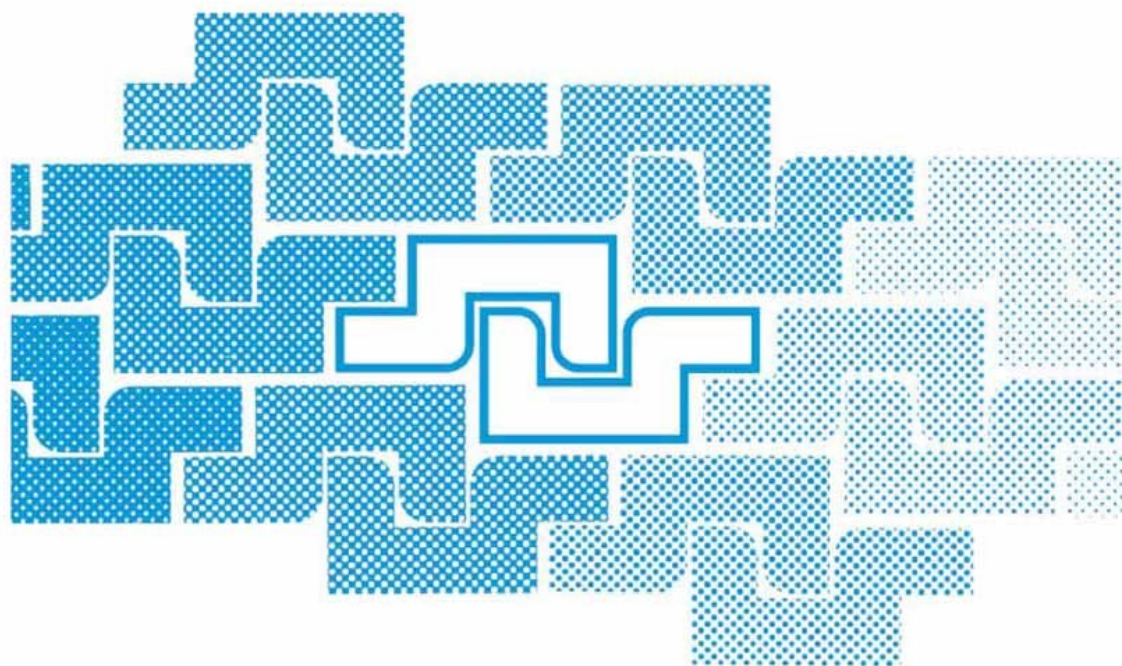




Frontiers of Multifunctional Integrated Nanosystems

Edited by

Eugenia Buzaneva and Peter Scharff

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Frontiers of Multifunctional Integrated Nanosystems

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Frontiers of Multifunctional Integrated Nanosystems

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KLUWER ACADEMIC PUBLISHERS

NEW YORK, BOSTON, DORDRECHT, LONDON, MOSCOW

eBook ISBN: 1-4020-2173-9
Print ISBN: 1-4020-2171-2

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Photographs of the participants to the NATO ARW in Imenau (July 2003)

PREFACE

Once again after ARW 2000, 2001, scientists and engineers from around the world come together here for an international exchange of information on the molecular-scale science and application of nanocarbon, nanosilicon and biopolymer integrated nanosystems.

A large number of exciting new developments in firstest years of XXI century are presented. Significant progress has been made in the deposition of device-quality and nanocrystalline silicon dots in *in situ* growth characterization techniques, and in state-of-the-art computer modeling of deposition processes. These issues are especially important for the successful future commercialization of silicon thin-film devices. The latest results concerning silicon thin-film solar cells are highlighted. A-Si:H tandem cells now approach stabilized conversion efficiencies of up to 10%, even for large-area modules. Similarly, $\mu\text{-Si}$ solar cells deposited on optimized TCO contacts by PECVD have reached conversion efficiencies of 9.4% on the laboratory scale. To achieve such high efficiencies in large-scale production is still a major challenge, but even here, many improvements have been made. Active matrix arrays for displays or sensors continue to be the second major application of thin silicon films, and again much progress has been made in that area. And experimental and theoretical tools for the investigation of the microstructure and structural processes in amorphous silicon and has also provided strong evidence for the so far elusive “paracrystalline” phase as a structural precursor of nanocrystalline silicon. Topics include:

The primary goal of a materials scientist is a predictive understanding of materials properties, and that requires a clear picture of the role played by electrons in determining the materials' behavior. Only then can one hope to design and build new materials with desired physical, chemical and engineering characteristics. Present-day research in this subject is carried out on the basis of quantum mechanics, through solution of the so-called single-particle Schrodinger equation that describes the behavior of electrons in a solid. This new volume from Antonios Gonis attempts to describe one formal approach to solving the Schrodinger equation developed within the framework of multiple scattering theory (MST). With 24 chapters and 1031 pages, the volume offers a comprehensive and welcome entrée to the field of electronic structure of solids and should serve as a treatise for advanced undergraduates, graduate students and researchers in the field. 2000, hardcover, 1031 pages.

It should be noted that the success of our multidisciplinary meeting and of this Book was guaranteed in advance by the enthusiastic work of: Androula Nassiopoulou, Greece; Giovanni Marletta, Italy; Hans Kuzmany, Austria; Ross Rinaldi, Italy; Clivia M Sotomayor Torres, Germany; Dunsch Lothar, Germany; Sergey Romanov, Germany; Gogotsi Yury, USA; Angel Rubio, Spain. We express our gratitude to all those, who have contributed to the workshop, especially to Key Speakers:

Prof. Wolfgang Jantsch, Austria
Prof. Hans Kuzmany, Austria
Prof. Ladislav Kavan, Czech Republic
Dr. Rio Yannick, France
Prof. Peter Scharff, Germany
Prof. Clivia M. Sotomayor Torres, Germany

Dr. Androula Nassiopoulou, Greece
 Prof. Giovanni Marletta, Italy
 Prof. Ross Rinaldi, Italy
 Prof. Per Hyldgaard, Sweden
 Prof. Sue Bayliss, UK
 Prof. Eugenia Buzaneva, Ukraine
 Prof. Yury Gogotsi, USA

We thank all the authors who responded eagerly to this demanding task and promptly delivered high quality manuscripts. This book would not have been possible without the efficient and cheerful help of our scientific secretary and editorial assistant, Dr. Oleksander Ivanyuta. We are most grateful to them for all their efforts.

We gratefully acknowledge the generous support of the NATO Scientific Affairs Division and our Universities, The Scientific and Training Center «Physical and Chemical Material Science» of the Kiev National Taras Shevchenko University and NAS of Ukraine, which made the workshop and this resulting book possible, and to Kluwer for efficient publication.

Eugenia Buzaneva

Peter Scharff

Ilmenau, Germany, November 2003

The Book includes the results of advanced investigation in Molecular-Scale Science and Technology of Nanocarbon, Nanosilicon and Biopolymer Integrated Nanosystems have been obtained at first years of 21th century:

- Modeling and Computer Simulation of Fundamental Characteristic of Nanosystems.
- Nanotechnology of Building Blocks and Integrated Nanosystems.
- Single and Assembled Molecules, Nanoparticles on Surfaces and Interfaces Investigations
- Fundamental Properties of Carbon Integrated Nanosystems
- Fundamental Properties of Silicon Integrated Nanosystems
- Multifunctional Characteristics of Nanosystems: Moletronics; Electronics and Photonics; Magnetic properties of Nanosystems on Spintronics and Magneto-optoelectronics; Sensory Nanosystems (chemical, biological and medical).

This Book demonstrates that researching nanocarbon, nanosilicon, biomolecular integrated nanosystems, and developing their new applications, has proven to be a complex and exiting topic that will no doubt continue to engage scientists and engineers for may years to come.

OPTICAL PROPERTIES OF SMALL-RADIUS SWNTS WITHIN A TIGHT-BINDING MODEL

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Abstract

The optical properties of single-walled carbon nanotubes (SWNTs) are studied within a symmetry-adapted density-functional-theory-based non-orthogonal tight-binding model using $2s$ and $2p$ electrons of carbon. The use of symmetry-adapted model for the calculation of the electronic band structure and the optical properties allows reducing significantly the size of the matrix electronic eigenvalue problem. Consequently, it could be possible to do these calculations for all 48 SWNTs with radii between 2 Å and 5 Å. The obtained band structures for several nanotube types agree well with ab-initio results up to ~ 3.5 eV above the Fermi energy. Similarly to the ab-initio calculations, the tight-binding model predicts deviations from the predictions of the band structure within the zone-folding method. It is demonstrated that, e.g., nanotube (5,0) is metallic while the zone-folding method predicts it as semiconducting. Secondly, the dielectric function for the same nanotube types is calculated within the random phase approximation for energies up to 7 eV. The peak positions of the imaginary part of the dielectric function for parallel light polarisation versus nanotube radius are illustrated on a chart.

1. Introduction

The discovery of the carbon nanotubes in 1991 [1] and the speculations about their amazing properties directed much attention to their experimental and theoretical study (for reviews, see, e.g. [2-4]). In the simplest case, a nanotube consists of a single graphitic layer, the so-called single-walled carbon nanotube (SWNT). The SWNT can be viewed as a long strip of graphene sheet rolled up into a seamless cylindrical surface and can be characterised uniquely by a pair of indices (L_1, L_2). Based on a π -band tight-binding model within the zone-folding approximation (π -TB ZFA) for the non-optimised (“rolled-up”) structure, the nanotubes were predicted to be metallic (zero-gap semiconductors) if $L_1 - L_2$ is a multiple of 3 or semiconducting else [5]. It was also shown that extending this model to encompass σ and π bands, some metallic nanotubes are very-small-gap semiconducting nanotubes [5]. The predictions of such π -band tight-binding models for the optical transitions energies has been widely used for assignment of the peaks in the optical absorption spectra of nanotube samples [6]. Recently, a π -tight-binding model with a chirality- and diameter-dependent nearest-neighbour hopping integral was used to relate well resolved features in the UV-VIS-

NIR spectra of individual SWNTs to electronic excitations in specific tube types [7]. Using a non-orthogonal σ - and π -band tight-binding approach [8], a first-principles, self-consistent, all-electron Gaussian-orbital based local-density-functional (LDA) approach [9], and a plane-wave ab-initio pseudopotential LDA approach [10] dealing directly with the optimised nanotube structure, it was possible to study in more detail the curvature-induced σ - and π -band mixing and deviation from the sp^2 hybridisation. In particular, these effects were found to alter significantly the electronic structure of small nanotubes compared to the predictions of the π -band tight-binding model [10]. In the case of small-radius insulating SWNTs, strongly modified low-lying non-degenerate conduction band states are introduced into the band gap due to $\sigma^*-\pi^*$ rehybridisation. As a result, the LDA gaps of some tubes are lowered by more than 50% and the tube (6,0) previously predicted to be semiconducting is shown to be metallic. Similar effects are observed in the electronic properties of carbon nanotubes with polygonised cross sections calculated within a plane-wave ab-initio pseudopotential LDA approach [11]. Recently, it was shown by extensive ab-initio LDA calculations that even for nanotubes with large radii R ($5 \text{ \AA} < R < 7.5 \text{ \AA}$) a shift of $\sim 0.1 \text{ eV}$ is predicted relative to the results of the π -TB (ZFA) [12].

The optical properties of SWNTs have been treated exclusively within π -band tight-binding models within the gradient approximation for the matrix elements of the linear momentum. The selection rules for allowed dipole transitions were first discussed by Ajiki and Ando [13] in the study of the low-energy optical absorption due to interband transitions as a probe of the Aharonov-Bohm effect. π -band tight-binding calculations of the plasmons and optical properties of carbon nanotube systems were presented by several groups [14-16]. A symmetry-adapted approach was implemented in Ref. [16]. Ab-initio calculations of the dielectric function were carried out for a (5,7) nanotube [17] and for three small-radius nanotubes, (3,3), (5,0), and (4,2) [18, 19]. The π -band tight-binding models cannot reproduce satisfactorily the electronic structure and optical properties of nanotubes with $R < 5 \text{ \AA}$. On the other hand, such calculations are much less computer-time consuming than within the ab-initio approaches. An alternative approach will be to use 1) a well-tuned non-orthogonal tight-binding model which reproduces fairly well the electronic structure of graphite up to $\sim 5 \text{ eV}$ and 2) a symmetry-adapted approach which will allow one to handle nanotubes with a large number of carbon atoms in the unit cell [20].

Here, the results of a non-orthogonal tight-binding study of the electronic band structure and the optical properties of all SWNTs with radii in the range $2 \text{ \AA} < R < 5 \text{ \AA}$ are presented. First, the main relations between the structural parameters of a nanotube are introduced in Sec. II. The symmetry-adapted non-orthogonal tight-binding model is presented in Sec. III. The obtained electronic band structure and the dielectric function for three SWNTs is given in Sec. IV together with the chart of the radius dependence of the optical transition energies for all 48 SWNTs with radii between $2 \text{ \AA}$ and $5 \text{ \AA}$. The report ends with conclusions (Section V).

2. The nanotube structure

The ideal single-walled carbon nanotube can be viewed as obtained by rolling up of an infinite strip of a graphene sheet into a seamless cylinder [5,8,21]. The seamlessness of the tube means coincidence of lattice points previously connected on the sheet by a lattice vector $L_1\mathbf{a}_1 + L_2\mathbf{a}_2$ ($\mathbf{a}_1$ and $\mathbf{a}_2$ are the primitive translations vectors of the sheet, L_1 and L_2 are integer numbers). This ideal nanotube can be specified uniquely by the pair (L_1, L_2) . We recall that a two-atom unit cell can be mapped onto the entire graphene sheet by use of two primitive translation vectors. Similarly, a two-atom unit

cell can be mapped onto the entire tube by use of two different screw operators. By definition, a screw operator $\{S_i | \mathbf{t}_i\}$ ($i=1,2$) executes a rotation of the position vector of an atom at an angle φ_i about the tube axis with rotation matrix S_i and a translation of the position vector at a vector $\mathbf{t}_i$ along the tube axis. Thus the equilibrium position vector $\mathbf{x}(l_1 l_2 k)$ of the k -th atom in the $(l_1 l_2)$ -th cell is obtained from $\mathbf{x}(k) \equiv \mathbf{x}(00k)$ as

$$\mathbf{x}(\mathbf{l}_1 \mathbf{l}_2 k) = \{S_1 | \mathbf{t}_1\}^{l_1} \{S_2 | \mathbf{t}_2\}^{l_2} \mathbf{x}(k) = S_1^{l_1} S_2^{l_2} \mathbf{x}(k) + l_1 \mathbf{t}_1 + l_2 \mathbf{t}_2 \quad (1)$$

We adopt the abbreviated notation $S_i(\mathbf{l}) = S_1^{l_1} S_2^{l_2}$ and $\mathbf{t}(\mathbf{l}) = l_1 \mathbf{t}_1 + l_2 \mathbf{t}_2$ and rewrite Eq. (1) in the form

$$\mathbf{x}(\mathbf{l}k) = \{S(\mathbf{l}) | \mathbf{t}(\mathbf{l})\} \mathbf{x}(k) = S(\mathbf{l}) \mathbf{x}(k) + \mathbf{t}(\mathbf{l}) \quad (2)$$

Here the vector index $\mathbf{l}=(l_1, l_2)$ labels the two-atom unit cells and $k = 1, 2$, labels the atoms in a given cell. In a similar way, one of the atoms in the two-atom unit cell can be mapped unto the other atom by use of a screw operation defined by the angle φ' and the translation $\mathbf{t}'$.

The primitive rotation angles and the primitive translations of the two types of screw operations can be found from the translational periodicity and rotational boundary conditions

$$N_1 \varphi_1 + N_2 \varphi_2 = 0, \quad L_1 \varphi_1 + L_2 \varphi_2 = 2\pi, \quad N_1 \mathbf{t}_1 + N_2 \mathbf{t}_2 = \mathbf{T}, \quad L_1 \mathbf{t}_1 + L_2 \mathbf{t}_2 = \mathbf{0}. \quad (3)$$

Here, $\mathbf{T}$ is the primitive translation vector of the nanotube. N_1 and N_2 are integer numbers determining the primitive translation vector and are given by the relations

$$N_1 = (L_1 + 2L_2) / d, \quad N_2 = -(2L_1 + L_2) / d. \quad (4)$$

Here d is equal to the highest common divisor d' of L_1 and L_2 if $L_1 - L_2$ is not a multiple of $3d'$ or d is equal to $3d'$ if $L_1 - L_2$ is a multiple of $3d'$. From Eqs. (3) and (4) one obtains

$$\varphi_1 = 2\pi N_2 / N_c, \quad \varphi_2 = -2\pi N_1 / N_c, \quad \mathbf{t}_1 = (L_2 / N_c) \mathbf{T}, \quad \mathbf{t}_2 = -(L_1 / N_c) \mathbf{T}. \quad (5)$$

Here, the total number of the atomic pairs in the unit cell, N_c , is

$$N_c = N_1 L_2 - N_2 L_1 = 2(L_1^2 + L_1 L_2 + L_2^2) / d \quad (6)$$

The atomic position vectors can be written as $\mathbf{x}(n\mathbf{l}k) = \mathbf{x}(\mathbf{l}k) + n\mathbf{T}$, where the integer number n labels the (translational) unit cells.

A nanotube can be characterised alternatively by its radius R and chiral angle (or wrapping angle) θ which is the angle between the tube circumference and the nearest zigzag of C-C bonds, $0^\circ \leq \theta < 30^\circ$ [5]. For the “rolled-up” structure these two quantities are given by

$$R = \sqrt{3(L_1^2 + L_1 L_2 + L_2^2)} a_{C-C} / 2\pi, \quad \theta = \tan^{-1}(\sqrt{3} L_2 / (L_2 + 2L_1)), \quad (7)$$

where a_{C-C} is the C-C bond length in graphene. The “rolled-up” structure is useful when the nanotube structure cannot be optimised as is the case with some tight-binding models of the electronic structure with fixed parameters or in dynamical models based on fixed force constants. However, in other tight-binding models with explicit dependence of the parameters on the interatomic separations and in all ab-initio models of the electronic structure, as well as in the potential-based dynamical models, one should optimise the tube structure. In the simplest case, only the bond lengths and

valence angles for the two atoms in the unit cell are varied in the optimisation procedure preserving the screw symmetry of the tube. Thus as independent structural parameters can be considered R , T , ϕ' , and t' . For the optimised structure the above relations between L_1 , L_2 and R , θ will generally no longer hold.

3. The symmetry-adapted non-orthogonal tight-binding model

The electronic band structure of a periodic structure is usually obtained solving the one-electron Schrödinger equation

$$\left[-\frac{\hbar^2 \nabla^2}{2m} + V(\mathbf{r}) \right] \psi_{\mathbf{k}}(r) = E_{\mathbf{k}} \psi_{\mathbf{k}}(r), \quad (8)$$

where $V(\mathbf{r})$ is the effective periodic potential, $\psi_{\mathbf{k}}(\mathbf{r})$ and $E_{\mathbf{k}}$ are the one-electron wavefunction and energy depending on the wavevector $\mathbf{k}$. This equation can be solved by representing $\psi_{\mathbf{k}}(\mathbf{r})$ as a linear combination of basis functions $\varphi_{r\mathbf{k}}(\mathbf{r})$

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_r c_{r\mathbf{k}} \varphi_{r\mathbf{k}}(\mathbf{r}) \quad (9)$$

In the tight-binding approach, the φ 's are constructed from atomic orbitals centered at the atoms. Let us denote by $\chi_r(\mathbf{R}(\mathbf{l}) - \mathbf{r})$ the r -th atomic orbital centered at an atom with position vector $\mathbf{R}(\mathbf{l})$ in the $\mathbf{l}$ -th unit cell. Bloch's condition for the electron wave function φ of a system consisting of N unit cells is satisfied for the linear combination of χ 's

$$\varphi_{r\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{l}} e^{i\mathbf{k} \cdot \mathbf{R}(\mathbf{l})} \chi_r(\mathbf{R}(\mathbf{l}) - \mathbf{r}). \quad (10)$$

Equation (10) is applicable to any nanotube as well. The number of atoms in the unit cell of the nanotube can be very large leading to large-size matrix equations for the band problem.

We notice, however, that any nanotube has a screw symmetry, which allows one to use only a two-atom unit cell for the electronic problem. In this case, Eq. (10) is still valid but for the transformed χ 's

$$\varphi_{r\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{l}} e^{i\mathbf{k} \cdot \mathbf{R}(\mathbf{l})} T_{rr'} \chi_{r'}(\mathbf{R}(\mathbf{l}) - \mathbf{r}). \quad (11)$$

Here $\mathbf{k}=(k_1, k_2)$ is an yet undefined two-component wave vector of the tube and $T_{rr'}$ is the matrix realizing a representation of the screw symmetry group in the space of the χ 's. Substituting Eq. (11) in Eq. (8), we obtain

$$\sum_{r'} c_{r'}(\mathbf{k}) H_{rr'}(\mathbf{k}) = E_{\mathbf{k}} \sum_{r'} c_{r'}(\mathbf{k}) S_{rr'}(\mathbf{k}), \quad (12)$$

where

$$H_{rr'}(\mathbf{k}) = \sum_{\mathbf{l}''} e^{i\mathbf{k} \cdot \mathbf{l}''} H_{rr''}(\mathbf{l}) T_{r''r'}(\mathbf{l}), \quad S_{rr'}(\mathbf{k}) = \sum_{\mathbf{l}''} e^{i\mathbf{k} \cdot \mathbf{l}''} S_{rr''}(\mathbf{l}) T_{r''r'}(\mathbf{l}) \quad (13)$$

and

$$H_{rr'}(\mathbf{l}) = \int d\mathbf{r} \chi_r(\mathbf{R}(\mathbf{0}) - \mathbf{r}) \hat{H} \chi_{r'}(\mathbf{R}'(\mathbf{l}) - \mathbf{r}), \quad S_{rr'}(\mathbf{l}) = \int d\mathbf{r} \chi_r(\mathbf{R}(\mathbf{0}) - \mathbf{r}) \chi_{r'}(\mathbf{R}'(\mathbf{l}) - \mathbf{r}). \quad (14)$$

The quantities $H_{rr'}(\mathbf{l})$ and $S_{rr'}(\mathbf{l})$ are the matrix elements of the Hamiltonian $\hat{H}$ and the overlap matrix elements, respectively.

The wave vector components k_1 and k_2 can be determined imposing the rotational boundary and translational periodicity conditions

$$k_1 L_1 + k_2 L_2 = 2\pi l, \quad k_1 N_1 + k_2 N_2 = k. \quad (15)$$

Here k is the one-dimensional wave vector of the tube ($-\pi \leq k \leq \pi$) and the integer number l labels the electronic energy levels with a given k ($l = 0, 1, \dots, N_c - 1$). From Eq. (14) we obtain k_1 and k_2

$$k_1 = (2\pi N_2 l - L_2 k) / N_c, \quad k_2 = (L_1 k - 2\pi N_1 l) / N_c. \quad (16)$$

The substitution of Eq. (15) in Eqs. (11) – (13) yields

$$\varphi_{\mathbf{rk}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{l}} e^{i(\alpha(\mathbf{l}) + z(\mathbf{l})k)} T_{rr'} \chi_{r'}(\mathbf{R}(\mathbf{l}) - \mathbf{r}), \quad (17)$$

$$\sum_{r'} c_{r'}(kl) H_{rr'}(kl) = E_{kl} \sum_{r'} c_{r'}(kl) S_{rr'}(kl), \quad (18)$$

$$H_{rr'}(\mathbf{k}) = \sum_{\mathbf{l}''} e^{i(\alpha(\mathbf{l}) + z(\mathbf{l})k)} H_{rr''}(\mathbf{l}) T_{r''r'}(\mathbf{l}), \quad S_{rr'}(\mathbf{k}) = \sum_{\mathbf{l}''} e^{i(\alpha(\mathbf{l}) + z(\mathbf{l})k)} S_{rr''}(\mathbf{l}) T_{r''r'}(\mathbf{l}). \quad (19)$$

The quantities $\alpha(\mathbf{l})$ and $z(\mathbf{l})$ are given by

$$\alpha(\mathbf{l}) = 2\pi(l_1 N_2 - l_2 N_1) / N_c, \quad z(\mathbf{l}) = (L_1 l_2 - L_2 l_1) / N_c. \quad (20)$$

The set of linear algebraic equations Eq. (17) has non-trivial solutions for the coefficients c only for energies E which satisfy the characteristic equation

$$|H_{rr'}(kl) - E_{kl} S_{rr'}(kl)| = 0. \quad (21)$$

The solutions of Eq. (21), E_{klm} , are the electronic energy levels; the energy bands are labeled by the composite index lm ($m = 1, 2, \dots$). The corresponding eigenfunctions are $c_r(klm)$ apart from an omitted index labeling the degenerate eigenfunctions belonging to the same energy level E_{klm} .

The total energy of a nanotube (per unit cell) is given by

$$E = \sum_{klm}^{occ} E_{klm} + \frac{1}{2} \sum_i \sum_j \phi(r_{ij}), \quad (22)$$

where the first term is the band energy (the summation is over all occupied states) and the second term is the repulsive energy, consisting of repulsive pair potentials between pairs of nearest neighbors. The force in α direction on atom with position vector $\mathbf{R}(\mathbf{0})$ is the sum of the band and repulsion contributions; the former is given by the Hellmann-Feynman theorem

$$F_\alpha = \sum_{klm}^{occ} \frac{\partial E_{klm}}{\partial R_\alpha(\mathbf{0})} = \sum_{klm}^{occ} \sum_{rr'} c_r^*(klm) \frac{\partial (H_{rr'} - E_{klm} S_{rr'})}{\partial R_\alpha(\mathbf{0})} c_{r'}(klm). \quad (23)$$

The imaginary part of the dielectric function in the random-phase approximation is given by [22]

$$\varepsilon_2(\omega) = \frac{4\pi^2 e^2}{m^2 \omega^2} \sum_{cv} \frac{2}{2\pi} \int dk |p_{cv,\mu}|^2 \delta(E_{kl'c} - E_{klv} - \hbar\omega), \quad (24)$$

where $\hbar\omega$ is the photon energy, and e and m are the elementary charge and the electron mass. The sum is over all occupied (v) and unoccupied (c) states. The matrix element of the momentum $p_{cv,\mu}$ in the direction μ of the light polarisation is

$$p_{cv,\mu} = \langle kl'c | p_\mu | klv \rangle = \sum_{rr'} c_r^* (kl'c) c_r (klv) f_\mu(l'l') \sum_{l''} e^{-i(\alpha(l'l'')/2 + z(l'l''))} p_{r',r'',\mu}(l'') T_{rr''}(l'). \quad (25)$$

Here, $f_x(l'l') = f_y(l'l') = (\delta_{l',l'+1} + \delta_{l',l'-1})/2$ and $f_z(l'l') = \delta_{l'l'}$ (z -axis is along the tube axis) are the conditions for non-zero matrix elements $p_{cv,\mu}$ and express the optical transitions selection rules (see [13]). From Maxwell's relation $\varepsilon = \tilde{n}^2$ ($\tilde{n}$ is the complex refractive index), the refractive index $n = \text{Re } \tilde{n}$ and the extinction coefficient $\kappa = \text{Im } \tilde{n}$ are readily obtained. The relations $\alpha = 2\omega\kappa/c$ (c is the light velocity in vacuum) and $R = |(\tilde{n}-1)/(\tilde{n}+1)|^2$ allow one to derive the absorption coefficient α and the reflection coefficient for normal incidence R .

Let us consider a single pair of v - and c -bands with maximum and minimum separated by a direct gap $E_{l'clv}$. Assuming that the matrix elements $p_{cv,\mu}$ are independent of k , it is straightforward to show that the contribution to ε_2 from these bands is given by

$$\varepsilon_2 = \frac{2\pi e^2}{m^2 \omega^2} \sqrt{\frac{2m_{l'clv}^*}{\hbar^2}} |p_{cv,\mu}|^2 \frac{1}{\sqrt{\hbar\omega - E_{l'clv}}}. \quad (26)$$

Here m^* is the reduced effective mass for the two bands. Alternatively, for a pair of v - and c -bands with minimum and maximum separated by energy $E_{l'clv}$ one readily obtains

$$\varepsilon_2 = \frac{2\pi e^2}{m^2 \omega^2} \sqrt{\frac{2m_{l'clv}^*}{\hbar^2}} |p_{cv,\mu}|^2 \frac{1}{\sqrt{E_{l'clv} - \hbar\omega}}. \quad (27)$$

In the general case, the graph $\varepsilon_2(\omega)$ will consist of two types of spikes close to those described by Eqn. (25) and (26). From the derivation of the latter two equations it is clear that the electron density of states (DOS) versus ω will have the same two types of spikes.

4. Results and discussion

The parameters of the non-orthogonal tight-binding model were taken from a density-functional-based study [23]. In the case of graphite, these parameters showed excellent performance in the calculation of the equilibrium lattice parameter and the cohesive energy. The tight-binding electronic structure of graphite corresponds fairly well to the ab-initio results for the valence bands and for the unoccupied bands up to ~ 3.5 eV above the Fermi energy. This implies that the optical properties of graphite should be reproduced well up to about 7 eV. The same reliability region should be valid for carbon nanotubes as well.

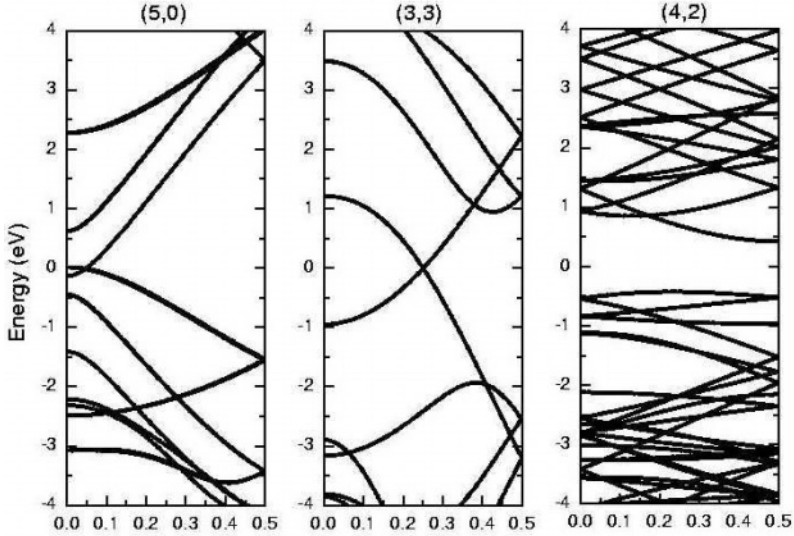


Figure 1. Calculated electronic band structure of SWNTs (5,0), (3,3), and (4,2) in the energy range between -4 eV and 4 eV with respect to the Fermi energy.

Here, the structure of all 48 SWNTs with radii R in the range from $2 \text{ \AA}$ to $5 \text{ \AA}$ was optimised. The optimisation was carried out under the constraint that all atom lie on a cylindrical surface and as independent structural parameters were considered R , T , φ' , and l' . The electronic band structure and the imaginary part of the dielectric function for parallel and perpendicular light polarisation were calculated for all mentioned SWNTs. In Fig. 1, the electronic band structure of three small-radius nanotubes, (5,0), (3,3), and (4,2), is shown. In all three cases, the predicted band structure corresponds semiquantitatively to the results in Refs. [18,19]. In particular, the expected large $\sigma^* - \pi^*$ rehybridisation in thin tubes due to curvature effects [10] is demonstrated here as in Refs. [18,19]: the (5,0) nanotube is metallic contrary to the predictions of π -TB (ZFA); the crossing of the bands at the Fermi level in (3,3) nanotube is at $k \approx 0.25 \pi/T$ instead at $k = 2/3 \pi/T$; nanotube (4,2) has an indirect band gap of $\approx 0.83 \text{ eV}$ which is twice smaller than the direct gap of the π -TB (ZFA) but is larger than the ab-initio one [18,19]. The effects of rehybridisation are found to decrease with the increase of the tube radius and to become unimportant for R close to $5 \text{ \AA}$.

The calculated imaginary part of the dielectric function of SWNTs (5,0), (3,3), and (4,2) for parallel and perpendicular polarisation in the energy range from 0 to 6 eV are shown in Fig. 3. The peaks in parallel polarisation originate from minima and maxima of occupied and unoccupied bands with the same quantum number l . For example, peak A1 in Fig. 1 (tube (3,3)) can be associated with an optical transition between a maximum of an occupied band of $\sim -2 \text{ eV}$ and a minimum of an unoccupied band of $\sim 1 \text{ eV}$. These minima and maxima give rise to spikes in the electronic density of states of the SWNTs. The peaks in perpendicular polarisation originate from minima and maxima of occupied and unoccupied bands as well from states on parallel parts of occupied and unoccupied bands with quantum numbers l and $l \pm 1$. For example, peaks B1 and B2 come from such transitions near the crossing point of the bands at the Fermi level; peak B3 comes from states near the Brillouin zone boundary; peak

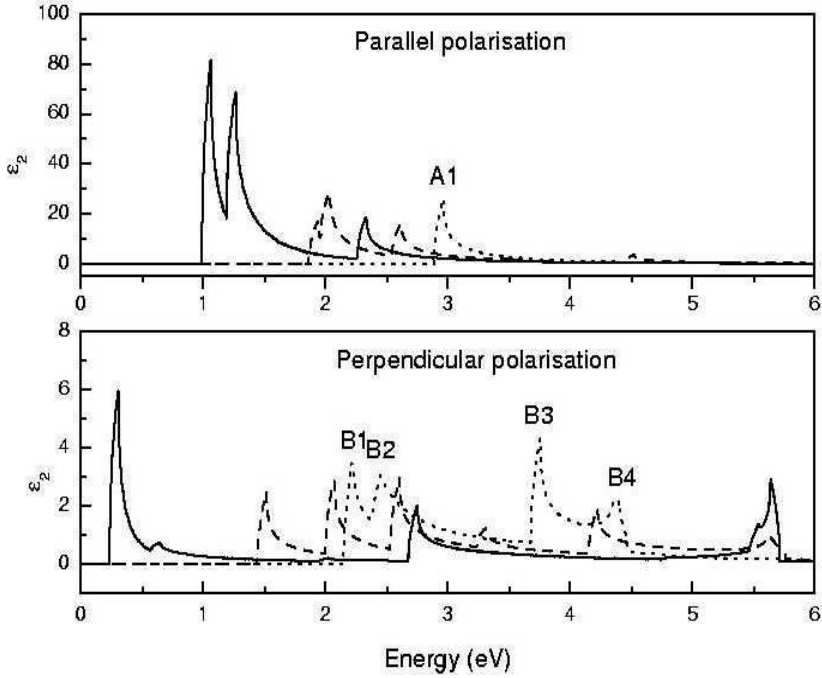


Figure 2. Calculated dielectric function ϵ_2 of SWNTs (5,0), (3,3), and (4,2) for parallel and perpendicular polarisation in the energy range from 0 to 6 eV.

B4 is due to transitions between minima and maxima of bands at the zone centre. It should be noted that in the calculation of ϵ_2 for perpendicular polarisation, the local field effects were not accounted for here. On the other hand, the small lateral size of the nanotubes leads to strong depolarisation effect and to significant reduction of the dielectric function [13]. The precise inclusion of the local field effects is expected to lead to improvement of the dielectric function for perpendicular polarisation mainly in the peak height. The importance of the knowledge of the dielectric function for both parallel and perpendicular polarisation has been stressed recently in a cross-polarised resonant Raman study of SWNTs [24].

The energies of the optical transitions in nanotubes determine the conditions for resonant Raman scattering of light from nanotubes. Previous results for these energies versus tube radius were derived within a π -TB (ZFA) [6]. In view of the inadequacy of these results for small-radius tubes it is important to correct them taking into account the curvature effects. Here, we present the transition energies versus tube radius for all 48 tubes with radii between 2 Å and 5 Å (Fig. 3). It is seen in Fig. 3 that as a result of curvature-induced hybridisation effects the nanotubes, predicted to be metallic within the π -TB (ZFA), are small-gap semiconducting tubes except for the armchair tubes that are always metallic due to their symmetry. In both metallic and semiconducting nanotubes, the energy bands come lower thus decreasing the energy of the optical transitions. These differences are large for very-small-radius nanotubes and tend to disappear for radii close to 5 Å.

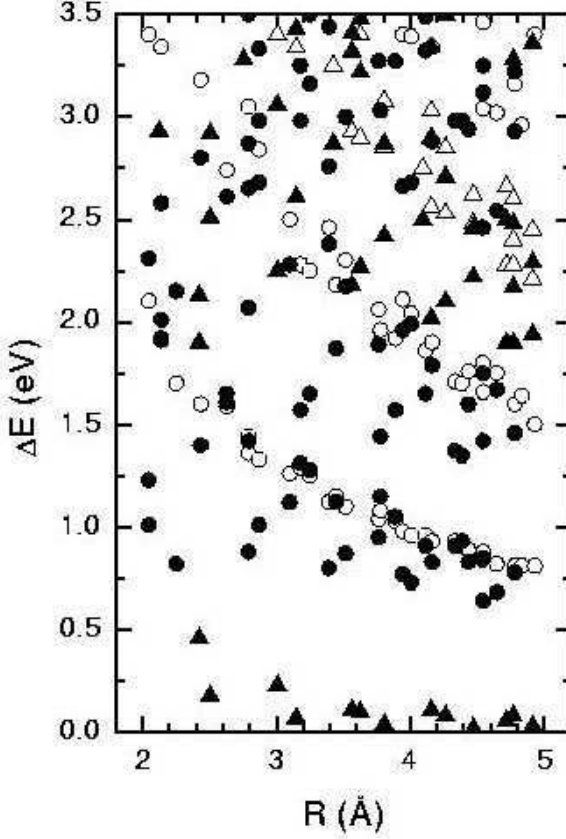


Figure 3. Calculated optical transitions versus tube radius for parallel polarisation for all 48 tubes with radii between 2 Å and 5 Å in comparison with π -TB (ZFA) results from Ref. [6]. The circles denote semiconducting tubes and the triangles denote metallic tubes (according to the π -TB (ZFA)); open symbols are data from Ref. [6] and solid symbols are results obtained here.

5. Conclusions

The optical properties of single-walled carbon nanotubes (SWNTs) are studied within a density-functional-theory-based non-orthogonal tight-binding model. The model is symmetry-adapted which allows for significant reduction of the size of the matrix electronic eigenvalue problem. It is shown that the calculated electronic band structure of three small-radius nanotubes agrees well with ab-initio simulations up to several eV above the Fermi energy and exhibits large differences with the π -TB (ZFA) results. For example, nanotube (5,0) is found to be metallic while the π -TB (ZFA) predicts it as semiconducting. Secondly, the dielectric function for the same nanotube types is calculated within the random phase approximation for energies up to 7 eV. The obtained peak positions of the imaginary part of the dielectric function versus nanotube radius can be useful for determination of the conditions for resonant Raman scattering from nanotubes.

Acknowledgments

This work was supported partly by a NATO Senior Fellowship and partly by the University of Antwerp (RUCA), Belgium, in the framework of the Visiting Professors Program.

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THE ELECTRONIC STRUCTURE OF NANOTUBES AND THE TOPOLOGICAL ARRANGEMENTS OF CARBON ATOMS

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Abstract

After summarizing the topological coordinate methods for fullerenes, tori and nanotubes, an extension is presented for two dimensional periodic carbon sheets. This was applied for four Haeckelite structures. Contrary to the expectation, the leapfrog transformed Haeckelite structures did not revealed intrinsic metallic behavior. The corresponding nanotubes were found semiconductors independent of tube orientations.

1. Introduction

The conductivity behavior of polyhex single-walled carbon nanotubes is mostly determined by the chirality of the tubes. A tube is metallic if the K-point of the Brillouin zone of the corresponding graphite sheet remains as an allowed k -state. These points are the only points where the two bands of the graphite sheet coincide, that is there is a zero energy band between the occupied and empty band [1, 2, 3]. Pentagons and heptagons can modify drastically the electronic structure of the polyhex nanotubes. In ref. [4] for example there are presented three Haeckelite sheets composed of ordered arrangements of pentagons, hexagons, and heptagons revealing intrinsic metallic behavior, independent of orientation, tube diameter, and chirality. The connection between the topological arrangement of carbon atoms and the electronic structure is not yet fully understood. In most of the cases only the connectivity structure is given, but for the sake of further investigations one needs Cartesian coordinates as well. The topological coordinate method [5, 6] is a very simple and transparent approach in overtaking this problem. It has already been used for fullerenes [5, 6], tori [7, 8] and nanotubes [9]. Here we present a natural application for two-dimensional periodic structures. Using only the topological arrangement of carbon atoms, we shall describe the electronic structure as well. Although the tight-binding method is a very crude approximation, many qualitative properties can be found with the help of the adjacency matrices of the atomic arrangement.

2. Topological coordinates for two-dimensional periodic carbon structures

Suppose that the atomic arrangement of a carbon structure is given by an n -vertex graph $G = (V, E)$ where V is the set of vertices (set of atoms) and E is the set of edges (set of inter atomic bonds). Let $\mathbf{A}$ be the adjacency matrix with elements $A_{ij}=1$ if i and j are adjacent and $A_{ij} = 0$ otherwise. From this definition follows that $\mathbf{H} = -\mathbf{A}$, where $\mathbf{H}$ is the Hückel Hamiltonian matrix with $\alpha = 0$ and $\beta = -1$. It is assumed further that

$$a_1 > a_2 \geq a_3 \geq \dots \geq a_n \quad (1)$$

if a_k is the k -th eigenvalue of $\mathbf{A}$ and $\mathbf{c}^k$ is the corresponding eigenvector.

In the construction of topological coordinates special kind of eigenvectors, the bi-lobal eigenvectors are used [5, 6]. Vectors having this bi-lobal property can be identified by the graph-disconnection test: for a candidate vector, color all vertices bearing positive coefficients black, all bearing negative coefficients white, and all bearing a zero coefficient gray; now delete all gray vertices, all edges incident on gray vertices, and all edges connecting a black to a white vertex; if the graph now consists of exactly two connected components, one of black and one of white vertices then the eigenvector is bi-lobal type [5, 6, 8].

If $\mathbf{c}^{k_1}$, $\mathbf{c}^{k_2}$ and $\mathbf{c}^{k_3}$ are the first tree bi-lobal eigenfunctions of $\mathbf{A}$ than Manolopoulos and Fowler [5, 6] introduced the x_i , y_i and z_i topological coordinates of the carbon atoms in a spherical carbon structure (fullerene) as,

$$x_i = S_1 c_i^{k_1}, \quad (2)$$

$$y_i = S_2 c_i^{k_2}, \quad (3)$$

$$z_i = S_3 c_i^{k_3}, \quad (4)$$

where $S_\alpha = 1$ or $S_\alpha = 1/\sqrt{(a_1 - a_{k_\alpha})}$ or any other appropriate scaling factors. In the case of toroidal structure we need four bi-lobal eigenvectors $\mathbf{c}^{k_1}$, $\mathbf{c}^{k_2}$, $\mathbf{c}^{k_3}$ and $\mathbf{c}^{k_4}$, and the topological coordinates of the torus are calculated as,

$$x_i = S_1 c_i^{k_1} (1 + S_4 c_i^{k_4}), \quad (5)$$

$$y_i = S_2 c_i^{k_2} (1 + S_4 c_i^{k_4}), \quad (6)$$

$$z_i = S_3 c_i^{k_3}, \quad (7)$$

where S_1 , S_2 , S_3 , and S_4 , are appropriate scaling factors as before. In the construction of this formula we supposed that the position of an atom i on the toroidal surface is the sum of vectors $\mathbf{R}_i$ and $\mathbf{r}_i$. The vector $\mathbf{R}_i$ points from the center of gravity of the torus to a point on the circular spine, and vector $\mathbf{r}_i$ points from there to the surface point i [8].

Transforming the torus into a nanotube, the topological coordinates of the nanotube are the followings [9]:

$$x_i = S_3 c_i^A, \quad (8)$$

$$y_i = S_4 c_i^A, \quad (9)$$

$$z_i = R \arccos(S_1 C_i^A / R) \quad \text{if} \quad C_i^A \geq 0, \quad (10)$$

$$z_i = R(2\pi - \arccos(S_1 C_i^A / R)) \quad \text{if} \quad C_i^A < 0, \quad (11)$$

We can repeat this idea by transforming the tube into a rectangle and obtain the topological coordinates for a two-dimensional periodic structure as:

$$x_i = r \arccos(S_4 C_i^A / r) \quad \text{if} \quad C_i^A \geq 0, \quad (12)$$

$$x_i = -r \arccos(S_4 C_i^A / r) \quad \text{if} \quad C_i^A < 0, \quad (13)$$

$$y_i = S_4 c_i^A, \quad (14)$$

$$z_i = R \arccos(S_1 C_i^A / R) \quad \text{if} \quad C_i^A \geq 0, \quad (15)$$

$$z_i = R(2\pi - \arccos(S_1 C_i^A / R)) \quad \text{if} \quad C_i^A < 0, \quad (16)$$

Here the radii R and r are the appropriate average values of $\mathbf{R}_i$ and $\mathbf{r}_i$ using the scaling of ref. [9].

Figures 1-4. are drawn by Eq.12-16. The structures A and B of Figures 1-2. are two pentaheptite modifications of the graphite sheet [10, 11] and structures LFA and LFB are the leapfrog transformation of A and B respectively. The terminology leapfrog transformation is developed for fullerenes and means the omni-capping and dualizing the original structure [6].

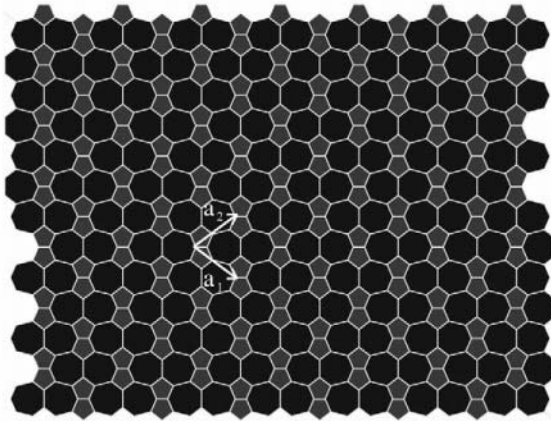


Figure 1. The structure A . Topological coordinates for a pentaheptite modification of the graphite sheet.

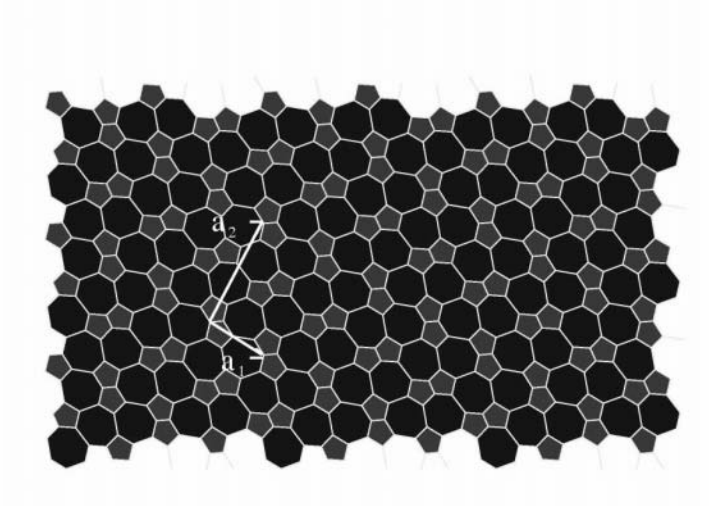


Figure 2. The structure B. Topological coordinates for a pentaheptide modification of the graphite sheet.

The two-dimensional periodic lattice structure can be generated by the translations, $\mathbf{t} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2$, where n_1 and n_2 are integers and $\mathbf{a}_1$, and $\mathbf{a}_2$ are unit vectors of the direct lattice. The unit vectors of the super cell are $\mathbf{S}_1 = m_{11} \mathbf{a}_1 + m_{12} \mathbf{a}_2$ and $\mathbf{S}_2 = m_{21} \mathbf{a}_1 + m_{22} \mathbf{a}_2$ with integers m_{11} , m_{12} , m_{21} , m_{22} . For the construction of the topological coordinates of a 2-dimensional periodic system we need the number of atoms in the unit cell (0, 0) and neighbors each of them in the unit cells (0,0), (1,0), (-1,0), (0,1), (0, -1), (1,1), (-1,-1), (1, - 1) and (-1, 1). Using then the integers m_{11} , m_{12} , m_{21} , m_{22} the matrix $\mathbf{A}$ of the

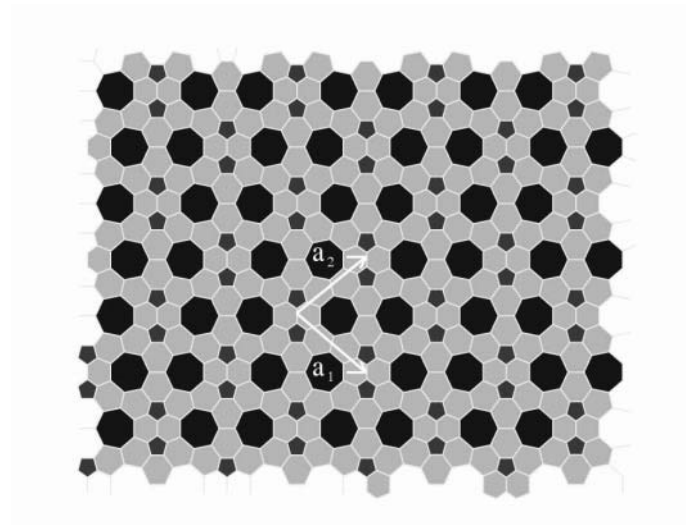


Figure 3. The structure LFA. Topological coordinates for the leapfrog transformed structure A.

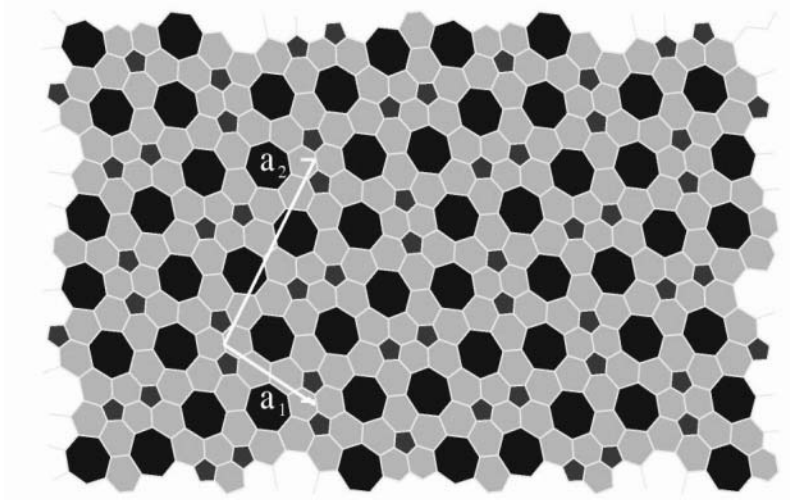


Figure 4. The structure LFB. Topological coordinates for the leapfrog transformed structure B.

corresponding torus can be constructed by identifying the opposite edges of the super cell, and finally the topological coordinates are calculated by the Equations 12-16. In the drawing, however, of the final figures the opposite edges of the super cell are not identified. Thus the topological coordinates can be obtained without knowing the unit vectors $\mathbf{a}_1$, and $\mathbf{a}_2$ and without knowing the coordinates of the atoms in the unit cell.

3. The electronic structure of single- walled carbon nanotubes

From the $\mathbf{a}_1$, and $\mathbf{a}_2$ unit cell vectors of the direct lattice the $\mathbf{b}_1$, and $\mathbf{b}_2$ unit cell vectors of the reciprocal lattice are calculated by the relations

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{z}}{(\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{z})}, \quad (17)$$

$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{z}}{(\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{z})}, \quad (18)$$

where $\mathbf{z}$ has the same direction as $\mathbf{a}_1 \times \mathbf{a}_2$ with $\mathbf{z} \cdot \mathbf{z} = 1$.

As there are only 2 carbon atoms in the unit cell of the polyhex carbon sheet, the 2×2 blocs of the tight binding Hamiltonian matrix can be diagonalized in an analytic way, and there are closed forms for the $-E_\mu(\mathbf{k})$ electronic energy values [12]. The $\mathbf{k}$ is a point in the reciprocal space and μ , is the band index. This is not the case for the structures A, B, LFA and LFB of Figures 1-4. as they have 8, 16, 24 and 48 atoms in the unit cell respectively. In the present paper the corresponding eigenvalues are

determined by numerical methods.

The electronic structure of a single-walled nanotube can be obtained from that of the corresponding infinite sheet [12]. The allowed k values are on parallel lines, which are parallel to the long axis of the unrolled super cell.

In Figures 5-8. the $E_{\text{LUMO}}(\mathbf{k}) - E_{\text{HOMO}}(\mathbf{k})$ values are shown in the function of the reciprocal space vector $\mathbf{k}$. $E_{\text{LUMO}}(\mathbf{k})$ is the lowest unoccupied molecular orbital and $E_{\text{HOMO}}(\mathbf{k})$ is the highest occupied molecular orbital at $\mathbf{k}$, supposing, that the first $r/2$ orbitals are occupied at each $\mathbf{k}$ and r is the number of carbon atoms in the unit cell. At the structures A and B the two bands (HOMO and LUMO) coincide at $\mathbf{k} = (0, 0)$. This is in agreement with the results of ref. [4], where it was found that the Haeckelite nanotubes of the structure A are metallic, independently of chirality and diameter. On Figures 7. and 8. these two bands do not coincide. This does not mean, however, that the nanotubes are semiconductors independent of the super cell, as it could happen that $E_{\text{LUMO}}(\mathbf{k}_1) - E_{\text{HOMO}}(\mathbf{k}_2) < 0$. Thus we have calculated for the structures LFA and LFB the values $E_{\min} = \min(E_{\text{LUMO}}(\mathbf{k}))$ and $E_{\max} = E_{\text{HOMO}}(\mathbf{k})$. The condition that a nanotube be insulator or semiconductor independent of the super cell, is $E_{\min} > E_{\max}$. We have found that the nanotubes of structures LFA and LFB are semiconductors independent of the super cell, as $E_{\min} = 0.057 > E_{\max} = -0.16$ for the structure LFA and $E_{\min} = 0.073 > E_{\max} = -0.17$ for the structure LFB.

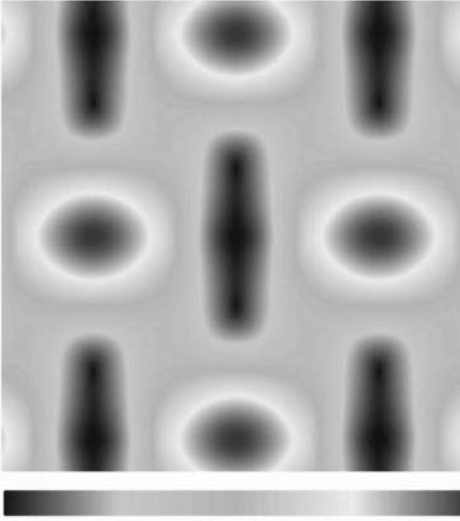


Figure 5. The $E_{\text{LUMO}}(\mathbf{k}) - E_{\text{HOMO}}(\mathbf{k})$ for the structure A. The axes of the components $-10.0 \leq k_x \leq 10.0$ and $-10.0 \leq k_y \leq 10.0$ correspond in order to the horizontal and vertical directions. The colors blue and red mark the values 0.0 and 2.0 respectively.

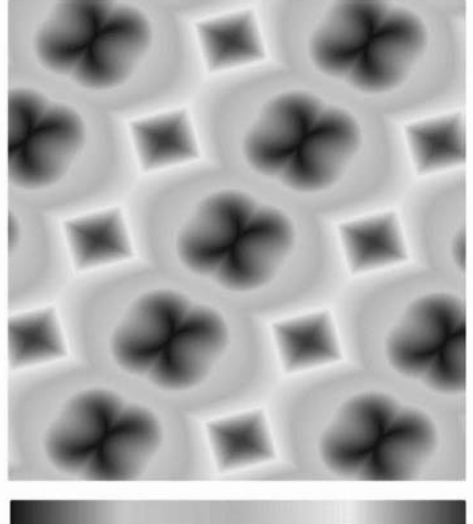


Figure 6. The $E_{\text{LUMO}}(\mathbf{k}) - E_{\text{HOMO}}(\mathbf{k})$ for the structure B. The axes of the components $-10.0 \leq k_x \leq 10.0$ and $-10.0 \leq k_y \leq 10.0$ correspond in order to the horizontal and vertical directions. The colors blue and red mark the values 0.0 and 1.5 respectively.

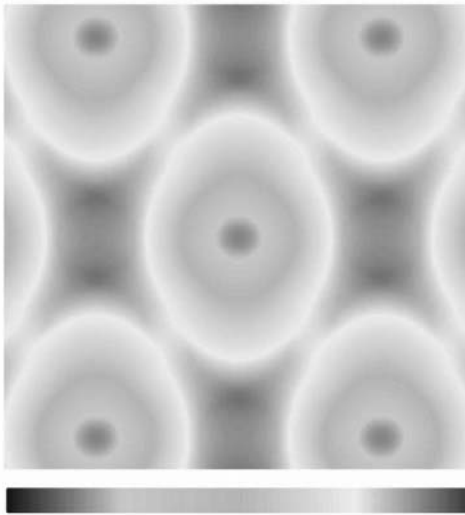


Figure 7. The $ELUMO(\mathbf{k}) - EHOMO(\mathbf{k})$ for the structure LFA. The axes of the components $-10.0 \leq k_x \leq 10.0$ and $-10.0 \leq k_y \leq 10.0$ correspond in order to the horizontal and vertical directions. The colors blue and red mark the values 0.0 and 1.4 respectively.

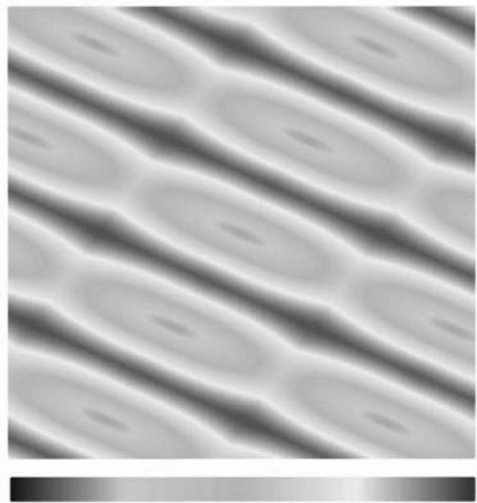


Figure 8. The $ELUMO(\mathbf{k}) - EHOMO(\mathbf{k})$ for the structure LFB. The axes of the components $-10.0 \leq k_x \leq 10.0$ and $-10.0 \leq k_y \leq 10.0$ correspond in order to the horizontal and vertical directions. The colors blue and red mark the values 0.0 and 1.2 respectively.

4. Conclusions

We have found that the topological coordinates can be defined for two-dimensional periodic carbon structures as well. The topological coordinates generate a natural pair of unit cell vectors $\mathbf{a}_1$, and $\mathbf{a}_2$. Using these unit vectors the $\mathbf{b}_1$, and $\mathbf{b}_2$ reciprocal lattice unit vectors can be constructed and the electronic structure of the infinite carbon sheet can be calculated. From the electronic structure of the infinite carbon sheet the nanotube electronic structure can be calculated in the usual way as parallel lines correspond to allowed $\mathbf{k}$ states of the nanotube.

With this method we studied four Haeckelite sheets, the structures A, B, LFA and LFB of Figures 1-4. For A and B we obtained intrinsic metallic behavior independent of the shape of nanotube as it was expected, but contrary to the expectation the LFA and LFB leapfrog Haeckelite structures were found semiconductors independent of the shape of the nanotube.

Acknowledgements

The author is grateful for grants from ARW2003:PST.ARW.979334 and OTKA (T 038191, T043231).

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IRRADIATION EFFECT ON THE ELECTRON TRANSPORT PROPERTIES OF SINGLE-WALLED CARBON NANOTUBE

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Abstract.

The conductivity of the metallic (10,10) single-walled carbon nanotube with simulated different types of local topological radiation defects was calculated and analysed.

1. Introduction

The advance of high technologies involves creation of materials and devices with new properties. The effective method for this creation is irradiation of matter by particles. As known, the most effect of the particle beam technology has been achieved in the microelectronics. Now this technology is intensively investigated with the purpose of creating and modification the different nanostructures [1].

Due to the unique physical properties [2] the single-walled carbon nanotubes (SWCNT) are very promising for applications in nanoelectronics, nanomechanics and in vacuum electronics. At present time, in the literature the influence of the particle irradiation on the electron transport properties of SWCNT is not currently known, and this problem is very important for nanotechnology.

2. Results and Discussion

In this work the radiating damages modeling in the SWCNT is carried out. These defects were generated by low energy single charged C6 and Ar18 ions. The calculations are carried out using a SRIM2000 package [3] for a carbon target of density 1.69 g/cm³, which corresponds to fullerite. The normal incidence was simulated. The sublimation heat and binding energy were taken for fullerite, and atom displacement energy was taken for carbon. These approximations cause discrepancy in accounts of sputtering, energy transferred to phonons system and numbers of recoil atoms. As we were interested with elastic and inelastic energy losses as a whole, it does not result in essential mistakes.

Energy of ions changed from 2 up to 7 keV for carbon ions and from 10 to 100 keV for Ar18 ions. The velocity of ions at these energies is within the limits of 0.1-0.15 and 0.1-0.3 Hartree units, accordingly. In these specified areas, the elastic energy losses exceed inelastic ones and they are compared between them on the top limit. We also have carried out estimations of electronic stopping and nuclear scattering with use screening radius by Firsov [4] and Lindhard-Scharff [5], and also electronic stopping by Firsov [4] and Brice [6]. These estimations differ up to 30% from SRIM-calculations and we expect that this value is our estimations exactness.

Results of modeling we used for an estimation of energy, which can receive into electronic and nuclear subsystems of SWCNT from projectiles. Excitation and ionization of atoms can result in significant change of their interaction potential. The lifetime of excited state can exchange on the orders [7], in depending on the excitation amount, electron-electronic and electron-vibrational interaction in target. It can result in the various scripts of its local damage, which is observed at the fullerene fragmentation [8]. To avoid these situations we considered such energy range, in which the elastic losses dominate. Therefore we neglected change of interatomic interaction caused by inelastic losses of ions.

The calculated depth dependencies of elastic and inelastic energy, transferred to target atoms, from Ar ion are given in the Fig.1 for Ar ions with energy of 10 keV. These curves were obtained using SRIM2000 package. It is visible, that on all depths of a target, if ion energies are less then 10 keV, the inelastic losses are less elastic ones more than three times. Therefore it is possible to expect, that the basic mechanism of local SWCNT fragmentation in this case is determined by kinetic energy received carbon's atom. For C6 ions with energy of 2 keV the elastic/inelastic losses ratio is not less two, and it is decreased at higher energies.

To account of average energy transferred to an individual atom by a collision we divided the calculated energy losses by the particles concentration and then multiplied of this result by the total cross section, which is equal to the interatomic distance square. As a result we have received the following estimations: $E_{el} \approx 41$ eV and $E_n \approx 137$ eV. If it to take into account, that the energy of excitation is distributed among several electrons, and the elastic scattering energy is transferred to the nearest atom, these values justify neglect of inelastic losses even in the first approximation. Since E_n exceeds of radiating defect energy ($E_d \approx 25$ eV for C6 ion) in some times, hence an Ar18 ion with energy of 10 keV can knock out from one to several nearest SWCNT atoms in depending to the collision conditions. The multiatomic damages probability decreases quickly with atoms amount increasing. Similar estimations for C6 ions with energy of 2 keV give $E_{el} \approx 19$ eV and $E_n \approx 37$ eV. Therefore in this case the inelastic losses are not neglect small, as the elastic scattering energy is not much more exceeds E_d . If the ion energy is increased, then the relative contribution of electronic excitation increases too and the local SWCNT fragmentation should be determine by both channels of energy losses.

Thus, the analysis of modelling results at the described above assumptions, allows to make such qualitative conclusions. At energy of Ar18 ions about 10 keV the local SWCNT damages will be determined by the elastic scattering of an ion, which results to knocking-out from one to several nearest carbon atoms. The electronic excitation can be neglected as

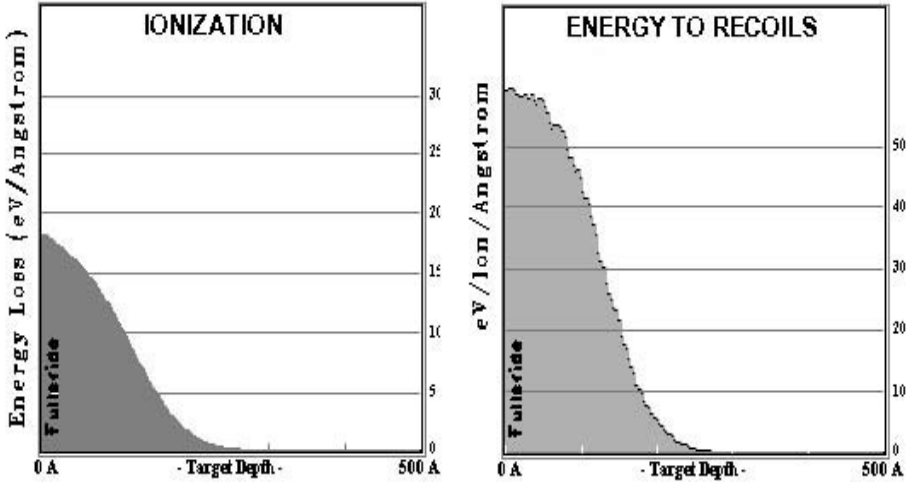


Figure. 1. The calculated depth dependencies of elastic and inelastic energy transferred to the target atoms from Ar ion.

a first approximation. For atoms of carbon the similar situation is absent at all energies large than 2 keV.

The obtained above results testify to the possible formation of different topological pentagon-heptagon pair defects under SWCNT irradiation, for example: a) (5-7-7-5) Stone-Wales defect [9] and b) (5-7-8-7-5) defect [10]. Therefore, the next task of our work was to calculate the conductivity of the metallic (10,10) SWCNT with such radiation defects.

The calculation of the conductivity was carried out by use the Landauer formalism [11]

$$C = \frac{2e^2}{h} T(E), \quad (1)$$

where $T(E)$ is a transmission function of the considered system:

$$T(E) = \text{Tr}[\Gamma_2 G \Gamma_1 G^+]. \quad (2)$$

Here G is a Green function for the SWCNT and Γ is a coupling function connected with defect formation in the SWCNT [12].

Fig. 2 shows the calculated conductivity for the both pure and imperfect SWCNT. As one can see the topological defects always sharply decrease the conductivity of metallic (10,10) SWCNT as a result of symmetry breaking along the SWCNT. It is to note also that this effect is strongly dependent on the number of created defects.

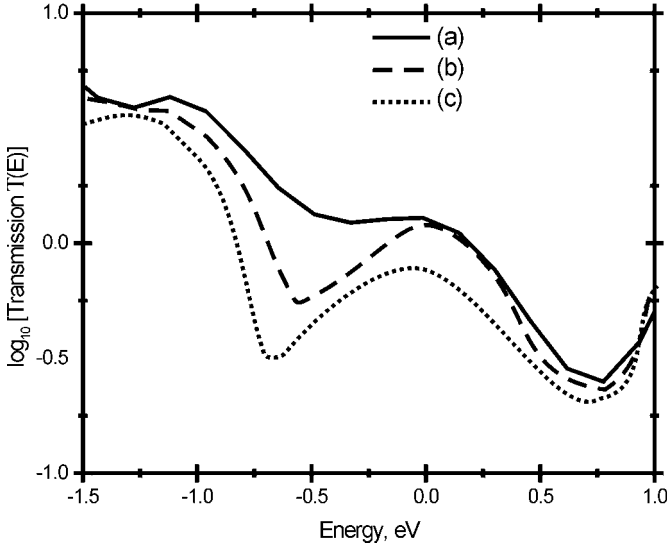


Figure. 2. Transmission function $T(E)$ for the pure (a) (10,10) SWCNT and with different defects: (b) 5-7-7-5 and (c) 5-7-8-7-5.

Acknowledgements

This work was partly supported by INTAS Grant (N 2136).

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CALCULATION OF THE DENSITY PROFILE OF LIQUID LOCATED IN THE MULTI-WALLED CARBON NANOTUBE

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Abstract

The density profile of liquid located in a multi-walled carbon nanotube was calculated using the solution to the isoperimetrical problem of the minimization of a free energy of the system in the limited volume for the constant number of particles. It was shown that far from the critical point a substantial change in the density occurs only in the near-wall layer, whereas near the critical point a significant change of density takes place in the entire volume of the liquid.

1. Introduction

Since their official discovery in 1991, [1] carbon nanotubes (CNTs) have been the target of a rapidly growing number of investigations, mainly due to their wide range of potential applications, from nanowires and molecular containers to biosensors [2, 3]. Many studies addressed the structure, mechanical properties and electronic properties of these CNTs, but only a limited attention has been paid to the thermal fluid aspects of their existence or their potential fluidic applications.

Multi-walled hollow CNTs (MWNTs) possess extremely high rupture strength [4] which, when combined with their ability to provide a conduit for fluid transport at near-molecular length scales, makes them attractive candidates for implementation in future micro- or nanofluidic devices. A new application of nanotubes in flow sensors has been recently suggested [5]. Therefore, understanding fluid behavior in nanochannels is important for the proper design and efficient operation of such devices.

Conventional experimental techniques using cylindrical capillaries with radii in the range 40-200 nm were employed [6] to reach the conclusion that the surface tension of water at these scales does not differ from the bulk values in the temperature range 281-343 K. Other experimental studies of capillary phenomena in subnanometer channels have also been performed [7], but the reported results were based primarily on bulk-type measurements. In some cases, CNTs have been filled, at least partially, with molten materials (liquid metals, salts, oxides) through capillary action [8-10], but little has been reported on the dynamic

aspects of fluid transport in CNT. Recently, studies of fluid interface motion in nanochannels of MWNTs with an outer diameter of about 100 nm and a length from 1 to 10 μm were performed using a transmission electron microscope [11-13]. Good wettability of the inner carbon walls in hydrothermal carbon nanotubes by the water-based fluid was shown. Fully reversible interface dynamic phenomena were visualized and an attempt was made to explain the origin of this fine-scale motion.

However, a fundamental question of whether fluids behave as continua at the length scales down to a nanometer or less is still to be answered. In particular, it is necessary to carry out the calculation of the spatial (along the tube radius) distribution of the density of liquid [14-16] for calculating the degree of the CNT filling by liquid. It is important to note that the generally accepted local relationship for calculating the density in nanosystems is not applicable far from the critical point. Therefore, it is necessary to use a relationship, which takes into account the correlations in the Percus-Lebowitz approximation⁹. Furthermore, in the case of a confined system, the obtained solution must satisfy not the standard condition of equality of the system density at infinity to the average density, but an integral condition relative to density (isoperimetrical condition). Thus, in our opinion, the above reasons can lead to significant deviations in density from the density in the local approximation. This is very important for the study of fluid dynamics in CNT.

2. Results and Discussion

2.1. THEORY.

For calculating the local density profile of liquid $\rho(\vec{r})$ in the presence of the external field $v(\vec{r})$, where $\vec{r}$ is the spatial coordinate, it is necessary to solve the problem about the minimization of free energy of system Ψ as functional $\rho(\vec{r})$ [17]

$$\Psi = \int_V d\vec{r} \cdot \psi(\rho(\vec{r})), \quad (1)$$

where $\psi(\vec{r})$ is the free-energy density, and V is the volume of system. Dependence $\psi(\vec{r})$ on the coordinate in the external field in the approximation of smooth heterogeneity (sufficiently low gradients of density) takes the form [18].

$$\psi(\vec{r}) = \psi_0(\rho(\vec{r})) + \frac{A}{2} [\nabla \rho(\vec{r})]^2 + (v(\vec{r}) - \mu) \rho(\vec{r}), \quad (2)$$

where $\psi_0(\rho(\vec{r}))$ is the free-energy density in the local approximation (i.e., it is determined by the equation of state of a uniform system), μ is the chemical potential of the ensemble; $A = \xi^2 / \chi$, where ξ is the correlation radius and $\chi = \left(\frac{\partial \mu}{\partial \rho} \right)_T$. Let us note

that both ξ and χ as functions of $\rho(\vec{r})$ depend in the general case on $\vec{r}$ ¹⁸. In the local approximation, the density profile is determined by the algebraic equation which follows from equation (2)

$$\mu_0(\rho(\vec{r})) + v(\vec{r}) = \mu, \quad (3)$$

where $\mu_0(\rho(\vec{r})) = \frac{\partial \Psi_0}{\partial \rho}$ is the local value of chemical potential¹⁸.

In the confined system, external field is created also by the limiting surfaces of the system and the problem of the calculation of dependence. $\rho(\vec{r})$ is complicated by the imposition of condition of the constancy of the number of particles N (mass m) of the system:

$$N = \int_V d\vec{r} \cdot \rho(\vec{r}). \quad (4)$$

After taking into account equation (1), equation (2) takes the form:

$$\Psi = \int_V d\vec{r} \cdot \left\{ \psi(\rho(\vec{r})) + \frac{A}{2} [\vec{\nabla} \rho(\vec{r})]^2 + (v(\vec{r}) - \mu) \rho(\vec{r}) \right\}. \quad (5)$$

In the one-dimensional case, when $v(\vec{r}) = v(x)$, the problems (3) - (4) take the form

$$\Psi = \int_V dx \cdot F(x, \rho, \rho'), \quad (6)$$

$$N = \int_V dx \cdot G(x, \rho, \rho'), \quad (7)$$

where

$$F(x, \rho, \rho') = \psi(\rho(x)) + \frac{A}{2} [\rho'(x)]^2 + (v(x) - \mu) \rho(x), \quad (8)$$

$$G(x, \rho, \rho') = \rho(x) \quad (9)$$

The problem of the minimization of function (6) under the condition of constancy (7) is known as the isoperimetrical problem [19]. Using the Lagrange indeterminate coefficients allows us to obtain a differential equation of the Euler-type

$$F_\rho - \frac{d}{dx} F_{\rho'} + \lambda \left(G_\rho - \frac{d}{dx} G_{\rho'} \right) = 0 \quad (10)$$

under the transversality conditions

$$\left(\frac{\partial F}{\partial \rho'} + \lambda \frac{\partial G}{\partial \rho'} \right) \Big|_{x=a} = 0, \quad \left(\frac{\partial F}{\partial \rho'} + \lambda \frac{\partial G}{\partial \rho'} \right) \Big|_{x=b} = 0 \quad (11)$$

and isoperimetrical condition (7), where λ is the Lagrange indeterminate coefficient; a and b are the coordinates of the system boundaries. Equation (10) under the conditions (7) and (11) takes form

$$\frac{d\psi}{d\rho} + v(x) + \lambda - \mu - \frac{d}{dx} A\rho' = 0 \quad (12)$$

under the transversality conditions

$$\rho' \Big|_{x=a} = 0, \quad \rho' \Big|_{x=b} = 0 \quad (13)$$

and isoperimetrical condition

$$\int_a^b dx \cdot \rho(x) = n, \quad (14)$$

where $n = \rho_0 \cdot (b - a)$ and ρ_0 is the average density of filling. Conditions (13) - (14) allow us to determine the Lagrange coefficient λ and two constants of the differential equation (12).

2.2. MODEL AND DISCUSSION.

As the simplified model of the multi-walled CNTs (with the inner radius L and a length which considerably exceeds the CNT diameter of $2L$) one can consider an infinite plane-parallel layer with the thickness of $2L$. The deviations of density ρ from the average density of the filling ρ_0 will be considered to be sufficiently small ($\rho_0 \ll \rho$). In this case, the average density of filling is determined by the expression:

$$N = 2L \cdot \rho_0. \quad (15)$$

Attracting or repulsive forces may act near the walls depending on the wettability of the tube surface. Their potential is determined by the following expression

$$v(x) = 2Be^{-kL}ch kx, \quad (16)$$

where B is the amplitude ($B > 0$ corresponds to the attracting forces, and $B < 0$ corresponds to the repulsive forces) and k^{-1} is the radius of action of these forces. Further, it is necessary to expand function $\Psi(x)$ in the Taylor series according to degrees $\rho - \rho_0$, limited by the quadratic term. In this case:

$$\frac{d\psi}{d\rho} = \chi^{-1} \cdot (\rho - \rho_0). \quad (17)$$

Then the fundamental equation for the calculation of $\rho(x)$ will take the form

$$2A\rho'' - \chi^{-1}\rho = \{\lambda - \mu - \chi^{-1}\rho_0\} + 2B \cdot e^{-kL}ch\kappa x, \quad (18)$$

or

$$\rho'' - \kappa^2\rho = E + 2F \cdot ch\kappa x, \quad (19)$$

where

$$E = \frac{\lambda - \mu - \chi^{-1}\rho_0}{2A}, \quad F = \frac{B}{2A}e^{-kL}, \quad \text{and} \quad \kappa = (2\chi A)^{-1/2} = \frac{1}{\sqrt{2\xi}}. \quad (20)$$

The obtained equation must be solved under the following transversality conditions

$$\rho'(L) = 0, \quad \rho'(-L) = 0 \quad (21)$$

and the isoperimetrical condition

$$\int_{-L}^L dx \cdot \rho(x) = n. \quad (22)$$

Solution (19) under the conditions (21) - (22) takes the form:

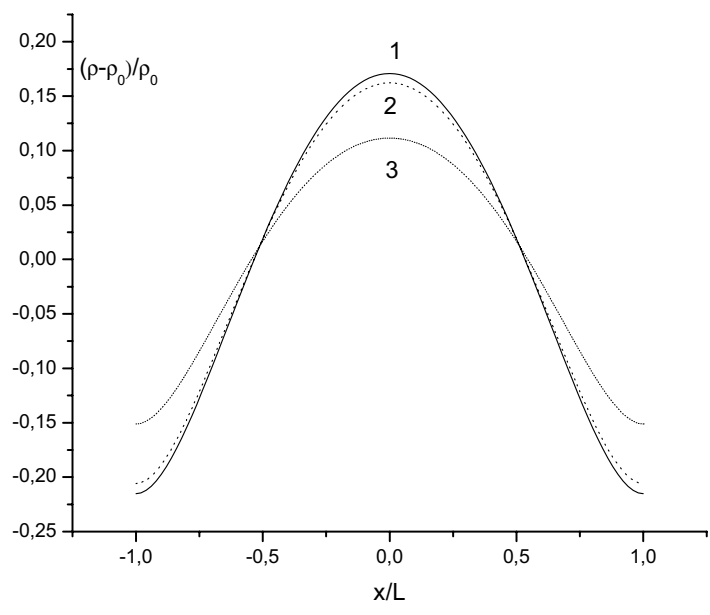
$$\rho(x) = -\frac{2Fk/\kappa}{k^2 - \kappa^2} \cdot \frac{sh\kappa L}{sh\kappa L} \cdot ch\kappa x + \frac{n}{2L} + \frac{2F}{k\kappa^2 L} \cdot sh\kappa L + \frac{2F}{k^2 - \kappa^2} \cdot ch\kappa x. \quad (23)$$

Fig. 1 shows the relative density profiles of liquid $\frac{\Delta\rho}{\rho_0}$ in the MWNT with different inner radia: a) $L=5$ nm; b) $L=25$ nm and c) $L=50$ nm at $k^{-1}=0.3$ nm under the various values of a correlation radius ξ . The case $\xi=L$ corresponds to the critical point in the limited system.

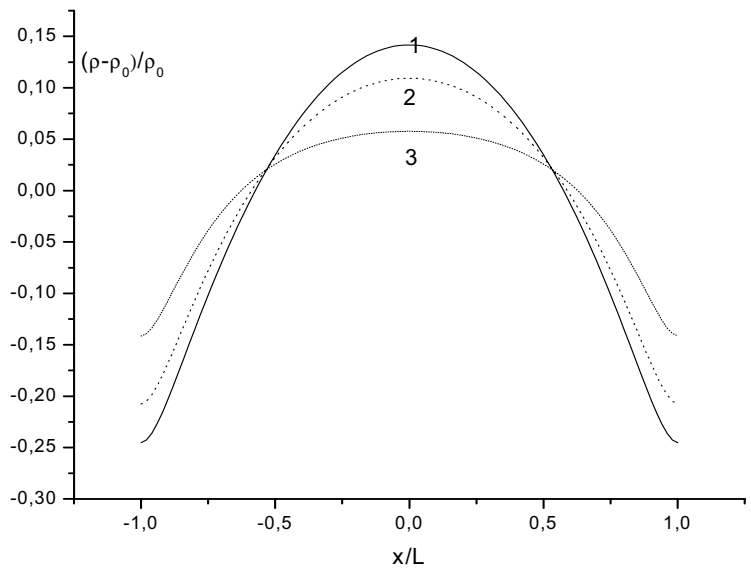
It is interesting to note that if the system is far from the critical point, then substantial changes in the density only occur in the layer whose thickness is of the order the radius of action of surface forces, i.e. k^{-1} . This is in agreement with previous work by Derjaguin.²⁰ However, when a critical point is approached, substantial changes in the density occur in the layer with the thickness of the order of a correlation radius ξ .

As one can see from Fig. 1, the deviation of density ρ from its average value ρ_0 exceeds 10% at $\xi > 10$ nm. Thus, for this nanosystem the assumption about $\frac{\Delta\rho}{\rho_0}$ being a small value

becomes unacceptable, i.e., it is necessary to take into account the terms of higher order on the $\rho - \rho_0$ in expansion (17). This leads to the fact that equation (17) becomes substantially nonlinear and does not have an analytical solution. However, even the solution obtained in the linear approximation suggests that the density of liquid essentially depends on the coordinate x near the critical point.



a)



b)

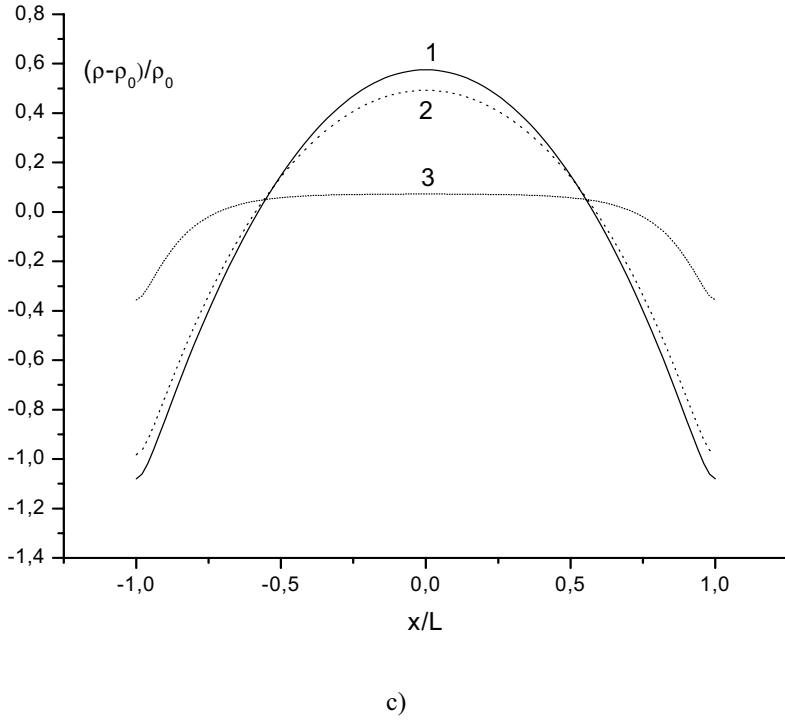


Figure. 1. Dependence of relative density $\frac{\Delta\rho}{\rho_0}$ on the coordinate x for the tube radius: a) $L=5$ nm; b) $L=25$ nm and c) $L=50$ nm at different values of correlation radius ξ : a) 1 – 5 nm; 2 – 3.5 nm; 3 – 1.5 nm ($B=10^{-22}$ J); b) 1 – 25 nm; 2 – 10 nm; 3 – 5 nm ($B=10^{-23}$ J); c) 1 – 50 nm; 2 – 25 nm; 3 – 5 nm ($B=2 \cdot 10^{-23}$ J).

3. Conclusions

The calculated in this work density profile of liquid in MWNT shows that a substantial change in the density occurs only in the near-wall layer, when the system is far from the critical point. Near the critical point, a significant change of density takes place in the entire volume of the system. Thus, the density of liquid essentially depends on the distance from the tube wall near the critical point.

The density profile of liquid obtained within the framework of the proposed model can be used for analysis of the pressure of water and other liquids located in the multi-walled CNTs.

Acknowledgements

Y.G. was supported by the US National Science Foundation under grant CTS-0196006. L.M. was supported by the STCU grant N1618.

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SMALL METAL CLUSTERS: *AB INITIO* CALCULATED BARE CLUSTERS AND MODELS WITHIN FULLERENE CAGES

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Abstract

Several models of small metal clusters Ag_n and Cu_n ($n < 5$) within the fullerene molecule C_{60} were constructed to estimate their possible stability and properties. With *ab initio* SCF MOLCAO method the bare metal clusters Ag_n , Cu_n and the structures $\text{C}_{60}\text{-M}_n$ with $n=1,2,4$ were calculated. Comparison of binding energies of the clusters shows that monoatomic $\text{C}_{60}\text{-M}$ are stable both for silver and copper, while in the case of di- and four-atomic $\text{C}_{60}\text{-M}_n$ the structures with copper atoms are much more favorable than those with silver. An embedding of metal clusters into C_{60} molecules is accompanied by its little distortion, but large distortion of the clusters does not correspond to stable structures. Stable structures reveal the effect of charge transfer from the fullerene cage to metal atoms resulting in positive charge for metal clusters. The models $\text{C}_{60}\text{-Cu}_2$ and $\text{C}_{60}\text{-Cu}_4$ with tetrahedron Cu_4 are proposed for search as possible candidates in experimental metal-fullerene systems.

1. Introduction

In the context of nanometer science and technology small clusters occupy a challenged place as objects with transitive features between atomic species and continuous bulk solids [1, 2]. There exists an eternal question “how closely cluster features approximate the corresponding bulk counterparts?” The fullerene family, including C_{60} and the larger molecules C_n , $n > 100$, is the clear example of similar “non-bulk” species. However, in the case of metals, M_n , too big number of atoms usually provides the behaviour like to bulk metals. The metal-doped fullerenes, both endohedral and exohedral [3-6], are formed due to electron-acceptor character of the fullerene electronic shell with which alkali or earth-alkali atoms can easily interact. On the other hand, few-atomic clusters of less active metals, like Ag, Cu, Au, can exist in the form of stable species in different media [7-10]. They can be easily produced in liquid and gaseous medium due to aggregation of metal atoms [8,11,12], however, the stabilization may be attained only through incorporation of the clusters into solids. Various nanoporous media and zeolites [13-17] are materials with stable few-atomic metal clusters, meanwhile copper and silver clusters and nanoparticles were produced also in carbon nanotubes [18]. The key mechanism of the stabilization can be simple geometrical one (cage effect), but a cluster-matrix interaction is also quite possible in similar systems. In the present paper, we consider the other example of the metal-cluster-in-a-cage system, few-atomic Ag_n and Cu_n within fullerene molecule C_{60} . This system now is just hypothetical one, and it is of interest both from the point of view of understanding the

metal- C_{60} bonding and as the unique stabilization of metal clusters with non-trivial optical, magnetic and catalytic properties [1,2,13-17]. A feasible size of metal clusters is dictated by their geometry and values of the equilibrium interatomic distances, Ag-Ag and Cu-Cu (about 2.8 Å and 2.3 Å), varied slightly from diatomic molecules to bulk. These data provide possibility of the clusters of these metals up to $M_{4,5}$ to be within the fullerene cages. We have calculated several models and compare them with data of the bare M_n clusters.

2. Calculation Technique and Cluster Models

For the simplest problem of small metal clusters within the fullerene cage we consider a series of clusters M_n with nuclearity $n < 5$ those can fit the C_{60} cage (Fig. 1). The structures of different geometry were taken for four-atomic species, and the whole set includes thus OD monoatomic structures, i.e. single atoms (M) within the cage, 1D structure (M_2) within the cage, 2D (planar M_4) and the 3D case (tetrahedral M_4). A final geometry of $C_{60}-M_n$ was searched by the full optimization and any distortion from the initial I_h symmetry of fullerene molecule was allowed. Location of the metal atoms within it was also arbitrary, and as the results the structures of minimum energy $C_{60}-M_n$ were obtained. Thus, an effect of “fullerene-shell” was considered upon geometrical characteristics of the clusters and vice versa – the effect of clusters upon the fullerene cage geometry. The task on equilibrium geometry was restricted for ground states of the whole molecules.

The calculation method used was *ab initio* self-consistent field Hartree-Fock (SCF HF) within the MOLCAO approach (molecular orbitals – linear combination of atomic orbitals). The basis sets were constructed from 19e effective core potential (ECP) for Ag, and the all-electronic basis sets of 6-31G and STO-3G quality for Cu and C, respectively, were used. The calculations were done with a NWChem 4.1 software [19] and the basis sets library within the standard package.



Figure 1. Metal cluster structures considered in the model of $C_{60}-M_n$

3. Results and Discussion

The first easy model is one metal atom within the fullerene cage $C_{60}-M$ (Fig. 2). They are stable both for $C_{60}-Ag$ and $C_{60}-Cu$ that was estimated via the values of binding energies as the difference of total electronic energies of the optimized $C_{60}-M$ and the separated constituents: C_{60} and M. The $C_{60}-Ag$ model possesses the essentially higher binding energy than $C_{60}-Cu$, 10.15 eV against 2.73 eV, respectively. These monoatomic metal endofullerenes appear noticeably deformed from the perfect initial geometry. In the case of silver this deformation is a slight whole extension of the whole cage, the minimum C-C distance grows from 1.38 Å up to 1.40 Å (our data on geometry of C_{60} molecule are in accordance with previous calculations, e.g. [20]), and the maximum one does from

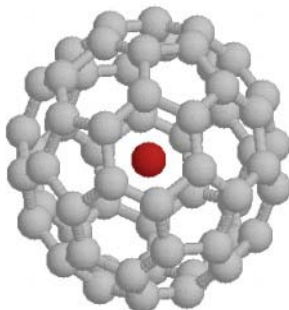


Figure 2. The structure considered in the model of C_{60} -M

up to 1.54 Å, respectively. Meanwhile, in the case of copper this deformation looks like the axial extension: the minimum value of C-C distance decreases by ~ 0.04 Å and the maximum one becomes 1.53 Å instead of 1.46 Å in the molecule without copper atom. The next essential factor of the difference between silver and copper single atoms stabilized within C_{60} is the conservation of initial symmetry of the C_{60} molecule, but the shift of Ag atom about 0.24 Å from the center. That effect can result in appearance of magnetic moment of this structure and was reported recently for the endohedral La atoms [21]. Metal atoms within C_{60} molecule acquire negative charges: $-0.1e$ in the case of silver and $-0.42e$ for copper. The charge transfer occurs, consequently, from the C_{60} cage to metal atoms. Thus, one copper atom has the more noticeable effect upon C_{60} molecule being inside it than one silver atom in C_{60} -Ag.

Table 1. The energies of HOMO and LUMO and the major contributed AOs

Model	HOMO, eV	Basic contributions	LUMO, eV	Basic contributions
C_{60}	-5.62	$p_z, p_x, p_y(C)$	+3.03	$p_z, p_x, p_y(C)$
C_{60} -Ag	-5.04	S(Ag)	+4.98	$p_x, p_y(Ag) + p_x, p_y(C)$
C_{60} -Cu	-0.90	S(Cu)	+4.05	$p_x(C)$
C_{60} -Ag ₂	-2.11	$d_{yz}(Ag) + p_z(C)$	-1.07	$p_z, p_y(C)$
C_{60} -Cu ₂	-3.02	s(Cu)	+3.04	$p_x, p_y(C)$
C_{60} -Ag ₄	-6.51	$d_{yz}, d_{yz}(Ag) + p_y(C)$	-1.67	$s(Ag) + p_y(Ag)$
C_{60} -Ag ₄ T	-1.99	$s, p_z(Ag) + p_y, p_z(C)$	-0.49	$s(Ag) + p_y, p_z(C)$
C_{60} -Cu ₄	-1.55	$s(Cu) + p_y, p_z(C)$	-0.40	$p_x, p_z(C)$
C_{60} -Cu ₄ T	-1.66	$s(Cu) + p_y, p_z(C)$	-0.45	$p_x, p_z(C)$

Table 2. The effective charges at metal atoms in the structures under calculation

C_{60} -Ag	-0.1			
C_{60} -Cu	-0.42			
C_{60} -Ag ₂	-1.34	-1.34		
C_{60} -Cu ₂	+0.27	+0.27		
C_{60} -Ag ₄	-0.81	-0.81	-1.01	-1.01
C_{60} -Ag ₄ T	-0.31	-0.31	-0.25	-0.25
C_{60} -Cu ₄	+0.29	+0.29	+0.01	+0.01
C_{60} -Cu ₄ T	+0.23	+0.23	+0.20	+0.20

The models with diatomic clusters within the fullerene molecule (Fig. 3) show very different stability for C_{60} -Ag₂ and C_{60} -Cu₂. The first appears to be instable, the second one has the binding energy (the difference between total electronic energies of C_{60} -M₂ and the sum of these values for C_{60} and M₂) 1.61 eV. This value of binding energy for C_{60} -Cu₂ is rather small, less than 0.03 eV per one atom. Hence, the structures C_{60} -M₂ appear to be more favorable with copper.

In the model C_{60} -Ag₂ the calculated Ag-Ag interatomic distance in the optimized structure is 2.37 Å, i.e. Ag₂ molecule is very strained that can be a reason of instability (Ag-Ag distance in Ag₂ is ~2.5 Å [22,23]). The interatomic distance for Cu₂ in C_{60} -Cu₂ is 2.18 Å that is only a little less than the distance of bare Cu₂, ~2.2 Å from the data of different authors [7,24-26]. In the case of C_{60} -Ag₂ a large deformation of the fullerene cage exists also: the minimum C-C distance becomes 1.36 Å, the maximum one extends to 1.51 Å. The C_{60} -Cu₂ model alters C-C distance in the range of 0.01 Å only.

Table 3. Selected interatomic distances in the optimized models, Å

Model	Minimum C-C	Maximum C-C	M-M			
C_{60}	1.38	1.46				
C_{60} -Ag	1.40	1.54				
C_{60} -Cu	1.34	1.53				
C_{60} -Ag ₂	1.36	1.51	2.37			
C_{60} -Cu ₂	1.38	1.47	2.18			
C_{60} -Ag ₄	1.39	1.58	2.30	2.31		
C_{60} -Ag ₄ T	1.40	1.55	2.40	2.44	2.52	2.54
C_{60} -Cu ₄	1.38	1.47	2.13	2.14		
C_{60} -Cu ₄ T	1.37	1.50	2.25	2.26	2.26	2.30

Another exponent of instability of C_{60} -Ag₂ is the big negative charge for each silver atom, -1.34e, showing that if this cluster would exist the large charge transfer is between the cage and silver atoms. In the case of C_{60} -Cu₂ model this effect is much less and reversed: each copper atom acquires the charge +0.27e, i.e. the transfer occurs from metal to the carbon cage. It should be remembered that in the case of models with monoatomic copper the direction of charge transfer was opposite. Thus, the clustering provides considerable changes in the bonding between the cage and metal atoms and appears to be very different for copper and silver, although in other aspects of small cluster properties these metals are similar.

A comparison of energies of the frontier orbitals in the models with diatomics, C_{60} -M₂, and the bare fullerene (Table 1) indicates that the rise of HOMO level occurs under formation of C_{60} -Cu₂, but formation of C_{60} -Ag₂ shifts up both HOMO and LUMO levels. HOMO is contributed mainly by s-orbitals of copper atoms in C_{60} -Cu₂, d-orbitals of silver together with p_z of carbon contribute in C_{60} -Ag₂. Orbitals of s-type from the metal atoms were also in HOMO of models with monoatomic metals, C_{60} -M. Hence, the stable binding of interior metal atoms and clusters is observed for active s-orbitals from metal atoms. That explains also known stability of C_{60} endohedral structures with alkali metals [5, 7].

The models with four-atomic clusters are most disputable within the scope of the present work since the proper size of these clusters provides evident restrictions on existence of stable structures. We have analysed the two types of these clusters: planar rhombus (that is known to be really stable in the case of bare clusters both Ag₄ and Cu₄ [27-30]), and tetra-

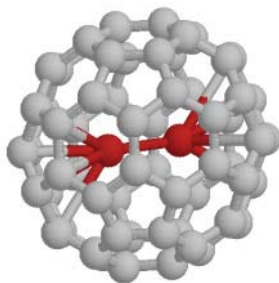


Figure 3. The structure considered in the model of $C_{60}-M_2$

hedron (Fig. 1). The latter bare cluster has the higher energy (1.54 eV for Ag and 0.58 eV for Cu), however, the tetrahedron is more compact to be embedable into fullerene cage.

According to our calculations the structures $C_{60}-Ag_4$ are instable with both types interior clusters, however, the structure with tetrahedron has the binding energy just -0.2 eV per atom. The planar rhombus results in the much more strained structure, -0.74 eV per atom and distorts the fullerene cage in the plane of silver atoms about 0.1 Ang. In spite of this deformation the interatomic Ag-Ag distances are about 2.30 Ang that is much less than the equilibrium Ag-Ag distance in bare clusters (2.7-2.8 Ang in different sources [26,28,29]). Thus the main reason of instability of this structure with planar rhombus Ag_4 is the strong effect of the cage upon silver cluster. HOMO in this structure includes big contribution of d-orbitals, that is not usual for small silver clusters in which d-orbitals are important for the whole bonding but lie rather low in the stable structures. This strain effect leads to large self-polarization of $C_{60}-Ag_4$ with charge transfer from the cage to silver atoms providing the charges of the order of $-1e$ at each atom. This direction of charge transfer was shown to correspond to instable structures also in the lower size interior silver atoms, $C_{60}-Ag_2$. Therefore, one can suppose that a large charge transfer to metal is not favorable for stability of endohedral fullerenes.

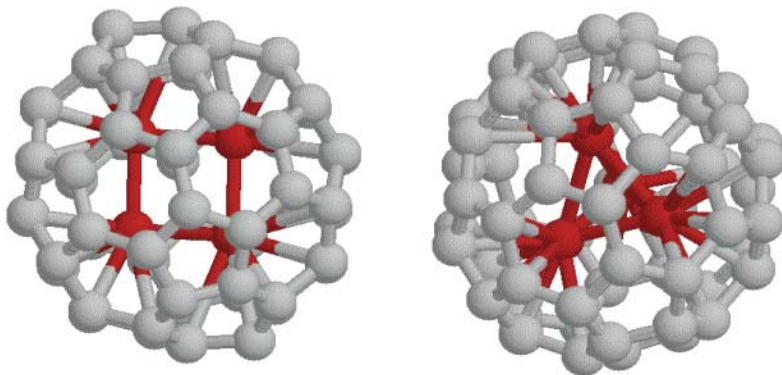


Figure 4. The structures considered in the model of $C_{60}-M_4$: planar M_4 and tetrahedron designed as M_4T

Both models of the four-atomic copper clusters within the fullerene cage, C_{60} -Cu₄, as well as C_{60} -Ag₄, possess negative binding energy, but its value is much lower for C_{60} -Cu₄ than for C_{60} -Ag₄. The planar rhombus Cu₄ in C_{60} -Cu₄ results in 2.73 eV, and the tetrahedron does 0.92 eV. An account of the number of atoms in the molecules gives the values of binding energy per atom 0.045 eV and 0.015 eV, respectively. Thus the stability of these models is very close to a threshold that means they should not be excluded as possible existing species. Our calculations include only electronic subsystem and do not count any temperature effects. Anyway, one can conclude that C_{60} -Cu₄ models appear to be much less strained than C_{60} -Ag₄, and one may suggest searching them in some experimental environment that admits both C_{60} and small copper clusters.

Among the two C_{60} -Cu₄ calculated we can observe that the model with tetrahedron has the optimized structure with distorted interior Cu₄. The four Cu-Cu distances obtained are different, from 2.26 Å through 2.30 Å while the equilibrium Cu-Cu distance of the bare tetrahedral Cu₄ is 2.28 Å (all four are equal) at the present theory level, while in another calculations this value appears to be rather variable, 2.2-2.5 Å [27,31,32]. The fullerene cage in this case are distorted slightly in axial direction (approximately on 0.04 Å). The rhombus in C_{60} -Cu₄ model, in contrast, is rather contracted: ~2.14 Å is the minimum Cu-Cu distance against the value in the bare cluster: 2.2-2.5 Å [27,29-32]. Thus, a reason of instability of C_{60} -Cu₄ can be the fact that Cu₄ clusters hardly fit the cage geometry, the tetrahedron Cu₄ can fit much better than the planar rhombus Cu₄ under the conditions that Cu-Cu distances should be not strongly deviated from equilibrium values of the corresponding bare clusters. Similar effect was in the case of C_{60} -Ag₄ models, but the values of these distortions are too large, and the models with Ag₄ are far to be stabilized. An analysis of effective charge distribution in C_{60} -Cu₄ models shows no large polarization (in contrast with C_{60} -Ag₄), and the direction of the charge transfer is from metal to carbon (Table 2). That is like to alkali atom appearance (those, evidently, are positive charged) within C_{60} molecules [4,5].

The results of calculations indicate also that in the four-atomic clusters in C_{60} the HOMO-LUMO gap shrinks strongly, HOMO goes up from -5.62 eV in C_{60} to 1.66 eV in C_{60} -Cu₄, HOMO is formed by s-orbitals of copper and p-orbitals of carbon. Instable C_{60} -Ag₂ and C_{60} -Ag₄ structures include contributions from other types of orbitals of silver atoms, either p- or d-ones (Table 1).

4. Conclusions

The present calculations of the C_{60} -M_n models with metal clusters embedded into the fullerene molecule are the first attempt, for our best knowledge, to analyse di- and four-atomic copper and silver clusters within C_{60} . There is *a priori* feasibility to embed Cu₂₋₄ and Ag₂₋₄ from the opinion of geometrical matching. The calculations performed at the *ab initio* SCF HF level with the ECP basis set for silver and all-electron basis sets for copper and carbon showed that these expectations are not too far from conclusions done on the basis of energetic positions. The models considered are very different in variation of electronic structure due to metal cluster embedding, the values of binding energy, change of geometrical parameters and charge distribution. The structures C_{60} -Cu, C_{60} -Cu₂ and C_{60} -Cu₄ (tetrahedron) can exist, being formed in some systems of simultaneous production of fullerene cages and metal clustering. In this case C_{60} molecule can serve as a selector of the

few atomic metal clusters since $C_{60}-M_n$ with $n>4$ may not exist because size of possible clusters is not allowed by the C_{60} geometry.

In the stable monoatomic $C_{60}-Ag$ and $C_{60}-Cu$ the fullerene cage is distorted in spite of spherical symmetry of embedded entities, and the charge transfer occurs from cages to metal atoms. The cage is less distorted in $C_{60}-Ag$, and this model is more stable than $C_{60}-Cu$. However, di- and four-atomic structures $C_{60}-M_n$ with silver show the reversed charge transfer and they are instable. The reason of their instability is a necessity for the silver cluster embedded to be strongly deformed in comparison with bare clusters. In contrast, Cu_2 retains its geometry of bare cluster, and Cu_4 (tetrahedron) is slightly disturbed only being within C_{60} . The frontier orbitals in both the stable and instable structures comprise s- and d-function of metal atoms together with p-functions of carbon, but the higher stability corresponds to contribution of s(Cu)- and s(Ag)-orbitals into HOMO. Therefore, $C_{60}-M_n$ can behave as s-metals in chemical and physical properties.

A searching of experimental verification of the models considered in the present work can be proposed under reactions of C_{60} molecules with metal atoms or clusters M_{2-4} and in the process of simultaneous formation of C_{60} combined with metal atom condensation [33-36]. A great tendency of silver and copper to clusterization can provide more probability of these metals to be incorporated in C_{60} as clusters than as single atoms.

Acknowledgements

The work was performed under partial support of Ministry of Education of Belarus. Author thanks attendees of ARW NATO in Ilmenau, 2003, for helpful discussions.

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NANOPARTICLE REACTIONS ON CHIP

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Abstract.

The handling of heterogenous systems in micro reactors is difficult due to their adhesion and transport behaviour. Therefore, the formation of precipitates and gas bubbles has to be avoided in micro reaction technology, in most cases. But, micro channels and other micro reactors offer interesting possibilities for the control of reaction conditions and transport by diffusion and convection due to the laminar flow caused by small Reynolds numbers. This can be used for the preparation and modification of objects, which are much smaller than the cross section of microchannels. The formation of colloidal solutions and the change of surface states of nano particles are two important tasks for the application of chip reactors in nanoparticle technology. Some concepts for the preparation and reaction of nanoparticles in modular chip reactor arrangements will be discussed.

Nanoparticles are of particular interest for nano construction technologies and for molecular recognition, because they can behave both as small robust solids and specifically reacting chemical species. Therefore, they moved into the focus of interest for labeling procedures in biochip applications for a few years. DNA-substituted Au nanoparticles are suited as labels for optical as well as for electrical detection of molecular interactions at DNA chips. A fast read-out of biochips and an optical detection of single binding events can be achieved if chemical amplification of nanoparticles by metal-catalyzed metal deposition is applied. It is assumed, that chip reactors will used for the preparation of nano particles and for their investigation. Nanoparticle technologies will promote biochip application as well as chip reaction technologies in near future.

1. Introduction

In chip fabrication, chemical processes play a crucial role. So, chemical liquid and gas phase processes are used for material preparation, thin film deposition and lithographic etching, e.g. The potential of chemical processes is connected with its high possible spatial resolution which is related to the molecular dispersity of the components in the media.

Particles must be avoided normally in all fabrication steps in lithographic micro and nano technology. But, nano particles are of interest for new materials and for the construction of nanosystems. Nanoparticles have been moved in to the focus of interest due to their

promising specific properties usable for nano architectures with new functions. Different types of micro fluid devices chip reactors were developed during the last decade [1]. Miniaturized reactors are addressed to the reduction of costs and risks in chemical, micro biological and microbiological processes. Micro reactors were developed for separation, detection and other analytical procedures [2-4]. Micro total analysis systems are focussed on miniaturized methods for analytics with small volumes [5-6]. Nanotiterplates were developed for applications in combinatorial chemistry and high throughput screening [7-9]. Chip thermocyclers were prepared for fast PCR processes in DNA analytics [10-15]. The problem of the choice of technologies for the constructions of nano systems cannot be longer defined as a size gap between biological or molecular features and microlithographic features. Biological micro objects as well as larger biological molecules cover the length range up to more than 10 microns. And, features made by nano lithography in the frame of planar technology are serially produced down to the sub-100nm-range (fig. 1). The problem consists of the gap between synthetic chemical and biological methods and preferred materials on the one hand and physical and inorganic chemical technologies in microfabrication on the other hand. The use of nano particles on chips and their generation and modification on chip surfaces and in chip devices show that this methodical and technological gap can be overcome [16]. Physical principles like laser tweezing or dielectrophoresis support precise manipulation of particles and cells inside micro channels [17]. In this contribution, production, modification and application of nano particles on chip surfaces and in chip devices is discussed and some examples are presented.

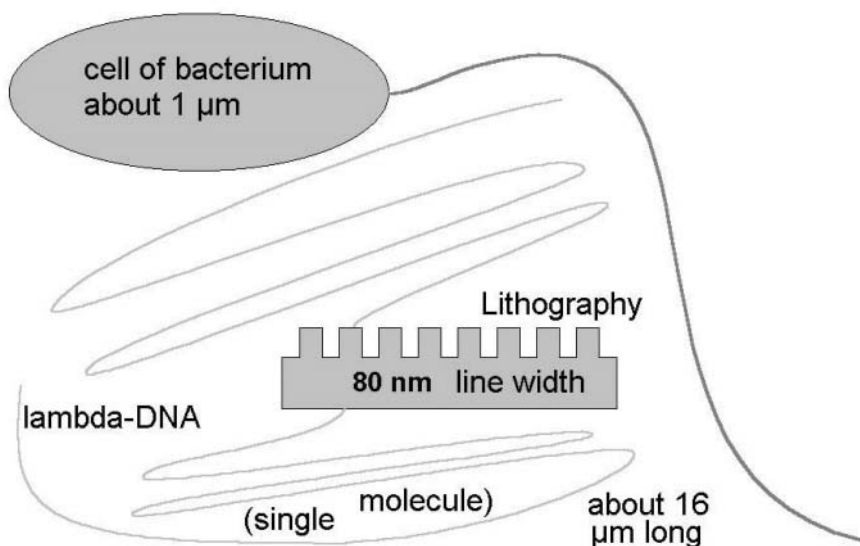


Figure. 1 Comparison of sizes of biological, molecular and technical micro objects

2. Particles for solid phase chemistry in chips

Solid-phase chemistry was introduced about four decades ago in order to improve the yield of synthesis processes consisting in a longer chain of synthetic steps. This method was particular succesful in the application of modular chemical processes like the solid-phase synthesis of peptides. The great advantage consists of the easy possibility of application of high excesses of reaction partners in the mobile phase leading to chemical equilibria in surface reactions, that are strongly shifted into the direction of products and in the possibility of stringent rinsing and, thus, the radical reduction of educts and byproducts.

Normally, larger ensembles of micro particles filled in columnes or filter cups are used for the solid phase synthesis. But, in microtechnical chemistry it is possible to use exactly one micro bead as reaction site. This microbead must be well defined by chemistry and geometrical situation. Therefore, micro chips are used for defining the position and the reaction environment in processing single beads.

By use of nanotiterplates, it was possible to arrange large arrays of single beads, each precisely adressable and distictable by its own position in the array (fig. 2). Typically, surface functionalized micro beads with diameters between about 40 μm and 0.2 mm diameter are used [8]. The volumes of a single micro fabricated chamber ranges between about 20 nl and 600 nl. The nanotiterplates for single-bead processing consist of arrays of micro compartments equipped with thin film bottom membranes containing micro pores of well defined size. So, liquids can be filled at moderate pressure into the micro chambers without loss through the bottom pores. But, after the reaction at higher pressure differences, the process liquid can be sucked out from the chamber in order to get beads with clean well-defined surface-attached products. Dispensing of process liquids, synthetic coupling, sucking-out and washing can be performed many times, if more complex synthesis programs are carried-out.

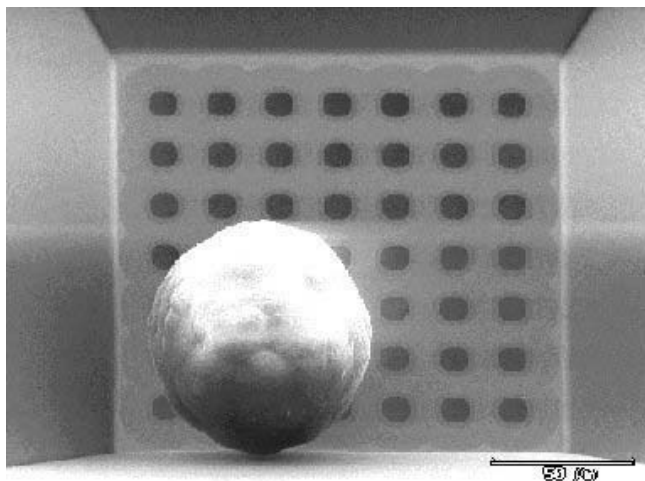


Figure. 2 Polymer micro bead for single-bead synthesis on chip at the micro sieve bottom of a 150-nl compartment in a Si nano titerplate made by thin film technology and microlithographic etching

Alternative to micro titerplates, synthetical and analytical operations can also be performed at surfaces of beads manipulated in flow channels. In contrast to conventional chromatographic columnnes, miniaturization opens the way to the handling of small particle ensembles and to single particle handling. Particles transported in micro fluidic networks can be processed by chemical coupling, cleavage of groups and cleaning. The solid phase gives the opportunity to change the ratio of transport rates of particles and surrounding liquids using dielectric manipulation, micro sieves or laser tweezers. So, particles can be operated through complex process chains.

3. Nanoparticles in planar chip arrangements for electronic devices

Specific properties of nano particles ("nano beads") related to their small size make them interesting for integration in planar structures in electronic chip devices. Nanobeads with chemically functionalized surface can be immobilized by specific binding like molecules. This behaviour is caused by the low number of atoms which are in contact with a plane surface at the same time, what reduces the effect of unspecific binding (adsorption) by a cooperative effect of a group of weak interactions. So, stronger specific bonds dominate in the interaction between nano particles and surfaces.

The specific chemical reactivity of functionalized beads can be used for the localized immobilization of chains of beads. So, a chain of metal nano beads can be produced, if they are coupled to a multifunctional molecule previously attached to the surface. A molecule supported nano electrode is formed by the chain of nano particles and can connect two lithographically prepared planar electrodes. The mesoscopic properties of metal nano beads are of particular interest for new types of electronic devices. So, the ability of nano beads to act as electron confinements can be used if the particles are immobilized in such a way inside a gap between planar electrodes, that two tunneling contacts are realized. This arrangement could become the key element of a planar single electron tunneling electronics ("SET electronics"). If a third electrostatically acting electrode is incorporated in the whole arrangement, a nano bead-based transistor (SET transistor) is formed [18].

4. Nanoparticles as labels for biochips

Labeling techniques are mostly used for the sensitive read-out of biochips. Good results were obtained by use of radionuclides as labels. But this technique can only be applied in highly equipped special labs and is, therefore, unsuited for a broader use of biochips.

Labeling by organic fluorescence dyes is the favored technique today. But, it suffers to some extend from low and environment-depending intensities and a lack in the quantitative reproducibility. Inorganic fluorescing materials could be an alternative, if they can be bound specifically. Therefore, flourescing dendrimers and nano particles are in discussion as substitutes for organic fluorescence markers [19].

The formation of adducts between molecules and nano particles and the formation of such adducts at chip surfaces and integration in nanoelectrode arrangements attracted a lot of

activities during the last years [20-24]. Beside basic investigations, such adducts have been quickly applied in the biomolecular diagnostics. Theory, the labeling of biochips by nano particles of heavy metals offers an efficient alternative to fluorescence labeling [25-28]. Such particles can be selectively react with molecules immobilized at a chip surface, if they are carrying complementary functional groups at their surface and an unspecific sticking at the chip surface can be suppressed. In general, specific binding can be realized up to particles diameters of several tens of nanometers. So, Au-beads of a diameter of 30 nm with a shell of immobilized oligo nucleotides can be selectively bond to a chip surface of immobilized complementary DNA.

If the binding of metal particles occurs in sufficient high density, it is possible to get an optical signal with high contrast by simple transmissive or reflective measurement. This optical methods allow a very fast read-out of informations from biochips.

If the Au nano particles are small or the binding density of labeling Au nano particles at the chip surface is not high enough, it is easily possible to improve the contrast by a chemical amplification process. In analogy to the photographic process, metal spots are enlarged by a local metal deposition by metal-catalyzed reduction of metal ions from solution. This process can also be used for getting electrical contacts, if nano particles are specifically bond inside gaps between nanoelectrodes or microelectrodes. Such a procedure allows to perform a simple electrical read-out of biochips.

The chemical amplification leads to the possibility of an optical detection of single binding events (fig. 3). If nanoparticle beads of a size of a few tens of nanometers or even a few nanometers are enlarged up to sizes of several hundred nanometers or a few microns, they can easily be detected by optical imaging (fig. 4). So, single binding events can be read-out with a fast working method. If the originally binding nano particles are small (lower nanometer range), they can be immobilized by single chemical bonds. Using this effect, it would probably become possible, to develop chip and read-out systems with very high data content and high data transfer rates adresssing the level of single molecule chemistry.

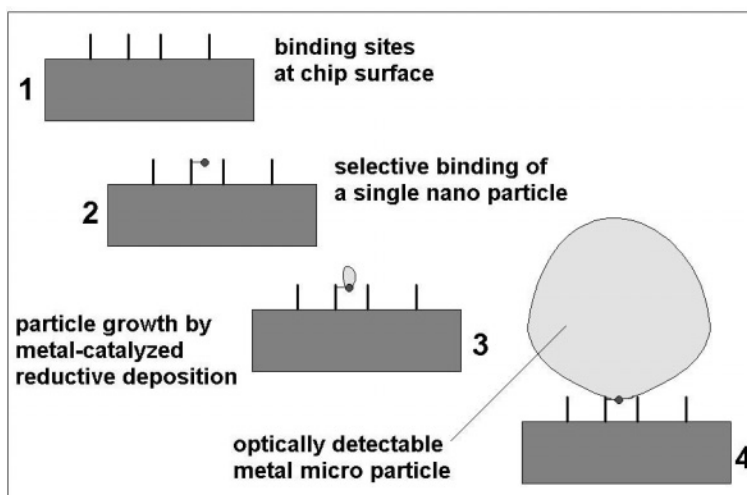


Figure. 3 Selectiv binding of chemically functionalized metal nano particle at a biochip surface and chemical amplification by metal catalyzed metal deposition from solution (schematically)

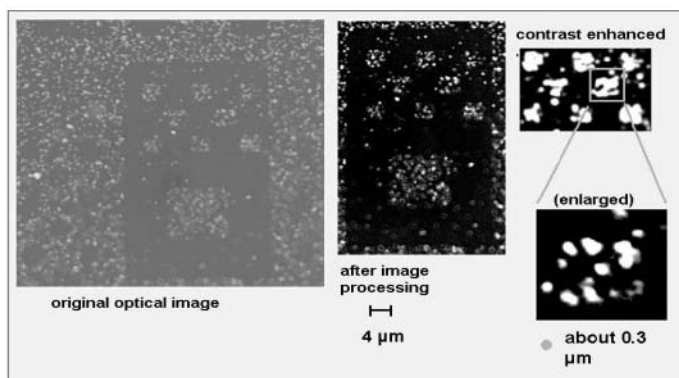


Figure. 4 Optical image of a chip surface with lithographically prepared micro chemotopes (smallest feature size $4\ \mu\text{m}$) after selective binding of Au nanoparticles and chemical in-situ amplification.

5. Nano particles in chip reactors

5.1. PRODUCTION OF NANO PARTICLES

Nano particles are not only of interest due to their use for chemical operations inside chip reactors and on chip surfaces. They can also be produced and modified in micro reactors. Micro reactors are in use for the preparation of nano particles with high homogeneity of particle size [16]. These processes are advantageously performed in the case of continuous nano particle formation in flow-through devices.

Colloidal solutions containing metal nanoparticles can be prepared in chip reactors working by interdiffusion and by a mix-and-recombine strategy. Therefore, interdiffusion channel reactors (fig. 5) or static micro mixers (fig. 6) are under investigation. In dependence on concentrations, different particle sizes with comparatively narrow size distribution can be addressed.

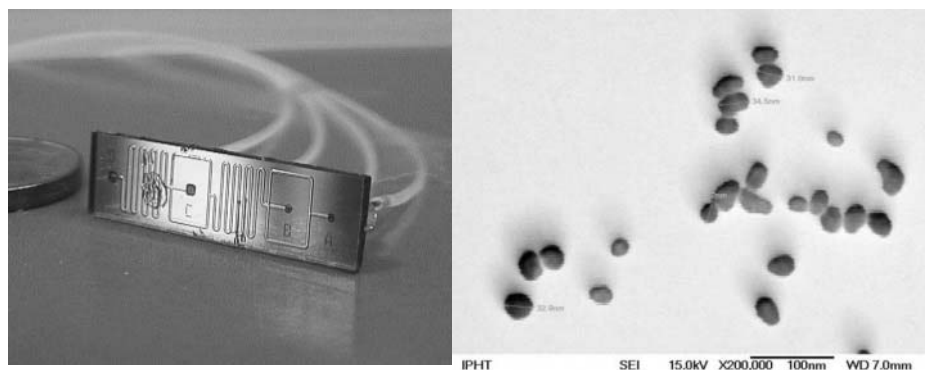


Figure. 5 Microchannel chip reactor for interdiffusion experiments

Figure. 6 Au nano particles at a Si surface. Preparation by chemical reduction of a tetrachloroaurate solution (SEM image)

A special opportunity for serial experiments with nanoparticles is offered by micro systems for segmented flow operations [29-34]. In small liquid volumes embedded inside a non-miscible organic carrier phase a serial formation of nano particle ensembles and a modification under stepwise changing conditions or composition of reaction mixtures can be achieved. The micro segmented flow represents a general experimental platform for parallelization of chemical as well as biochemical and micro biological investigations (fig. 7). Segments of aqueous solutions can be produced in micro fluidic chip reactors as well as in mechanically prepared devices (fig. 8). Generation frequencies with regular segment formation are observed up to 30 Hz [32, 34].

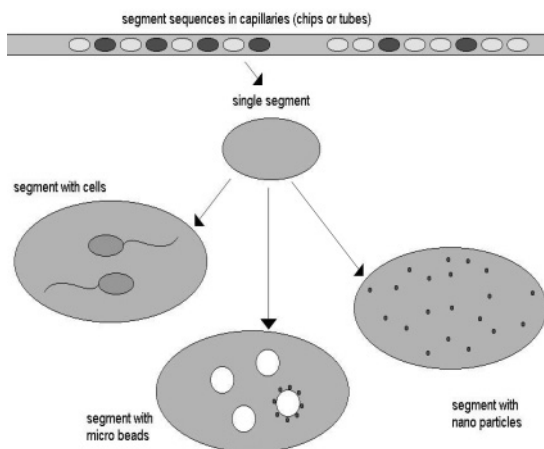


Figure. 7 Application variants of the micro segmented flow principle for the investigation of heterogeneous systems in combinatorial experiments and screening procedures

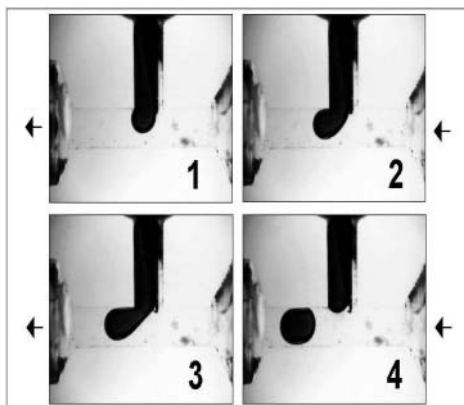


Figure. 8 Formation of aqueous segments in a nonmiscible carrier liquid (mineral oil). Optical image of a 0.5 mm micro injector (T-configuration) prepared mechanically in PMMA (optical imaging is supported by adaptation of refractive indexes of device material and carrier liquid, aqueous solution dyed by malachit green)

In the future, this concept will be developed to a experimental method for generation and modification of nano particles in a frame of automated combinatorial high-throughput experiments. Beside inorganic chemical investigations, interactions between nano particles and between particles and biomolecules, viruses or cells can be involved in these investigations. Segmentation can be used, e.g. for the subdivision of a certain volume of colloidal solutions in larger series of small reaction volumes (fig. 9). Studies under variation of the surface state of nano particles could be realized by integrated or micro modular arrangements of micro segment flow set-ups with two or more injector units. In combination with computer-controlled fluid actuators it is possible to apply step-wise changed concentrations of surface-active substances, which are injected into single reactions volumes in a serial flow. So, molecular shells of nano particles could be substituted by different amounts of active molecules (fig. 10). This principle is also of

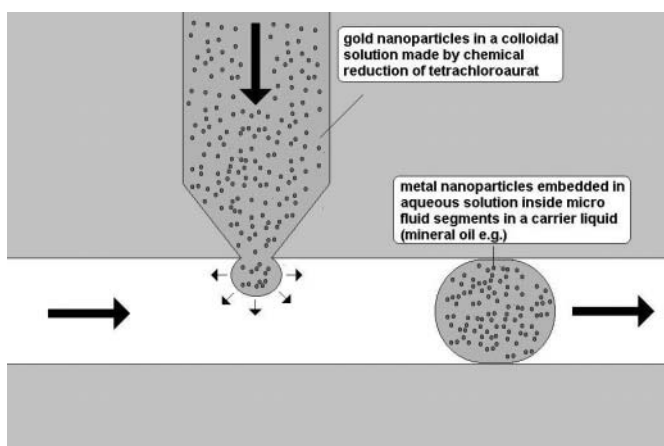


Figure. 9 Formation of micro fluid segments containing nano particles by a micro fluidic T-injector (schematically)

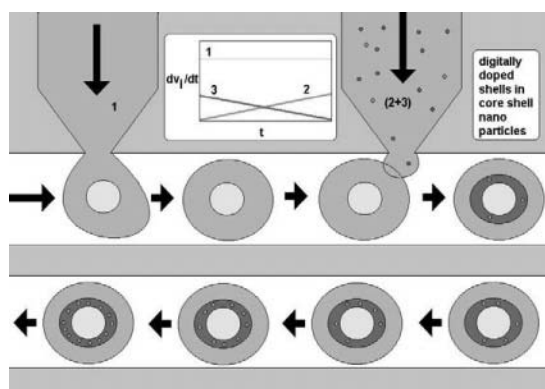


Figure. 10 Application of a double injector arrangement for the production of micro fluid segments containing core/shell particles with stepwise variation of shell composition (schematically)

interest for the quantitative variation of loading of binding sites at the surface of nanoparticles (fig. 11).

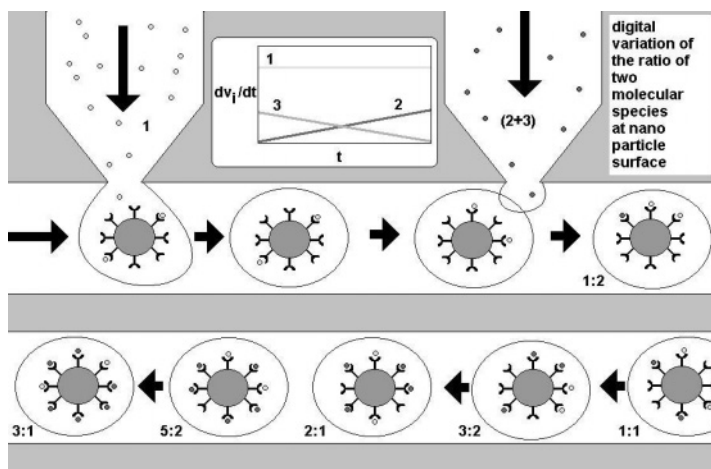


Figure. 11 Application of a double injector arrangement for the production of micro fluid segments containing functionalized nanoparticles with stepwise variation of the ratio of two types of molecules specifically attached to the particle surface (schematically)

5.2. ENLARGEMENT OF NANO PARTICLES BY METAL-CATALYZED GROWTH IN MICRO FLOW-THROUGH REACTORS

A growth of nano particles is induced, if a solution containing a noble metal salt as well as a reducing agent are brought together with small particles in a microchemical flow-through arrangement. The metal particles are working as nuclei for a metal deposition due to their electrochemical activity. They act like catalysts and accelerate the reduction of metal ions from solution in to metal depositing at the particle surface.

The increase in particle size is dependend on the original density of nano particles and on concentration of limiting substance (metal salt or reduzing agent). The reaction rate, and therefore also the particle growth rate, is influenced by concentrations as well and additionally by temperature.

Beside particle growth, the formation of new particles by a *de-novo* nucleation can not be avoided completely. For growth experiments, the conditions should be choosen in a way, that the ratio of nucleation rate to growth rate is low.

5.3. FORMATION OF CORE-SHELL PARTICLES BY DEPOSITION OF SECOND METAL FILMS AT NANO PARTICLES

Core-shell nano particles can be prepared by consecutive electrostatic immobilization of molecules on the nano particles surface. This method was applied, e.g., in the preparation of surface-functionalized luminescent particles [35].

Micro chip reactors can be used for two and more step reactions. So, it becomes possible to

make an *in-situ* modification of nano particles immediately after their formation. In batch experiments, ligand molecules are involved in or added to the reaction mixture in order to get the formation of surface substituted electrically charged nano particles, which are thermodynamically stable. Particle formation in micro reactors allows the decoupling of formation and stabilization to a certain extend, if the ligands are added to the reaction mixture shortly after the starting of the particle nucleation or growth process.

Organic thiols are particular suited for the functionalization of Au particle surfaces, because they form self assembled monolayers (SAM). Beside the formation of inert shells by application of alkylthiols, functionalized thiols like thiobiotine, thiooligonucleotides, thioglycerole and other can be applied for the preparation of nano particles with different chemical and physical properties.

The immobilization of other substances forming a second layer around the metal core can occur in a further chip reactor modul. A chain of immobilization steps or ligand exchange processes can be implemented in a chain of chip reactor moduls. So, micro reaction technology is a promising tool for the development of new types of nano particles in automated experiments.

6. Nanotechnical architectures using nano particles

6.1. INTERACTION OF FUNCTIONALIZED NANOPARTICLES

It is well known, that surface-functionalized nano particles can react to particle aggregates. In case of a DNA hybridization reaction between oligonucleotide-substituted Au particles, the formation of aggregates results in a shift in the plasmon resonance absorption due to the electronic interaction between particles of different size.

In analogy, to the formation of core-shell particles, the chemical reaction between different particles could be implemented in chip reactors. Reactive intermediate states are necessary. They can be handled using the short distances and short residence times in different regions of multifunctional or multi-step reactors. A very promising way would be the integration of photochemical steps in order to get an efficient activation of particles surfaces for subsequent coupling steps.

6.2. MODULAR CONSTRUCTION SCHEME FOR NANOARCHITECTURES USING MULTIFUNCTIONAL NANO PARTICLES

The chemical activation and coupling reactions between beads represent an important precondition for the construction of nanosystems by self-assembling of components. Therefore, a certain stiffness, differentiated regional chemical functionalities and a controlled mobility are necessary. Natural macromolecules like proteins and nucleic acids possess all this properties. But they are not well compatible to technical surroundings. The necessity of water or buffer solutions for formation and use of this molecular systems is a handicap for its technical use. In principle, synthetic polymers should be suited for molecular nanotechnology. But this application suffers, in most cases, from high mobility inside polymer chains and, therefore, the low definition and precision of molecular geometry.

Stiffness is an intrinsic property of colloidal metal particles and most other nano particles. If particles are stiff, not only binding topologies, but the geometry of the particles is much better defined than the geometry of particles with a multitude of rotational labile bonds like the most synthetic polymer molecules. That is the reason, why nano particles are particular suited for the construction of nano devices. But beside stiffness, a second precondition is the necessity of relative orientation of reacting particles. Local chemical functionality is needed for this. Since particles with three or more specifically adressable regions for local binding must be produced. It is expected, that chip reactors could support orientation and functionalization of nano particles in order to give them localized chemical binding groups and arrange them to well designed aggregates.

7. Conclusions

The combination of particle technologies with chip technologies leads to different fields of miniaturized chemical, biochemical methods and nanotechnology. Particles can act as carriers for molecules immobilized at their surface. They can be generated, transported and modified inside micro channels or can be processed in 2-dimensional arrays of micro chambers.

Surface-functionalized metal nano particles are applied as new labels for biochips. Nanoparticles are of interest for the construction of nano devices, too. Chip reactors and modular micro reactor arrangements can be used for the production of nanoheterogeneous systems and, therefore, contribute to a microtechnical environment for self-assembling systems with nano particles.

Acknowledgement

The fruitful collaboration with G. Mayer, J. Albert, A. Schober, T. Henkel, A. Grodrian and J. Metze is gratefully acknowledged. We thank M. Sossna (micro lithography) and F. Jahn, Jena (SEM images) as well as F. Möller, V. Möller and A. Schreier, Ilmenau (segmented flow) for technical support. Financial support of BMBF and DBU is gratefully acknowledged.

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ELECTROCHEMICAL CHARGING OF NANOCARBONS: FULLERENES, NANOTUBES, PEAPODS

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Abstract:

Electrochemical doping of nanocarbons is easy, versatile and precise in terms of the defined amount of doping charge. Electrochemical reduction of thin solid films of C_{60} is irreversible, and is accompanied by a structural reconstruction, which can lead to a formation of regular clusters of C_{60} . The Vis-NIR spectroelectrochemistry of single walled carbon nanotubes (SWCNT) points at reversible and fast bleaching of the electronic transitions between Van Hove singularities. The bleaching causes reversible quenching of resonance Raman scattering of both radial breathing and tangential modes of SWCNT. Fullerene peapods, $C_{60}@SWCNT$ and $C_{70}@SWCNT$ exhibit similar quenching of the tube-related modes. The Raman intensities of intratubular C_{60} increase considerably upon anodic doping, but not at cathodic charging. In contrast to that, all the relevant Raman modes of intratubular C_{70} show symmetric charge-transfer bleaching of the tube-related modes.

Key words: fullerenes, nanotubes, peapods, Raman spectroscopy, optical spectroscopy, electrochemistry

1. Introduction

The last two decades of the 20th century have witnessed three pioneering discoveries in the field of nanostructured carbons: fullerene C_{60} in 1985 by Kroto et al. [1], nanotubes in 1991 by Iijima [2] and peapods in 1998 by Luzzi et al. [3]. There were also significant early works on the same subject [4, 5], but these three milestones were the starting points for a new era in the synthesis and characterization of nanocarbons.

Carbon materials accompany electrochemistry since its early days [6]. Hence, the new discoveries in the area of nanocarbons have also inspired many electrochemists. Along with the characterization of electrochemical properties of carbons, the fullerenes [7, 8], nanotubes [7, 8] and other interesting nanocarbons [8, 9] can also be synthesized by electrochemical methods.

Electrochemical properties of the fullerenes C_{60} and C_{70} have been studied since the early 1990s, when these molecules became ordinarily available. Both C_{60} and C_{70} are reducible in acetonitrile-toluene mixtures in six reversible one-electron steps between -0.97 to -3.26 V vs.

Fc/Fc^+ (Fc = ferrocene) at lower temperatures [10]. This fact, along with the absence of anodic electrochemistry of fullerenes matches clearly the electronic structure of fullerenes. For instance, the LUMO of C_{60} can accept six electrons to form C_{60}^{6-} , but the energy of the HOMO of C_{60} is too low to be depleted from electrons at the usual electrochemical conditions. Higher fullerenes and endohedral fullerenes, such as C_{82} and C_{84} , both pure and filled with Sc and Er, provide new redox-active structures [11].

Electrochemical studies on carbon nanotube have focused on doping [12] and energy storage [13]. The latter theme splits into three sub-topics: hydrogen storage [14], Li batteries [15, 16] and supercapacitors [13]. The electrochemical hydrogen storage capacities of nanotubes were reported to be 110 mAh/g, (0.39 wt% H_2) [17] or 800 mAh/g, (2.9 wt%) [14], which is smaller than for the sorption from the gas phase [18]. The lithium-insertion into nanotubes is characterized by larger capacity compared to that of graphite (372 mAh/g for LiC_6), faster kinetics and absence of staging [15]. Since the intercalation between graphene layers is ruled out (especially in the single walled carbon nanotubes, SWCNT), Li is accommodated in nano-channels between the nanotube bundles [15]. Carbon nanotubes typically achieve capacitances of ca. 15-100 F/g [13].

Fullerene peapods represent interesting supramolecular complexes, which are formed *via* filling of SWCNT by fullerenes from the vapor phase [3, 19]. Several works relate to $\text{C}_{60}@\text{SWCNT}$ and $\text{C}_{70}@\text{SWCNT}$, but there are also scarce data on higher fullerenes and endohedral fullerenes included in carbon nanotubes [19]. Previous experimental [3, 20, 21] and theoretical [22] studies have shown that encapsulation of C_{60} requires the diameter of SWCNT to be 1.3-1.4 nm. Apparently, the preferred structure exhibits the "graphite-like" distance (0.3 nm) between C_{60} and the tube wall [3, 21]. Electrochemistry of peapods was studied in much less extent compared to the works on empty tubes and fullerenes. Nevertheless, there is a clear challenge to explore the electrochemical [23] and chemical [24] doping behaviour of peapods. As both of the components of peapods, i.e. SWCNT and $\text{C}_{60}/\text{C}_{70}$, show specific redox response, these studies should address fundamental problems of electronic and redox properties of carbon nanostructures.

1.1. SPECTROELECTROCHEMISTRY OF NANOCARBONS: FUNDAMENTALS

Electrochemistry provides data on nanocarbons in terms of the charge-transfer and population of electronic states near the Fermi level. This information is upgraded by investigations of allowed optical transitions by Vis-NIR spectroscopy. Valuable data can be obtained, if electrochemistry and Vis-NIR spectroscopy are applied simultaneously, i.e. by *in-situ* spectroelectrochemistry. Further information on the structure of nanocarbons on electrochemical interface is acquired by vibrational (IR and especially Raman) spectroscopy.

The free C_{60} molecule (I_h symmetry group) has 10 Raman active vibrations ($2A_g + 8H_g$) [25, 26]. The vibrational structure of C_{70} is more complex: the free molecule (D_{5h} symmetry group) has 53 Raman active vibrations ($12A_1' + 22E_2' + 19E_1''$) [26], whose complete assignment is still a subject of debate [26]. For the excitations around 2.5 eV, the Raman features of C_{60} are

resonance-enhanced *via* the first allowed transition in C_{60} ($h_u \rightarrow t_{1g}$) [25]. Also the C_{70} spectra are resonance enhanced around 2.5 eV *via* several electronic transitions in this region [26].

Optical and electronic properties of SWCNT are controlled by the tube structure (helicity), which is described by the so-called Hamada vector or chiral indexes (n, m). They characterize rolling of graphene sheet into each individual SWCNT: if $n = m$, the tubes have an "armchair" structure and are metallic. If $m = 0$, the tubes are "zig-zag" oriented and for $m \neq n \neq 0$, the tubes are of "chiral" structure. The tubes are metallic if $(m-n)$ is divisible by 3, otherwise they are semiconducting. The electronic structure of SWCNT is further characterized by van Hove singularities (vHs) in the density of states. The singularities extend symmetrically around the Fermi level. Hence, we can distinguish four sets of singularities: filled valence-band semiconducting ($v_s^{1,2,3,\dots}$), empty conduction band semiconducting ($c_s^{1,2,3,\dots}$) and analogous sets for metallic tubes ($v_m^{1,2,3,\dots}$, $c_m^{1,2,3,\dots}$).

Allowed optical transition between the singularities give rise to characteristic optical spectra in the Vis-NIR region. As samples are always polydisperse in diameters and chiralities, (m, n) we can usually distinguish three pronounced optical absorption bands, assigned to ($v_s^1 \rightarrow c_s^1$), ($v_s^2 \rightarrow c_s^2$) and ($v_m^1 \rightarrow c_m^1$) transitions. Their energies increase in the same sequence. For instance, tubes of ca. 1 nm in diameter exhibit the corresponding transitions energies at ca. 0.7, 1.2 and 1.8 eV, respectively. The dependence of transition energies on the tube diameters has been calculated theoretically for varying (n, m) [27] and this function became familiar under the nickname "Kataura plot".

The optical transitions between vHs are also responsible for resonance enhancement of Raman scattering in SWCNT. The enhancement is ca. 2-4 orders of magnitude, if the transition energy matches the energy of incident photon. Consequently, Raman spectra of SWCNT are very selective, displaying dominantly the tubes, which resonate with the particular optical transition. Raman spectra of SWCNT exhibit three major components: the radial breathing mode (RBM), and the high-frequency G and D modes. Whereas the G and D modes are found in also other graphene-like structures (multiwalled nanotubes, graphite), the RBM is characteristic for SWCNT only. It corresponds to the "breathing" of tube in direction perpendicular to its axis (A_1 mode). The G-band, also called tangential displacement mode (TM), comprises several graphene in-plane vibrational (A_1 , E_1 and E_2) modes. The RBM allows easy determination of the diameter of SWCNT (d) from the RBM frequency (ω) [20, 24, 28, 29]:

$$d = \frac{k_1}{\omega + k_2} \quad (1)$$

Constants k_1 and k_2 vary in the literature; typical values are 239 and 8.5, respectively for ω in cm^{-1} and d in nm [28,29]. The constant k_2 characterizes the interaction of SWCNT in a bundle, i.e. it is zero for isolated SWCNT. Optical spectra of peapods are similar to the spectra of empty tubes, they are dominated by allowed transitions between vHs. The peapods $C_{60}@SWCNT$ exhibit small red-shift of optical transitions (14 - 25 meV) compared to empty SWCNT, which corresponds to a diameter increase of 0.03 nm due to the C_{60} -encapsulation [30]. The optical transitions of intratubular fullerenes are poorly distinguishable. Raman spectra of C_{60}/C_{70} peapods display, in general, the superposition of weak lines of the parent fullerenes and strong lines of SWCNT [24, 31, 32].

2. Electrochemistry of fullerene films

The electrochemistry of molecular fullerenes in solution is well defined [10, 11], and is exemplified by a reversible uptake of up to six electrons in C_{60} or C_{70} (see Section 1). The films of solid C_{60} are normally insulators, but can be made metallic in reduced (n-doped) state [33, 34]. The chemical reductive doping of C_{60} is highlighted by a discovery of superconductivity in alkali-metal doped fullerene like K_3C_{60} [33] and Cs,Rb_3C_{60} [34]. The pristine films of C_{60} or C_{70} show irreversible cathodic reduction and various peculiar morphological changes [35, 36]. Electrochemistry of fullerene films is complemented by investigations of chemical redox reactions of solid fullerenes, which can be conveniently followed by Raman spectroscopy [25]. The n-doping manifests itself by overall drop of Raman intensities and by softening of the $A_g(2)$ mode by ca. 6 cm^{-1} per electron per C_{60} molecule. Doping of C_{60} by potassium vapor gives distinguishing characteristic Raman lines for three fullerenes: KC_{60} , K_3C_{60} and K_6C_{60} [25].

The easiest method to produce fullerene film for electrochemical applications consists in their casting from solution on suitable metallic substrates [35]. However, such films are polycrystalline and not very uniform. Bard et al. [35] have shown that cathodic reduction of such C_{60} or C_{70} films is irreversible in acetonitrile electrolyte solution, and is accompanied by structural reorganization, intercalation of the electrolyte cation and partial dissolution. The film dissolution can be avoided in aqueous medium, but in most aprotic solvents the C_{60}^- is soluble. However, hydrogen evolution at cathodic potentials limits the potential window in aqueous electrolyte solution.

Good-quality fullerene films on highly oriented pyrolytic graphite (HOPG) and Au (111) can be prepared by heteroepitaxial growth [36–38]). Their characterization by simultaneous application of electrochemistry and *in situ* scanning probe microscopy provides data on supramolecular arrangement. An attractive issue is the spontaneous self-organization of C_{60} molecules into defined clusters upon reductive doping [36, 38].

Fig. 1 demonstrates an example of C_{60} aggregation visualized by scanning tunneling microscopy of heteroepitaxially-grown C_{60} upon charge injection from the tip. The electron tunneling triggered surface aggregation of C_{60} to nanoclusters 5–10 nm, in pseudo close-packed arrangement [36, 38].

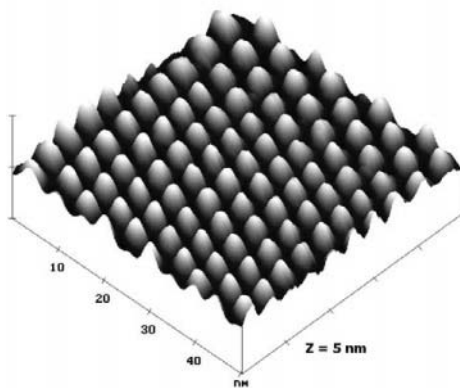


Figure 1. Fullerene C_{60} nanocluster array formed by electron tunneling from the STM tip to the fullerene film epitaxially grown on the HOPG (basal plane)

Electrochemical reduction of the same fullerene-film in alkaline aqueous electrolyte solution (KF+KOH) leads to its complete re-structuring towards nanoclusters of ca. 5 to 20 nm in size [36,38]. The driving forces for the electrochemical nanostructuring are electrostatic interactions between electrolyte cations (K^+) and C_{60} , and repulsive interactions of C_{60} - C_{60} electronic shells. Monte Carlo simulations showed that the layers of the composition K_xC_{60} , $0.1 < x < 3$, decompose predominantly into K_3C_{60} clusters enclosed by regions with very low potassium content. The K_3C_{60} clusters are metallic and act as nanoelectrodes for localized charge transfer. Such knowledge is important for applications of C_{60} in films for microelectronic devices. The self-organization of C_{60} into supramolecular clusters allows making templates for subsequent deposition of metal superstructures. Nothing is known about electrochemically driven self-organization of C_{70} and other fullerenes including endohedral fullerenes.

3. Electrochemistry of single walled carbon nanotubes

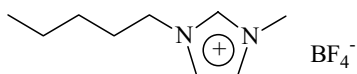
In contrast to the well-defined faradaic redox processes in molecular fullerenes (Section 2), the electrochemical properties of carbon nanotubes resemble the behavior of graphite electrode. The electrochemistry of SWCNT is dominated by double-layer charging with a small contribution, if any, of faradaic pseudocapacitance of surface oxides [13, 39-41]. The latter is represented by a generic Equation (2): [41]



Charge-transfer doping of SWCNT has been studied since the pioneering work by Rao et al. [42] (for review see Ref. [12]. Reductive doping by alkali metals [42, 43] and anion radicals [44, 45] and oxidative doping by Br_2 and I_2 [42-44] was followed by Raman [42], Vis-NIR [43, 44, 46] and resistivity measurements [43, 46]. The most characteristic issue was bleaching of optical transitions between vHS [27, 39, 40, 44, 46, 47]. Doping is associated with amphoteric depleting or filling of vHS [42, 44-46]. In turn, this bleaching also decreases the resonance Raman enhancement.

Alternatively, the population of singularities can be also easily and precisely controlled by electrochemistry [13, 39, 40, 48-52]. SWCNT exhibit reversible bleaching of the optical electronic transitions between vHS upon doping [39, 40, 49]. The bleaching of optical transitions also causes reversible quenching of resonance Raman scattering of both radial breathing (RBM) and tangential-modes (TM) of SWCNT [40, 49].

The Raman and Vis-NIR spectroelectrochemistry of SWCNT was studied both in aqueous [39] and acetonitrile [40] solutions. In order to increase the electrochemical window in aqueous media towards negative potentials, a mercury electrode was also used as a support of SWCNT [39]. Furthermore spectroelectrochemistry was also done in ionic liquids like butylmethylimidazolium tetrafluoroborate:



This medium allows the broadest window of electrochemical potentials to be applied (-2.4 to 1.7 V vs. Fc/Fc^+). It presents a very stable, solvent-free electrolyte, which even permits *in situ* spectroelectrochemical studies by Vis-NIR and Raman spectroscopy to be carried out.

Commercial SWCNT, fabricated usually by catalytic laser-ablation of graphite, show relatively narrow distribution of tube diameters between ca. 1.1-1.4 nm [39,40]. On the other hand, the so-called HiPco tubes [40], which result from catalytic pyrolysis of carbon monoxide [53,54] have diameters between ca. 0.7 to 2 nm [28,29,40,53,54]. This makes them useful for investigations of diameter-selective effects. Wider tubes were efficiently doped because of better accessibility of intertube channels in the bundle [28,29]. This effect was predicted to depend also on the size of the dopant molecule, which dictates the isotropic expansion of the trigonal lattice of SWCNT [28,29]. The efficient doping of wide tubes can also be simply interpreted in terms of the diameter-selective transition energies between the vHS [39,40]. Consequently, the relevant singularities of wide tubes are depleted/filled before those of narrower tubes, when the p-/n-doping progresses [39,40].

The somewhat unexpected good doping of the narrowest tubes was ascribed to smaller van der Waals forces, keeping the bundle together [29] and/or to the fact that the dopant/carbon ratio is relatively higher for thin tubes, if we assume the number of C-atoms forming the nanotube perimeter [28]. Figure 2 demonstrates an example of Raman spectra of a HiPco nanotubes in 0.1 M NMe_4BF_4 +acetonitrile (Me = methyl) at varying potentials. Similar spectra were recorded also in acetonitrile containing LiClO_4 [40].

The diameter of SWCNT (d) can be calculated from the RBM frequency (ω) according to Eq. (1). For the sample shown in Fig. 2 the corresponding tube diameters were between 0.79 to 1.34 nm. In terms of the zone-folding [27,46,47], the photons of 2.41 eV energy resonate with the transition ($\nu_m^1 \rightarrow c_m^1$) in tubes of narrower diameters and with the transition ($\nu_s^3 \rightarrow c_s^3$) in tubes of wider diameters from this set.

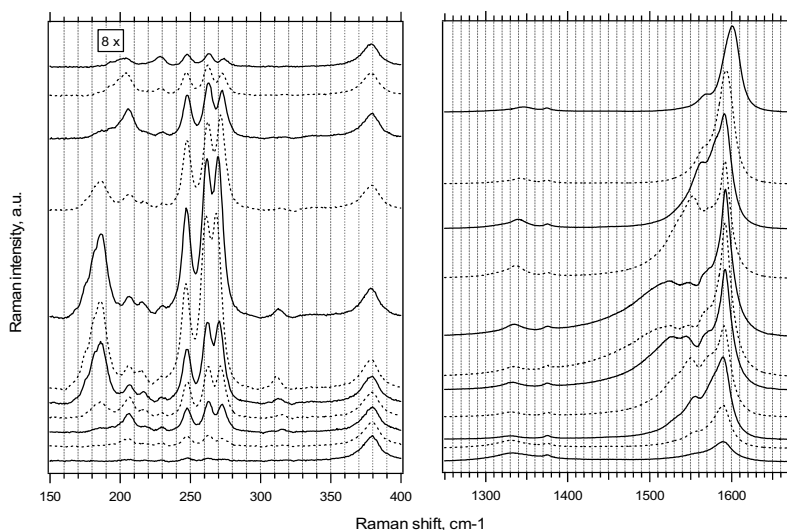


Figure 2. Potential-dependent Raman spectra of SWCNT on Pt electrode (excited at 2.41 eV) in 0.1 M NMe_4BF_4 +acetonitrile. The electrode potential varied by 0.3 V from 1.01 to -1.99 V vs. Fc/Fc^+ for curves from top to bottom. Spectra are offset for clarity, but the intensity scale is identical for all spectra in the respective window. The intensity is zoomed by a factor of 8 in the first window. Peaks of acetonitrile are apparent at 378.5 cm^{-1} and 1375.5 cm^{-1} .

The TM band shows the characteristic Breit-Wigner-Fano broadening, which is a signature of narrow metallic tubes in the HiPco sample [28, 40]. This broadening disappears upon doping, because the v_m^1/c_m^1 levels are depleted/filled at lower potentials than the v_s^3/c_s^3 states [28, 40]. The TM-band shows a blue shift upon anodic charging at larger potentials (Fig. 2) which reflects the stiffening of the graphene mode if holes are introduced into the π band [40]. The shifts of TM-band, generated by n-doping are more complex. In contrast to p-doping which always causes a blue-shift of the TM-band [23, 39, 40, 42, 48], the n-doping carried out electrochemically [40, 49, 51] or chemically [42, 55, 56] may cause both blue- or red-shifts depending on the counter-ion used (Li^+ , K^+ , Rb^+), doping level and the excitation wavelength. The interpretation is far from being clear and consistent [40, 42, 49, 51, 55, 56].

The overall intensities of RBM mode decrease as a result of both cathodic and anodic charging, which matches the behavior in aqueous [39, 48, 57] and aprotic [23,40,49] electrolyte solutions. However, the individual tubes in the HiPco sample (cf. Fig. 2) showed different intensity-voltage profiles, depending on their diameter [40].

By detailed analysis of the spectra exemplified in Fig. 2, we may confirm the effect of diameter-selectivity [28, 29]: the tubes of intermediate diameters (between 1 to 1.2 nm) are less affected by doping, while both the narrower and wider tubes respond more efficiently to doping. In general, the cathodic doping (compensated by extra cations in the double layer) leads to more pronounced attenuation, compared to anodic doping (compensated by extra anions in the double layer).

4. Electrochemistry of fullerene peapods

Charge-transfer on fullerene peapods ($C_{60}@SWCNT$ [23] and $C_{70}@SWCNT$) was studied by electrochemistry in 0.2 M $LiClO_4$ + acetonitrile and in butylmethylimidazolium tetrafluoroborate (ionic liquid). No distinct redox peaks of the reduction of fullerenes [35] were detected by cyclic voltammetry. The capacitance of empty SWCNT was ca. 40 F/g in 0.2 M $LiClO_4$ + acetonitrile [40]. For an ideal double layer capacitor, the change in number of electrons transferred per one carbon atom, Δf equals:

$$\Delta f = \frac{M_C C \Delta U}{F} \quad (3)$$

where M_C is atomic weight of carbon, ΔU is potential difference and F is Faraday constant. Equation (3) yields $\Delta f = 0.005$ e⁻/C-atom for $\Delta U = 1$ V and $C = 40$ F/g. A one electron reduction of C_{60} represents $\Delta f = 0.017$ e⁻/C-atom (for C_{70} : $\Delta f = 0.014$ e⁻/C-atom). Hence, the redox-process C_{60}/C_{60}^- or C_{70}/C_{70}^- corresponds to ca. 3 times more electrons per C-atom compared to double layer charging of the wall. Cyclic voltammetry evidences that the electroreduction of intra-tubular C_{60}/C_{70} is hampered [23]. This matches the fact that even a stronger chemical reduction of $C_{60}@SWCNT$ with K-vapor was sluggish, starting with a charge transfer to the nanotube wall [24].

Figure 3 presents the Vis-NIR spectra of $C_{60}@SWCNT$ on indium-tin oxide electrode (ITO) in 1-butyl-3-methylimidazolium tetrafluoroborate. Similarly to empty SWCNT [40], dry peapods (or in the electrolyte at open-circuit potential) showed three optical bands: at 0.7 ($v_s^1 \rightarrow c_s^1$), 1.25 ($v_s^2 \rightarrow c_s^2$), and 1.8 ($v_m^1 \rightarrow c_m^1$) eV. No optical transitions of C_{60}/C_{70} (expected at

ca. 2.3 - 2.6 eV) were found. Anodic polarization shifts the Fermi level, and the singularities are depleted in the sequence: cs1, cs2, cm1. Analogously, cathodic polarization leads to sequential filling of the singularities: vs1, vs2, vm1. In both cases, the optical bands reversibly disappear in the same sequence [23, 40]. In ionic liquids, the Vis-NIR spectra can be recorded up to 2.45 V vs. Fc/Fc⁺. At high positive potentials, a new optical band appears between 1.1 eV to 1.3 eV (Fig. 3). It reminds the doping-induced transitions [43, 46] for chemically (Br₂) p-doped SWCNT (vs_n→vs₁, vs_n→vs₂; n≥3) [23, 40, 43, 46].

Inset in Figure 3 shows the NIR absorbance at 0.7 eV of the same peapod-covered electrode, on which square-wave potential pulses were applied between -0.5 V and 1.2 V. Similar to the charging of SWCNT in acetonitrile electrolyte solution [23] the switching is reversible, while ca. 90% of the absorbance shift occurs in times <1 s (Fig. 2, inset). Apparently, the optical switching is driven by fast double-layer charging (cf. Eq. 3).

In Figure 4 the *in situ* Raman spectra of C₆₀@SWCNT and C₇₀@SWCNT (in 0.2 M LiClO₄ + acetonitrile) are given in the area of the most intense bands of fullerenes (cf. arrows in Figure 4). Complete spectra are listed in Table 1. Anodic charging discloses the C₆₀ H_g(8) line at 1573 cm⁻¹ due to the blue-shift of TM band. The H_g(8) mode is normally hidden in the G-band and cannot be observed in dry peapods. The Raman spectrum of C₇₀ peapods is more complicated, because of the lower symmetry of the molecule [26] (cf. Section 1.1). Cathodic doping of C₆₀@SWCNT causes overall decrease of Raman intensities (Fig. 4). However, at positive potentials, an interesting enhancement of Raman intensities of intratubular C₆₀ (Fig. 4) is detected. The "anodic enhancement" of intratubular C₆₀ is not reproduced in C₇₀@SWCNT (Fig. 4). The relevant Raman modes of C₇₀ show the "normal" symmetric potential-dependence (as the RBM/TM lines). As in C₆₀@SWCNT, doping discloses two lines (1332 cm⁻¹ and 1564 cm⁻¹; the latter being the strongest Raman lines of bare C₇₀). These bands are normally hidden in peapods by overlapping D- and G-lines.

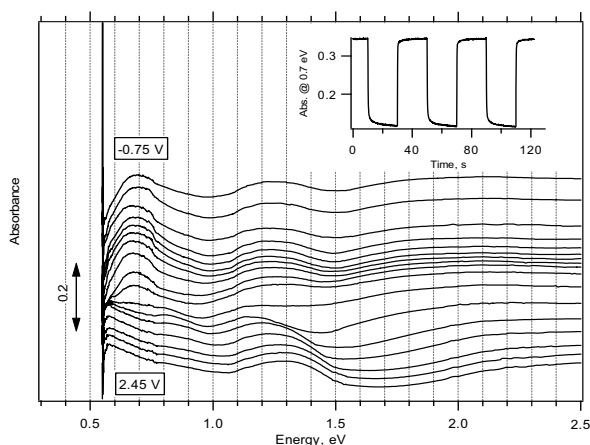


Figure 3. Potential dependent Vis-NIR spectra of C₆₀@SWCNT peapods deposited on ITO electrode in 1-butyl-3-methylimidazolium tetrafluoroborate. The applied potential varied by 0.2 V from -0.75 to 2.45 V vs. Fc/Fc⁺ for curves from top to bottom. Spectra are offset for clarity, but the absorbance scale is identical for all spectra (see scale bar). Inset shows the absorbance at 0.7 eV as a function of time, if the applied potential was switched between -0.5 (higher plateau) and 1.2 V (lower plateau) vs. Fc/Fc⁺.

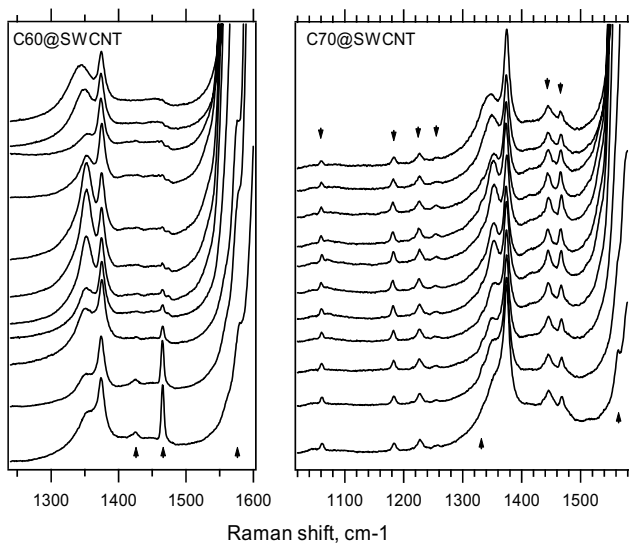


Figure 4. Raman spectra of $C_{60}@SWCNT$ and $C_{70}@SWCNT$ (excited at 2.54 eV) in 0.2 M $LiClO_4$ + acetonitrile. The electrode potential varied by 0.3 V from -1.7 V to 1.3 V vs. Fc/Fc^+ for curves from top to bottom. Spectra are offset for clarity, but the intensity scale is identical for the respective window. Arrows indicate the expected Raman lines of C_{60}/C_{70} .

Table 1. Raman spectra of peapods, $C_{60}@SWCNT$ and $C_{70}@SWCNT$ in 0.2 M $LiClO_4$ + acetonitrile: spectral assignment of the main lines (cf. Figure 4).

$C_{60}@SWCNT$		$C_{70}@SWCNT$	
ω , cm^{-1}	Assignment	ω , cm^{-1}	Assignment
(165-185)	RBM (SWCNT)	(165-185)	RBM (SWCNT)
270	$H_g(1)$	260	A_1, E_2
379	(δ CN, acetonitrile)	379	(δ CN, acetonitrile)
430	$H_g(2)$	450	A_1, E_1''
494	$A_g(1)$	563	A_1, E_1''
709	$H_g(3)$	699	A_1, E_1, E_2
769	$H_g(4)$	740	A_1, E_1, E_2
1350	D-mode (SWCNT)	1061	A_1, E_2
1374	(δ CH, acetonitrile)	1181	A_1, E_1, E_2
1424	$H_g(7)$	1226	A_1, E_1, E_2
1465	$A_g(2)$	1256	E_1, E_2
1573	$H_g(8)$	1350	D-mode (SWCNT)
1593	TM (SWCNT)	1374	(δ CH, acetonitrile)
		1443	A_1, E_1, E_2
		1466	A_1, E_1
		1593	TM (SWCNT)

The non-symmetric anodic Raman enhancement in $C_{60}@SWCNT$ can be interpreted as follows: The LUMO level of C_{60} (t_{1u}) is unusually close to the Fermi level of SWCNT [22]. This anomalous position is due to the hybridization of nearly free electron state of SWCNT and the π -state of C_{60} [22]. Extra electrochemical charge interacts primarily with the peapod wall, causing the depletion/filling of states close to the Fermi level. This leads to symmetric anodic/cathodic bleaching of the RBM/TM intensities and the frequency shifts of TM. Cathodic charging of $C_{60}@SWCNT$ causes that the extra electrons efficiently quench the HOMO-LUMO transition. However, anodic charging virtually does not influence the electronic structure of C_{60} . In $C_{70}@SWCNT$, the LUMO of the fullerene is located above the conduction band of SWCNT. This is the case also for wider tubes, in which the intratubular C_{70} can rearrange from lying to standing configuration [31]. Such a steric compensation is inherently excluded for C_{60} because of its spherical symmetry. The “thick” C_{60} peapods have their LUMO-band very near the Fermi level, while it can even be partly filled and the Raman resonance is partly quenched [22]. Anodic charging of thick C_{60} peapods will deplete the half-filled LUMO, which efficiently enhances the overall Raman intensity.

Acknowledgement

This work was supported by IFW Dresden and by the Academy of Sciences of the Czech Republic (contract No. A4040306).

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NANO-ENCAPSULATION OF FULLERENE IN DENDRIMERS

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Abstract.

Two series of dendrimers with peripheral triethyleneglycol chains and a fullerene core have been prepared and characterized. The photophysical properties have been investigated in different solvents (toluene, dichloromethane and acetonitrile). In particular, we have shown that the fullerene triplet lifetimes are steadily increased with the dendrimer volume in all the investigated solvents. Interestingly, the triplet lifetimes of the largest fullerodendrimer in the three solvents lead towards a similar value suggesting that the fullerene core is in a similar environment whatever the nature of the solvent is. In other words the C₆₀ unit is, to a large extent, not surrounded by solvent molecules but substantially buried in the middle of the dendritic structure, which is capable of creating a specific site-isolated nanoenvironment around the fullerene moiety.

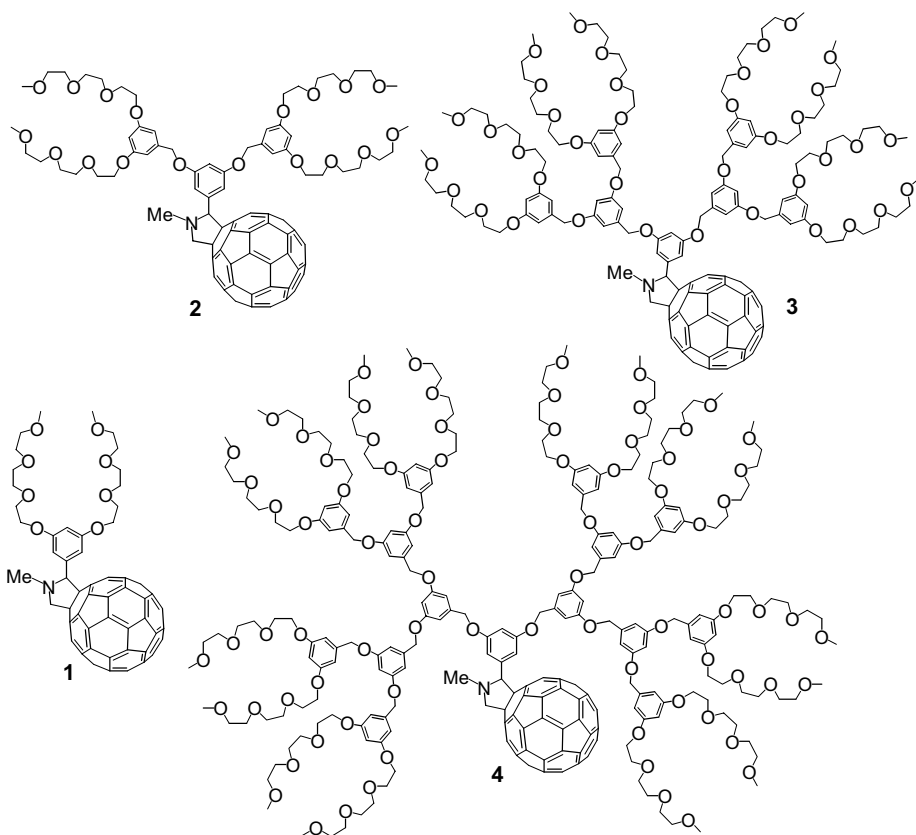
1. Introduction

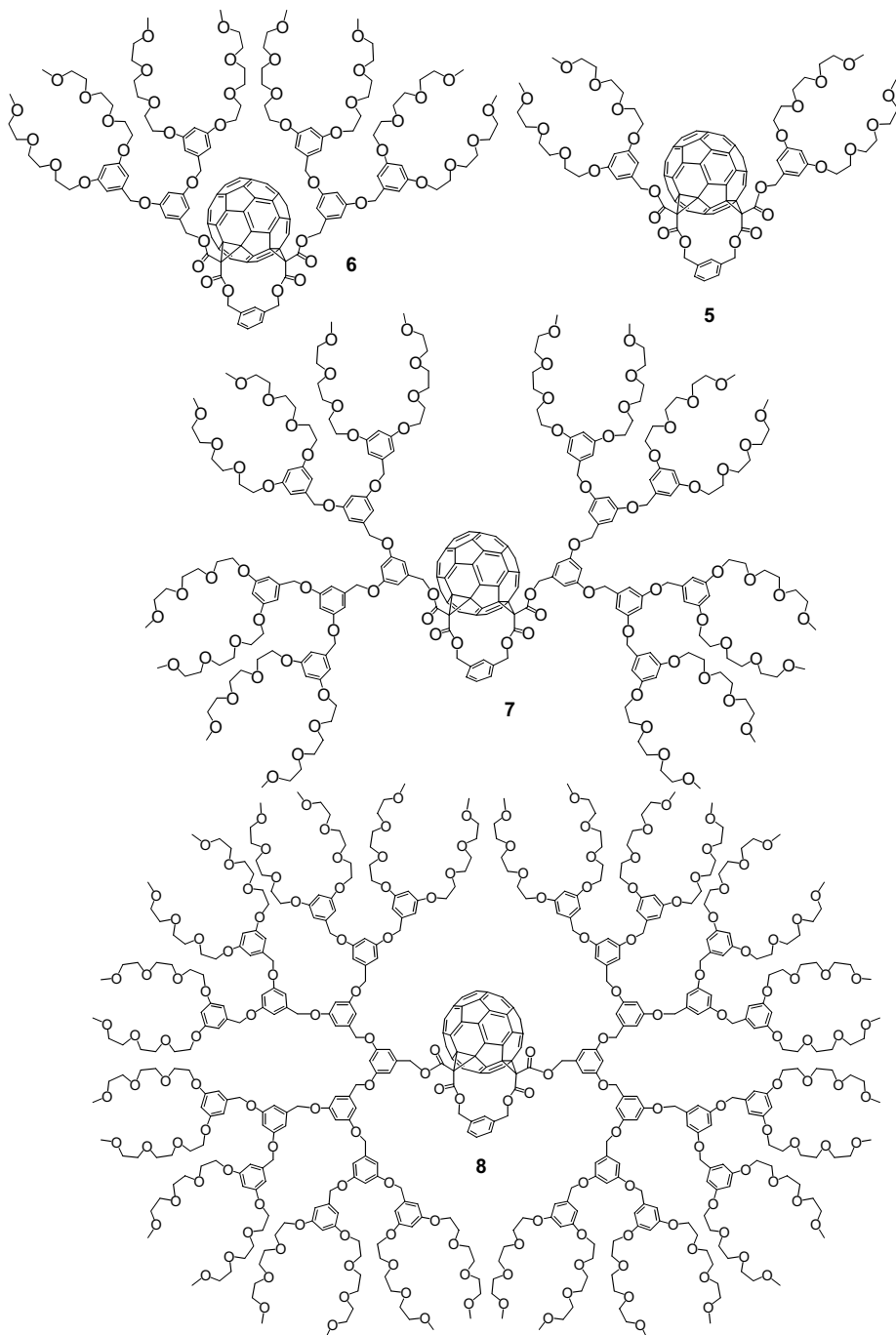
In light of their unique molecular structure, dendrimers have attracted increasing attention in the past years [1]. With regard to the development of suitable procedures to synthesize monodispersed dendrimers, more and more emphasis is being placed on the design and study of functionalized dendrimers [1]. Of particular current interest is the use of dendritic architectures to mimic globular proteins owing to the ability of such macromolecules to surround active core units, thus creating specific site-isolated nano-environments capable of affecting dramatically the properties of the core moiety [2]. A variety of experimental techniques have been employed to provide evidence for the shielding of the core and to ascertain the effect of the surrounding dendrons. For example, kinetic studies of chemical reactions involving the central core unit give insight into substrate diffusion through the dendritic shell and allow for an evaluation of the accessibility of the core [2]. On the other hand, specific changes in the nano-environment of electroactive and/or photoactive cores are conveniently analyzed by monitoring the redox and/or photophysical properties as a function of the generation number [2]. As a part of this research, we have prepared various

series of dendrimers with a fullerene core to study specific effects resulting from the attachment of dendrons on the C_{60} chromophore [3-5]. These results are summarized in the present chapter to illustrate our current understanding of macromolecular encapsulation using dendrimers.

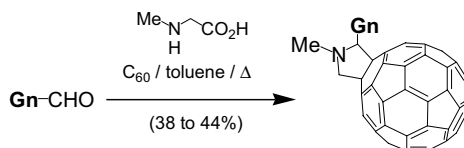
2. Results and discussion

The synthesis of fullerene-functionalized dendrimers is currently an area of considerable interest [5-6]. Dendrimers with a C_{60} core, peripheral C_{60} subunits or a C_{60} sphere at each branching unit have been already described. As far as fullerodendrimers with C_{60} -type cores are concerned, it should be noted that the functionalization of the fullerene sphere with dendritic branches dramatically improves the solubility of the C_{60} . In the design of fullerodendrimers **1-8**, it was decided to attach poly(aryl ether) dendritic branches terminated with peripheral triethyleneglycol chains to obtain compounds soluble in a wide range of solvents [7].

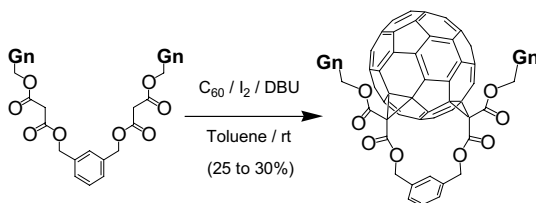




The synthetic approach to prepare compounds **1-4** relies upon the 1,3-dipolar cycloaddition of the dendritic azomethine ylides generated in situ from the corresponding aldehydes and *N*-methylglycine. This methodology has proven to be a powerful procedure for the functionalization of C_{60} due to its versatility and the ready availability of the starting materials [8]. The reaction of the dendritic aldehydes with *N*-methylglycine and C_{60} in refluxing toluene gave the corresponding fulleropyrrolidines **1-4** in 37 to 44% isolated yield after column chromatography on silica gel followed by gel permeation chromatography [3].



Fullerodendrimers **5-8** were obtained by taking advantage of the versatile regioselective reaction developed in the group of Diederich [9], which generated macrocyclic bis-adducts of C_{60} by a cyclization reaction at the C sphere with bis-malonate derivatives in a double Bingel cyclopropanation. Reaction of dendritic bis-malonates with C_{60} , I_2 , and DBU in toluene at room temperature afforded the corresponding cyclization products **5-8** [9]. The relative position of the two cyclopropane rings in **5-8** on the C_{60} core was determined based on the molecular symmetry deduced from the ^1H - and ^{13}C -NMR spectra (C_s).



The structure of fullerodendrimers **1-8** was confirmed by analytical and spectroscopic data. The unequivocal characterization of these dendrimers also requires their mass spectrometric analysis. Electrospray (ES) and/or matrix-assisted laser desorption/ionization (MALDI) mass spectrometries are the most appropriate tools for such a purpose owing to their gentle ionization processes preventing high levels of fragmentations. Compounds **1-7** have been characterized by both techniques. As far as ES-MS is concerned, the compounds are uncharged in solutions and their analysis requires the addition of 1% formic acid to charge the fullerene derivatives [3-4]. For MALDI-MS measurements, several matrices have been tested, such as α -cyanohydroxycinnamic acid, 2,5-dihydrobenzoic acid or 1,8,9-trihydroxyanthracene (dithranol). Singularly, the expected peaks were only detected with dithranol. The ES and MALDI mass spectra of **1-7** (not represented here) are all characterized by two singly charged peaks corresponding to the protonated and cation bound (with Na^+) compounds. Due to the high molecular weight of **8**, its characterization was only possible by MALDI-MS. As a matter of fact, the mass range of the ES instrument (an ES triple quadrupole mass spectrometer with a mass-to-charge (m/z) ratio range of 8000) was not sufficient to allow the characterization of **8**.

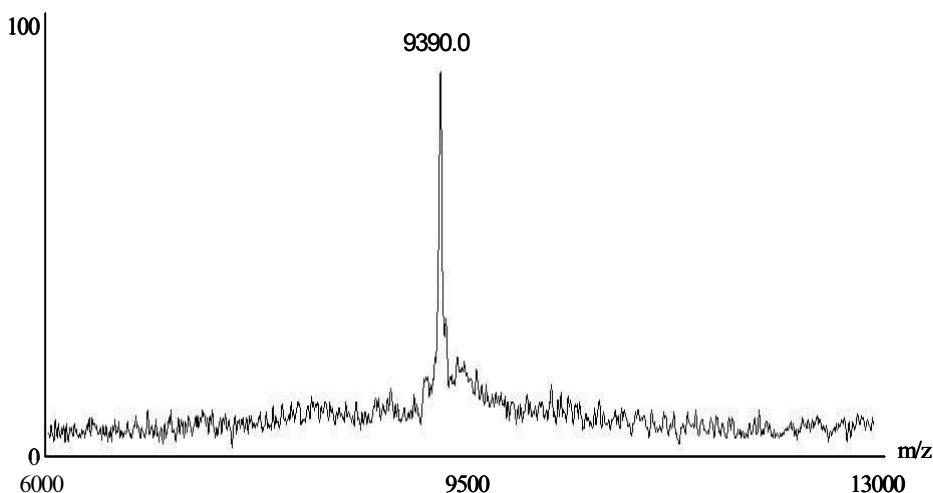


Figure 1. MALDI mass spectrum of fullerodendrimer **8**.

(MW= 9391.5). Since, a MALDI mass spectrometer is typically equipped with a time of flight (TOF) analyzer with a theoretically unlimited m/z range, its use was therefore an alternative and a complementary method to complete the unambiguous characterization of these compounds. The MALDI mass spectrum of **8** (Figure 1) presents only one mono-charged peak corresponding to $[M+Na^+]$ at $m/z = 9390.0$ (calculated $m/z = 9391.5$).

The photophysical properties of **1-8** have been studied in different solvents (PhMe, CH_2Cl_2 and CH_3CN). The lifetimes of the lowest triplet excited states are summarized in Table 1. For both series of dendrimers interesting trends can be obtained from the analysis of triplet lifetimes in air-equilibrated solutions (Table 1). A steady increase of lifetimes is found by increasing the dendrimers size in all solvents, suggesting that the dendritic wedges are able to shield, at least partially, the fullerene core from external contacts with the solvent and from quenchers such as molecular oxygen. For compounds **1-4**, the increase is particularly marked in polar CH_3CN , where a better shielding of the fullerene chromophore is expected as a consequence of a tighter contact between the strongly nonpolar fullerene unit and the external dendritic wedges; in this case a 45% lifetime prolongation is found in passing from **2** to **4** (23 % and 28% only for PhCH₃ and CH_2Cl_2 , respectively). It must be emphasized that the triplet lifetimes of **4** in the three solvents are rather different from each other, likely reflecting specific solvent-fullerene interactions that affect excited state deactivation rates. This suggests that, albeit a dendritic effect is evidenced, even the largest wedge is not able to provide a complete shielding of the central fulleropyrrolidine core in **4**. The latter hypothesis was confirmed by computational studies (Figure 2).

Table 1. Life time of the first triplet excited state of **1-8** in air equilibrated solutions determined by transient absorption at room temperature.

Compound	τ (ns) in PhMe	τ (ns) in CH ₂ Cl ₂	τ (ns) in CH ₃ CN
1	279	598	[a]
2	304	643	330
3	318	732	412
4	374	827	605
5	288	611	314
6	317	742	380
7	448	873	581
8	877	1103	1068

[a] not soluble in this solvent.

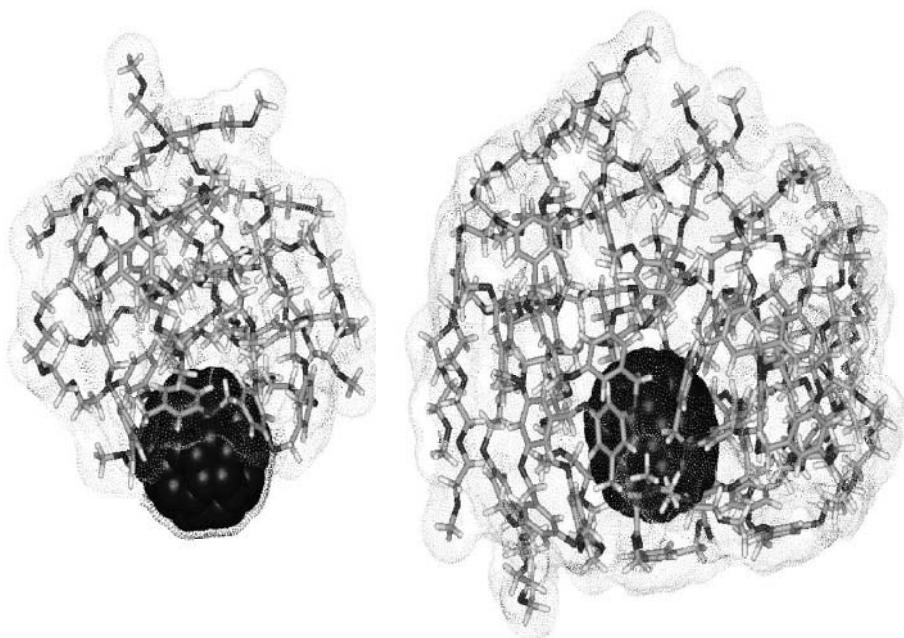


Figure 2. Snapshots of the theoretical structure of fullerodendrimers **4** (left) and **8** (right) at 300 K obtained from Molecular Dynamics calculations. These studies have been performed on SGI Origin 200 and Octane² workstations using the Discover 3 software from Accelrys (www.accelrys.com) with the pcff forcefield. The previously minimized structures were allowed to equilibrate for 500 ps at a 300 K isotherm by the MD simulation (in the NVT ensemble with a time step of 1 fs).

As shown in Figure 2, the calculated structure of **4** reveals that the dendritic shell is unable to completely cover the fullerene core (it must be noted that the calculations have been performed in the absence of solvent, our aim being only to estimate the possible degree of isolation). In contrast, the triplet lifetimes of **8** in the three solvents lead towards a similar value suggesting that the fullerene core is in a similar environment whatever the nature of the solvent is. In other words the C_{60} unit is, to a large extent, not surrounded by solvent molecules but substantially buried in the middle of the dendritic structure which is capable of creating a specific site-isolated microenvironment around the fullerene moiety. The latter hypothesis is quite reasonable based on the calculated structure of **8** (Figure 2) showing that the dendritic branches are able to fully cover the central fullerene core.

3. Conclusion

Owing to their special photophysical properties, fullerene derivatives are good candidates for evidencing dendritic effects. In particular, we have shown that the triplet lifetimes of a C_{60} core can be used to evaluate its degree of isolation from external contacts. The dendritic effect evidenced for **1-8** might be useful to optimize the optical limiting properties characteristic of fullerene derivatives. Effectively, the intensity dependant absorption of fullerenes originates from larger absorption cross sections of excited states compared to that of the ground state [10], therefore the increased triplet lifetime observed for the largest fullerodendrimers may allow for an effective limitation on a longer time scale. For practical applications, the use of solid devices is largely preferred to solutions and inclusion of fullerene derivatives in sol-gel glasses has shown interesting perspectives. However, faster de-excitation dynamics and reduced triplet yields are typically observed for fullerene-doped sol-gel glasses when compared to solutions [10]. The latter observations are mainly explained by two factors: (i) perturbation of the molecular energy levels due to the interactions with the sol-gel matrix and (ii) interactions between neighboring fullerene spheres due to aggregation. Therefore, the encapsulation of the C_{60} core evidenced by the photophysical studies for both series of fullerodendrimers might also be useful to prevent such undesirable effects. The incorporation of fullerodendrimers **1-8** in sol-gel glasses has been easily achieved by soaking mesoporous silica glasses with a solution of **1-8**. For the largest compounds, the resulting samples only contain well-dispersed fullerodendrimer molecules. Preliminary measurements on the resulting doped samples have revealed efficient optical limiting properties [3] and further studies are underway in order to determine the influence of the dendritic branches on the optical limiting behaviour of these composite materials.

Acknowledgements

This work was supported by the CNR, the CNRS and the French Ministry of Research (*ACI Jeunes Chercheurs*). G. A. thanks Italian MIUR (Progetto 5%) and Y. R. the French Ministry of Research for their fellowships. We further thank H. Nierengarten, J.-M. Strub and A. Van Dorsselaer for MS measurements.

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IRRADIATION-CONTROLLED ADSORPTION AND ORGANIZATION OF BIOMOLECULES ON SURFACES: FROM THE NANOMETRIC TO THE MESOSCOPIC LEVEL

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Abstract.

The basic principle of ion – polymer interactions and parameters are discussed in view of their use to modify the absorption and organization processes of proteins and cell adhesion and spreading onto polymeric surfaces.

In particular, experimental results are presented on the surface interaction processes of Human Serum Albumin, complex proteins mixtures from Fetal Bovine Serum and fibroblast cells with polyhydroxymethylsiloxane (PHMS), polyethyleneterephthalate (PET), amorphous carbon phases ($a\text{-C:H}_x$) and silicon-carbon-oxygen phases ($\text{SiC}_x\text{O}_y\text{H}_z$).

The surface chemical structure and properties of the unirradiated and irradiated surface, before and after the interaction with the biological systems have been characterized by using Small Spot X-Ray Photoelectron Spectroscopy, Near Field Microscopies, and Surface Free Energies measurements techniques.

The interaction processes of the biological systems are discussed in view of the ion-induced chemical and thermodynamical modifications of polymer surfaces, with a specific attention to the Surface Free Energy and related components.

In particular, dramatic effects of modification of the single protein adsorption kinetics have been demonstrated to depends on a critical value of the total surface free energy for unirradiated and ion-treated surfaces of PET and PHMS. Also, the evidence for complex protein aggregation phenomena could be related to the free energy of interaction of the protein solution with the ion-modified and unmodified polymer surfaces. Finally, spatially selective cell adhesion and spreading has been demonstrated to depend on a critical threshold value for the electron donor Lewis basic component of surface free energy.

1. Introduction

The need for having a breakthrough in fields like biocompatible surfaces, bioelectronics, biosensors etc., is triggering an enormous interest in the realization of hybrid systems based on the controlled adhesion of biological systems, going from amino acids and peptide sequences till proteins and cells, on polymers and inorganic surfaces [1].

It is to note that most of the relevant applications in these fields need a spatially resolved process of adsorption/adhesion of the biological systems of interest, as far as the properties like biocompatibility and cytocompatibility depend in a direct way on physical and chemical structure at the micro- and nanometer scale [2]. In fact, it has been shown that for instance cell adhesion can be driven by well-defined physical and chemical features at the

surfaces, as trenches, holes and patterns in the micrometer scale both on polymers and silicon substrates [2, 3]. As an example, various types of cells, including the neuronal ones have been shown to be able to create connected networks guided by spatial structures in polymers or silicon, in view of producing a kind of cell circuitry [4, 5]. It is important to note that in these cases a non-trivial dependence upon the lateral dimensions is observed and that different types of cells behave in different way on the spatial constrains [6].

Still in the micrometer range, the development of highly integrated multipurpose microsystems, including biosensor arrays, DNA-chips and related technologies, as well as the Lab-on-chip devices critically depend on the ability to functionalise specific micrometer-scale areas in very complex three-dimensional structures, mostly based on silicon and related compounds [7].

On the other hand, at the nanometer scale, at least two different aspects of controlled biomolecule adsorption/organization must be considered, i.e., the interest in achieving nanosized patterns of biological molecules in a general perspective of bio-electronics devices, and the specificity of nanostructured surfaces in stimulating specific response of large systems, as cells or protein aggregates, opening new very interesting views on the way the cells can “sense” nanometric surface features [8-10].

In view of the above sketched areas of application, it is clear that suitable and application-specific methods and techniques must be developed to obtain the spatially-resolved structuring of surface.

Basically, in the current research the problem is faced at two different level: a first, simple “spatial” approach involves the featuring the morphology of a surface with topographical features, as grooves, steps, and trenches. The second approach involves the spatially resolved modification of the chemical structure of the surfaces.

In the present paper we will discuss basically the second approach, based on the controlled modification of the chemical structure of the surfaces and the related properties [11]. This specific approach is in fact in our opinion closer to the fundamental nature of the adhesion/adsorption processes, and is based on the combined approach of understanding the basic mechanisms in terms of the very fundamental properties of the surfaces and the feedback to use the understanding of the processes in order to set up specific and selective approaches.

More in particular, we will address essentially processes of surface modification based on the use of radiation treatments, including essentially low- and medium-energy ion beams. The reason for this is clearly related to the quite good understanding of the beam-induced chemical modifications in polymers [12, 13] and the outstanding capability of focused ion beams of achieving a direct surface patterning [14].

In this paper, after a short introduction to the main features of ion-matter interaction processes, we basically focus the attention on the adsorption/organization processes of proteins and cells onto respectively carbon- and silicon-based surfaces obtained by using well-defined ion irradiation treatments. The modified adsorption/organisation processes are therefore discussed in view of the chemical and physical structure of the irradiated surfaces, obtained by using Small Spot X-Ray Photoelectron Spectroscopy (XPS), Near Field Microscopies (NFM), and Surface Free Energies (SFE). Thus, properties including the surface chemical structure and the related thermodynamical properties, as well as the morphology at the nanometric scale, are related to the observed aggregation and ordering effects.

The biomolecules of interest included human serum albumin, as an example of a single protein, the Fetal bovine Serum, as an example of the behaviour of a complex multiprotein system and fibroblasts as one of the most characteristic example of cell of interest in biomaterials applications. The synthetic surfaces included inorganic surfaces as SiO_2 (pyrolytic oxides), silicon-carbon alloys (a-Si:C,H) and two model polymers as different as polyhydroxymethylsiloxane (PHMS) and polyethyleneterephthalate (PET).

2. Why Ion Beams?

2.1 FUNDAMENTALS OF BEAM-MATTER INTERACTION

The use of ion beams to modify materials properties is prompted by a number of unique features of this tool, which turn in processing advantages. In particular, ion beam induced processes in polymers are characterized by the following peculiar features:

- 1) The particle-solid beam involves a very high and spatially localized energy deposition process, occurring according to different and competing energy deposition pathways, mostly consisting in ionisation and excitation processes of the electronic system, and displacements of atoms (collision cascades) [15];
- 2) The energy deposition processes induces in turns a very complex “cascade” of chemical events, following the thermalization of the primary physical events, which completely modify the initial chemical structure as well as the related physical properties [16];
- 3) The basic schemes of chemical reactions depends upon the predominant energy deposition mechanism [12].
- 4) It is possible to tune in a quite simple and reproducible way the type and amount of chemical and physical modification as well as the thickness of the modified layer just by setting a few characteristic parameters [16].

Let us discuss in some details the points above summarized.

2.1.1 - Energy deposition mechanisms. Since long time the energy deposition events have been rationalized in terms of a linear model, the Lindhard-Scharff-Schiøtt theory, describing the energy loss or stopping process of an ion of given energy in a given target in terms of three terms of electronic stopping (S_e), collisional or nuclear term (S_n) [15] and charge-exchange term (S_{c-e}) [17].

The electronic term S_e essentially accounts for the ionisation and excitation processes produced by the interaction of the ion electric field with the electron system of the materials. This specific step in itself includes also the “secondary” effects induced by the low-energy electrons produced in the primary ionisation events and ejected around the first ion-atom impact site.

The collisional (or “nuclear”) term S_n consists in the loss of energy in the knock-on impact between the incoming ion and the screened nucleus of the target atom. The process then involves the displacement of the struck atom from its original site, with a fraction of the energy of the primary ion, this energy being sufficient to produce secondary recoiling atoms originating the well-known effect of “collision cascades” around the primary ion trajectory, as well as the diffusion of phonons or, more in general, vibrational modes across the material.

Finally, the charge-exchange term S_{c-e} is important only when very high energy and high charge ions are used, consisting roughly in the electron capture of electrons from the target atoms [17]. We will neglect this last effect, as it has a negligible importance in the commonly used energy and charge states for practical applications, i.e., in the range of keV-MeV ions.

The amount of deposited energy can simply be accounted as a monotonously decreasing function of the ion path, the useful parameter being the deposited energy per length unit dE/dx , or Linear Energy Transfer (LET), often expressed as eV/nm [15].

2.1.2 - Localized energy deposition and Ion tracks. The described primary energy deposition process occurs basically through a series of spatially correlated discrete events of energy absorption by the atoms included within a small volume around the trajectory of the primary ion. This volume is designated as “ion track”. It is to note that the spatial features of the “ion track”, i.e., length and radius, depend upon the energy and mass of the primary ion as well as on the type of atoms of the target materials.

The effective parameter considered for practical purposes is the projected range, R_p , intending by this the distance of the implanted ion at rest from the surface. The higher is the ion energy and the lower the mass, the higher will be R_p . It is to note that the concept of ion track is in some way an idealisation, as the only experimentally observable effect is the late product of the energy deposition within the ion track, i.e., the result of the related chemical processes, mostly seen as modification of the solubility (and then etching behaviour) of the irradiated region, or the secondary physical events, as the colour centre formation in suitable solids. However, this concept is useful to connect in an intuitive way the ion trajectory and the energy deposition process. In fact, according to the above summarized points, the energy deposition process can be completely characterized by two simple experimental parameters respectively consisting in the ion energy, E_i , and the total number of ion per unitary area Φ (fluence). In fact, each ion will deposit along the stopping path an amount of energy, easily calculated in terms of the LSS theory [15], and reduced to an average energy deposited per unit of length S_t (eV/nm). Therefore, the total deposited energy within a given layer will be simply given by the product

$$\langle E_d \rangle = S_t \times \Phi \quad (1)$$

2.1.3 - Beam-induced chemistry. In the last 15 years, it has been shown that the chemical events induced by the energy deposition can be rationalized if we consider two relatively well-distinct regimes of energy deposition.

The first one involves the energy deposition for ions in the keV range, depositing energy in the target materials by both electronic and collisional mechanisms, with ion tracks of the estimated average diameter of less than 1 nm and an average energy deposition ranging between 1-100 eV/nm [12].

The second regime involves ions in the MeV-GeV energy range (Swift Heavy Ions), losing energy only through electronic stopping (and obviously also by charge-exchange processes). The related track sizes are in this case in the range of a 5-50 nanometers and the typical energy deposition ranges between 1-20 keV/nm [18, 19]. In this paper we will not deal with the processes related to this last energy regime, which mostly affect the bulk properties of the irradiated polymers, due to the high range of the employed ions (tens of micrometers up to millimetres).

The chemical events in the keV regime can be rationalized in terms of the fluence and $\langle Ed \rangle$ (see equ.1). In particular, a first quite general classification can be done by considering three distinct ranges of ion fluence. A graphic summary of the classification of the class of chemical effects as a function of the ion fluence (in the keV regime) is reported in fig. 1.

The first fluence regime, roughly up to 5×10^{13} ions/cm², corresponds to a physical situation of single tracks, in which the polymer primary structure is modified only in the isolated impact region, by simple radiation-induced chemical processes producing primary products which, in general, do not interact each others, as is sketched in fig. 2a. Creation of radical sites on a monomeric unit, ready to react with a close chain, or the rupture of the backbone (“chain scission”), are the typical examples of the described phenomena [19]. The modification of properties related to the Molecular Weight Distribution (MWD) of the polymer, as solubility (and the related resist properties) and crystallinity occur essentially in this first fluence regime [20, 21]. Furthermore, in this regime the primary structure of the polymer and probably most of the secondary structure are still almost intact.

The second fluence range roughly includes the fluence between 5×10^{13} and 5×10^{14} ions/cm². This range corresponds to the situation in which already a substantial part of the surface is covered by the single impact regions, reaching finally the complete geometrical coverage by the single ion tracks, as is sketched in fig.2b. In this regime the local modification of the monomer chemical structure occurs, summing up (until the surface is geometrically saturated) in a process which depends linearly on the fluence. This regime has been therefore indicated as a “mild chemistry regime” [12, 16]. During this step a new material of completely different chemical and electronic structure is progressively produced and the related properties, including the optical and electrical ones as well as the surface density of chemical groups, closely reflect the ion-beam induced changes [12, 16].

A particularly important point is that also the interactions of the irradiated surfaces with biological objects as cells, proteins and amino acids are strongly modified in this regime

Fluence (ion/cm ²)	Chemical effect:	Property changes:
10^{12}	1 crosslinks, chain scission	1. solubility
10^{13}	2. loss of volatile molecules (H ₂ , CO, ...)	2. resist properties
10^{14}	3. mild chemistry	3. adhesion, biocompatibility I optical properties
10^{15}	4. backbone rearranges three-dimensional branched polymers	4. density hardness
10^{16}	5. H-amorphous carbons graphitic clusters	5. electrical conductivity biocompatibility II

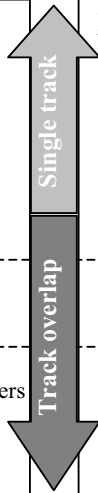


Figure 1.: Evolution of chemical effects as a function of the ion fluence

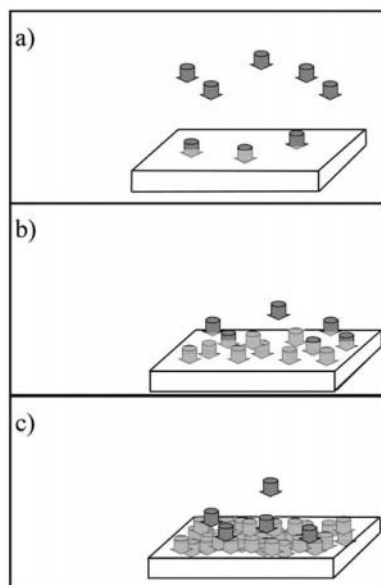


Figure 2.: Fluence regimes: a) single track; b) saturated track regime; c) overlapped tracks or “re-implantation regime”

[22-24]. We stress that in this step we find essentially a somewhat primary product of the ion irradiation., not yet modified by more successive interactions.

Finally, the third fluence regime includes the processes occurring from 5×10^{14} to 1×10^{17} ions/cm². In this range, the primarily modified areas (i.e., the areas modified in single impact events) undergo a further drastic modification, due to the many re-implantation events occurring at increasing fluence (fig.2c). Thus, we can estimate that at 10^{15} ions/cm² each unit area on the surface has been struck about 5-10 times. In this fluence regime a drastic reorganization of the re-irradiated region occurs, producing the well known effect of massive carbonization of carbon-based polymers [25]. The properties of the materials obtained in this fluence range are essentially those of hydrogenated amorphous carbons, also if the structure of these carbons may be quite different, according to the predominant energy deposition mechanisms [12, 25]. The materials obtained in this regime in general exhibit a good biocompatibility, in agreement with what has been shown for pyrolytic carbons [26]. Therefore, we consider this class of processes and materials less interesting in view of the possibility of modulating the biomolecules adsorption/adhesion and the related biocompatibility properties.

2.1.4 – Beam parameters for surface modification - According to the above discussion, we can now define in a clear way the best suited irradiation conditions to be used to drive the biomolecule adsorption/organization conditions. In particular, in the present work we will consider basically ions of energy suitable to concentrate the modification effects within a few nanometers at the polymer surfaces, i.e., low energy ions with energy ranging from 1-50 keV, furthermore, we will discuss only the effects of irradiation with inert gases, in such

a way to focus only the energy deposition effects. To this purpose, we will exploit essentially the intermediate fluence regime, between 5×10^{13} and 5×10^{14} , so that the “primary” modifications of the polymer can be exploited, without reaching the carbonisation. In fact, in this regime we can modulate in a quite simple way the wished chemical modifications by tuning the fluence as well as the energy deposition mechanisms. We know already that the produced surface phases are very highly “reticulated” amorphous phases [27], which may exhibit signs of nano-structuring, due to the chemical reorganization processes, producing clustering or local densification of the irradiated polymers [28]. Furthermore, the irradiated regions are well-adherent to the underlying unmodified region, as they are intrinsically compositionally graded phases. In fact, the modification process in this energy regime is linearly dependent on the total deposited energy and it is expected to decrease with it, so that at the end of the track only a very mild modification is expected [12, 16]. This fact is in itself one of the important advantages of the ion beam irradiation with respect to other surface modification techniques, as not only it implies a high mechanical stability of the irradiated surfaces, but also it implies that the processes of surface recovery, linked to the inward/outward diffusion of polymer segments, or low molecular weight fragments, are in fact hindered by the formation of the relatively thick and reticulated layer in the selected irradiation conditions.

Low energy ion beams are easily adapted to patterning processes, either by using suitable masks, or by using focused ion beams. It is clear that in the saturation fluence regime of interest for our experiments (5×10^{13} - 5×10^{14} ions/cm²) the patterning will rely on the spatially resolved chemical modification of the surfaces, allowing to study in an exclusive way the effect of the progressive surface chemistry on the adsorption/organization processes of biomolecules interacting with the irradiated surfaces.

Last but not least, we will show in the paper that the ion beam effect on different class of polymers can be discussed in terms of quite general rules, by checking in particular the modification of crucial features as the electronic structure of the irradiated materials and then their electrical and optical properties, the density of specific chemical groups or chemical domains formed under irradiation, and in turn the interfacial energy and the chemical reactivity.

3. Experimental

3.1 PREPARATION, SURFACE MODIFICATION AND CHARACTERIZATION OF THE POLYMER FILMS

Poly(hydroxymethylsiloxane) (PHMS) and poly(ethyleneterephthalate) (PET) (from Aldrich) were deposited as thin films on either p-doped silicon (100) wafers or gold-covered quartz crystals by spin coating (3000 rpm, 60 s, room temperature). The thickness of the deposited films were respectively of $500(\pm 30)$ nm for PHMS and $600(\pm 50)$ nm for PET, as measured from an alpha-step profilometer. The surface irradiation was performed either with 5 keV and 50 keV Ar⁺ or 25 keV He⁺ at fluences ranging from 5×10^{14} to 1×10^{16} ions/cm² (RT, chamber pressure better than 10^{-5} Pa, current density of $1.5 \mu\text{A}/\text{cm}^2$) or by direct patterning by using a highly focused 15 keV Ga⁺ beam. After irradiation the samples were aged in the laboratory atmosphere for 1 week before both surface physico-chemical characterization and adsorption/adhesion experiments.

3.2 – SURFACE CHARACTERIZATION TOOLS

3.2.1 Chemical structure. *X-Ray Photoelectron Spectroscopy (XPS)*. XPS analysis was carried out with a PHI 5600 Multi Technique Spectrometer equipped with a dual Al/Mg anode, a hemispherical analyzer and an electrostatic lens system (Omni Focus III). The electron take-off angle was 45° and the analyzer was operated in FAT mode by using the Al $K\alpha_{1,2}$ radiation with pass energies of 187.85 eV and 11.75 eV for survey and detailed scans, respectively. According to the attenuation length value of $\lambda=2.8$ nm for N 1s photoelectrons [29] in organic materials, the estimated sampling depth 3λ is about 6.0 nm. The spectra were analyzed by using an iterative least squares fitting routine based on Gaussian peaks and Shirley background subtraction. Binding energies (BE's) of all the spectra were referenced to the intrinsic hydrocarbon-like C1s peak at 285.0 eV or 284.6 eV for unirradiated PHMS [24].

3.2.2 Micro- and Nanoscale Morphology. Optical Microscopy (OM) was performed by means of a Leika DM-RME microscope with 50 to 1000x magnification equipped with a Polaroid digital camera. The surface micro- and nano-topography as well as the roughness were measured with a Multimode/Nanoscope IIIA Atomic Force Microscope (AFM) (Digital Instruments) in tapping mode in air with a standard silicon tip. The relative room humidity was 30% and the room temperature was 25°C . Data were acquired on square frames having edges of 10 μm , 1 μm and 350 nm. Images were recorded using height, phase-shift and amplitude channels with 512x512 measurement points (pixels). Measurements were made at least three times on different zones of each sample. Surface roughness values were determined in five random areas per sample, scanning across areas 10×10 and $1\times 1 \mu\text{m}^2$. Roughness parameters (Ra and Rms) calculation and image processing were performed using the Nanoscope III software.

3.2.3 Surface Free Energy. *Contact angle and Surface Free Energy (SFE) measurements.* Measurements of Surface Free Energy were performed by evaluating both static and dynamic contact angles of three different liquids onto the untreated and irradiated surfaces. Half automatic video-based measurements of contact angle were performed at 25°C and 65% relative humidity by using an OCA30 instrument (Dataphysics). The advancing (θ_{adv}) and the receding (θ_{rec}) contact angles were measured by the needle-syringe method [30]. At least five measurements were made for each sample and then averaged. The Surface Free Energies, in terms of apolar Lifshitz-van der Waals (γ^{LW}) and polar Lewis acid (γ^+) and basic (γ^-) components, were evaluated by using the Good-van Oss model [31], with ultrapure Millipore water, glycerol and tricresyl phosphate (Aldrich).

3.3 PROTEIN ADSORPTION AND CELL ADHESION TESTS.

3.3.1 In-situ characterization of the Mass adsorption and Viscoelastic properties. *QCM-D (Quartz Crystal Microbalance with Dissipation monitoring)*. The simultaneous measurements of both frequency (f) and energy dissipation (D) of the sensor consisting of polymer thin film-covered 5 MHz-crystals (Q-Sense) were performed on a Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D) instrument (Q-Sense AB, Gothenburg, Sweden). The changes in D and f were measured on the addition of the adsorbing solution for both the fundamental frequency ($n=1$, i.e. $f \sim 5$ MHz) and the first

three overtones ($n=3, 5$ and 7 , corresponding to $f \sim 15, \sim 25$ and ~ 35 MHz, respectively). Both solutions and measurement cell were stabilized at the temperature of 37°C .

3.3.2 Ex-situ characterization. Protein adsorption experiments. Solutions of Human Serum Albumin (HSA) and Human Fluorescein IsoThiocyanate Albumin (FITC-albumin) (purchased as lyophilized powders from Sigma Chemical Co.) were prepared at a concentration of $20\text{ }\mu\text{g/ml}$ in phosphate buffer (PB) ($\text{pH} = 7.4$). The Fetal Bovine Serum (FBS) (from Sigma), used for testing the multiple protein adsorption, was diluted to 10% (v/v) in ultrapure Millipore water. The incubation steps with single or serum proteins were carried out by soaking respectively PET or PHMS substrates in Petri dishes containing 2 ml protein solution. During the incubation period the samples were kept at 37°C in 5% CO_2 atmosphere. After that the samples were gently washed by using ultra pure Millipore water with a micropipette performing a number of sucking-rinsing steps, in order to wash out the non-adsorbed proteins. The samples were then dried in atmosphere before the measurements. Fluorescence measurements were performed on solutions of FITC-albumin detached from the polymer surfaces by trypsin/EDTA. A Jasco FP-777 Spectrofluorometer with an excitation wavelength of $\lambda = 488\text{ nm}$ was employed, and the intensity at the maximum emission wavelength $\lambda_{\text{max}} \cong 524\text{ nm}$ was measured.

Cell culture experiments. BHK21 and VERO Fibroblast cell lines (Clonetics, Bio-Whittaker) were routinely maintained in Dulbecco's Modified Eagle Medium (D-MEM, Gibco) supplemented with 10% Fetal Calf Serum (FCS, Gibco), Penicillin (0.1 mg/ml), Streptomycin (0.5 mg/ml), L-Glutamine (2 mM), at $70\text{--}80\%$ confluence on polystyrene flasks (Corning). The cell adhesion as well as proliferation and tendency to spreading were evaluated respectively after 2 and 48 hours of incubation at 37°C in a humidified 5% CO_2 atmosphere. At least 10 microscopic fields per sample were randomly acquired with $\times 5$ and $\times 20$ magnification by a COHU High Performance CCD Camera and Leica Qwin software. Quantitative evaluation of adhered cells was performed using the Scion Image software (Windows version of NIH Image software), which allowed to evaluate the cell coverage in terms of integrated density ($\text{I.D.} = N \times [M - B]$), where N is the number of pixels in the selection, M is the average gray value of the pixels and B is the most common pixel value). Results of the image analysis are expressed as mean-standard deviation for each group of treated samples. Differences among groups were established by T-student test analysis by a two population comparison. Statistical significance was considered at a probability $P < 0.05$.

4. Results

4.1 – PATTERNS OF CHEMICAL MODIFICATION OF PET AND PHMS

In this section we will shortly report two specific cases of ion beam-induced modifications relevant for the adsorption processes of biological systems. In particular we will compare the effects of ion irradiation for polyethyleneterephthalate (henceforth PET) and polyhydroxymethylsiloxane (henceforth PHMS). Both these polymers are relevant for applications in the area of biocompatible materials, and they can also be assumed as the model cases of the beam-induced modification respectively in carbon- and silicon-based polymers [32, 33].

The ion-induced chemical modifications may be considered to imply properties at different

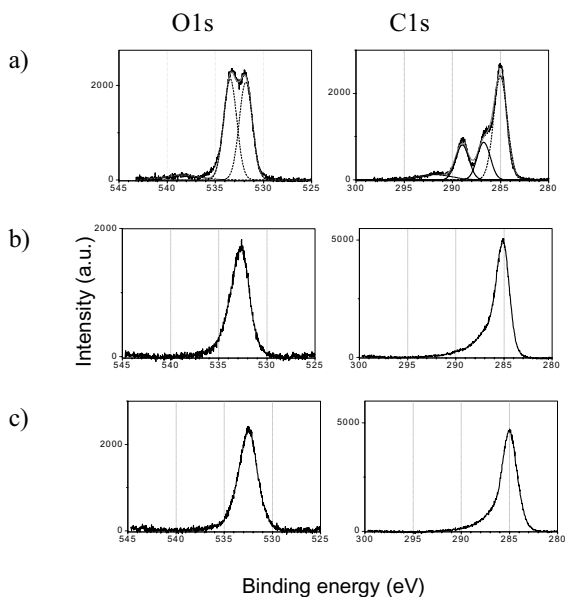


Figure 3.: XPS photoelectron peaks of O 1s and C 1s peaks for PET surfaces: (a) unirradiated, (b) 50 keV Ar⁺ irradiated and (c) 25 keV He⁺ irradiated.

spatial scales, going from “local” properties, as compositional domains and specific chemical functionalities as well as acid/base region and the local electronic structure, to spatially averaged properties, like the Surface Free Energy.

Let us show the typical trends of chemical modification induced by ion irradiation in the second fluence regime (see section 2.1.3 above), i.e., the so called “mild chemistry regime”, corresponding to the first modification level of the polymer.

Figure 3 shows the XPS C 1s and O 1s peaks for PET before (fig.3a) and after irradiation respectively with 50 keV Ar⁺ at 5×10^{14} (fig.3b) and 25 keV He⁺ at 5×10^{15} ions/cm² (fig.3c). It can be seen that for both irradiations with Ar⁺ and He⁺ the change of the C 1s and O 1s photoelectron peakshape is similar, with the strong decrease of C(=O)O groups, indicated by the decrease of the components respectively at ~289 eV of BE for C 1s and ~531.8 eV of BE for O 1s, and the disruption of the aromatic rings (the disappearance of the *shake-up* components, related to the $\pi \rightarrow \pi^*$ transitions, respectively at ~538.5 eV of BE for O 1s and ~292.0 eV of BE for C 1s). This modification of the surface chemical structure corresponds to the change of the stoichiometry from the original C_{2.4}O₁ of unirradiated PET surfaces to that of C_{5.5}O₁ for the irradiated ones.

Figure 4 reports the XPS O 1s, C 1s and Si 2p peaks for PHMS in the same irradiation conditions as for PET. Also in this case the pattern of modification is comparable for the two kinds of irradiation and essentially involves the progressive conversion of the initial [-SiO₃C-] units into [-SiO₄-] clusters, with a marked depletion of the -CH₃ groups, involving either their ejection from the surfaces or their conversion in small hydrogenated amorphous carbons clusters (a-C:H) [28]. Accordingly, the structure of the modified surfaces may be shortly described as an amorphous SiO₂-like matrix, with inclusions of a-C:H clusters, as discussed in details in previous papers [32-34].

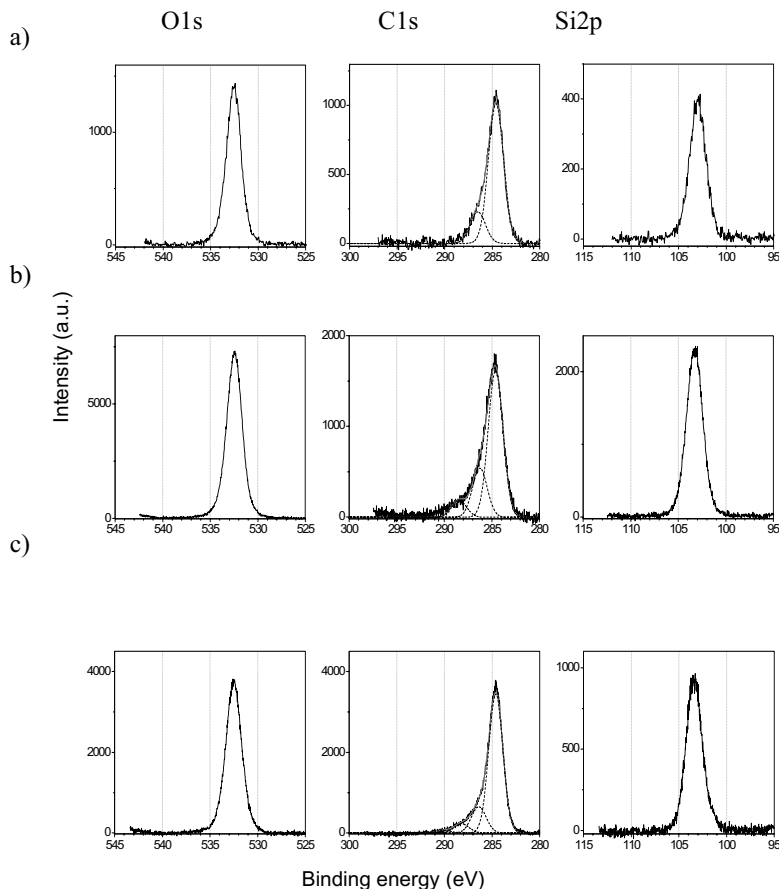


Figure 4.: XPS photoelectron peaks of O 1s, C 1s and Si 2p peaks for PHMS surfaces: (a) unirradiated, (b) 50 keV Ar⁺ irradiated and (c) 25 keV He⁺ irradiated.

It is to point out the fact that, according to the analysis in the preceding section 2.1, the ion energy and fluence have been set in such a way that the total deposited energy $\langle Ed \rangle = S_t \times \Phi$ is the same for the Ar⁺ and He⁺ treatments, i.e., about 4.2×10^{16} eV/cm². The XPS results show indeed that the “degree” of chemical modification is very similar for both treatments and it depends, in the selected ion energy regime, uniquely on the $\langle Ed \rangle$. Furthermore, again following the analysis in section 2.1, in the employed fluence the polymer surface can be considered as completely saturated with the primary ion track, with a negligible track overlap, so that the modification of the primary structure of the polymer can be considered concluded.

This point is in fact supported by the observation that both the decrease of the COO⁻ groups, assumed as a marker of the modification of the PET monomer structure, as well as the formation of the [-SiO₄-], assumed as marker of the PHMS modification, saturates at 5×10^{14} ions/cm² for Ar⁺ ions and 5×10^{15} ions/cm² for He⁺, independently on the very

different chemical structure of the two polymers. Obviously, in the two cases the difference of one order of magnitude in fluence for Ar^+ and He^+ irradiation is just related to the different density of the deposited energy, which corresponds to a smaller “effective radius” for the He^+ ions [35].

4.2 – SURFACE FREE ENERGY MODIFICATION

In order to understand the effect of irradiation on the adsorption/organization processes, we have considered in a specific way the correlation between the ion-induced chemical modification and Surface Free Energy (SFE).

It is well known that SFE for irradiated polymer surfaces in a general way tends to increase, as it is easily indicated by the modification of the water dynamic contact angle [36]. Furthermore, by using the well-known technique of the three liquids, it is also possible to quantify the modification of the various components of the SFE, i.e., the Lifshitz-Van der Waals dispersive term γ^{LW} , and the acid-base ones, corresponding to the Lewis acid γ^+ and base γ^- terms, according to the relationships reported below [31]:

$$\gamma^{\text{total}} = \gamma^{\text{LW}} + \gamma^{\text{AB}} \quad (2)$$

$$\gamma^{\text{AB}} = 2\sqrt{\gamma^+ \cdot \gamma^-} \quad (3)$$

Tables 1 and 2 show the modifications induced in SFE of respectively PHMS and PET by several types of ions in different conditions.

Table 1. PHMS

Treatment	ACID (γ^+) (mJ/m ²)	BASE (γ^-) (mJ/m ²)	AB (γ^{AB}) (mJ/m ²)	LW (γ^{LW}) (mJ/m ²)	TOTAL SFE (mJ/m ²)
Untreated	0.4	8.7	3.7	27.0	30.7
5 keV Ar^+ F = $5 \times 10^{14} \text{ cm}^{-2}$	2.1	23.9	14.2	28.7	42.9
5 keV Ar^+ F = $1 \times 10^{15} \text{ cm}^{-2}$	3.0	19.7	15.4	30.2	45.6
50 keV Ar^+ F = $1 \times 10^{15} \text{ cm}^{-2}$	1.5	26.9	12.6	39.3	52.0
15 keV Ga^+ F = $1 \times 10^{15} \text{ cm}^{-2}$	1.3	36.8	13.8	39.1	52.9

Table 2. PET

Treatment	ACID (γ^+) (mJ/m ²)	BASE (γ^-) (mJ/m ²)	AB (mJ/m ²)	LW (mJ/m ²)	TOTAL SFE (mJ/m ²)
Untreated	0.4	16.9	5.2	39.1	44.3
5 keV Ar^+ F = $5 \times 10^{14} \text{ cm}^{-2}$	1.7	14.6	10.0	26.1	36.1
5 keV Ar^+ F = $1 \times 10^{15} \text{ cm}^{-2}$	0.9	16.0	7.6	33.2	40.8
50 keV Ar^+ F = $1 \times 10^{15} \text{ cm}^{-2}$	1.0	11.7	6.8	39.2	46.0
15 keV Ga^+ F = $1 \times 10^{15} \text{ cm}^{-2}$	0.4	12.9	4.5	39.0	43.5

It can be seen that the ion irradiation generally increases the SFE of PHMS, in correspondence to the decrease of the water contact angle from $\sim 90^\circ$ of the unirradiated hydrophobic surfaces to values ranging from $\sim 40^\circ$ to $\sim 50^\circ$, the relative magnitude of the effect being closely related to the ion beam parameters, with particular attention to the total deposited energy, i.e., to the primary ion energy and fluence. These parameters in fact are responsible for the more or less modification of the chemical structure of the irradiated surfaces. In the case of PET the modification of SFE is much less marked, as expected on the basis of the fact that the water contact angle value is nearly unchanged around the value of $\sim 65^\circ$ for untreated and irradiated surfaces.

4.3 - ADSORPTION OF BIOMOLECULES ONTO IRRADIATED POLYMER SURFACES.

4.3.1 A model case of single protein adsorption: Human Serum Albumin (HSA). Figure 5 shows the HSA adsorption kinetics obtained from fluorescence measurements for PHMS and PET surfaces irradiated with 5 keV Ar^+ at 5×10^{14} and 1×10^{15} ions/cm². Both for the two selected ion doses the irradiation induces a severe modification of the protein adsorption for the two different polymers.

In fact, for PHMS (fig. 5a), while the irradiation with 5×10^{14} ions/cm² produces a peaked curve with a maximum of the adsorption at 1 hour of incubation time, the samples irradiated at the higher fluence of 1×10^{15} ions/cm² exhibit smooth adsorption behavior with small increase and an adsorption plateau. At variance of this, PET surfaces unirradiated and irradiated to 1×10^{15} ions/cm² exhibit a peaked HSA adsorption kinetics with more or less pronounced maxima (Fig. 5b), while PET irradiated to 5×10^{14} ions/cm² shows a relatively smooth curve of adsorption [33].

The two different adsorption behaviors have been interpreted in terms of the two following basic models of adsorption: i) for the smooth kinetics, a completely reversible adsorption mechanism with no interaction among the adsorbed molecules, (Langmuir-like behavior); ii) for the peaked kinetics, adsorption processes in which the protein molecules are adsorbed in one conformation but may change to a second irreversibly bound form, which

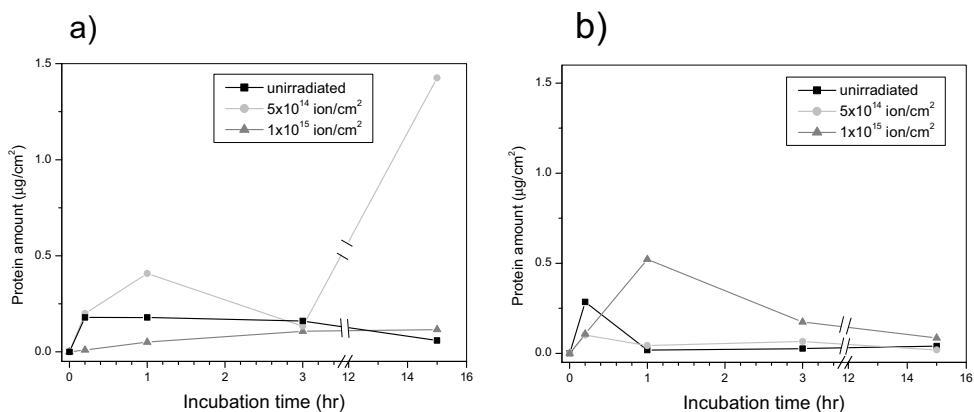


Figure 5.: FITC-HSA adsorption kinetics on unirradiated and 5 keV Ar^+ irradiated surfaces of PHMS (a) and PET (b).

need a larger contact area with the surface and induce the extra-desorption of the initially adsorbed macromolecules [37].

It seems to be clear that, on the basis of these models, ion irradiation is able to drastically change the nature of the adsorption mechanism for PHMS and PET depending on the ion dose.

This findings have been related to the different ion-induced patterns of chemical and physical modification of the two polymers, which have been already discussed in the previous section, according to the XPS and Surface Free Energy results. In particular, Figure 6 shows the change of both the total surface free energy γ_s^{tot} and the atomic concentrations with increasing ion fluence for 5 keV Ar^+ irradiation of PHMS (Fig.6a) and PET (Fig.6b) surfaces, respectively.

One can see that ion beam readily modifies PHMS into a carbon-depleted $\text{SiC}_x\text{O}_y\text{H}_z$, the rough formula being changed from $\text{Si}_{1.2}\text{C}_0\text{O}_2$ (unirradiated samples) to $\text{Si}_{1.3}\text{C}_{0.3.4}$ (5×10^{14} ions/ cm^2) and $\text{Si}_{1.5}\text{C}_{0.4.2}$ (1×10^{15} ions/ cm^2), while for PET irradiation induces a relatively small depletion process of the oxygen-containing groups. Indeed, before irradiation the oxygen content was about 26.5%, quite close to the theoretical one of 28.6%, while after irradiation it becomes 23.1% at 5×10^{14} ions/ cm^2 and 21.5% at 1×10^{15} ions/ cm^2 , respectively.

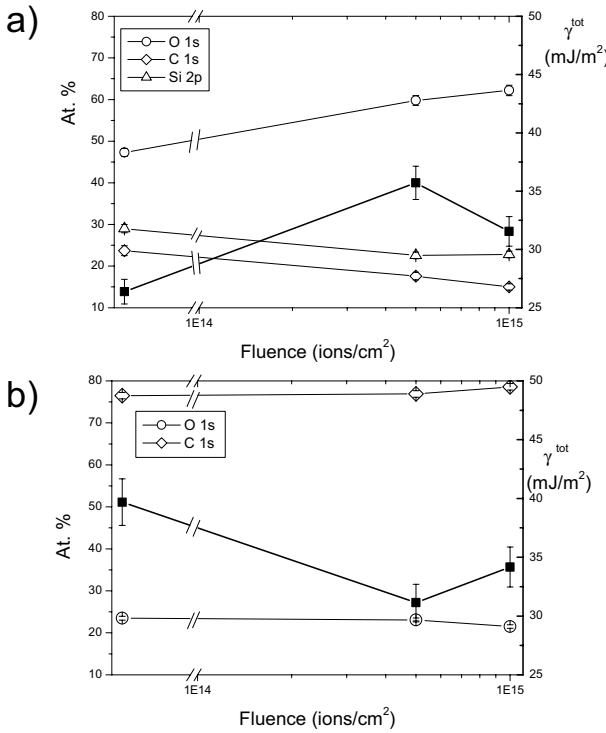


Figure 6.: γ_s^{tot} (solid squares, right axis) and atomic concentrations (open symbols, left axis) vs. ion fluence for PHMS (a) and PET (b) surfaces.

It can also be seen that at variance with the compositional modifications, which behave quite linearly, the SFE exhibit a non linear modification trend. Furthermore, the trends of SFE modification are opposite for PHMS and PET. In fact, for PHMS γ^{TOT} shows an initial increase from 26.4 mJ/m² (before irradiation) to 35.7 mJ/m² (at 5x10¹⁴ ions/cm²) and then a small decrease to 31.5 mJ/m² (at 1x10¹⁵ ions/cm²). On the other hand for PET γ^{TOT} initially decreases from 39.7 mJ/m² to about 31.1 mJ/m² (at 5x10¹⁴ ions/cm²) and then slightly increases to 34.2 mJ/m² (at 1x10¹⁵ ions/cm²).

The modifications of HSA adsorption kinetics above described can be discussed in terms of observed non-linear changes in the surface free energy γ^{TOT} . Indeed, for PHMS, the modification of the adsorption kinetics from a Langmuir-type (before irradiation) to a peaked-type (at the fluence of 5x10¹⁴ ions/cm²) can be interpreted as to be due to the strong increase of the hydrophilic character of the irradiated surface (corresponding to the maximum value of the total surface free energy). In turn, it is known that the increase of the hydrophilic character of the solid surface lowers the adsorption tendency of the HSA molecules [37]. It is interesting to note that at higher ion fluence the decrease of γ^{TOT} corresponds to the recovery of the initial Langmuir-type profile. As for PET, the modification of adsorption kinetics follows an opposite trend, as discussed above. In this case in fact, the initially peaked kinetic (untreated surfaces) evolves to a smoothed one in connection with the decrease of the SFE (at the fluence of 5x10¹⁴ ions/cm²), while the initial adsorption trend is restored when γ^{TOT} increases again at higher fluence. Accordingly, we conclude that peaked adsorption behaviour is observed only above a critical value of the surface free energy (about 31 mJ/m² in the present experiment), while below this critical value a smooth Langmuir-type kinetic is observed [33].

Hence, the ion irradiation treatments modify the HSA adsorption mechanisms through the change of the SFE above and below a characteristic critical value.

4.3.2 - Serum Proteins adsorption. Here we report an example of the adsorption process from a complex protein solution system (Fetal Bovine Serum, FBS) on three model surfaces: untreated PHMS and the corresponding silicon-based (SiO_xC_yH_z) and carbon-based (a-C:H_x) phases obtained by ion beam irradiation, respectively representative of irradiated PHMS and PET. Figure 8 shows the plots of frequency shifts (Δf) and dissipation shifts (ΔD) upon exposure of the three examined surfaces to the FBS solution.

One can see that the frequency and dissipation changes are completely different for the various samples. In fact, the hydrophobic surfaces of untreated PHMS (Fig. 7a) displays the lowest values of frequency decrease (less than 10 Hz) and ΔD shift ($\sim 0.2 \times 10^{-6}$), suggesting a low mass adsorption at the sensor surfaces as well as the invariance of the viscoelastic properties (i.e., $\Delta D \sim 0$) of the thin adsorbed film.

Regarding the SiO_xC_yH_z surfaces (Fig. 7b), although the dissipation curve still does not change significantly ($\Delta D \sim 0.1 \times 10^{-6}$), the frequency curve exhibits a noticeable shift to the saturation value of $\Delta F \sim -65$ Hz, after 1 hour of incubation time. Finally, the a-C:H_x surfaces (Fig. 7c) show the intermediate Δf shift of ~ 15 Hz, and the relatively high dissipation change of $\sim 1.5 \times 10^{-6}$, which indicates a not negligible viscoelastic behaviour of the adlayer.

By applying the Sauerbrey relation for the frequency to mass conversion [38], in the approximation of a rigid adlayer, the estimated adsorbed mass on PHMS, SiO_xC_yH_z and a-C:H_x surfaces should be of 100, 700 and 300 ng/cm², respectively.

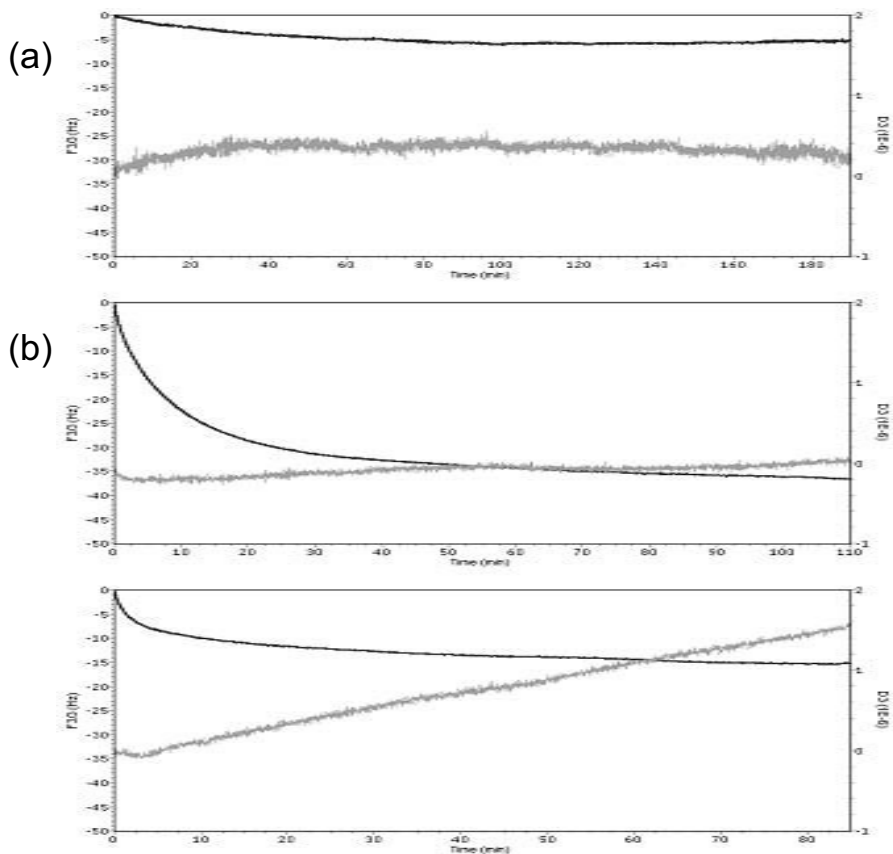


Figure 7.: Frequency (left axis) and dissipation (right axis) shift for FBS protein adsorption on: (a) unirradiated PHMS, (b) SiO_xC_y and (c) $\alpha\text{-CH}_x$.

However, it has to be noted that the QCM-D frequency shift is actually related to the total mass coupled to the oscillating sensor surface [39], including the surface-trapped solvent molecules. In fact, as far as the XPS results evidenced an almost complete and comparable protein coverage for all the investigated surfaces, the QCM-D data must be interpreted in terms of different viscoelastic properties of the overlying protein solution in proximity to the interface or also in terms of different aggregation state of the protein adlayer.

As to the first hypothesis, the SFE analysis indicated different water wettability of the three surfaces, the unirradiated PHMS being the most hydrophobic surface ($\theta_s \sim 90^\circ$), while the $\alpha\text{-CH}_x$ and $\text{SiO}_x\text{C}_y\text{H}_z$ are respectively mildly hydrophobic ($\theta_s \sim 65^\circ$) and hydrophilic ($\theta_s \sim 35^\circ$) surfaces. Accordingly, the frequency shifts at the $\alpha\text{-C:H}_x$ and $\text{SiO}_x\text{C}_y\text{H}_z$ irradiated surfaces could just be the effect of the different solution behaviour depending on the different SFE values. Thus, this effect can involve the water adsorption, the surface swelling as well as the different density at different interfaces, all processes producing an apparent increase of the adsorbed mass.

The correlation between the obtained QCM-D curves and the SFE properties of the three examined surfaces is evident from Figure 8, showing the Dissipation vs. Frequency (Df) plots (Fig.9a), and the free energy of interaction in water ΔG_{iwi} (Fig. 9b), given by:

$$\Delta G_{iwi} = -2\gamma_{iw} = -2\left(\sqrt{\gamma_i^{LW}} - \sqrt{\gamma_w^{LW}}\right)^2 - 2\left(\gamma_i^{AB} + \gamma_w^{AB} - 2\sqrt{\gamma_i^+ \cdot \gamma_w^-} - \sqrt{\gamma_i^- \cdot \gamma_w^+}\right) \quad (4)$$

where $\Delta G_{iwi} > 0$ or < 0 indicates a hydrophilic or hydrophobic surface, respectively [31]. In particular, the Df plots in Fig. 8a provide information about adsorption kinetics and absolute viscoelastic properties. It is possible to see that three different kinetic regimes are

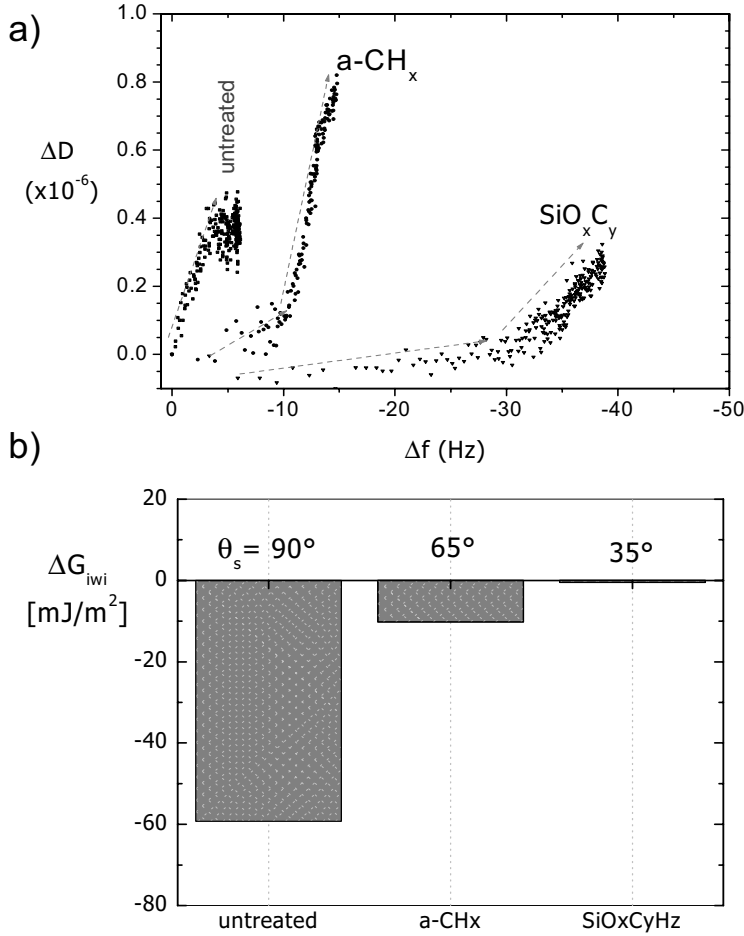


Figure 8.: Df plots from QCM-D data (a) and Free energy of interaction in water ΔG_{iwi} (b) for unirradiated PHMS, a-CH_x and SiO_xC_yH_z surfaces. Dashed arrows are drawn to guide the eye.

obtained for the three examined surfaces: a one-step kinetic (a curve with a large slope, corresponding to a viscoelastic layer) and a two-step kinetics for the irradiated a-C:H_x and SiO_xC_yH_z surfaces.

However, while for the a-C:H_x, after the initial short step at low-slope, the second regime exhibits a slope similar to that of unirradiated PHMS, for the mildly hydrophilic SiO_xC_yH_z surfaces the low $\Delta f/\Delta D$ value for both regimes points out the rigidity of the adlayer.

The second hypothesis above formulated, i.e., the occurrence of different aggregation phenomena, has been investigated by AFM measurement on the dry samples reported in Figure 9. One sees clearly that on the untreated PHMS and a-C:H_x only few and relatively small aggregates are formed, while on the SiO_xC_yH_z surfaces, relatively few but very large aggregates (having a typical dimension ranging between 100-200 nm of size) are unevenly distributed through the surface [40].

As noted above, the XPS results clearly indicated that an almost complete coverage is found for all the investigated surfaces. i.e., the aggregates seen in AFM lay on a smooth and probably continuous protein film [41]. The effect is also observed when AFM phase images are obtained (in the insets), showing that the effect has also a chemical nature.

4.3.3 - Beam-modified Cell-Surface interaction. In general, the cell-surface interaction is studied in terms of the attachment or adhesion, proliferation, and spreading processes of a given cell line on surfaces having well-defined structural and chemical features.

It is to note that there is a large living debate about the nature of the critical factors for different types of cells and surfaces, in view of the peculiar and often unpredictable behaviour of the various cell systems [41]. However, several correlations have been established involving the surface topography and its chemical structure as “primary” factors, and in turn the concentration of specific functional groups, the chemical and/or crystallographic “defects”, serving as “anchoring” sites [42-45], the surface free energy [46-48], the electrical properties (charge state and electronic structure) [49, 50].

Furthermore, it has been pointed out that the first event in a common cell adhesion experiment consists in the adsorption of serum proteins and peptides on the surfaces, so that the cell-surface interaction is intrinsically mediated by the preliminary coating of the

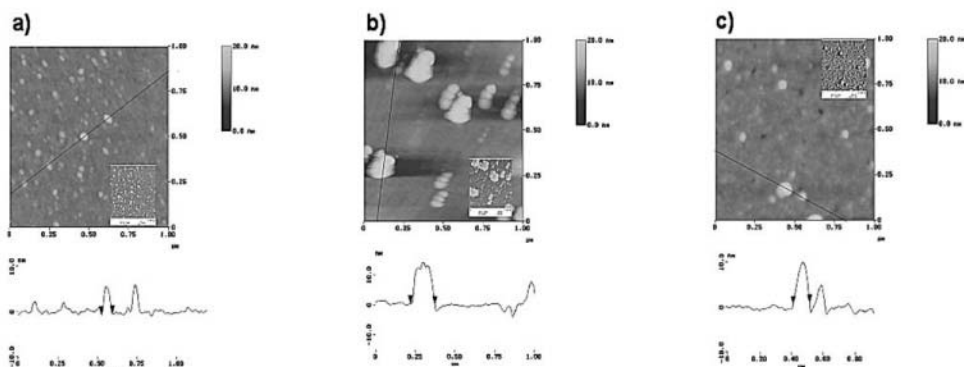


Figure 9.: AFM tapping mode topographical and (in the insets) phase images for FBS-incubated surfaces of: unirradiated PHMS (a) , SiO_xC_yH_z (b) and a-C:H_x (c).

surface with a proteinaceous or peptidic layer. In a more general way, the cell-surface interaction is rationalised according to two basic time-dependent steps:

- Diffusion-guided short term “physico-chemical” attachment (mostly depending on the surface structure): steps of “cell attachment and adhesion”;
- Biochemically-guided long term response, involving the modification of the cell membrane, expression of adhesive proteins, etc. (mostly depending on the cell type): steps of “cell spreading and proliferation”

Figure 10 shows the characteristic effect induced by ion irradiation on the first two interaction steps for a very common cellular system onto an ion-irradiated polymer surface.

In this case BHK21 fibroblasts in the Dulbecco's Modified Eagle Medium, were put in contact for 24 hours with a PHMS surface partially irradiated with 5×10^{14} ions/cm² of 5 keV Ar⁺. It can be clearly observed that most of the cells tend to be preferentially attached to the irradiated area, on the left hand side of the photo, while only a few of them seem interacting with the unirradiated area, on the right hand side of the picture.

Figure 11 reports the quantitative evaluation of the cell adhesion at two different incubation times, corresponding to the two time-steps in cell-surface interaction above sketched. In particular, the bars at 2 hours represent the cell adhesion step, i.e., a process which is driven by very basic physico-chemical parameters as the surface free energy, the surface charge, the roughness, etc. The bars at 48 hours of incubation time are representative of the second biochemically-guided interaction step, involving the complex building-up of the protein-cell system on the surfaces.

It can be seen that the ion irradiation induces a fluence-dependent enhancement of both adhesion and spreading processes, with an enhancement factor of about 5 times in the cell-covered surface for the spreading processes with respect to the adhesion step [48]. Furthermore, it appears that the cell coverage tends to reach the saturation at fluence of 5×10^{14} ions/cm². The close analysis by Scanning Electron Microscopy of the cell covered surfaces at this fluence indicated that a fully confluent cell monolayer is indeed obtained at this fluence [24].

The enhancement effect has been indeed demonstrated to be quite general for a large number of polymers, including polystyrene, polyethylene, polypropylene, polyurethane and silicone rubbers, and cell systems, including endothelial cells, fibroblasts, astrocytomas, pericytes, etc. [22-24, 51-53].

However, a recent experiment from this Laboratory has shown that the effect is not as general as one could believe. In fact, the cell response for beam patterned PET and PHMS surfaces showed that while in the case of PHMS the cell response is selective for the irradiated areas, in the PET case the cells do not exhibit any selective adhesion and adhere in a massive way to both the irradiated and unirradiated areas.

Figure 12 reports the results obtained for Fibroblast Vero cells adhesion experiments (5 hrs. incubation time) on simple patterns, consisting of stripes 80-, 30- and 10- micrometer wide, obtained respectively onto PET and PHMS surfaces by using 15 keV Ga⁺ to a fluence of 1×10^{15} ions/cm².

The observed improvement of the cell response on the irradiated surfaces has been basically discussed in terms of the modification of contact angle (i.e., the surface free energy) [24] and composition, put in relation to the formation of peculiar hydrogenated amorphous carbon-or silica-like phases, depending on the original structure of the irradiated polymers [24, 32-34].

Accordingly, we could establish a quite fair correlation between the relative contribution of

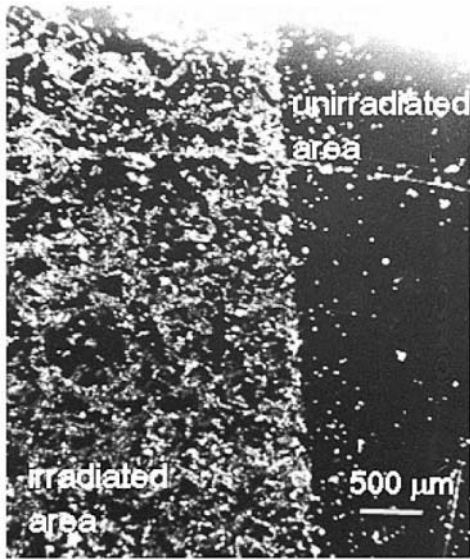


Figure 10.: BHK21 cells (white dots) adhered on a 5 keV Ar^+ irradiated PHMS.

the different components of the SFE with the enhancement of cell adhesion and spreading. In fact, figure 13 reports the contact angle modification and the analysis of the polar components γ^+ and γ^- of SFE for the two irradiated PET and PHMS surfaces.

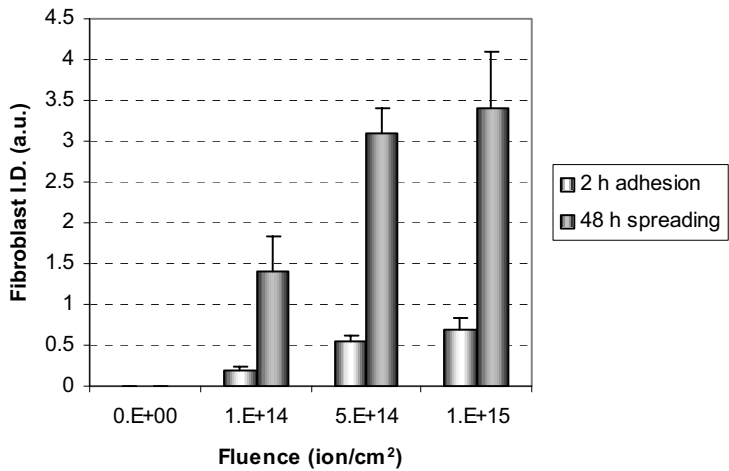


Figure 11.: Integrated density I.D. values of BHK21 cells on unirradiated and 5 keV Ar^+ irradiated PHMS surfaces.

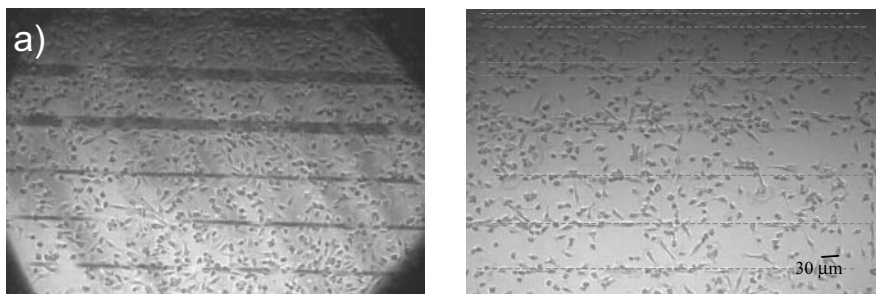


Figure 12.: Optical micrographs of patterned and cell-incubated surfaces of: (a) PET, (b) PHMS. Dashed arrows are drawn to guide the eye.

It can be seen that in the case of PHMS the Ga^+ irradiation induces a quite marked modification of the water contact angle, from about 90° to 35° , while for PET the contact angle modification is much smaller, from about 70° to 60° (fig.13a and b).

Moreover, figure 13c and d shows that the ion irradiation essentially involves the basic Lewis polar component γ^- , which for irradiated PHMS increases from about 0.1 to about 40 mJ/m^2 , while for irradiated PET the same component changes from about 15 to about 22 mJ/m^2 . This effect, along with the almost constant value of the dispersive Lifshitz – van der

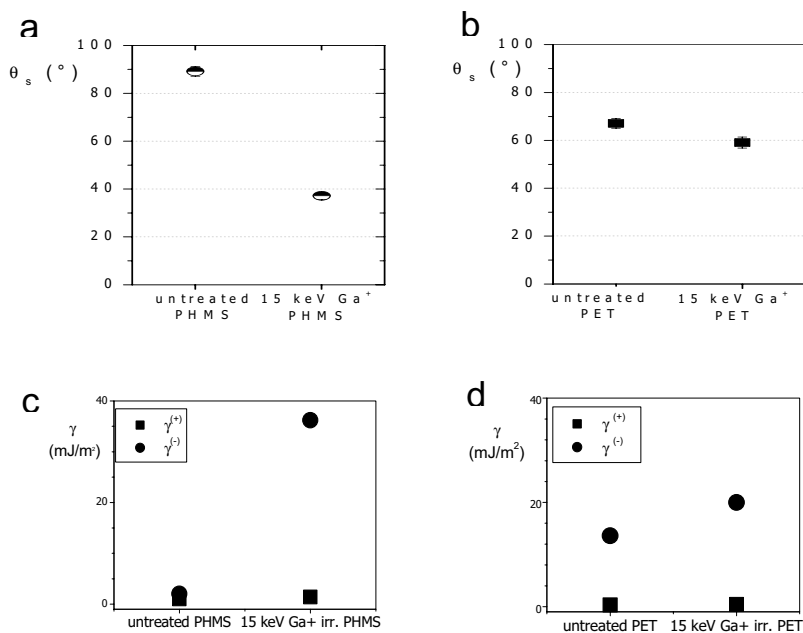


Figure 13.: Static water contact angle change for PHMS (a) and PET (b). Lewis acid (+) and base (-) components of SFE for PHMS (c) and PET (d).

Waals component, suggests that is just the enrichment of the concentration of basic polar groups on the surface above a critical value, which induces the surface selectivity for cell adhesion.

It seems therefore possible that important effects of selectivity can be obtained only for polymers having a large difference among the γ^- value before and after ion irradiation. It remains an open question the importance of the electronic structure of the irradiated phases in the determination of the γ^- values. In fact, it is well known that electrically conducting domains have a strong electron-donor character, and in turn a high γ^- value [31].

5. Conclusions

Experimental findings on the modification of the process of single and complex protein adsorption as well as cell adhesion and spreading enhancement have been described for ion irradiated polymer surfaces.

The effects for protein adsorption have been shown to be strongly dependent on the characteristic ion-induced modification of the chemical structure of a very thin surfacial layer and the related Surface Free Energy properties, which appears capable of influencing the protein adsorption and aggregation mechanisms.

The comparison of the properties of ion-modified carbon- and silicon based model polymers (i.e., PET and PHMS) respectively consisting in a-C:H_x and $\text{SiO}_x\text{C}_y\text{H}_z$ phases, allowed to demonstrate that dramatic differences in the protein adsorption process could be obtained. In fact, remarkable surface-dependent effects of protein aggregation were observed, with small and scarce aggregates found on the carbon-based a-CH_x surfaces, and large aggregates observed on the silicon-based $\text{SiO}_x\text{C}_y\text{H}_z$ materials.

The peculiar features of the adsorbed protein layers on the two different types of surfaces could be related to the overall cell adhesion and spreading behaviour in terms of the Surface Free Energy modification. In particular, the experimental results allowed to identify a very critical role for the electron donor Lewis basic component of SFE, which appears as the factor triggering the cell adhesion properties of a given surface and in turn its selectivity behaviour.

Acknowledgements

The Authors gratefully acknowledge the financial support from FIRB and PRIN 2002 programs.

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ORIENTED IMMOBILIZATION OF C-REACTIVE PROTEIN ON SOLID SURFACE FOR BIOSENSOR APPLICATIONS

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Abstract

An attempt of surface modification with receptor layers to achieve a maximal signal from antigen-antibody interaction on the solid surface has been undertaken. Interaction of *C-reactive* protein (CRP) with monoclonal anti-CRP has been investigated by comparative study by chemical cross-linking or electrostatic interaction in the framework of Layer-by-Layer approach. The processes of gold surface modification have been monitored by a wavelength interrogation-based surface plasmon resonance (SPR) sensor. Atomic force microscopy has been used for visualization of the surfaces modified with protein layers. The influence of *biotinylated protein G-streptavidin* (bPG/STV) complex on the SPR signal shift by antigen-antibody interaction has been studied. The influence of different cross-linking chemicals, such as di(N-succinimidyl)-3,3'-dithiodipropionate, 3-(2-pyridyldithio)-propionic acid N-hydroxysuccinimide ester, and N-hydroxysuccinimide/N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide on antigen immobilization of anti-CRP/bPG/STV system has been also examined. The film morphology of the first immobilized layer is very important for protein interactions. Maximum SPR-shift by CRP coupling with anti-CRP has been observed on the surface modified by streptavidin and di(N-succinimidyl)-3,3'-dithiodipropionate. AFM method can be used to directly monitor CRP/anti-CRP interaction on polyelectrolyte support.

1. Introduction

Bioengineering on solid surface is a multi-disciplinary research field including biotechnology, chemistry, physics, microelectronics, material science and etc. Instrumentation for bioanalytical purposes is now well elaborated and includes various techniques [1], such as mass spectrometry, X-ray photoelectron spectroscopy, ellipsometry, infrared reflection-absorption, fluorescence spectroscopy and SPM methods (AFM, STM, NSOM and etc). These methods can provide the essential tools to analyze the presence of proteins on solid surface, to register the morphology change and to measure the biospecific interactions at the molecular level. Detection of molecule interactions by biosensors is mainly based on the optical and electrochemical techniques, such as surface plasmon resonance (SPR), total internal reflection fluorescence microscopy, time-resolved fluoroimmunoassay, the displacement flow immunoassay, electrochemical impedance spectroscopy [2-6] and etc.

SPR is one of prevalent methods for biosensors [2, 3] because of its direct detection of analytes in real time. SPR sensors have been widely used for the analysis of antigen-antibody interactions [7], and also used to characterize the conformational changes of protein molecules [2]. Recently, there has been an intensive investigation on the imaging of protein arrays by SPR, especially, using white lights rather than lasers as the light source [8]. One drawback of SPR sensors is the detection limit of low concentration or low molecular weight analytes, but the detection limit has been improved by oriented immobilization of proteins, enhancing the response signal by streptavidin-biotinylated protein complex [3], or using modified colloidal gold particles [4].

For application of biosensors, it is essential to immobilize receptors on sensor surfaces, which are directly attached to solid substrates and used to detect specific target molecules. So, surface modification is a key technique for biosensor elaboration. Various biomolecules, such as antibodies, nucleic acids, proteins, or catalytic ones like enzymes, microorganisms and biomimetic catalysts can be used as receptors [9, 10]. We have chosen the interaction of *C-reactive* protein (CRP) with monoclonal anti-CRP at investigation of optimal protein immobilization on SPR chip surface. That choice was determined by a number of circumstances. In particular, C-reactive protein is widely used as a diagnostic tool for clinicians [11]. During the acute phase response, CRP concentration of serum increases rapidly from less than one to several hundred micrograms per milliliter in response to inflammation or injury [12, 13]. High levels of circulating CRP are usually present within one to three days following acute tissue damage, infection or systemic inflammation. Two major functions are well documented for CRP now, namely: (i) innate immunity against infection [14, 15] by recognition of pathogens and to mediate their elimination by recruiting the complement system and phagocytic cells and (ii) removal of membrane and nuclear material from apoptotic and necrotic host cells [16]. These functions of CRP are stipulated by its specific binding to the phosphocholine or residues of C-polysaccharide (PnC). Indeed, phosphocholine, the principal CRP ligand, is widely distributed in capsular carbohydrates and lipopolysaccharides of bacteria and other microorganisms. CRP also binds to microbial polysaccharides and to ligands exposed on damaged cells. Binding of CRP to these substrates activates the classical complement pathway leading to their uptake by phagocytic cells. CRP has been found on necrotic cells and invading microbes at inflammation sites. It was shown [17] that CRP is associated with cell membranes of damaged and necrotic, but not normal cells. Thus, rapid determination of CRP level in sera of patients is very important task for medical diagnostics. Not less important task is correct immobilization of CRP on solid support for subsequent separation of damaged cells as well as bacteria or other microorganisms with the aim of subsequent identification. So, the goal of the work is to apply the different approaches for CRP/anti-CRP molecules immobilization on a solid surface and to compare the protein activity for antigen-antibody interaction depending on the surface used.

2. Experiment

2.1. MATERIALS

3,3'-Dithiodipropionic acid di(N-succinimidyl ester) (DTSP), N-succinimidyl-3-(2-pyridyldithio)propionate (SPDP), *N*-ethyl-*N'*-(diethylaminopropyl)-carbodiimide (EDC),

N-hydroxysuccin-imide (NHS), Poly(diallyldimethylammonium chloride) (PDPA), $M_w \sim 100000$, and poly(sodium 4-styrenesulfonate) (PSS), $M_w \sim 70000$ were obtained from Aldrich Chemical Co. (Milwaukee, WI). PSS was dialyzed against Milli-Q water for two days and then lyophilized before use. Streptavidin (STV) was purchased from Kem-En-Tec (Denmark) and recombinant biotin labeled protein G (bPG) was obtained from Sigma (USA). C-reactive protein (CRP) was purchased from Life biotech (Switzerland) and anti-CRP antibody (α -CRP) was purchased from Boditech (South Korea). Other chemicals were reagent grade.

2.2. SUBSTRATE PREPARATION AND MODIFICATION

Gold-coated (420Å) slide glasses were prepared by sputtering gold on glass plate. Thin (30Å) titanium sub-layer was used to improve adhesion of gold film to glass. Then, the slide glass was cleaned by incubation with a cleaning solution of $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (1:1:5, v/v) at 80°C for 10 min and washed with dH_2O . Muscovite mica for AFM observation was cleaved with adhesive tape. After extensive rinsing with water, the surfaces were dried under N_2 . After incubation with protein solutions, surfaces were also washed in phosphate buffer (pH 7.4) containing 1.2 mM potassium phosphate monobasic, 2.7 mM potassium chloride, 8.1 mM sodium phosphate dibasic, 138 mM sodium chloride.

Surface activation with polyelectrolyte solutions: Gold surfaces of slide glass or fresh cleaned mica were modified by alternative adsorption of 1 mg/ml PDPA and PSS solutions for 15 min. The treated surfaces were rinsed three-five times with dH_2O between each deposition and finally dried under N_2 gas. The outermost layer becomes «negatively» or «positively» charged after last treatment with PSS and PDPA.

Immobilization of proteins on SPDP-functionalized gold substrates: The cleaned gold surfaces were activated by dipping in 1 mg/mL SPDP dissolved in DMF for 1 h at room temperature. The derivatized substrates were cleaned by rinsing with DMF and subsequently with the phosphate buffer (pH 7.4) to remove unbound SPDP. The surfaces of the *N*-succinimidyl-derivatized substrate were then modified by an appropriate protein, via the surface amine groups by dropping several tens microliters of protein solution (1 mg/mL in 20 mM sodium phosphate buffer, pH 7.0) onto the prederivatized surfaces and incubating for 1 h at 25 °C. After the substrates were rinsed thoroughly with phosphate buffer, to remove any unbound and loosely bound protein.

Immobilization of proteins on DTSP-functionalized gold substrates: A conditioned gold substrate was immersed in 10mM DTSP in DMSO for 30 min at room temperature. The corresponding monolayer containing the active succinimidyl esters was rinsed in DMSO and water. Afterward, the functionalized substrate was incubated with various proteins in phosphate buffer for 1 h. The immobilized proteins were thoroughly rinsed with phosphate buffer and dH_2O for 15 min.

Immobilization of proteins on NHS/EDC-functionalized gold substrates: The activated gold surface with presumably free hydroxylic groups were incubated with 150 mM EDC and 30 mM NHS for 30 min to attach the NHS group to the -OH terminus. Then, the surfaces were incubated with 1mg/ml proteins in the phosphate buffer (pH 7.4) at room temperature for 1 hour. All the samples were washed with phosphate buffer, extensively rinsed with dH_2O and dried under N_2 gas.

2.3. INSTRUMENTATION

Surface modification with polyelectrolytes or protein binding on the modified surfaces has been monitored by a SPR system (self-assembled). White light from a quartz tungsten halogen lamp was focused on a gold-coated slide glass and totally reflected light was analyzed by a fiber optic spectrometer with a linear charged coupled device detector (AVS-S2000, Avantes), which monitors the whole range of 500 to 700 nm, simultaneously. Index matching between a fused silica right angle prism and the slide glass was achieved by a drop of distilled water. Resulting data were processed by the 4th order polynomial curve fitting technique. System control and data acquisition were performed using a LabVIEW-based software (self-developed).

AFM images were obtained with a Nanoscope IIIa (Digital Instruments, USA). The device was equipped with a <E> calibrated scanner using the manufacturer's grating. AFM images were obtained by both contact mode (CM) and tapping mode (TM). 100 mm and 200 mm nanoprobe cantilevers (spring constants of 0.12 and 0.38 N/m) with oxide-sharpened Si_3N_4 integral tips were used for CM regime and tapping silicon cantilevers with resonance frequency 280-320 kHz were used for TM regime. The applied force was varied over a wide range from several nN up to tens of nN in contact mode. Film thickness was estimated by measuring a depth of an artificial hole that was scratched preliminary in CM regime. Film roughness was measured on images obtained in less destructive TM regime.

3. Protein immobilization schemes

3.1. IMMOBILIZATION VIA PHYSICOSORPTION OR ELECTROSTATIC INTERACTION

Protein-substrate and protein-protein interactions on substrate are quite complex. Protein properties, especially, their conformation, can be changed by the contact with sensor surfaces, since proteins are affected at the sensor surface by van-der-Waals hydrophobic and electrostatic interactions, interfacial perturbations by multipoint attachments to the surface, pH environment, surface charge, co-adsorption of low molecular weight ions, and isoelectric points of proteins [18]. Bound proteins may lose their activity resulting from the immobilization chemistry or inappropriate orientation. Hence, the biological activity of biomolecules upon immobilization on the chip surface should be preserved. Immobilized molecules must retain their native conformation to ensure proper function at the surface without denaturation. That is why, during the last few years, special interest has been paid to the studies on the nature of the protein-surface interaction to control the biomolecule adsorption process [19]. Biomolecules can be immobilized on the surfaces by different methods, for example, physisorption or chemisorption, copolymerization, covalent chemical coupling, and supramolecular interactions [20, 21]. Immobilization of antibody molecules from immunoliposomes has been also used in several biotechnological applications [22].

Simplest approach includes incorporation of antibodies [23] or enzymes [24] onto thin films. This approach is quite promising because repeated assays by regeneration is possible. Indeed, protein interactions on surfaces have physical natures and the interactions are easily disturbed by salt concentration (PBS solution, for example), pH environment and competitive reactions in the solution. A whole range of antibodies with

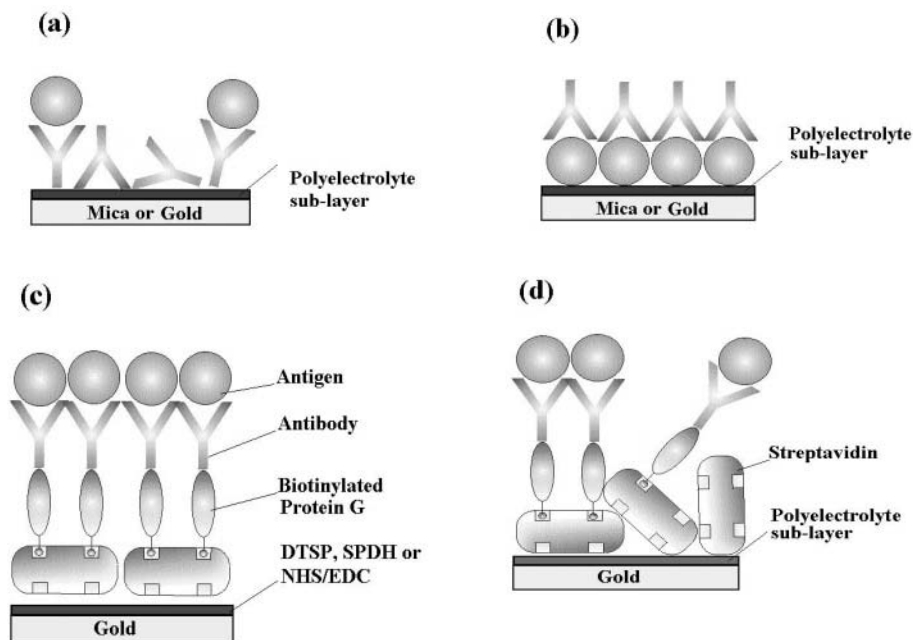


Figure 1. Possible schemes for antigen-antibody immobilization on solid support: (a,b, d) polyelectrolyte support and (c) chemical cross-linker one for protein molecules fixation on solid surface.

different specificities can be bound to and dissociated from the surfaces simply by lowering the pH of the solutions [25].

Layer-by-Layer (LbL) method has been introduced by Decher [26], and it provides a way to fabricate functional films on solid surfaces with nanometer resolution. By the LbL method, it is possible to change the property of inorganic surfaces and create “friendly” monolayer environments (hydrocarbon, charged and etc.) for non-specific protein binding. The method has been extended and successfully applied to the surface formation with various biomolecules such as globular proteins [27], enzymes [28], and even viruses [29].

It has been reported [30] that the structure and orientation of adsorbed proteins is dependent on the charge of the film. It was interesting to clear up the opportunities of LbL method for recognition of CRP and a-CRP proteins on polyelectrolyte support. Strong polyelectrolytes (PDDA and PSS) were chosen in that study for gold surface modification with aim of subsequent direct immobilization of a-CRP and CRP molecules (figs. 1a, b).

3.2. COVALENT OR AFFINITY-BASED IMMOBILIZATION

Covalent coupling of molecules is irreversible and thus stable. Majority of works have been focused the gold surface immobilization due to its better-elaborated chemistry based on thiols using self-assembling molecules (SAM) approach [31]. Indeed, SAMs provide an alternative means by which molecules are self-organized into densely packed structures on a surface [39]. The antibodies are usually linked to gold substrates using bifunctional reagents with a thiol group on one side (fig. 2).

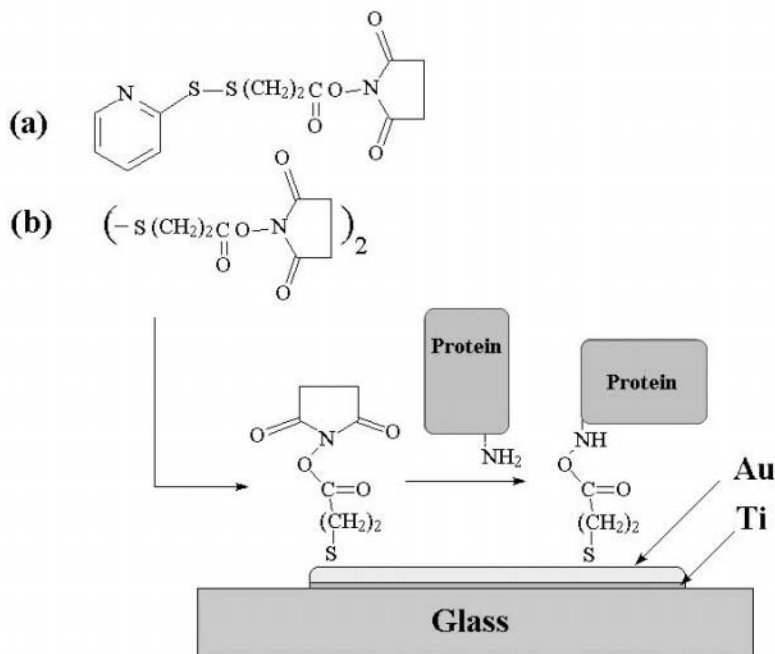


Figure 2. Schematics of chemical immobilization of protein on gold surface via (a) SPDP or (b) DTSP cross-linker reagent

SAMs prepared by bifunctional compounds are extremely important and promising for bioengineering of sensor surfaces. Usually, covalent coupling of proteins and peptides is achieved by the conjugation of COOH-terminated SAMs with NHS esters [33]. NHS/EDC cross-linking is one of most popular methods for immobilization of proteins and nucleic acids on sensor surfaces [34, 35]. The NHS/EDC covalent coupling results in the formation of mainly amide bonds between enzymes and SAM molecules [36]. Proteins are covalently coupled to chemically activated surfaces through the reaction of lysine side chains. However, immobilization by the covalent coupling may results in the random orientation of biomolecules because the functional groups used for the attachment can be found in more than one location of the biomolecule surfaces. So, the biomolecules may lose their biological activities by the random orientation on their support surfaces [37].

The best approach to control the orientation of immobilized biomolecules is to selectively attach a predetermined site of the protein on the sensor surface. There have been reports on the methods to control the orientation of immobilized proteins on the surface [38-41], such as (i) site-specific oriented attachment of biomolecules to gold surfaces through thiol- or cysteine-containing enzyme, (ii) orientation with heterobifunctional photoactivatable cross-linking agents, and (iii) oriented immobilization of antibodies by the use of immobilized protein A or G, or biotin-streptavidin interaction. We have chosen the way of CRP antigen-antibody immobilization through bPG-streptavidine protein bridge. Indeed, the universal tools to properly orient antibody molecules are protein A and G from *Staphylococcus*

which specifically bind to the Fc regions of antibodies. After immobilizing protein A or G to the surface by cross-linking reaction, it is possible to attach antibodies with the desired orientation for the antigen binding.

Using the bPG–streptavidin system, ligands and targets can be immobilized via such an affinity bond if they are linked to a biotin molecule: the small biotin molecule is able to bind to one of four equivalent binding sites of the tetrameric proteins avidin or streptavidin [42]. This binding is specific and about four orders of magnitude even stronger than typical antigen–antibody interactions. Moreover, streptavidin is highly resistant to denaturing reagents, extremes in pH and temperature [43]. Thus, when streptavidin is attached to gold surface via one or two binding sites, the other binding sites are exposed to the solution [44]. Hence, the appropriate binding of streptavidin to the solid surface can help to produce an oriented protein film. Indeed, immobilization of a biotinylated protein G with a specific antibody is possible on solid surface after immobilizing a streptavidin monolayer (fig. 1c,d). In such a way, in the present work, the optimal modification method of gold surface is reported to improve the immobilization of protein molecules. To understand the difference between electrostatic attachment of complex to polyelectrolyte support and covalent immobilization via chemical cross-linker reagents, we have analyzed antigen–antibody interaction on STV/bPG complexes. That is why antigen–antibody interaction on the surface modified by covalently bound bPG/STV complex or directly by polyelectrolytes has been examined.

4. Results and discussion

It was shown earlier [41] that such polyelectrolytes as positively charged PDDA and negatively charged PSS could be used for immobilization of protein molecules on solid surface. It was found that both mica under water and gold surfaces treated with $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2$ could be modified with polyelectrolyte films because the surfaces are negatively charged. First, the surfaces were incubated with the polyelectrolytes to immobilize STV, which can make oriented immobilization of bPG monolayer with subsequent antibody immobilization for antigen binding (fig. 1d). The processes of surface modification were analyzed by AFM after incubating, washing and drying the surfaces. The results of section analysis through artificial hole in protein layer are shown in figs. 3a and 3b, which suggested the interaction between STV and bPG molecules on polyelectrolyte surfaces.

Unfortunately, bound biotinylated protein G lost its activity since anti-CRP and CRP didn't react with surface bPG molecules. As shown in Figs. 3a and 3b, there was no significant difference in the film thickness before and after incubating anti-CRP and CTP on STV/bPG surfaces. On the contrary, STV/bPG complex was quite active for antigen–antibody immobilization when STV was immobilized on the gold surface via bifunctional SAM bridge (fig. 1c). With the aim to find the best cross-linking reagent we have examined various bifunctional chemicals. In particular, we have compared two different cross-linking protocols for STV molecules immobilization on gold surface, namely, using DTSP and SPDH chemicals. Additionally, it was established that commonly used NHS/EDC procedure can be also used for STV molecules binding to gold surface, probably, due to hydroxyl groups appearance on the surface after $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2$ treatment of gold spots on chip plate. There were an essential differences (Table 1) in SPR signal shift as well as in

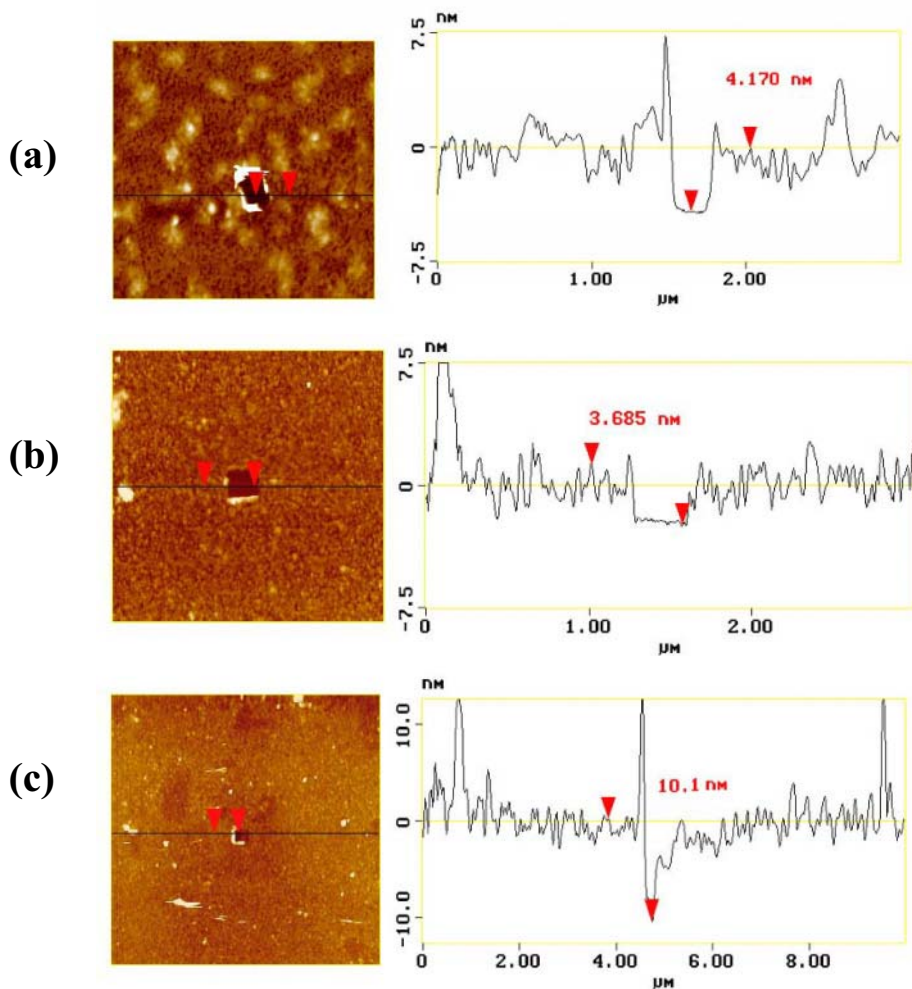


Figure 3. AFM analysis of protein layer thickness through artificial scratched hole (a) in streptavidin-biotinylated protein G complex on negatively charged (PSS/PDDA/mica) surface; (b) for CRP antigen-antibody fixation on bPG/STV/PSS/PDDA/mica surface and (c) for protein CRP/anti-CRP layer on bPG/STV/Gold after STV cross-linking with DTSP reagent.

surface roughness after each step of successive immobilization of protein molecules: STV, bPG, a-CRP, and CRP.

As shown in Table 1, the SPR shift was approximately the same after cross-linking streptavidin by different chemicals, but the roughness was different for all cases and minimal in case of DTSP-treated surface. It is likely that subsequent coupling of STV molecules with biotinylated protein G was the best in the case of DTSP activated surface because both SPR wavelength shift and film thickness were maximal (Table 1 as an example). As a result, DTSP provided good surface for the binding of anti-CRP on bPG, but only partial adsorption of anti-CRP was observed by SPDP and NHS/EDC. The final

Table 1. SPR and AFM analysis of surface during STV/BG/ACRP/CRP system construction on solid surface

Protein	STV		bPG		anti-CRP		CRP	
Chemicals	Δ SPR, nm	Rm s	Δ SPR, nm	Rms	Δ SPR, nm	Rms	Δ SPR, nm	Rms
DTSP	12.0	1.05	8.5	1.62	5.6	1.22	11.5	1.99
SPDH	10.9	1.2	2.35	1.24	8	1.21	2.8	1.61
NHS/EDS	10.05	1.55	4.5	1.17	9.1	1.38	1.05	1.45

result of CRP antigen interaction testifies the optimal immobilization of CRP antibody for the first case. Constant shift of SPR signal was observed during successive immobilization of proteins on gold spots of chip plate (fig. 4). It was found that SPR signal shift was correlated with thickness of total protein layer (fig. 5) on the DTSP cross-linking surface. It was observed that 3.6 nm shift in SRP wavelength was caused by 1nm increase of film thickness.

High resolved AFM images of protein surfaces made by step-by-step immobilization are shown in Fig. 6. One can see the changes in protein film morphology for each step and even recognize separate protein molecules. High degree of film uniformity was obtained by DTSP. Strong condensation of CRP molecules on Au/DTSP/STV/bPG/anti-CRP and Au/SPDP/STV/bPG/anti-CRP complexes was observed even with the naked eye during chip plate incubation for more than 1 hour. The similar results were also obtained by polyelectrolyte sub-layer (PSS), and shown in fig. 7. These results suggested that PSS surface can be considered as quite friendly for a-CRP molecules. So, we have checked the

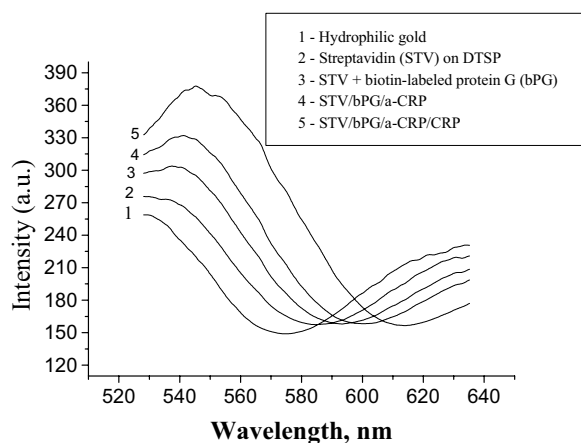


Figure. 4. SPR signal shift for step-by-step protein film construction for antigen-antibody immobilization on bPG/STV/Gold after STV cross-linking with DTSP reagent.

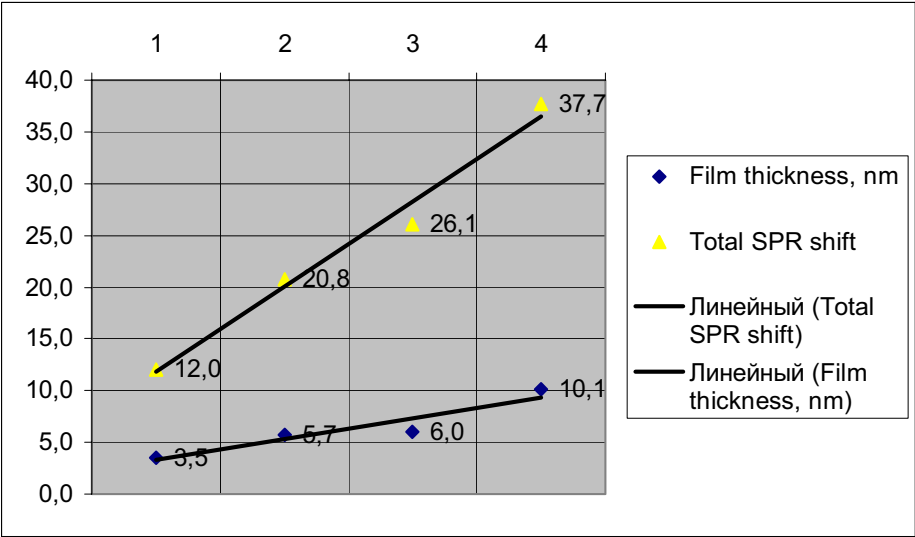


Figure 5. Increasing of the film thickness and SPR shift for STV/bPG/a-CRP/CRP system, when DTSP was used as cross-linker reagent.

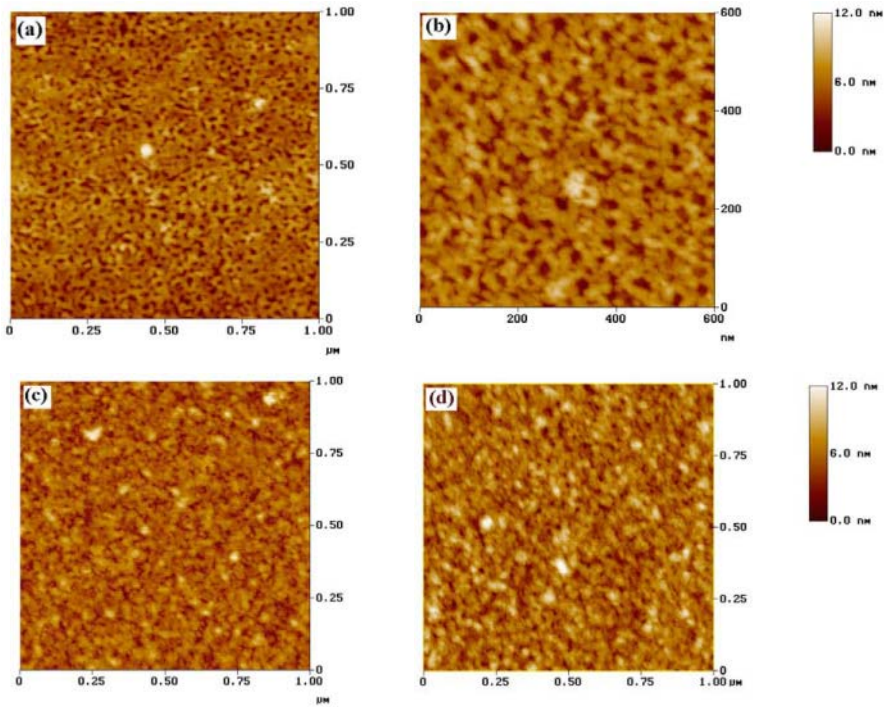


Figure 6. Changing in protein film morphology during successive fixation on gold surface: (a) STV, (b) bPG, (c) a-CRP and (d) CRP molecules for the case of STV molecules coupling with DTSP.

possibility of anti-CRP and CRP immobilization directly on polyelectrolyte sub-layer in attempt to simplify laborious procedure of preliminary stage of surface activation via bPG/STV intermediate layer. It was found that CRP molecules were quickly (within 20 min) adsorbed onto PSS and PDDA films (Fig. 8a, for example).

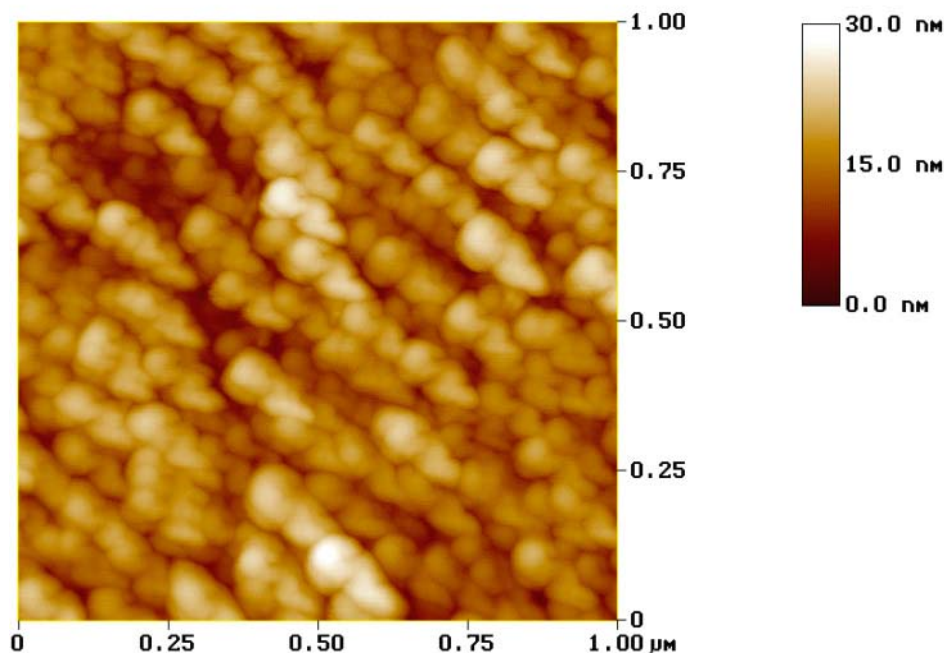


Figure 7. AFM image of oriented adsorption of α -CRP aggregates from 0.1 mg/ml solution on PSS/PDDA/mica support after mica plate incubation in saline phosphate buffered solution of α -CRP

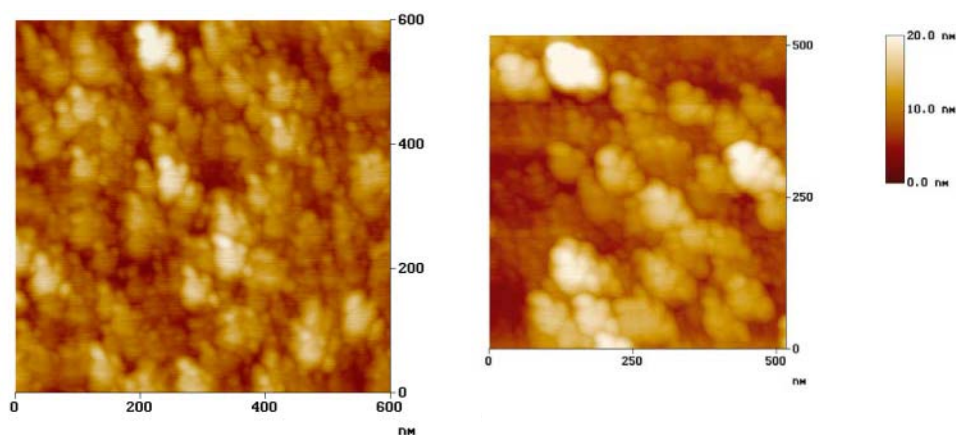


Figure 8. High resolved AFM images of (a) CRP and (b) α -CRP on CRP binded to polyelectrolyte PDPA/PSS support.

Subsequent interaction of CRP-activated surface with CRP antibody is possible (fig. 8b). One can see high-resolved AFM image (fig. 8b) of anti-CRP molecules attached to PSS sub-layer. Such protein system on the polyelectrolyte surface can be used for subsequent fixation of mole complex objects like damaged cells. Undoubtedly, the degree of packing of anti-CRP molecules depends on the concentration. So, AFM method can be additionally used directly for monitoring anti-CRP/CRP interaction on polyelectrolyte support. We believe that it will be possible to determine the concentration of anti-CRP molecules from direct AFM imaging from CRP antibody precipitation on activated surface in nearest future.

5. Conclusions

Cross-linking procedures (DTSP, SPDH or NHS/EDS) affect on antigen immobilization on STV/bG/anti-CRP system. The final result depends on straptavidin film morphology. The most closely packed STV monolayer (maximal SPR shift as well as minimal Rms, mean surface roughness) was observed by the use of DTSP cross-linker reagent. More rough and thick STV layer was found in NHS/EDC cross-linker protocol. It may be due to aggregation and deactivation of STV molecules on NHS-modified surface. As a result, maximum shift of SPR wavelength by coupling of CRP with anti-CRP has been observed on DTSP-modified gold surface. Correlation between film thickness and SPR shift by STV/bG/anti-CRP/CRP system was observed. Ratio between SPR shift and thickness was equal ca. ~ 3.6 for protein film. Additionally, AFM method can be used to directly monitor CRP/anti-CRP interaction on polyelectrolyte support.

Acknowledgements

This work was supported in part by the 21C Frontier functional Human Genome Project From Ministry of Science and Technology of Korea and the Advanced Backbone IT Technology Development Project from the Ministry of Information and Communication.

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MESOPOROUS ALUMINOSILICATES AS A HOST AND REACTOR FOR PREPARATION OF ORDERED METAL NANOWIRES

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Abstract

The creation of functional nanomaterials with the controlled properties is emerging as a new area of great technological and scientific interest, in particular, it is a key technology for developing novel high-density data storage devices. Today, no other technology can compete with magnetic carriers in information storage density and access rate. However, usually very small (10-1000 nm³) magnetic nanoparticles shows para- or superparamagnetic properties, with very low blocking temperatures and no coercitivity at normal conditions. One possible solution of this problem is preparation of highly anisotropic nanostructures. From the other hand, the use of purely nanocrystalline systems is limited because of their low stability and tendency to form aggregates. These problems could be solved by encapsulation of nanoparticles to a chemically inert matrix. One of the promising matrices for preparation of highly anisotropic magnetic nanoparticles is mesoporous silica or mesoporous aluminosilicates. Mesoporous silica is an amorphous SiO₂ with a highly ordered uniform pore structure (the pore diameter can be controllably varied from 2 to 50 nm). This pore system is a perfect reactor for synthesis of nanocomposites due to the limitation of reaction zone by the pore walls. One could expect that size and shape of nanoparticles incorporated into mesoporous silica to be consistent with the dimensions of the porous framework.

Here we suggest a novel synthetic route for the preparation of ordered magnetic nanowires in mesoporous silica matrix. The method is based on intercalation of a hydrophobic metal compound, into the hydrophobic part of silica-surfactant composite. Nanocomposites were characterized by TEM, ED, SAXS, SANS, BET and magnetic measurements. It was shown that shape and size of the particles are in good agreement with the shape and size of the pores. This approach leads to functional materials, which could find an application as high-density data storage devices.

However this method has some disadvantages: the quantity of metal intercalates could not be varied or set, and maximal quantity is rather small. Therefore, we suggested another approach based on charging of matrix by replacing part of silicon atoms by aluminum. It gives rise to possibility of controlling loading of metal to pores by varying silicon to aluminum ratio, besides that, the use of mesoporous aluminosilicates as nanoreactors enables one to load cations by simple ion exchange. In the present study mesoporous

aluminosilicates prepared by different methods were compared. Incorporation of silver ions into mesoporous silica matrix was studied as a model system. It was shown that shape and size of the particles are in good agreement with that of the pores. Thus, the suggested method leads to one-dimensional anisotropic nanostructures.

1. Introduction

Modern information technologies require development of novel high-density data storage devices due to colossal growth of digital information volume. The main branch of industry of the information carriers today, relies upon magnetic information storage. The further improvement of the density requires the development of principally new magnetic materials with high saturation magnetic flux density, large enough coercitivity and suitable magnetic characteristics for information carriers, reading heads, etc. The special role in creation of the components for such devices belongs to high-quality anisotropic nanostructures and nanocomposites [1], because of the possibility to exploit the effect of quantum tunneling of magnetization observed for nanomagnets [2].

The synthesis of high-quality nanostructures usually involves the use of geometrically confined systems at nanolevel as a reactor for preparation or crystallization of particles. Usually, a nanoreactor is formed by colloidal species, such as in Langmuir-Blodgett films, self-assembling multilayers, reversed micelles etc. However, colloidal chemistry routes usually require inert atmosphere and thus obtained nanoparticles are not stable enough to be suitable for applications. One possible alternative is to use solid state nanoreactors since solid state materials often possess nanoscale cavities and stabilize nanoparticles in matrix. Here we report the use of mesoporous aluminosilicates and mesoporous silica as a matrices for the preparation of metal nanoparticles. Mesoporous aluminosilicates as well as mesoporous silica were first synthesized by "Mobile Oil Corporation" researchers in 1992. These materials possess some unique properties: they have well-ordered hexagonal array of uniform cylindrical mesopores, diameter of which can be controllably varied between 20 and 500 Å, and extremely high surface area (about 1000 m²/g). These properties suggest their possible application for the preparation of nanomaterials by chemical reactions of intercalated compounds. One can expect that the presence of the ordered pore system will provide conditions required for the formation of low dimensional anisotropic nanostructures. During chemical reactions, pore walls spatially constrain the reaction zone, thus rendering the conditions similar to those in the 1D nanoreactors.

Synthesis and characterization of one-dimensional magnetic nanoparticles (nanowires) in the mesoporous silica films is of great technological and scientific interest, because this system is promising for developing high-density data storage devices. Recently, the formation of mesoporous silica films with highly ordered system of mesochannels was reported on silicon (110) substrates [3]. In the case of encapsulation of a magnetic material (for example, iron) into the pores, we will get a perfect system of isolated nanomagnets inside the diamagnetic matrix (fig. 1). The main advantage of this approach is the presence of the ordered system of magnetic domains, which gives rise to possibility of the precision positioning of the writing/reading head. However, characterization of films is complicated. Thus, at the first step it is necessary to carry out synthesis of magnetic nanowires in bulk mesoporous silica matrix.

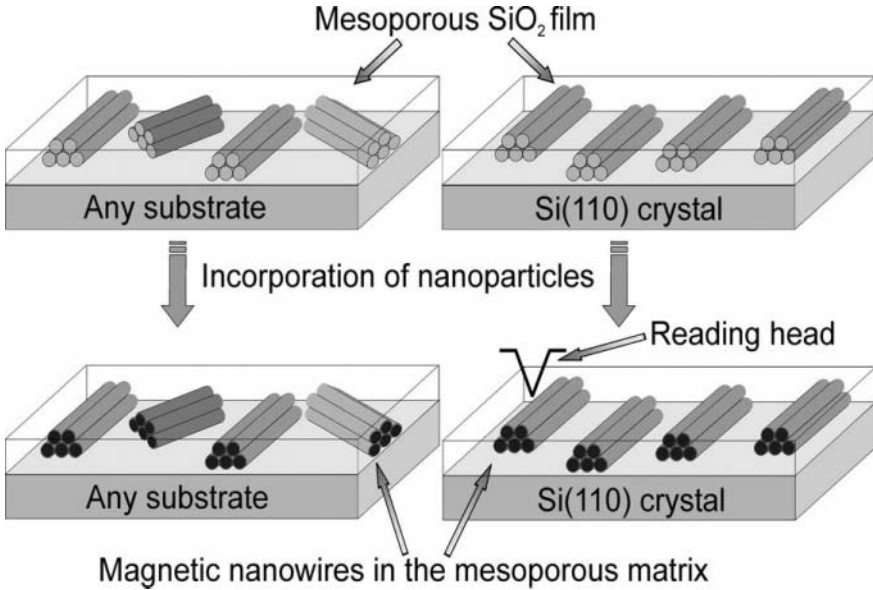


Figure 1. Magnetic storage devices based on the mesoporous silica films.

Recently, several attempts have been made to prepare metal nanowires in mesoporous silica matrix by simple soaking mesoporous SiO_2 in an aqueous solution of corresponding metal salt with subsequent reduction [4]. However, it was found that the size of metal particles exceeds the size of the pores and the particle size distribution is not uniform. The reason for the formation of nanoparticles outside the pores is probably the hydrophobic nature of the pore walls [5], which prevents filling the pores by an aqueous solution. Another approach involves vapor deposition of a volatile metal compound into the pores with subsequent reduction. However, this method cannot be used for the preparation of magnetic nanowires since reduction of volatile compounds of magnetic metals occurs at relatively high temperature, which results in the collapse of nanowires.

Here we suggest a novel variant of synthesis of ordered magnetic iron nanowires in the mesoporous silica matrix. The method is based on the introduction of a hydrophobic metal compound, into the hydrophobic part of silica-surfactant composite (fig. 2) with following reduction of metal. Formation of anisotropic particles is evident. The atoms of transition metal in this case are homogeneously distributed in the pore volume. During the reduction

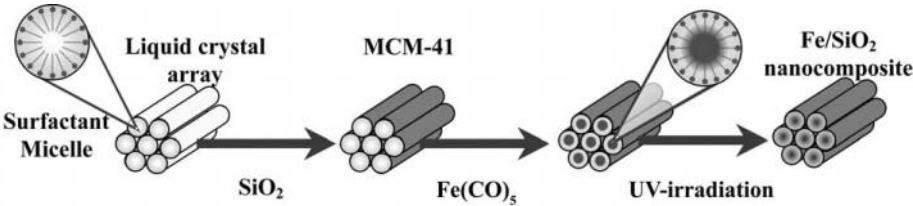


Figure 2. Schema of the synthesis of Fe/SiO_2 nanocomposites.

process the growth of metal nanoparticles is limited by the pore walls, which leads to the formation of anisotropic crystals.

2. Results and Discussion

2.1 Fe/SiO₂ NANOCOMPOSITES

To prove the presence of mesoporous structure after intercalation of iron the comparison between the SAXS patterns for the obtained nanocomposite and as-synthesized mesoporous silica was performed (fig. 3). 1D hexagonal pore structure filled with surfactant molecules has the lattice parameter, $a = 4.10$ nm, while the lattice parameter of nanocomposite was found to be 4.06 nm. It confirms that preparation procedure does not brought considerable influence on the mesoporous matrix.

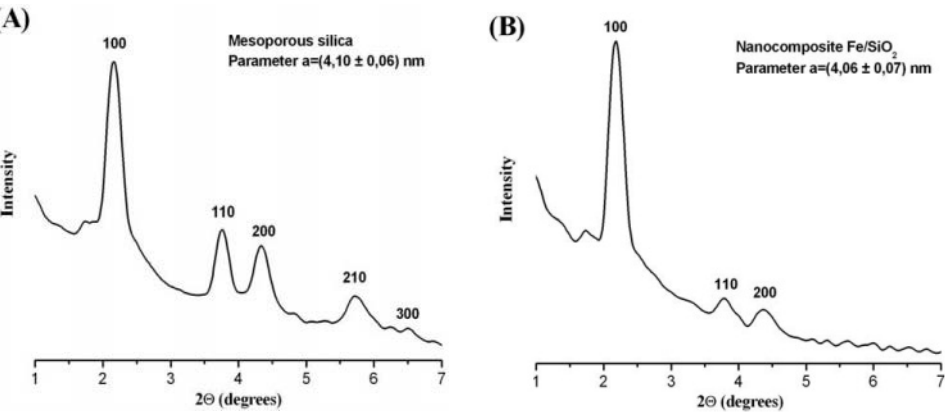


Figure 3. Small angle X-ray diffraction patterns for as-prepared mesoporous silica–surfactant composite (A) and Fe/SiO₂ nanocomposite obtained by UV-induced decomposition of Fe(CO)₅ (B).

The removing of template molecules after thermal modification was verified by the method of capillary absorption of nitrogen at 77K and carbon analysis. It was expected that during

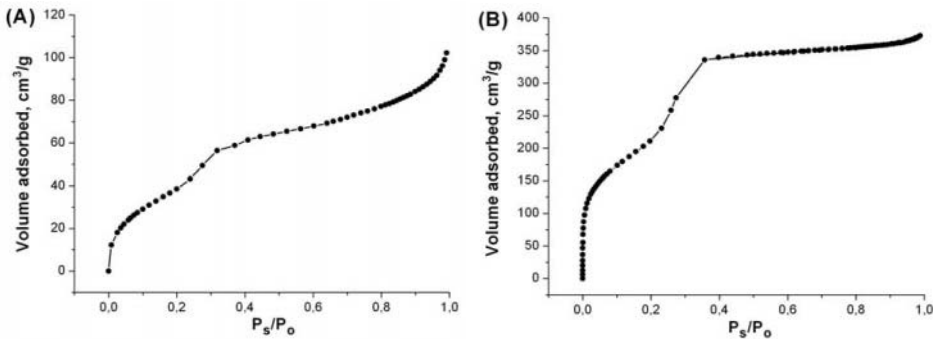


Figure 4. Nitrogen sorption isotherm for FeSiO₂-350 (A) and FeSiO₂-400 (B).

annealing procedure CTAB molecules are decomposed giving volatile organic compounds (CTAB decomposition temperature is 230°C). However, according to BET surface area values, it was found that a complete removing of CTAB occurs only at the annealing temperatures higher than 350°C, while at the temperature of 300°C and 350°C residual carbon was observed by carbon analysis (<2 and 0.28 weight percents). But even these samples have specific step-like increase in absorbency value at $\sim 0.3 P_g/P_0$ which is characteristic for mesoporous structures (fig. 4). The surface area values and residual carbon content for the obtained samples are presented in table 1.

Table 1. Specific surface areas and carbon content for Fe/SiO₂ composites.

Sample	Residual carbon, weight %	Surface area, m ² /g
FeSiO₂-300	<2	
FeSiO₂-350	0.28	151.68
FeSiO₂-375	0.070	697.9
FeSiO₂-400	0.044	775.5

The amount of iron intercalated into the mesoporous matrix was measured by chemical analysis. In all samples it corresponds well to with the molar ratio SiO₂ : Fe = 9:1. The calculation of the mean diameter of iron nanowires (assuming infinite length and crystallographic density of iron 7.87 g/cm³) for this ratio gives the value of 0.7 nm. At the same time, direct transmission electron microscopy observations indicates the presence of nanowires with characteristic width of 1-1.5 nm and length more than 100 nm (fig. 5). Electron diffraction studies confirm the formation of metallic iron in the system.

The most important parameter of the obtained system is anisotropy (or the length) of iron nanoparticles. Unfortunately, it could not be estimated by direct electron microscopy studies since the boundary between adjacent particles could not be clearly seen. Therefore, physical methods are required for the comparison of sample's microstructure. Anisotropy parameters of magnetic particles obtained by reduction of iron-containing MCM could be calculated using temperature dependence of magnetic susceptibility or small angle neutron scattering technique.

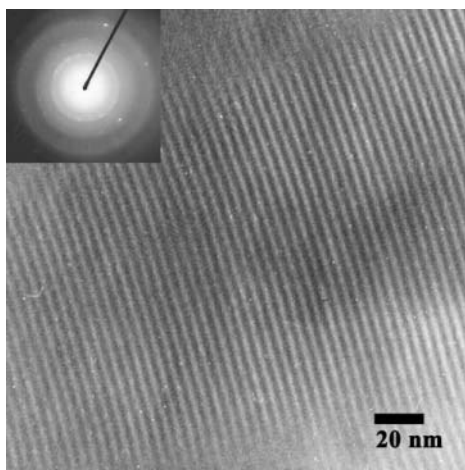


Figure 5. TEM image and electron diffraction pattern for FeSiO₂-375.

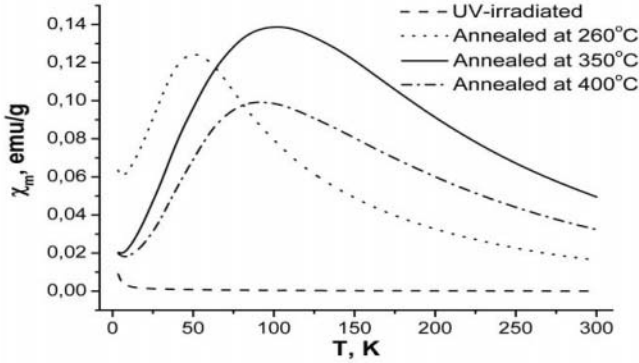


Figure 6. Temperature dependence of magnetic susceptibility for Fe/SiO₂ nanocomposites.

Temperature dependence of magnetic susceptibility for all samples was studied in the temperature range 2-300K (fig. 6). All samples are superparamagnetic, but blocking temperature tends to increase with the increase of annealing temperature. The length of the particles could be calculated from blocking temperatures (Eq. 1 [6]) assuming cylindrical shape of them, radius of the particles was obtained by TEM:

$$T_B = \frac{\Delta E}{k \ln(\tau \cdot f_0)} \approx \frac{[0.25 \cdot I_s^2 (N_{||} - N_{\perp}) + K_I] V}{25k}, \quad (1)$$

where ΔE – activation barrier, k – Boltzman constant, τ - relaxation time, f_0 – frequency factor, $N_{\perp}$ and $N_{||}$ - demagnetization coefficients perpendicular and along the axes of easy magnetization, I_s – saturation magnetization, K_I - magnetic anisotropy constant, V – mean particle volume.

The increase of reduction temperature up to 350°C leads to increase of the particles length (see table 2). However, the higher reduction temperature gives the shorter particles, that identifies the process of particle formation as a percolation process. The calculations, shows that the average form factor attains the value of 38, i.e. at the particle diameter of 1 nm the average domain length will be of 38nm. At the same time the magnetic hysteresis measurements of samples indicates the coercive force values up to 650 Oe at 4K and 80 Oe at room temperature, which is nearly sufficient for modern magnetic data storage (fig. 7).

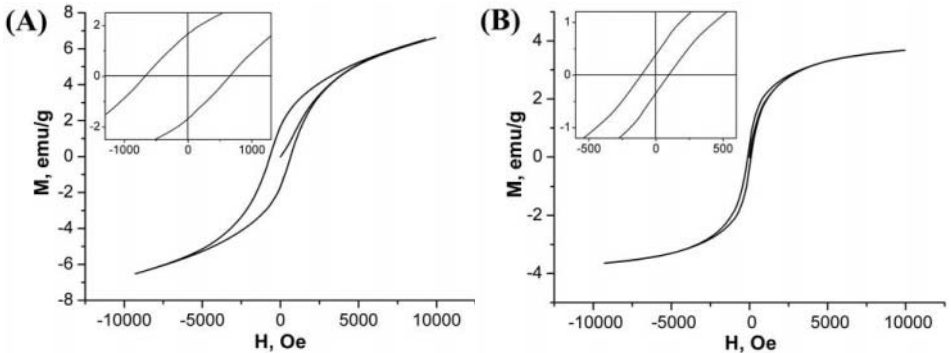


Figure 7. Magnetic hysteresis loop for FeSiO₂-400 measured at 4K (A) and 300K (B).

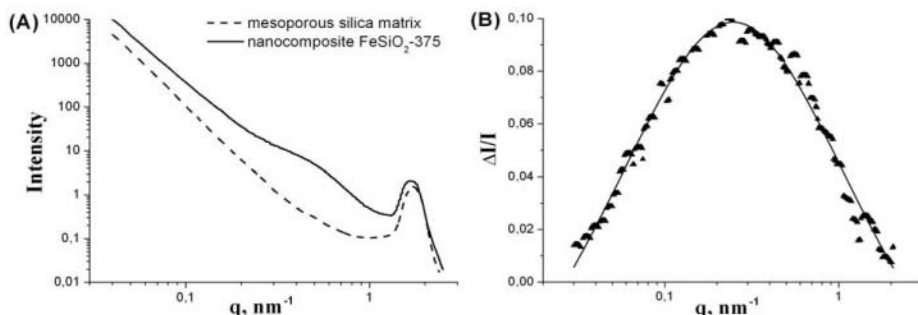


Figure 8. Small angle polarized neutron scattering patterns for mesoporous silica matrix and nanocomposite $\text{FeSiO}_2\text{-375}$ (A) and difference curve (B).

The room temperature magnetic susceptibilities also were found to be relatively high.

Table 2. Magnetic data for Fe/SiO_2 nanocomposites.

Sample	Blocking temperature, K	Form factor	Coercive force, Oe		Saturation magnetization at 300K, emu/g
			4K	300K	
FeSiO₂-260	50.8	21	397.6	11.6	2.56
FeSiO₂-350	100.5	38	563.1	28.9	3.63
FeSiO₂-400	89.1	35	665.0	84.4	3.68

To get more information about anisotropy of magnetic nanoparticles the small angle polarized neutron scattering measurements were carried out. The spectra for sample crystallized at 375°C and pure mesoporous silica is presented in figure 8a. The difference between these two curves could be used for calculation of correlation lengths in the system (fig. 8b). The average correlation length was found to be 20 nm. It should be noted that obtained value is an integral correlation length of all randomly directed particles in the powder. In the approximation of cylindrical particles the calculations shows the form factor of 40, which is in good agreement with magnetic measurements.

The next step of the work involves preparation of analogous Fe/SiO_2 composites in epitaxial films of mesoporous SiO_2 with all pores parallel to the surface and aligned in a certain direction. The transmission electron photograph of the film shows the presence of well-ordered anisotropic particles in the transparent matrix. Thereby such films may serve as a test system for information storage. Thus, the proposed method enables the formation of highly

anisotropic magnetic nanostructures in the mesoporous silica matrix, where the pore system serves as one-dimensional solid state nanoreactor.

However this method also has some disadvantages: the quantity of metal intercalated using this method could not be varied or set and maximal quantity is rather small. Therefore, we suggest another approach based on charging silica matrix by replacing part of silicon atoms by aluminum, which enables one to control loading value by varying silicon to aluminum ratio.

2.2 MESOPOROUS ALUMINOSILICATES

Mesoporous aluminosilicate is mesoporous silica, where silicon atoms are partially substituted by aluminum (aluminum is coordinated to four framework oxygen atoms), which causes a negative excess charge of the framework. This charge is compensated by cations of alkali metals or protons, which are located in the channels of the mesoporous matrix and bonded by Coulombic interactions. The amount of cations present in the pore volume is proportional to the charge of the matrix, which can be easily controlled during the synthesis. These cations can be substituted by simple ion exchange in an aqueous solution. Due to this features mesoporous aluminosilicates exhibit specific adsorption behavior; Bronsted and Lewis acid sites which provides their catalytic activity; and wide flexibility for adjustments by the isomorphic substitution of the framework constituents or by the ion exchange of counter ions. Besides that, as a result of high diffusion rates of gases in the mesoporous structure, the thermal decomposition of the template proceeds without destruction of mesoporous structure. Chemical reactions of cations present inside the pores also proceed without the destruction of the matrix, which in turn provides spatial constraints for the reaction zone. These properties make mesoporous aluminosilicates the most promising one-dimensional solid state nanoreactors for preparation of metal nanowires.

The most important parameters for usage of the mesoporous aluminosilicates as a nanoreactors are well-defined mesoporous structure and high aluminum loading value. To understand the dependence of the properties of mesoporous aluminosilicates from the preparation conditions it is necessary to regard the process of the formation of the mesoporous structure in detail. The difference between hydrolysis rates of alumina and silica sources usually leads to two competing reactions: the first is the copolycondensation (aluminum atoms incorporate into silica structure which provides tetrahedral coordination of aluminum), and the second is the formation of the amorphous aluminum hydroxide (octahedral coordination of aluminum atoms). Aluminum hydroxide could be bonded to mesoporous structure or can form aggregates which have no connection to the mesoporous structure. This form does not affect on the matrix charge, and blocks mesopore channels. Usually it could not be removed by conventional methods. Thus, it is necessary to avoid the formation of aluminum hydroxide on the synthetic stage for preparation of the aluminosilicates with well-defined structure.

Today, there are two well-known techniques for preparation of the mesoporous aluminosilicates. The first one is sol-gel synthesis based on copolycondensation of silicon and aluminum containing hydroxocomplexes in the presence of the surfactant molecules in alkali medium (pH~10-11). Usually tetramethylortosilicate (TMOS) or tetraethylortosilicate (TEOS) [7] and aluminum alkoxides or inorganic salts are used as silica and alumina sources [8]. Surfactant molecule, typically, consists of hydrophilic "head" and hydrophobic "tail" groups, and form liquid crystalline phases in water solution. Partially hydrolyzed aluminum and silicon alkoxide molecules condense giving a framework on the micelle surface. The capped micelles subsequently organize yielding periodic arrays. Thus, incorporation of aluminum into the silica framework is influenced not only by the synthesis conditions, but also by chemical composition (or hydrolysis rates) of the silicon and aluminum progenitors. Another traditional preparation route is hydrothermal synthesis. In this case the formation of the aluminosilicate framework is a result of aggregation of

oligomeric species containing silicon and aluminum in the presence of the template during high pressure and temperature treatment [9]. However, despite the affluence of information on synthesis and properties of the mesoporous aluminosilicates, it is impossible to perform full comparison of different methods.

Thus, in the frame of the present study we analyzed different techniques of synthesis of the mesoporous aluminosilicates with high aluminum loading. Three synthetic procedures were applied:

- 1) copolycondensation of TEOS and $\text{Al}(\text{NO}_3)_3$ (**Si_nAl** series);
- 2) copolycondensation of TEOS and $\text{Al}(\text{O}i\text{-Pr})_3$ (**Si_nAl*i*P** series);
- 3) hydrothermal synthesis (**MAS Si_{15/n}Al** series).

The main objective here was to choose the best technique according to the difference in nonframework $\text{Al}(\text{OH})_3$ content and maximal arrangement of the structure. A well-known method to indicate the position of aluminum atoms is NMR spectroscopy. Typical ^{27}Al NMR solid state spectrum of mesoporous aluminosilicate shows two peaks with shifts of 0-5 and 55-62 ppm. These shifts can be ascribed to aluminum in octahedral and tetrahedral coordination respectively. The ratio of peak areas enables us to estimate distribution of aluminum atoms in mesoporous silica walls (tetrahedral aluminum), and nonframework species of aluminum hydroxide (octahedral aluminum) [10].

The NMR spectra of the aluminosilicates prepared by copolycondensation of aluminum nitrate and tetraethylortosilicate (**Si_nAl** series) show a rather high number of Al atoms in tetrahedral sites (fig. 9). The increase of tetrahedral aluminum on the first stage and decrease on the second stage with increase of overall aluminum in the sample must be attributed to the competition between the copolycondensation and the hydrolysis processes.

SAXS spectra, surface properties and TEM imaging indicate that the obtained samples show better results in case of low aluminum content (table 3), while in case of high aluminum loading (Al:Si ratio higher than 1:4) well-ordered structure was not obtained at all. It should be noted that according to TEM studies the size of aluminosilicate tends to decrease with increase of aluminum content. Therefore the destruction of mesoporous structure could be attributed to the high hydrolysis rates of silicon and aluminum sources which prevent the formation of large periodic structures. Thus very small particles (less than 10 nm) with low periodicity are formed.

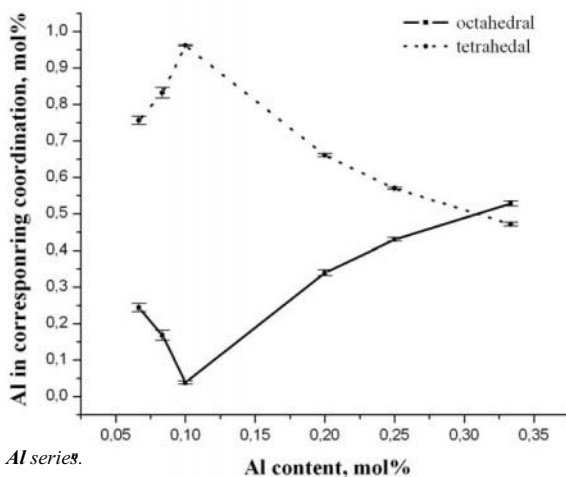


Figure 9. NMR data of **Si Al** series.

The next technique we used was the copolycondensation of aluminum isopropoxide and tetraethylortosilicate. The NMR study indicates the increase of Al atoms in the tetrahedral sites with increase of Al content in the sample, which points out the hydrolysis stage as a

Table 3. NMR, SAXS data and specific surface area values for mesoporous aluminosilicates.

Sample	Tetrahedral aluminum content, mol %	Lattice constant, $a_{90\%}$ (a mean), nm	Surface area, m ² /g
MCM-41	--	3,9-4,3 (4,1)	~1100
Si₁₄Al	0.76	3,7-4,4 (4,0)	450
Si₁₁Al	0.83	3,4-4,5 (4,0)	390
Si₉Al	0.96	3,1-4,7 (3,9)	390
Si₆Al		2,5-4,9 (3,7)	400
Si₄Al	0.66	2,5-5,5 (3,3)	300
Si₃Al	0.57	2,5-6,0 (3,7)	260
Si₂Al	0.47	--	140
Si₁₄Al_iP		3,1-5,3 (4,2)	1120
Si₁₁Al_iP		3,0-5,6 (4,3)	1070
Si₉Al_iP	0.56	2,9-4,9 (3,9)	970
Si₆Al_iP	0.54	2,4-6,0 (4,2)	930
Si₄Al_iP	0.51	2,8-5,1 (3,8)	760
Si₃Al_iP	0.49	2,9-3,9 (3,4)	560
Si₂Al_iP	0.42	2,8-4,0 (3,3)	420
MAS Si_{15/4}Al	0.57	--	35
MAS Si_{15/2}Al	0.44	3,3-5,8 (4,5)	450
MAS Si_{15/1}Al	0.42	4,1-5,3 (4,7)	550

limitation stage of this process (fig. 10). This system behavior differs from the first method used, due to the change of the limitation stage. Moreover nearly linear dependence of the amount of tetrahedral (or octahedral) aluminum on overall aluminum content gives the evidence of the first order reaction by aluminum.

The SAXS patterns of **Si_nAl_iP** series are shown on figure 11. All samples exhibit diffraction

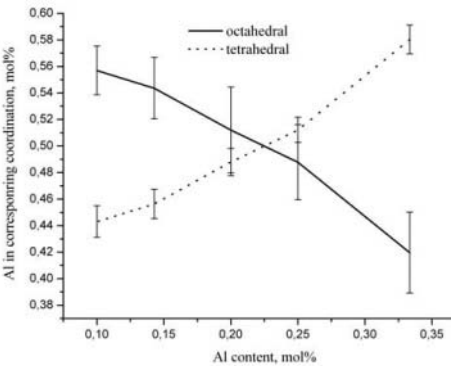


Figure 10. NMR data for **Si_nAl_iP** series.

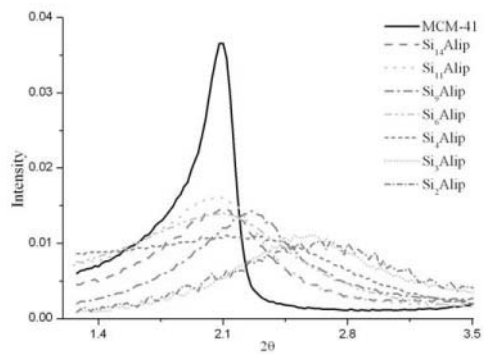


Figure 11. Small angle X-ray diffraction patterns of **Si_nAl_iP** series.

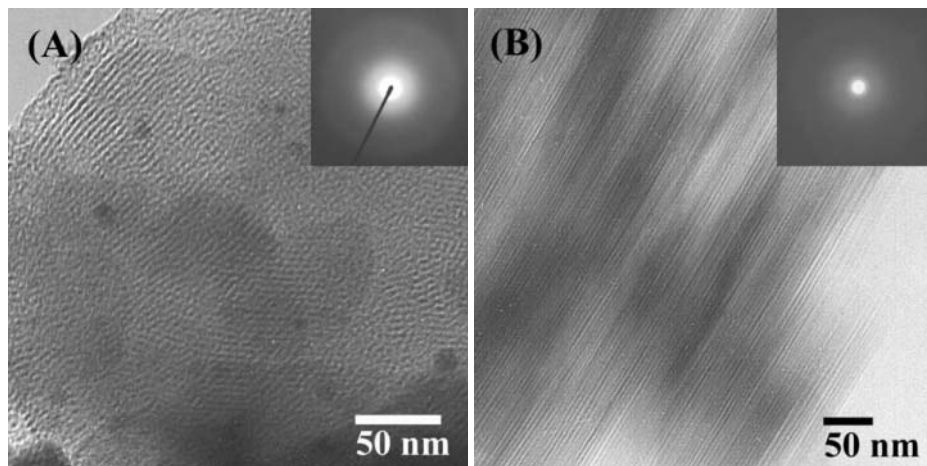


Figure 12. TEM image and electron diffraction patterns for nanocomposites **Ag/Si₉AlIP** (A) and **Ag/Si₁₁AlIP** (B).

maxima (nm) corresponding to the regular hexagonal structure of cylindrical pores. It was found that the diffraction maximum position shifts to higher 2θ values with increase of aluminum content, i.e. the lattice parameter of mesoporous structure decreases. Besides that, the growth of peak's halfwidth indicates the reduction of the mesoporous structure regularity and the growth of the pore size distribution. These results are in good agreement with N_2 adsorption-desorption studies: all samples exhibit high surface area values and the surface area decreases with increase of aluminum content (table 3). However even the highest Al content in **Si₂AlIP** results in extremely high specific surface area of $420 \text{ m}^2/\text{g}$. Therefore the second technique appears to be acceptable for preparation of nanocomposites based on mesoporous aluminosilicates with high aluminum loading.

The third method based on the hydrothermal synthesis shows well defined mesoporous structure for low aluminum content ($<7\%$). Unfortunately higher loading values lead to shrinkage of mesoporous structure. The tetrahedral aluminum content, surface areas and pore sizes for **MAS Si_{15/n}Al** series are also presented in table 3.

Thus, the approach based on $\text{Al}(\text{O}i\text{-Pr})_3$ hydrolysis was found optimal for preparation of mesoporous aluminosilicates with high aluminum content. While for aluminosilicates with low aluminum content ($<10\%$) the hydrothermal synthesis or copolycondensation of aluminum nitrate and tetraethylortosilicate are also acceptable. Since the hydrolysis of $\text{Al}(\text{O}i\text{-Pr})_3$ give mesoporous matrices in the widest range of Si:Al ratio **Si_nAlIP** series was used as nanoreactors for preparation of metal nanowires.

It's necessary to note that the incorporation of the metal cation into mesoporous aluminosilicate and the formation of metal nanowires should be studied on the model system first. Here one should choose such cation which provides a minimal charge and rather high atomic number due to the better contrast with the matrix for electron microscopy. Therefore silver was mentioned to be an optimal ones.

Incorporation of silver ions into mesoporous silica matrix was proved by TEM and ED. It was proved that particles shape and size are in good agreement with that of the pores (fig. 12). Thus, the suggested method leads to preparation of one-dimensional anisotropic nanostructures.

3. Conclusions

Thus, in the present study we suggested and successfully realized synthesis of ordered metal nanowires in the mesoporous matrices using two novel techniques. The first method is based on the introduction of a hydrophobic metal compound, into the hydrophobic part of silica-surfactant composite. The second approach involves charging of silica matrix by replacing part of silicon atoms by aluminum with subsequent ion exchange and reduction of metal cation. Both routes results in the formation of nanowire arrays. Besides that, an approach based on charging of matrix enables one to control the metal loading value.

Acknowledgments

The authors are thankful to Prof. A.T. Dembo, Dr. K.A. Dembo and A.P. Malakho for carrying out small angle X-ray diffraction measurements. We also would like to acknowledge Dr. A.V. Knotko and A.V. Garshev for TEM imaging; Dr. N.A. Grigorieva and M.P. Nikiforov for fruitful discussions. This paper was partially supported by the scientific program "Universities of Russia" (UR.06.02.001), RFBR (03-03-32182), INTAS (No. 2001-204).

Experimental details

PREPARATION OF MESOPOROUS SILICA (MCM-41)

Mesoporous silica was prepared by the method described elsewhere [11]. The method is based on polycondensation of a silica source (tetraethylorthosilicate (TEOS), 98%, Aldrich) in the presence of template (cetyltrimethylammonium bromide, CTAB, 99.9%, Aldrich) in ammonia aqueous solution. The resulting molar ratio was 1 TEOS : 0.152 CTAB : 2.8 NH_3 : 141.2 H_2O . The precipitate was filtered out, washed by deionized water to pH=7, and dried at 363 K for 12 h. The mesoporous silica films on Si(110) were obtained by spin coating technique.

PREPARATION OF Fe/SiO₂ NANOCOMPOSITES

Intercalation of iron was performed using iron pentacarbonyl because this non-polar molecule can be expected to dissolve well in the hydrophobic part of the SiO₂/surfactant micelles and could be easily decomposed to give elemental iron [12]. Dried mesoporous silica-surfactant matrix (~1 g, for powder samples) was soaked in 10 mL of liquid Fe(CO)₅ for 2 days. After filtration the sample was washed with heptane in order to get rid of Fe(CO)₅ absorbed on the external surface. Decomposition of Fe(CO)₅ to amorphous iron was carried out under UV-irradiation (DRT-1000 lamp, 1000 W) in vacuum (10^{-5} bar) for 10 hours. In order to achieve a formation of crystalline, anisotropic nanoparticles the sample was annealed in hydrogen flow in temperature range from 300 to 400°C for 3 hours. Powder samples were denoted as **FeSiO₂-260**, **FeSiO₂-350**, **FeSiO₂-375** and **FeSiO₂-400**, respectively.

PREPARATION OF MESOPOROUS ALUMINOSILICATES

To obtain mesoporous aluminosilicates using sol-gel technique CTAB was used as surfactant, TEOS (Aldrich, 98%) and $\text{Al}(\text{O}i\text{-Pr})_3$ (Aldrich, 98+%) or $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99+%) were used as Si and Al source respectively.

The first approach involved, does not require any expensive reagents and was earlier described in [13]. The Si/Al ratio was varied by controlling the TEOS to $\text{Al}(\text{NO}_3)_3$ ratio. CTAB was dissolved in deionized water (1,5g in 60 ml), then TEOS and an appropriate amount of 0,1 M $\text{Al}(\text{NO}_3)_3$ water solution were added. Mixtures were stirred for 1 h in order to achieve polycondensation of Si and Al hydroxocomplexes. The aqueous ammonia (18 wt.%) was dropped into the suspensions to form alkali medium. Obtained samples were denoted **Si_nAl** (n=2,3,4,6,9,11,14,19).

The second series of samples was prepared according to Ref. [14]. This approach is based on copolycondensation of $\text{Al}(\text{O}i\text{-Pr})_3$ and TEOS in alkali medium. The hydrolysis rate of $\text{Al}(\text{O}i\text{-Pr})_3$ exceeds TEOS ones, however aluminum hydroxide produced during hydrolysis process has high concentration of non-hydrolyzed and non-condensed groups, which can react with TEOS silanol groups, yielding large amount of aluminum incorporated into the SiO_2 lattice [15]. As a result the series **Si_nAl_iP** (n=2,3,4,6,9,11,14,19) was obtained.

The third approach, to obtain mesoporous aluminosilicates was hydrothermal synthesis [9]. At the first stage tetraethylammonium hydroxide (TEAOH, 20 wt % aqueous solution, Aldrich) was used as a structure directing agent: fumed silica (Aldrich, 99+%), NaAlO_2 and NaOH were stirred in TEAOH solution until a homogeneous mixture was obtained. The resulting mixture was transferred to stainless steel autoclave and heated at 150 °C for 24 hours, yielding aluminosilicate precursors. The precipitate was filtered out and washed by deionized water. At second aluminosilicate precursors was added into a CTAB water solution and transferred to autoclave and heating again at 180 °C for 48 hours. After that the solid product was filtered out, washed by deionized water, and dried at 363 K in air for 12 h. This series was denoted as **MAS Si_{1.5n}Al** (n=1,2,4).

PREPARATION OF $\text{Ag/Si}_{1-x}\text{Al}_x\text{O}_2$ NANOCOMPOSITES

Si_nAl_iP series was used as one-dimensional nanoreactor to obtain silver nanowires. Aluminosilicates were calcined at 500 °C to get rid of organic template. Intercalation of silver ions was performed by ion exchange using 1,0 M AgNO_3 water solution. Obtained samples were washed, dried and annealed in H_2 atmosphere for 1 h at different temperatures.

CHARACTERIZATION

To determine regular pore structure of aluminosilicates small-angle X-ray scattering (SAXS) was carried out at Rigaku D-max/RC (40kV 120mA) diffractometer using $\text{Cu K}\alpha_1$ radiation ($\lambda=1.5406 \text{ \AA}$) in the 2θ range $0.5^\circ - 10^\circ$ (2θ scan step 0.02°). The powder X-ray diffraction (XRD) analysis was carried out with Siemens D5000 (2θ scan step 0.03°) with $\text{CuK}\alpha$ radiation ($\lambda_{\text{ave}}=1.54184 \text{ \AA}$) in the 2θ range $5^\circ - 70^\circ$.

The specific surface properties were characterized by nitrogen capillary adsorption method using COULTERTM SA 3100TM instrument using N_2 as the working gas. Specific surface area and pore size distributions were calculated from absorption-desorption isotherms using BET (Brunauer-Emmett-Teller) and BJH (Barrett-Joyner-Halenda) procedures, respectively [16].

^{27}Al NMR spectra of the powdered samples were recorded on a Bruker MSL-300 spectrometer ($B_0=7.05\text{ T}$) at a resonance frequency of 78.207 MHz; external $\text{Al}(\text{H}_2\text{O})_6^{3+}$ standard in a 1 M aqueous $\text{Al}(\text{NO}_3)_3$ solution. Peaks for tetrahedral and octahedral coordinated aluminum was fitted by two lines (0-5 ppm and 52-56 ppm respectively).

Transmission electron microscopy (TEM) and electron diffraction was performed on a JEM-2000FXII electron microscope (JEOL) with the acceleration voltage of 200 kV. The powders for TEM studies were dispersed in ethanol and placed on a copper grid.

The MPMS-5S SQUID magnetometer (Quantum Design) was used for magnetic measurements.

Small angle neutron scattering (SANS) measurements were carried out at the IBR-2 pulse reactor in Dubna, Russia (2 MW, pulse frequency 1500 Hz). Neutron beam density was 10^{16} sm^{-2} . The scattered neutrons were detected with a position sensitive detector, exposition time 40 min.

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SCANNING PROBE MICROSCOPY OF BIOMACROMOLECULES: INSTRUMENTATION AND EXPERIMENTS

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Abstract.

The present paper is focused on the novel experimental implementations of scanning probe microscopy for the study of morphology and properties of biomacromolecules: chemical and biosensing using AFM cantilever system for measuring small attached masses.

1. Introduction

Our present analytical bionanoscopia activity is focused on the studies of nucleic acids, proteins, viruses and other biological systems performed in cooperation with several scientific groups of Moscow State University. The main directions of the investigations are the following: 1) molecular resolved lysozyme protein crystal growth in solution, surface reconstruction and kinetics parameters, 2) mechanical properties of individual plant viruses and RNA-protein complexes, 3) the effect of different factors on the morphology and biopolymers of living bacterial cell, 4) mechanics of nucleic acids absorbed on solid substrate.

The environmental control is extremely important feature for providing the study of dynamic processes in biological systems. We have implemented a simple liquid cell with precise temperature control in the range from room temperatures up to 60°C for contact and resonant modes. The effect of different factors on the morphology of biopolymers of cellular wall of living bacteria in liquid environments is witnessed.

The applications of FemtoScan Online microscope for ultrasmall mass measurements, chemical and biological sensing are discussed in the present paper.

The main features of FemtoScan Online probe microscope for long-term bionanoscopia experiments with full remote control are the following. This microscope may be used in real time operation by many remote scientists through the Internet especially in the field of analytical bionanoscopia, when a single experiment may last several days or weeks. It is very important, that the experimental data may be obtained simultaneously by several remote scientific groups for further independent analysis and processing. FemoScan Online microscope is also used for education of students as a key device in the Internet practical studies. At present time we have launched two biological-oriented practical studies:

"Mechanical rigidity of tobacco mosaic virus" and "Atomic force microscopy of biopolymers of bacterial cells".

Atomic force microscopy has become recently a practical tool for the measurements of ultrasmall masses [1]. This method has some advantages in comparison with quartz microbalance measurements [2] because the actual amount of mass to be defined is smaller. The mass equal to $30 \cdot 10^{-15}$ g was measured in a special vacuum design by V.de Heer in 1999 using static and resonant modes [3].

As mentioned in [4] the right choice of cantilever coating plays a crucial role in the design of chemical sensors. Hydrophopization of the cantilever surface is needed to reduce the effect of water adsorption in the case of variable humidity. The present chapter is mainly focused on the description of calibration procedures and sensitivity of AFM cantilever sensors in air conditions.

2. Materials and Methods

2.1. EXPERIMENTAL SETUP

FemtoScan Online scanning probe microscope (Advanced Technologies Center) and commercial cantilevers from Nanosensor and Mikromasch were used in the experiments.

The resonant oscillations of the cantilever were activated by the piezoceramic transducer installed in the cantilever holder as it is shown in fig.1. The oscillation amplitude is detected by the laser optical system. The incident focused light is reflected by the mirror backside surface of the cantilever towards the four-segment photodiode. High stable quartz direct frequency synthesizer (20 MHz, 0.01 Hz discrete) control the frequency of cantilever oscillation, RMS and lock-in amplifiers were used to detect the amplitude and phase of the oscillations. The shift of the resonance peak was controlled during the measurement of the mass of the adsorbed matter.

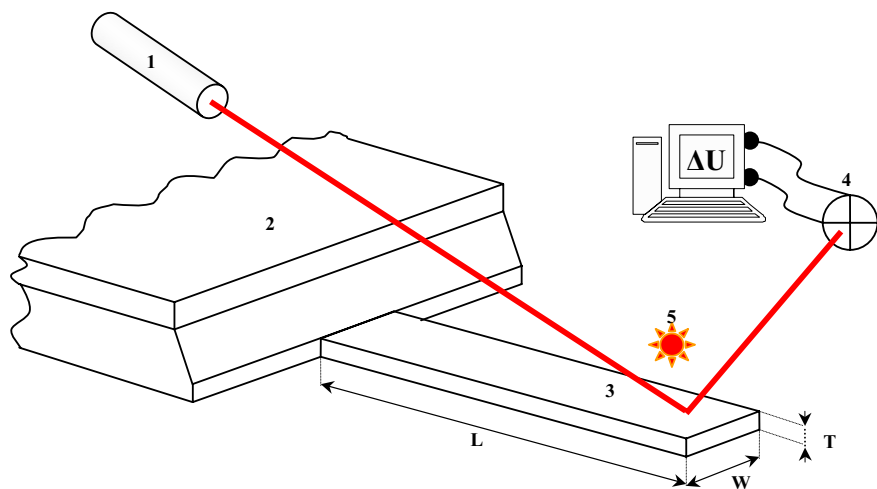


Figure 1. AFM cantilever resonance sensor: 1 – laser, 2 – piezoceramic transducer for inducing cantilever oscillations, 3 – cantilever, 4 – photodiode, 5 – thermostat.

The technical parameters of the cantilevers are listed in the Table 1.

Table.1. *Nanosensor u Micromasch cantilevers parameters* [5, 6].

Cantilever type	Thikness T, μ			Width W, μ			Length L, μ			Mechanical rigidity K, N/m.		
Value	min	typical	max	min	typical	max	min	typical	max	min	typical	max
Nanosensor	3	4	5	22.5	30	37.5	115	125	135	10	42	130
Mikromasch	0.7	1.0	1.3	32	35	38	345	350	355	0.01	0.03	0.08

Thermostat was used to reduce the possible thermal drift of the cantilever geometrical parameters.

2.2. CALIBRATION PROCEDURE

The calibration of the cantilever was performed by the consequent attachment of 15 polystyrene microspheres to the its free end. This was done by the method described elsewhere [7]. Epoxy glue was used in the experiments.

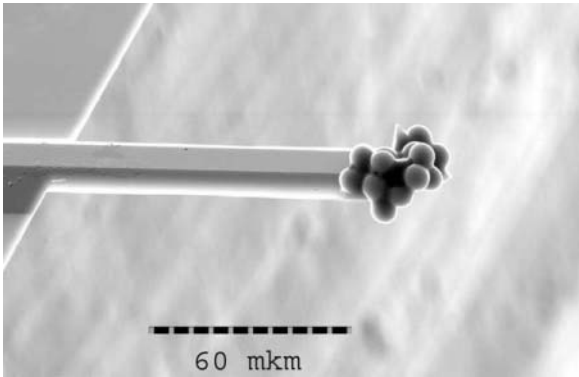


Figure. 2. Scanning electron microscopy image of 15 polystyrene microspheres $9.08 \pm 0.11 \mu$ in diameter and $47.01 \pm 1.73 \text{ ng}$ in mass attached to the Nanosensor cantilever.

The cantilever resonant frequency was measured after attachment of each of the microspheres.

2.3 MEASUREMENT PROCEDURE

The activated charcoal was used as an attached particle in the absorption measurements of organic compound (acetone and ethanol). The experiments were performed in the following sequence. The resonant frequency of the free cantilever was measured first. Then its end was covered with a thin sticky layer (epoxy glue without hardener component). The sticky layer remained in a liquid-like state during the whole time of the experiments and its influence on the mechanical rigidity of the cantilever was negligible. The adhesive force was strong enough so that the removal of the particles from the cantilever during experiments was never noticed. The small amount of activated

charcoal was attached to the cantilever. The mass of the attached particle was control by the resonance frequency measurements. The hysteresis in the adsorption/desorption process was revealed: the mass of the adsorbed acetone or ethanol was larger than the desorbed mass. The masses of the adsorbed/desorbed vapors were defined by frequency control of the resonant cantilever oscillations as described in the theoretical part below.

3. Theory of nanosensor operation

3.1. CANTILEVER OSCILLATION PROBLEM

The rod oscillations is described by the hyperbolic differential equation of 4th order. In the case of transverse rod oscillations (the rotational movement is neglected) the equation is written in the following form [8])

$$\frac{\partial^2 u}{\partial t^2} + a^2 \frac{\partial^4 u}{\partial x^4} = 0 \quad \left(a^2 = \frac{EJ}{\rho S} \right), \quad (1)$$

where E – Young modulus, ρ - density of the rod material, S and J – the cross section of the rod and inertia momentum of the cross section respectively its longitudinal axis x , u – lateral deflection of the rod from x axis.

The boundary conditions of the fixed end of the bar ($x = 0$) are

$$u|_{x=0} = 0, \quad \left. \frac{\partial u}{\partial x} \right|_{x=0} = 0.$$

The bending momentum for the free end ($x = l$) and the tangential forces inside the rod are the following [8,9]:

$$EJ \left. \frac{\partial^2 u}{\partial x^2} \right|_{x=l} = -I_t \frac{\partial^3 u}{\partial t^2 \partial x}, \quad EJ \left. \frac{\partial^3 u}{\partial x^3} \right|_{x=l} = -M_t \frac{\partial^2 u}{\partial t^2};$$

I_t – inertia momentum of the added end mass, M_t – added end mass.

Our aim is to find the eigenvalues ν_n of resonant frequency of the loaded cantilever (rod) which are derived as following:

$$\nu_n = \frac{\sqrt[4]{\lambda_n}}{2\pi l^2} \sqrt{\frac{EJ}{\rho S}}. \quad (2)$$

3.2. THERMAL DRIFT OF THE SYSTEM

Thermal drift inevitably leads to changes in the geometry of the system, also it influence the Young modulus. The theoretical dependencies for the cantilever resonant frequencies versus the value of the attached mass for two different temperatures are shown in fig.3. The temperature change equal to 1⁰C lead to the frequency drift about 890 Hz. According to the calibration curve (fig. 4) such a frequency change is also produced by the attached mass equal to 10⁻¹⁰ g. Temperature instability may drastically reduce the sensitivity of the system. In our case we use a thermostat to eliminate thermal instabilities.

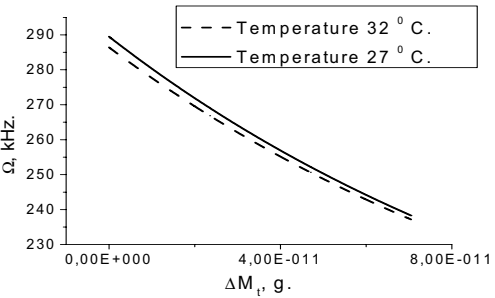


Figure. 3 Theoretical calibration curves for 27 u 32 °C.

The Young modulus dependence upon temperature may be neglected. For example, for silicon nitride, one of the most convenient material for cantilevers, $\Delta E/\Delta T = -10.31 \text{ MPa/K}$, $E = 314 \text{ GPa}$, one degree change in temperature leads to relative change in Young modulus less than $3 \cdot 10^{-5}$.

4. Result and discussions

4.1. EXPERIMENT AND THEORY COMPARISON

The experimental data is in good comparison with theoretical values (fig. 4).

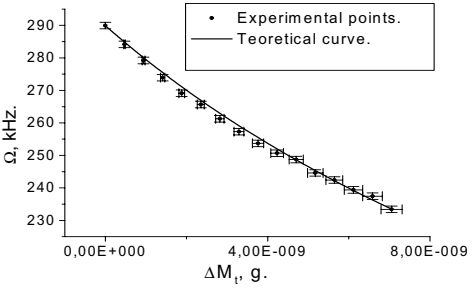


Figure 4. The frequency dependence of the frequency upon the attached mass. Experimental points correspond to 1,2, 3 ... 16 polystyrene microspheres, attached to the cantilever

Table. 2. Technical parameters of cantilever used in the measurements (fig.4) .

Cantilever type	Thickness T, μ			Width W, μ			Length L, μ			Mechanical rigidity K, N/m.		
Value	min	typical	max	min	typical	max	min	typical	max	min	typical	max
Nanosensor	3	4	5	22.5	30	37.5	115	125	135	10	42	130
Value chosen	4.00			30.0			125.0			42.4		

The Young modulus for silicon is 190 GPa [10]. For theoretical estimations the very exact microsphere position was not taken into account. The relative error was estimated as about 5%.

4.2. ADSORPTION OF ORGANIC VAPOR

The activated charcoal was attached to the cantilever as shown in fig.5. The mass of the charcoal is estimated as $M = 1.73 \cdot 10^{-8}$ g. The adsorbed mass of the ethanol in the near saturated vapor in our experiments was $M = 4.43 \cdot 10^{-10}$ g and corresponds to 2,5% of adsorbent mass. The sensitivity of the method is about $1 \cdot 10^{-12}$ g. We use amplitude method for the detection of frequency shift, phase modulation technique is supposed to reveal more sensitivity.

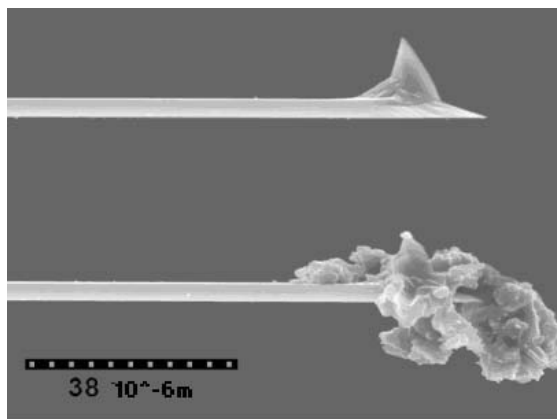


Figure.5 Scanning electron microscopy image of the Nanosensor cantilever before and after the attachment of activated charcoal.

The experiments performed with measurement of 17 pg mass (estimated value) are shown in fig.6. The adsorbed mass led to the clear noticeable shift of the resonant cantilever frequency.

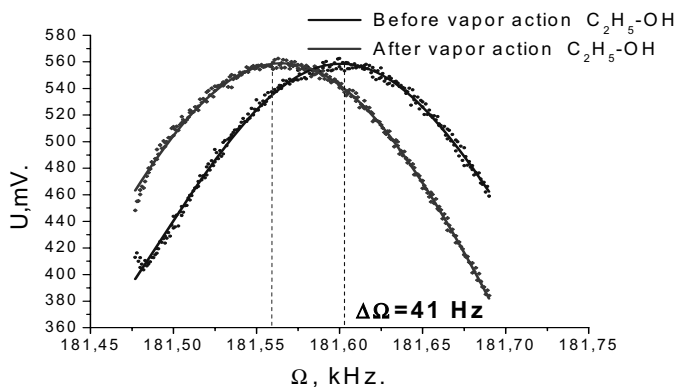


Figure. 6. The frequency shift is caused by the placement of the cantilever into the ethanol vapor of constant concentration. The frequency shift corresponds to 17 pg of ethanol molecules in the near surface layer. The measurements are performed at the temperature equal to 27 °C.

4.3. DETECTION OF WATER VAPOR

The water vapor concentration was defined by the resonant shift of the second harmonic oscillation of the Mikromasch CSC12 cantilever. The water in the small reservoir was put under the cantilever. Electric heater was used to increase the water temperature. The consumed electric power of the heater was regulated during the experiment, while the resonant frequency and Q factor were measured. The experimental data is presented in fig. 7. The decrease of the Q factor may be explained due to the increase of vapor concentration in the close vicinity of the oscillating cantilever. The viscous-elastic properties of the water vapor enlarge the energy dissipation of the moving cantilever as described in [10].

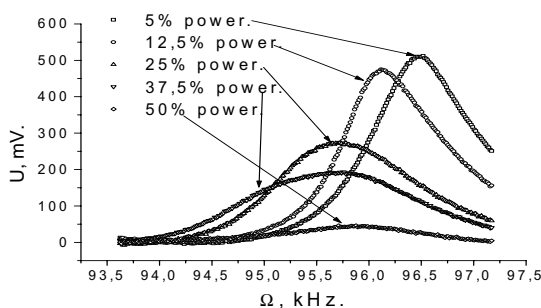


Figure. 7 Resonant curves of the cantilever for different heater power. X axis: 100 mV corresponds to 10 nm amplitude of the resonant cantilever oscillations.

The first and second resonances of the Micromasch cantilever are shown in fig 8.

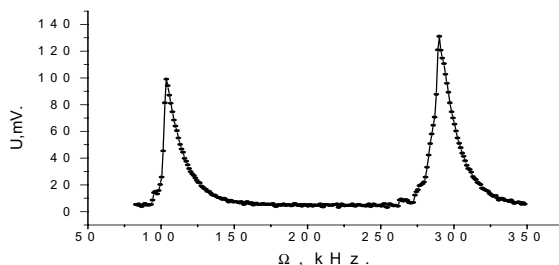


Figure. 8 First and second resonances of CSC12 (E) Mikromasch cantilever. X axis: 100 mV corresponds to 10 nm amplitude of the resonant cantilever oscillations.

5. Application of the developed method for biosensing

The developed technique may be used both for detecting and also for measuring the weight of biological objects. Taking into account the typical dimensions of Escherichia coli as $350 \text{ nm} \times 700 \text{ nm} \times 2000 \text{ nm}$ (as it can be witnessed using AFM in fig.9) and the density about 1 g/cm^3 the mass of the bacterium may be found as $500 \times 10^{-15} \text{ g}$. With the achieved sensitivity it becomes possible to measure two bacterial cells of the mentioned above size.

The sensitivity in measurement of protein molecules is about 10^6 , if size of the protein molecule is estimated as about $5 \text{ nm} \times 5 \text{ nm} \times 5 \text{ nm}$.

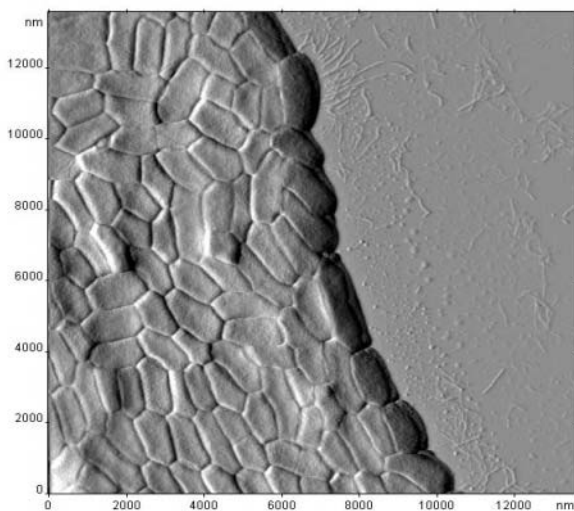


Figure. 9. AFM image of the monolayer of *Escherichia coli* bacteria. The typical bacteria dimensions are $350\text{ nm} \times 700\text{ nm} \times 2000\text{ nm}$.

Acknowledgment

The supports of Russian Foundation for Basic Research (00-04-55020 and 03-02-16113), INTAS (grant N 01-0045), Fund for Assistance to Small Innovative Enterprises (project N 3679) and Russian Ministry of Industry, Science and Technology (projects 40.012.1.1.1151 and 32.400.11.3215) are acknowledged.

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SURFACE SCIENCE TOOLS AND THEIR APPLICATION TO NANOSYSTEMS LIKE C₆₀ ON INDIUM PHOSPHIDE

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Abstract.

The growth of fullerene C₆₀ films on InP(001)-(2x4) was studied by a set of surface science techniques under ultra-high vacuum (UHV) conditions. Spectral signature measured by photoelectron and electron energy-loss spectroscopies (UPS, XPS, EELS, HREELS) corresponds to that of bulk C₆₀ both at low (1-2 monolayers (ML)) and high (10 ML) coverage. The result shows a weak bonding, most probably van der Waals interaction, at the molecule-substrate interface. Spectroscopic and microscopic data indicate, that C₆₀ forms 3D clusters at the initial stages of deposition. Electron diffraction (LEED) and tunnelling microscopy (STM) measurements reveal, that further molecule deposition leads to the formation of a well ordered single domain film. From the analysis of our microscopic data a C₆₀-film structure with fcc (111) orientation follows.

1. Introduction

During the last decade a large number of comprehensive investigations of fullerenes [1-3] on various substrates was performed. The interaction of C₆₀ with different semiconductor surfaces attracts continuous interest with respect to possible applications in technology [4-10]. For most applications of molecular structures in semiconductor devices, the key problem is the formation of homogeneously ordered molecular films on semiconductor substrates. In-plane epitaxial growth remains a challenge, in particular due to the formation of multiple symmetry – equivalent domains. From this viewpoint, searching for complementary materials and growth parameters, which allow the manufacturing of well ordered molecular structures, is a very relevant topic. Due to a good coincidence of the C₆₀ diameter with the unit cell of the (2x4) reconstructed InP(001) surface [11, 12], we expect the growth of commensurate close packed fullerene overlayers on the substrate. The growth mode of molecular layers is determined also by interface interactions. Strongly interacting substrates usually limit the surface mobility of the molecules during film formation, thus

leading to a high density of grains, whereas weakly interacting systems in many cases lead to an islanding of the films. Moreover, an interaction between the substrate and the molecular layers defines charge carrier transitions through the interface and also plays an important role in the design of electronic devices. Therefore, growth and characterisation of C_{60} on InP attracts our main interest.

So far InP was not studied in detail as a substrate material, in contrast to some other semiconductor substrates like silicon [4-7] or gallium arsenide [8-10]. Spectroscopic studies of the C_{60} /InP interface were performed only by Y. Chao *et al* [13].

In this contribution we present an investigation of C_{60} growth on InP(001) and its properties by a number of surface sensitive techniques like HREELS (High Resolution Electron Energy Loss Spectroscopy), LEED (Low Energy Electron Diffraction), STM (Scanning Tunnelling Microscopy), XPS (X-ray Photoelectron spectroscopy) and UPS (Ultraviolet Photoelectron Spectroscopy).

Our spectroscopic data reveal a relatively weak interaction between C_{60} and InP(001), strong predominance of fullerene bonding to indium or phosphorous was not registered. As a consequence, 3D islands were observed at the initial stage of molecular film growth. Further C_{60} deposition leads to the appearance of well ordered single domain molecular film. The structure of the film was characterised by STM and LEED and corresponds well to the known fcc ordering in C_{60} crystals.

2. Experiment

The experiments were carried out in different UHV-systems with a base pressure below 3×10^{-10} mbar. The vibrational spectra of the samples were measured by HREELS (Delta 0.5, developed by the Ibach's group), providing a nominal resolution of 8 cm^{-1} . Both specular and off specular regimes were exploited for registering dipole and impact active molecular vibrations, respectively [14]. Omicron STM-AFM and VT-STM were applied for structure characterisation. Micrographs of crystal substrates (InP(001), Si(111), Ag(111)) with atomic resolution were used for device calibration. The surface order was examined by LEED. Photoelectron spectroscopy (XPS, UPS) was used for examining the electronic structure of the core levels as well as the valence band. In addition, the film thickness was estimated by the evaluation of our XPS and microbalance data.

In order to study interactions at the boundary of C_{60} and InP(001) with respect to the bulk data, spectra obtained at various coverages are compared. At 1 ML the spectroscopic data show the response from the interface, whereas at 10 ML bulk properties of C_{60} are studied.

For the analysis of peak positions, HREELS data were deconvoluted. The procedure uses Razor Library software with implementation of Richardson - Lucy maximum likelihood algorithm [15]. In the process of deconvolution reducing of the spectrometer broadening was done by subtraction of the instrument response function from the experimental data. The instrument response function was defined from the elastic peak of the measured spectrum.

InP(001) substrates from MCP Wafer Technology Ltd (undoped and S-doped with a carrier concentration of 10^{19} cm^{-3}), were used. The preparation of clean InP(001) surface followed procedures already used in earlier studies [16-18]. At first, InP was etched in 40% HF for 30 sec, then rinsed in distilled water. Preliminary heating below 370 K for 10 hours was used for removing of surface contaminants. Gentle sputtering at an energy of 0.5 keV for 6

min with a sample current of about 2 μA at an ion beam angle plus and minus 45° with respect to the sample normal was the next cleaning step. Formation of (2x4) InP(001) was completed by substrate heating up to 620 K for 5 min.

C_{60} was deposited from a Knudsen cell, which was degassed by heating at 600 K for about 20 hours. During the deposition of molecules the sample was kept at room temperature in all our experiments. A deposition rate of 0.25 ML/min at a source temperature of 670 K was used. For the calibration of molecular source dosing we used consecutively depositions of C_{60} on Ag(111) with the film thickness measurements at every step. Fullerenes form a homogeneous film on the substrate [19]. For such structures film thickness can be evaluated from XPS peak intensities. The film thickness is determined by the attenuation of the Ag3d core level peak intensity relative to the change of C1s line intensity, which increases together with C_{60} exposure. In addition, quartz microbalance was measured in a different chamber for calibration purposes.

3. Results and discussion

3.1 SPECTROSCOPIC PROPERTIES

We start with the analysis of our XPS data. The attenuation of the substrate peaks In3d, In4d, P2s, and P2p with respect to C1s provides information about the molecular film thickness and the growth mode. In particular we estimate the thickness of annealed molecular layers by this technique. However the accuracy of that estimation is not very good. Since the layer structure after annealing is uncertain we used the simple model of a homogenous adlayer thickness.

XPS peak positions for various coverages (2 – 4 ML) of C_{60} were carefully measured and compared in order to study the chemical interaction of C_{60} with InP. In most cases chemical bonding leads to the appearance of energy shifts of peaks of the interacting species, so lines of both bonded components should be shifted. In our experiments indium and phosphorous peaks were not shifted by C_{60} deposition. However, small chemical shifts of the substrate components could be hidden by a signal from areas which are not covered by molecules. So, XPS does not register any chemical shifts of components which could point to strong bonding at the interface. The conclusion corresponds to measurements by other techniques (see below).

UPS results are presented in Fig. 1. The valence band structure of the clean reconstructed substrate (Fig. 1 a) corresponds to previously reported data, peaks at 6.8 eV and 3.7 eV correspond to density of bulk states, while peaks at 1.9 eV and 1.3 eV are related to surface states [20, 21]. The photoemission spectra of the $\text{C}_{60}/\text{InP}(001)$ system have characteristic fullerene signature that originates from electronic levels HOMO at 2.2 eV and HOMO-1 at 3.5 eV, and from the σ bands at 5.7 eV and 8.2 eV as well [22]. Note, that the InP related photoemission feature is visible as a shoulder towards E_F even if the substrate is covered by 2 ML C_{60} . That indicates inhomogeneous covering of the substrate by molecules, or cluster growth. Fig. 1b shows the In4d line after C_{60} deposition and restoring after desorption of C_{60} by annealing. The behaviour of the peak intensities confirms cluster growth of C_{60} on InP(001). Small changes in the peak position (about 0.1 eV) are not discussed here.

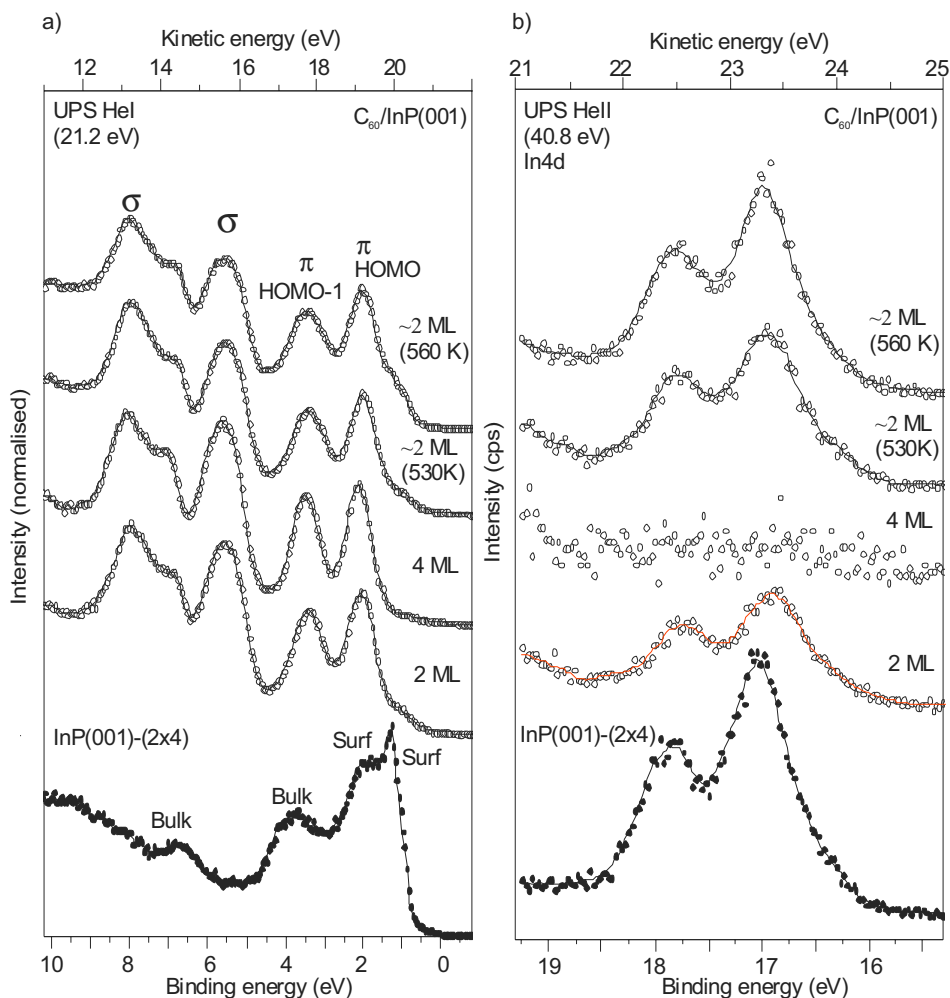


Figure 1. UPS HeI (a) and HeII In4d (b) spectra of $C_{60}/\text{InP}(001)$. The spectra are referenced to the Fermi edge of Au, attached to the sample holder. Subsequently deposited 2 and 4 ML and annealed up to 530 and 560 K structures were measured. Substrate peaks are totally attenuated by a coverage of 4 ML. Restoring of In4d peaks after C_{60} desorption by the sample annealing is registered (some discrepancies in annealed film thickness determination take place due to inhomogeneity of the film (see text)).

In Fig.2 HREEL spectra are presented. Fuchs-Kliwer phonons at 339 cm^{-1} (and its double losses at 678 cm^{-1}) dominate the spectrum of clean $\text{InP}(001)$ (2x4). Broad excitation centred at 760 cm^{-1} corresponds to carrier plasmons. These features are also present in spectra of $C_{60}/\text{InP}(001)$. After C_{60} deposition new peaks related to the molecule vibrations appear in the HREEL spectra.

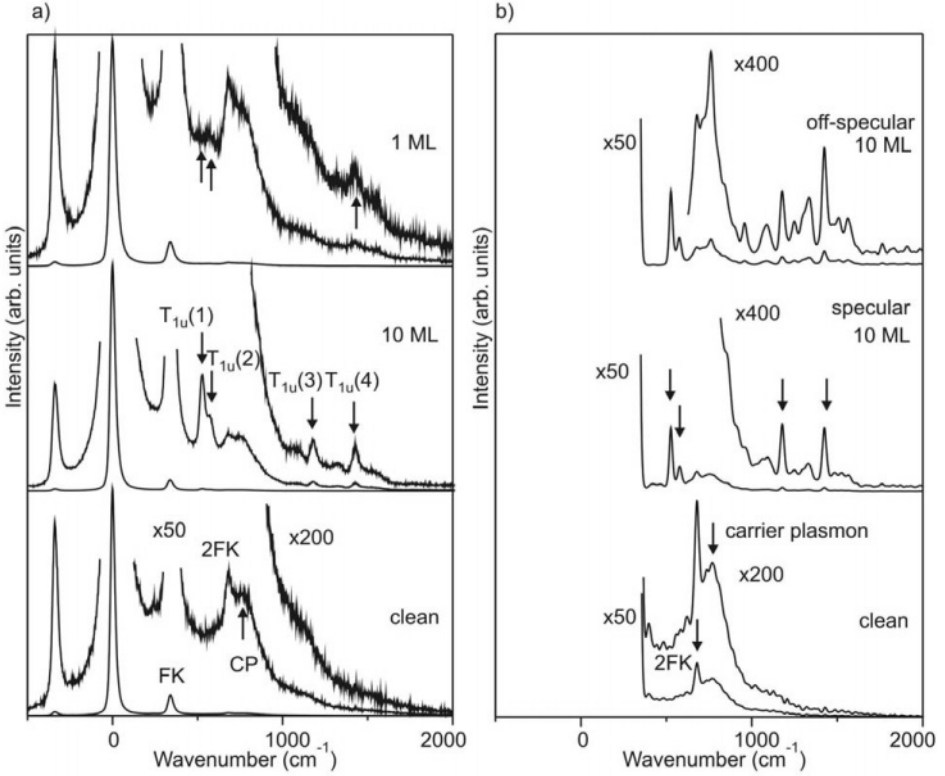


Figure 2. HREEL spectra of C₆₀/InP(001)-(2x4) (primary beam energy 4.5 eV, incident angle with respect to surface normal 64°). Spectra presented in a) as measured, b) deconvoluted (see text). The four dipole active modes are marked by arrows. No significant peak shifts are registered at 1 and 10 ML spectra (a). Non dipole active modes are registered in off-specular regime (b).

Table 1. HREELS mode assignment and comparison with published data.

HREELS	HREELS [25]	IRS [23]	Raman [23]	Calculations [24]	Mode symmetry [24]
426	428		437	438	H _g
526	528	527		547	T _{1u}
572	577	577		578	T _{1u}
855				829	G _u
903				931	G _u
959	961			994	G _u
1086	1078		1099	1094	H _g
1178	1183	1183		1208	T _{1u}
1250	1252		1250	1226	H _g
1295				1274	T _{3u}
1423	1428	1428		1445	T _{1u}
1481			1458	1431	H _g
1562	1567		1575	1568	H _g

Four dipole active modes with T_{1u} symmetry at 526, 572, 1178 and 1423 cm^{-1} are the most prominent in the curves. The same peak positions in the 1 and 10 ML spectra again point to a very weak interaction of C_{60} with the substrate. The bonding of C_{60} to InP (001) 2×4 is very weak due to the In – rich surface, which is electron deficient and therefore almost no charge transfer is possible.

In Fig.2b deconvoluted spectra for specular and off-specular geometries after 10 ML deposition are shown. New peaks in the off-specular spectrum are assigned to non dipole active vibrations of C_{60} . The positions correspond to published experimental and calculated data [23-25]. Our and literature data are summarised in Table 1. HREELS, infrared spectroscopy (IRS), Raman spectroscopy and calculated data are presented.

3.2. STRUCTURAL PROPERTIES

Due to the weakness of the C_{60} interaction with InP one can expect 3D cluster growth in the system. Slow substrate peak attenuation together with adlayer thickness increasing gives us indirect prove of this kind of growing process at the initial stages of molecules deposition. At low coverages (about 1ML) no molecular order was registered by LEED, STM data give evidence, that molecules form separate ordered clusters. In Fig. 3a an STM image of 1 ML coverage is shown. Hexagonal packing of C_{60} is clearly resolved. It is important to note, that at this coverage 3D islands are observed as well (not shown here). Furthermore molecules on the substrate are rather mobile, its positions are not stable under STM probe influence, this observation also corresponds to weak bonding at the interface.

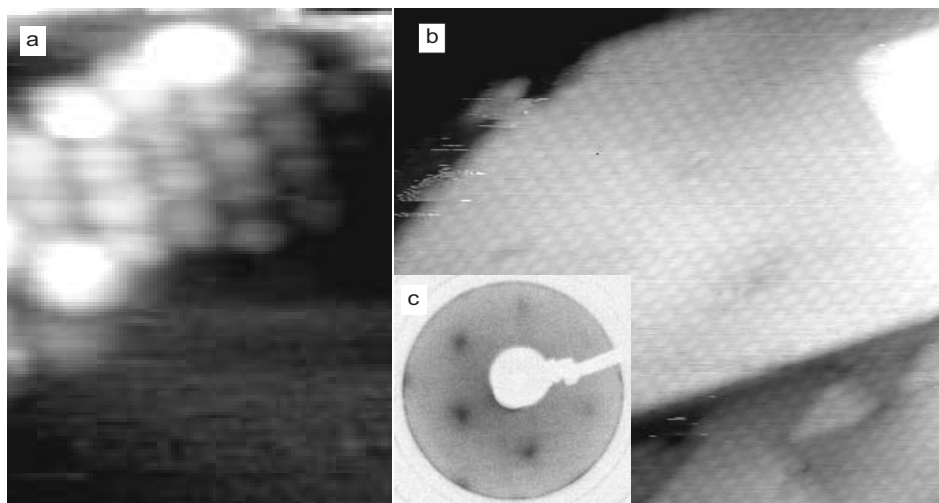


Figure 3. STM micrographs of $\text{C}_{60}/\text{InP}(001)$. a) Molecular cluster at 1 ML coverage ($6 \times 8 \text{ nm}^2$, $U_T=3.1 \text{ V}$, $I_T=0.1 \text{ nA}$), close packed molecules are resolved; b) Fullerene layer, coverage 10 ML ($34 \times 32 \text{ nm}^2$, $U_T=3.1 \text{ V}$, $I_T=0.09 \text{ nA}$), well ordered structure corresponds to fcc (111) lattice; c) LEED image of $\text{C}_{60}/\text{InP}(001)$ (primary beam energy 18 eV), shows single domain hexagonal molecular structure.

Further deposition of fullerenes leads to the appearance of well ordered single domain molecular structures. It was registered by both LEED and STM. In Fig. 3 STM micrographs and the LEED pattern of the structure are presented. Orientation of LEED spots and molecular rows in STM images are rigidly defined by initial substrate orientation, the rows are parallel to $[-110]$ direction of the (2×4) reconstructed $\text{InP}(001)$. Analysis of mutual positions of C_{60} rows in neighbouring terraces provides detailed information about the molecular film structure. ABC configuration of layers corresponds to the (111) orientation in a fcc lattice, which is found for bulk crystals of C_{60} with a spacing of 1 nm between the C_{60} molecules [10].

Our observations can be explained by the following model for the growth mode. Small molecular clusters are uniformly ordered with respect to the orientation of the substrate even at the initial stages of deposition. Most likely the C_{60} fills the grooves of the reconstructed (001) substrate surface, which plays the role of a template for cluster formation.

During further molecule deposition 3D cluster grow until the surface is completely covered. It takes place at a coverage of about 4 ML. In that case molecules form a single domain fcc structure in registry with the $\text{InP}(001)-(2 \times 4)$ substrate surface. The bonding of C_{60} to $\text{InP}(001) - (2 \times 4)$ seems to be very weak, most probably van der Waals interaction, that fullerene - fullerene interaction dominates, and a fcc (111) surface structure results.

Conclusion

In this study the growth of C_{60} films on $\text{InP}(001)-(2 \times 4)$ was analyzed by surface sensitive UHV spectroscopic and microscopic techniques. The interface interactions and its consequences for the molecular film structure are discussed. Advantages of investigations of such systems under UHV conditions are illustrated. Formation of a single domain molecular film on the substrate is very attractive for the manufacturing of simple electronic devices based on these materials. More surface properties of fullerenes need to be known for further successful application of this material to devices.

Acknowledgement

Authors are kindly thankful to L. Carta-Abelmann and P. Scharff (TU Ilmenau) for providing us C_{60} material for our experiments.

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POLARIZED RAMAN SPECTROSCOPY OF SINGLE LAYER AND MULTILAYER Ge/Si(001) QUANTUM DOT HETEROSTRUCTURES

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Abstract

Polarized Raman spectroscopy in backscattering geometry has been applied here for investigation of Ge/Si(001) quantum dot multilayer structures (ranging from 1 to 20 layers) grown by the Stranski-Krastanov technique. The characteristic Raman spectra of Ge dots have been obtained by taking the difference between the Raman spectra of the dots sample and the reference Si substrate, registered with the same polarization in the scattering channel. We found that Raman spectra of Ge dots obtained in such a manner are strongly polarized, in particular for Si-Ge (at $\sim 413\text{ cm}^{-1}$) and Ge-Ge (at $\sim 295\text{ cm}^{-1}$) vibrational modes. The dependence of peak intensity and peak position of Si-Ge and Ge-Ge modes versus the number of Ge dot layers, and versus the growth temperature for single layers, have been studied. The intermixing effect and stress have been obtained using the ratio of the integrated intensities and the peak positions of the aforementioned bands.

1. Introduction

In recent years, a considerable amount of work has been devoted to the study of semiconductor self-assembled quantum dots (QDs). Self-assembled QDs can be successfully grown with III-V [1], II-VI, and IV [2] lattice-mismatched semiconductors using a Stranski-Krastanov growth technique. Ge/Si self-assembled QDs are attracting a specific interest because of their compatibility with Si-based electronics. The growth of high-quality Ge/Si self-assembled QDs can be achieved either by molecular beam epitaxy [2, 3] or chemical vapor deposition [4-6]. Naturally, the electronic properties of the nanostructures depend on many parameters, including the size, shape, strain profile and composition of the QDs. A knowledge of these parameters is of crucial importance for future optoelectronic applications of the QD nanostructures.

The structure of the Ge quantum dots and other nanostructures formed on silicon has been studied using atomic force microscopy [7], transmission electron microscopy [8,9], X-ray photoemission spectroscopy [10] and other techniques. Raman spectroscopy was also found to be a powerful tool for the characterisation of the nanostructure formations. The position, intensity and width of Raman lines allows one to obtain information on composition, strain and quantum confinement in the nanostructures [11-13]. However, there is controversy regarding the analysis of Raman spectra of Ge/Si QDs due to overlapping of the LO-like phonon mode of Ge dots with two-phonon spectrum (transverse acoustical, TA modes) of Si substrate (or Si spacers) at ~ 435 and 302 cm^{-1} (see discussion in Refs. [14-16]). In particular Raman spectra of Ge/Si nanostructures are often dominated by a two-phonon peak originating from the silicon substrate. This fact has been largely ignored in many studies. Because the two-phonon spectrum of Si is strongly polarized [17], some authors recently used polarized Raman measurements of Ge/Si nanostructures in configuration, which allows to suppress gradually the contribution of the silicon acoustic phonons to the Raman spectra in the region of $\sim 200\text{--}460\text{ cm}^{-1}$ [15,18]. Nevertheless, our recent investigations [19] have shown that this suppression is not always large enough to obtain a pure Raman spectrum from the Ge dots.

This paper reports on an attempt to use polarized Raman spectra, obtained by cross-referencing the Raman spectra of a sample with dots, and a Si reference substrate, as a characteristic spectrum of QDs. The information on the intermixing effect and stress in QD layers is deduced based on this characteristic Raman spectrum analysis.

2. Experimental

Ge dots were grown using an ultrahigh-vacuum chemical-vapor deposition (UHV-CVD) system. Pure SiH_4 and hydrogen-diluted (10%) GeH_4 were used as gas sources. The system has a base pressure better than 1×10^{-10} Torr, and the pressure during growth was about 5×10^{-4} Torr. The growth chamber is equipped with a differentially pumped RHEED system, allowing us to probe the growing surface even at high partial pressures of hydrides (up to 10^{-1} Torr). During experiments, RHEED patterns were recorded using a camera-based video recording system. Transmission electron microscopy (TEM) measurements were performed on cross sections using a 400 kV microscope. Details of the experimental set-up and the growth conditions have been reported elsewhere [20, 21].

Two sets of samples were investigated here. One set included samples grown using approximately identical conditions, but having a different number of Ge/Si (001) dot layers. Another set included samples with single dot layers grown at different temperatures and with different thickness of the top Si cap layer. For the first set of samples the Ge growth temperature was chosen to be 550°C , since growing at this temperature results in a relatively narrow size distribution of the Ge islands (see Ref. [22]). The Ge growth rate determined from RHEED oscillations was 1 monolayer (ML) per minute ($1\text{ ML}=1.457\text{ \AA}$). Due to a very low Si growth rate at 550°C , Si deposition was carried out at 600°C and without growth interruption, to avoid island coalescence (Si deposition was started at 550°C , the growth temperature was then slowly raised to 600°C). The Si growth rate determined from high resolution TEM was of the order of 2.2 nm/min . To obtain Ge islands of identical size in each layer, Ref. [22], the Ge amount was adjusted to the effective critical thickness. The Ge islands thus formed have a pyramidal shape and are highly oriented along the Si crystallographic axes [23].

For the second set of samples the temperature of Ge layer growth was varied from 460°C to 800°C. Moreover, at each of these temperatures a pair of samples (with and without Si cap layer) was grown. The Ge islands were capped by Si at the same deposition temperature as was used for Ge growth. This resulted in layers of Ge dots with different shape, size, areal density and interdiffusion effect. The growth conditions and properties of these samples are summarised in Table 1 and Table 2. A schematic of the multilayer structure is shown in Fig. 1 *a*. Finally the Raman spectra of a number of thin (10 nm) SiGe alloys grown by MBE on Si substrates were also investigated for comparison. A schematic of these layer structures is shown in Fig.1 *b*.

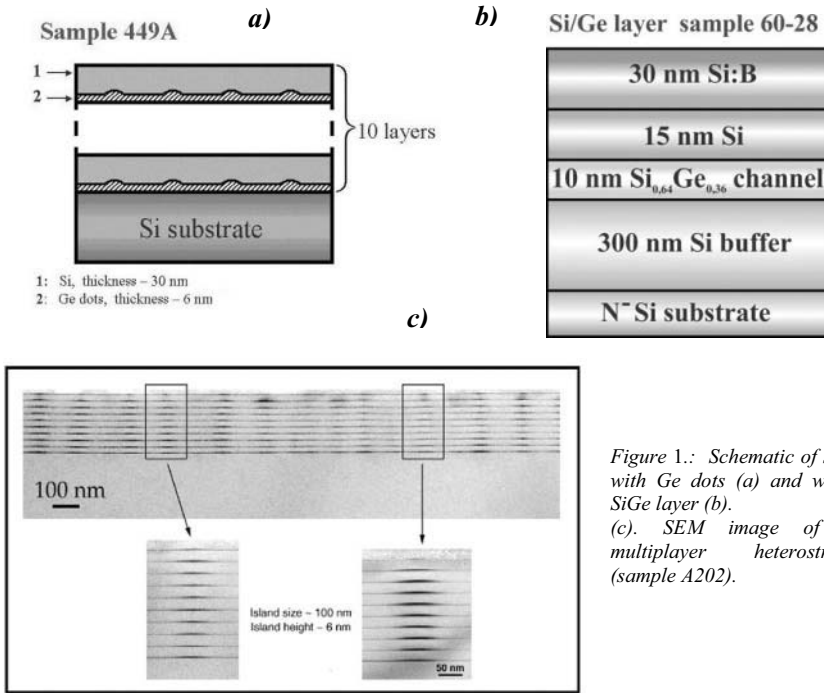


Figure 1.: Schematic of samples with Ge dots (*a*) and with thin SiGe layer (*b*). (*c*). SEM image of Ge/Si multilayer heterostructures (sample A202).

Raman spectra were registered in backscattering geometry using a RENISHAW 1000 micro-Raman system equipped with a Leica microscope. To prevent sample heating the power density was kept below 10^5 W/cm². The measurements were performed at room temperature with an Ar⁺ laser, 514.5 nm wavelength. An 1800 lines/mm grating was used in all measurements, which corresponds to a spectral resolution of ~ 2.5 cm⁻¹ per 3 pixels. In order to define the position of the phonon lines with a higher accuracy, the spectral lines, used for the analysis, were fitted with Lorentzian or Gaussian functions.

During Raman measurements we have used different polarization configurations according to selection rules to distinguish the signals from the Ge dot layers and the Si substrate. The position of sample, directions of the Si wafer crystallographic axes, and polarizations of the incident and scattered light are shown in Fig. 2. The polarization of light in the scattering channel was obtained by using the polarizer in one case and polarizer plus $\lambda/2$ plate in

another case in front of the spectrometer slit. Therefore, Raman spectra were obtained in two configurations, VV or [001(110,110)00-1] where scattering by the 2TA mode (peak at $\sim 302 \text{ cm}^{-1}$) is allowed, and in VH or [001(100,010)00-1] where scattering by the 2TA mode is forbidden but scattering by the LO-like Si and Ge modes are allowed. All the spectra were registered with the same accumulation time of 30s. Forty accumulations were taken for each Raman spectrum measurement.

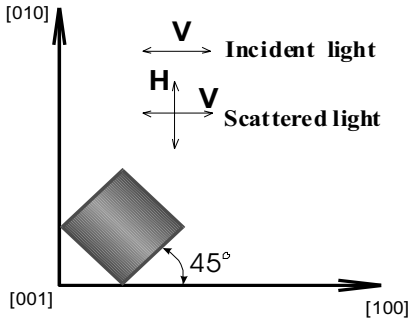


Figure 2.: Schematic of electric vector orientation in incident and scattered channels during polarised Raman measurements.

Table 1. Parameters of the first set of samples with Ge QDs multilayers.

Sample name	Number of layers	Layer thickness, nm			Areal density, cm^{-2}	Ge content x
		Si, barrier	Dots height	Si Cap		
A365	21	30	5	0	10^{11}	0.25
A202	10	22	5	0	$2,5 \cdot 10^{10}$	0.31
A449	10	30	6	30	$2,5 \cdot 10^{10}$	0.28
A224	5	22	5	22	$2,5 \cdot 10^{10}$	0.38
A374	3	160	5	0	$1,4 \cdot 10^9$	0.48
A328	2	22	5	22	$1,4 \cdot 10^{10}$	0.44
A338	1	—	6	<20	$1,5 \cdot 10^{10}$	0.5

3. Results and discussions

Figure 1c shows a representative [011] cross-sectional TEM image of a sample with 10 Ge/Si bi-layers. Regions of dark contrast correspond to the thin Ge wetting layers (WLs) and Ge islands, while light contrast regions correspond to the Si substrate and spacer layers. As was mentioned in the previous section, the Raman spectra of all samples were collected with high numbers of accumulations, which allows us to increase signal to noise ratio and to obtain a reliable spectra even from one layer of Ge dots. However, under such experimental conditions the weak features in the Raman spectrum of Si, which is always dominated by a strong LO-like phonon band at 520 cm^{-1} , becomes noticeable. These features at $\sim 229, 300, 435, 600 \text{ cm}^{-1}$ and higher were revealed and described in detail in Refs. [17,24]. Uchikora et al. [17] have assigned these features to the two-phonon (or

Table 2. Parameters of the second set of samples with single layer of Ge QDs.

Sample name	Growth T, °C	Thickness of layers, nm		Shape of dots,	Areal density, cm ⁻²	Ge content, x	Strain, ϵ
		Si cap	Dots, base/height				
A360	800	0	220/21	Pyramids	$2,3 \cdot 10^8$	0.44	-0.0022
			270/40	Domes			
A350	800	70	220/21	Pyramids	$2,3 \cdot 10^8$	0.35	-0.0065
			270/40	Domes			
A321	700	0	100/12	Pyramids	10^9	0.52	-0.0047
			110/22	Domes			
A320	700	60	100/12	Pyramids	10^9	0.39	-0.0041
			110/22	Domes			
A324	600	0	100/15	Domes	$1,4 \cdot 10^9$	0.66	-0.0066
A286	600	46	100/15	Domes	$1,4 \cdot 10^9$	0.45	-0.015
A208	550	0	95/14	Domes	$3 \cdot 10^9$	0.66	-0.0081
A198	550	22	95/14	Domes	$3 \cdot 10^9$	0.52	-0.013
A336	525	0	95/14	Domes	$3 \cdot 10^9$	~1.0	
A338	525	<20	~50/5-6	Hut clusters	$1,5 \cdot 10^{10}$	0.50	-0.016
A384	460	0	~48/5-6	Hut clusters	10^{10}	~1.0	
A361	460	<20	~48/5-6	Hut clusters	10^{10}	0.61	-0.017

density of states) Raman spectra of Si and have shown that these spectra are strongly polarized. In order to avoid the confusion of Raman spectra of Ge/Si quantum dots at frequencies of our interest (~ 430 and ~ 300 cm⁻¹) with two-phonon spectra of Si, spectra of the samples and Si substrate were measured in VV and VH configuration under the same conditions. As an example, a set of analyzed spectra for sample A202 is presented in Fig. 3. The difference in sample and substrate spectra obtained at different polarizations can be seen. Importantly, a prominent difference is clearly discernible between the sample and

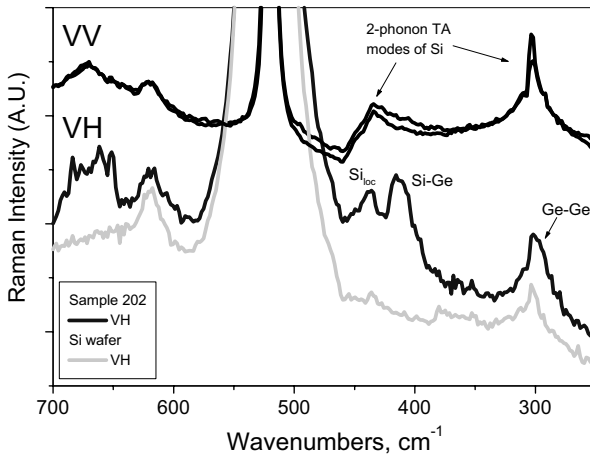


Figure 3.: Raman spectra of sample A202 and Si substrate collected at VV and VH polarization.

reference (Si) spectra in the region of interest. Although the 2TA phonon is observed at $\sim 300 \text{ cm}^{-1}$ in both spectra at the VH geometry, the Ge-Ge peak with intensity sufficient for analysis appears as a low-energy shoulder of the more intense Si 2TA phonon band in the sample spectrum. Note that the high orientation of the Ge islands on the Si substrate in studied samples results in highest intensity of the Ge-Ge peak. For random orientation of the islands (for example domed-shape islands) the Raman signal will be at least twice as weak and may be inaccessible for the analysis.

Therefore, the characteristic Raman spectra of Ge dots (I_{dots}) have been obtained by taking the difference between Raman spectra of dot sample (I_{sample}) and reference Si substrate (I_{Si}) registered with the same polarization in the scattering channel

$$I_{dots} = I_{sample} - f \cdot I_{Si} \quad (1)$$

Here f is the subtraction factor which can be obtained by taking the ratio of LO-like bands of the Si substrate at 520 cm^{-1} in the Raman spectra of the dot sample and the reference one $f = (I_{sample}/I_{Si})_{520}$. I_{dots} will hereafter referred to as the “difference spectrum”. We believe that by using this approach the contribution of both the Si substrate and Si spacers to the Raman spectrum of sample with dots will be taken into account. It should be noted that great care must be taken when choosing the reference for subtraction. We observed during this work that if the Si substrate or Si buffer layer are heavily doped, their TA phonon Raman spectrum will be slightly different from that for the normally doped Si substrate. In such a case the reference spectrum must be chosen as a mixture of these two or the reference

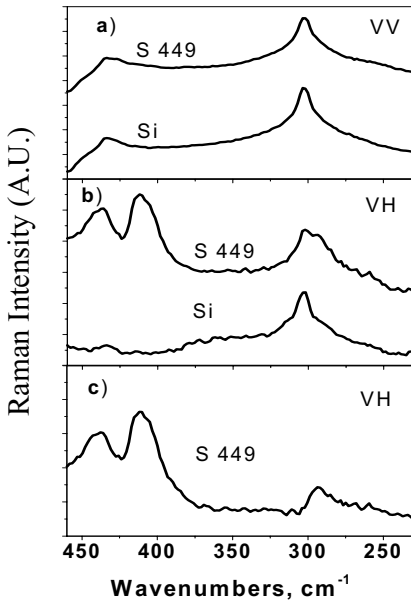


Figure 4.: Raman spectra of sample with 10 QD layers registered in VV and VH polarization (a and b, respectively) and the difference spectrum of this sample in VH polarization (c).

sample must be specially grown with the same structure of Si layers. Only in this case the subtraction can be done correctly.

The difference Raman spectrum of sample with ten layers of Ge dots (sample A449) together with the original spectra of sample and spectra of Si substrate at different polarizations are shown in Fig. 4. Three features at frequencies of ~ 413 , ~ 435 and $\sim 298 \text{ cm}^{-1}$ can be seen in the difference spectrum (Fig. 4c). The first two peaks belong to Si-Si local and Si-Ge modes respectively and the third one belongs to Ge-Ge mode. We can also see that the position of the Ge-Ge peak after the subtraction is shifted to the low-frequency side by a few cm^{-1} and the shape of this band is changed.

The difference spectra for a number of samples from the first set in the region of $200\text{--}470 \text{ cm}^{-1}$ are shown in Fig. 5, while Fig. 6 demonstrates the spectra for the second set of the samples. As can be seen, the Raman spectra deviate from each other depending on the growth conditions and number of layers deposited.

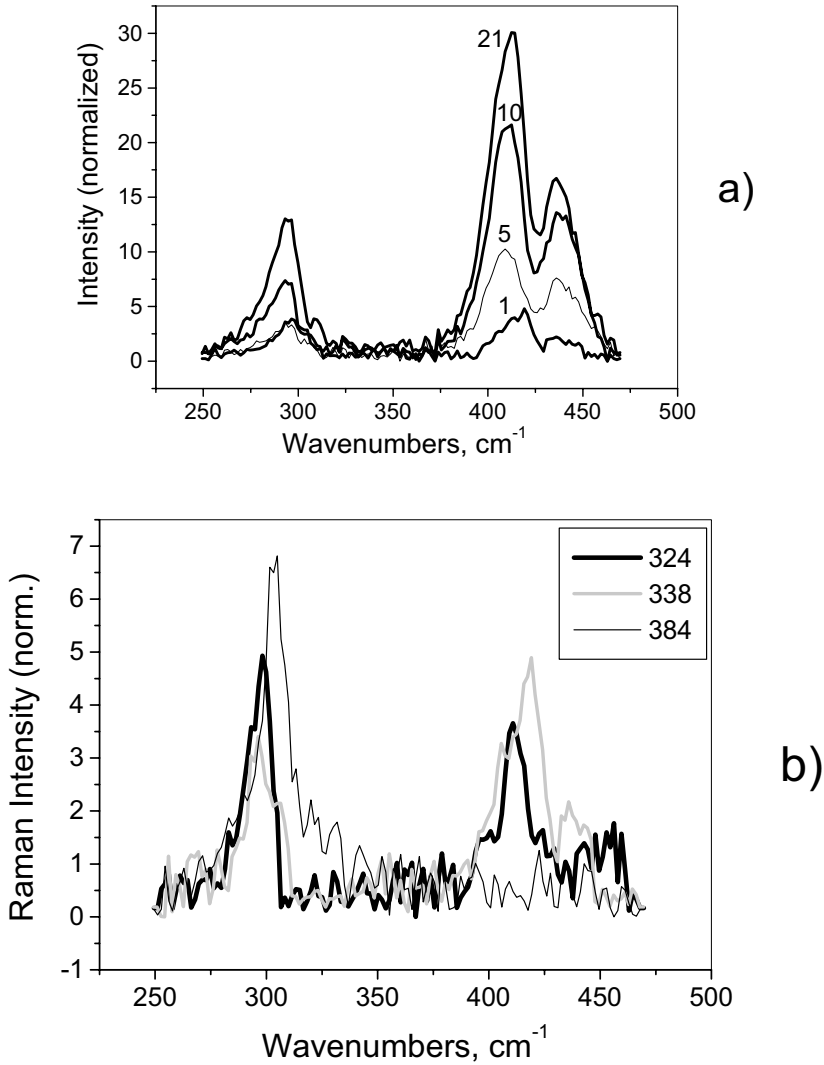


Figure 5.: The difference Raman spectra for QGs samples with different number of layers (a) and for single layers grown at different temperatures (b). Note that the number of layers in (a) shown beside the corresponding spectrum.

The dependences of the Si-Ge and Ge-Ge peak intensities and peak positions for both sets of samples are shown in Figs. 6 and 7. The intensities of these peaks have been normalised to that of the Si optical phonon. Quite surprisingly, the intensities of both peaks still increase, even for samples with 21 layers of the Ge dots, despite the depth of penetration for visible light into Si and Ge being substantially different. The depth of penetration of laser light into Si and Ge can be calculated using the simple expression:

$$d_p = 2.3/\alpha \quad (2)$$

where $\alpha_{\text{Si}} = 15080 \text{ cm}^{-1}$ and $\alpha_{\text{Ge}} = 600000 \text{ cm}^{-1}$ for the wavelength of $\lambda = 514 \text{ nm}$, which gives the values of $d_p(\text{Si}) = 763 \text{ nm}$ and $d_p(\text{Ge}) = 19.2 \text{ nm}$. It is obvious from these estimations that for many of the multi-layer samples studied in this work (with Ge dots height $> 5 \text{ nm}$) light will not reach more than 3-4 layers (see Fig. 8 and Table 3) resulting in saturation of the related Raman signals with increase in number of layers. However, as can be seen from Fig. 6 (a and b) this is not the case, since the intensity of both bands still increases. There are two options for the explanation of this effect i) the Raman signals come mainly from the Ge WLs (Fig. 8) or ii) there is diffusion of Si into Ge dots layer (so called intermixing effect).

As far as the Raman signal from the wetting layer is concerned, we can refer readers to the papers [25, 26], where the results on Raman line-mapping experiments with big Ge islands with small areal density ($\sim 9 \times 10^8 \text{ cm}^{-2} = 9/\mu\text{m}^2$) were published. In both reports no Ge-related signal was detected in between these islands despite the high sensitivity of the Raman probe (measurements have been performed using Raman microscope). Therefore we can conclude that the Raman signal from the very thin ($\sim 1.5\text{-}3\text{\AA}$) wetting layer is negligible. Another argument on behalf of the absence of the Raman signal from the wetting layer is that the surface modes, which can propagate in such layers, are forbidden in backscattering geometry [27]. Also, in general their position is shifted to low frequencies (390 cm^{-1} for Si-Ge and $\sim 288 \text{ cm}^{-1}$ for Ge-Ge peaks).

On the other hand, the Raman intensity dependence on the number of QD layers can be easily explained by the intermixing effect that causes the reduction of the light absorption by the Ge-Si dots and hence the increase of the depth of penetration of the laser light. Indeed, the depth of penetration of 514 nm radiation into $\text{Si}_{1-x}\text{Ge}_x$ layers can be easily estimated by the use of the well-known expression

$$d_p(\text{Si}_{1-x}\text{Ge}_x) = (1-x) \cdot d_p(\text{Si}_{1-x}) + x \cdot d_p(\text{Ge}_x) \quad (3)$$

which shows that at $x=0.5$, $d_p(\text{Si}_{0.5}\text{Ge}_{0.5}) = 391.1 \text{ nm}$. This value is large enough to allow the light to pass through all 21 layers of Ge dots and Si spacers.

Therefore we can conclude that the Ge-Si intermixing become apparent in the Raman spectra of the Ge dots and this is essential in the studied Ge/Si quantum dot structures. As was shown in a number of papers [28-30], this effect will depends on Ge and Si layer deposition conditions and for Ge dots grown at high temperature we can expect that more than 50% of Si diffuses into the dots interface [28]. For one layer of dots, Ge/Si intermixing may occur at both interfaces: at the dot/substrate interface, intermixing is mainly thermally activated while at the interface between dots and capped layers, it may be enhanced by the strain field distributed over the dot surface. It is expected that intermixing will also depend on the shape and size of dots. This will be analysed in the next section.

Based on Raman measurements the intermixing effect can be found from the ratio of the integrated intensities of Ge-Ge and Si-Ge peaks [31]

$$I_{\text{Ge-Ge}}/I_{\text{Si-Ge}} = Bx/2(1-x) \quad (4)$$

where x is the Ge content and B is a constant which depends on the experimental

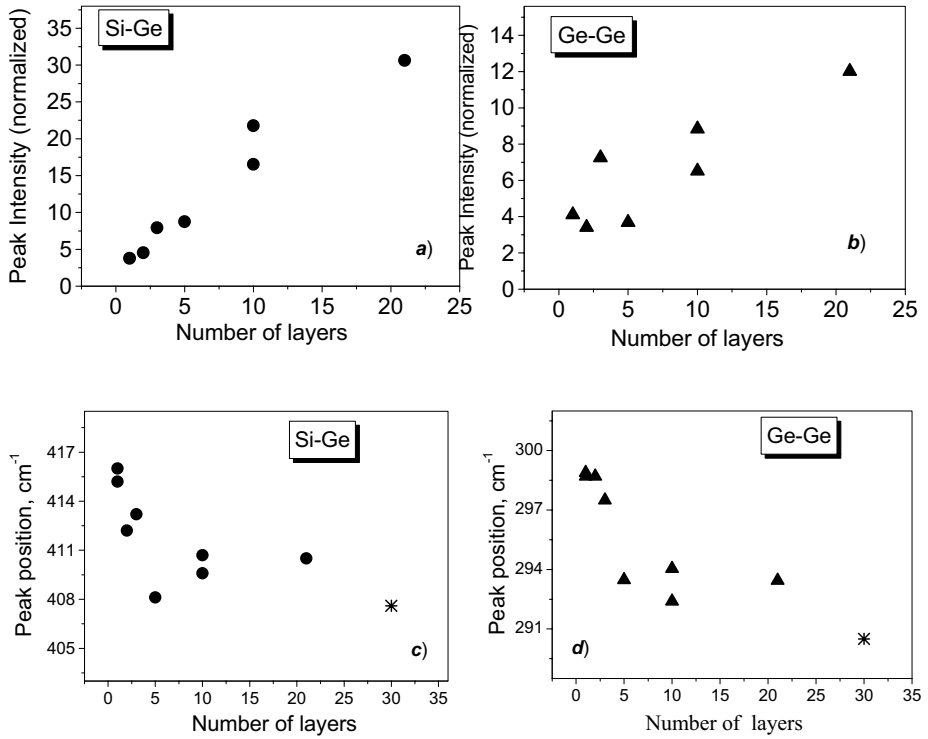


Figure 6. : The dependences of the Si-Ge and Ge-Ge peak intensity (a, b) and peak position (c, d) vs. number of layers for multilayer Ge dot heterostructures. Stars in (c) and (d) show the estimated values of frequencies for both modes using Eqns. (6) and (7) at $x=0.5$.

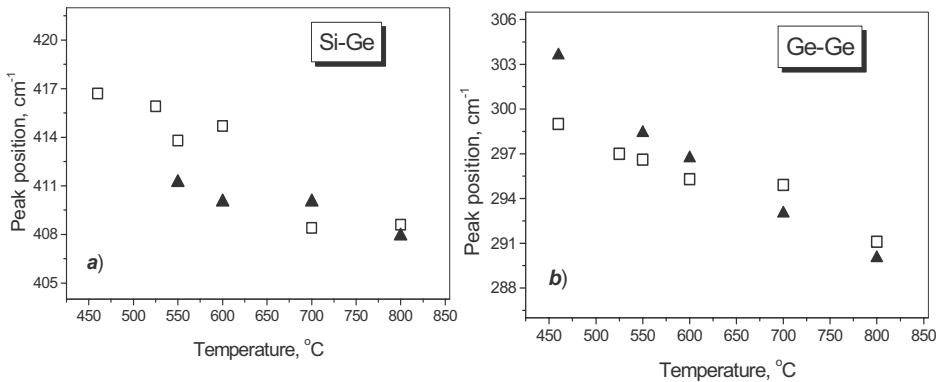


Figure 7. The dependence of peak position of Si-Ge (a) and Ge-Ge (b) modes vs. growth temperature for single layer of Ge dots with (squares) and without (triangles) Si cap layer.

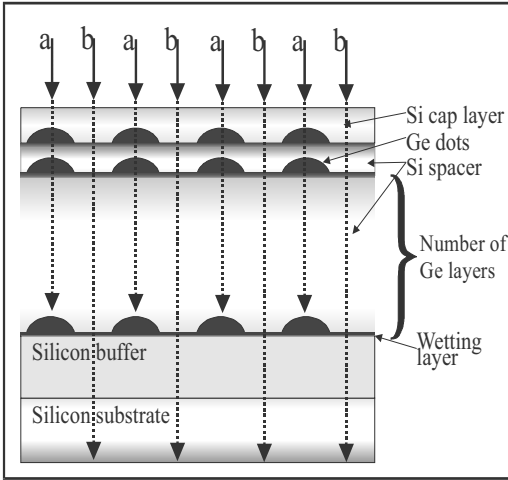


Table 3.

<i>Pass (a)</i>	<i>Pass (b)</i>
Sample A202 (10 layers)	
Si- 198 nm	Si- 198 nm
WLs- 3 nm	WLs- 3 nm
	Ge dots- 50 nm
Sample A238 (2 layers)	
Si- 44 nm	Si- 44 nm
WLs-0.6 nm	WLs- 0.6 nm
	Gw dots- 10nm

Figure 8.: Schematic and the thickness estimation for light passing through wetting layers (WLs) and QDs layers for samples with different number of layers.

conditions. We must stress that Eq. (4) was obtained and checked for a number of SiGe alloys using non-polarized Raman spectra. Since we used polarized Raman measurements in our study, we first checked the validity of the Eq. (4) for a number of thin SiGe layers with known Ge content. In such a way we determined the coefficient B for our experimental conditions. The calculations performed for the set of samples with multilayers of Ge dots show that the Ge content is reduced from 49% (for one layer) down to 25% for 21 layers (see Table 1). These results are in agreement with data obtained for similar samples in Ref. [28] by the selected area transmission electron diffraction (TED) of a *single* quantum dot and with the results obtained by different methods of analysis for Ge dots grown by other techniques [29, 30].

We are now moving to the analysis of the peak positions and try to see what kind of information we can extract from this. From our point of view there is again controversy in the literature regarding this analysis. In most of the published papers the bulk Ge-Ge phonon modes is considered as a reference in order to extract the information on the shift of these modes which directly relate to the stress in Ge dots. For practically all the samples studied in the present work such a consideration will lead to the conclusion that the Ge dot layer is under tensile stress, since it can be seen from Figs. 7 and 8 that Ge-Ge peaks for nearly all the samples are shifted to the low-frequency side. This contradicts the results obtained by other methods (and in particular TEM and photoluminescence measurements), which show that the stress is in fact compressive. Therefore, in the case of Raman data analysis, a proper reference must be chosen in order to extract reliable information for stress in Ge dots.

In general, the shift of the Ge-Ge peak in Ge quantum dots from the bulk value is mainly due to the three reasons i) confinement effect, ii) intermixing effect and iii) stress in a layer. The confinement effect shifts the position of the Ge-Ge phonon peak downwards [32, 33]. However, the size of Ge dots appears too large to expect a substantial confinement effect

especially in the plane of growth. As was shown in Refs. [32, 33], this effect can play a crucial role for Ge nanostructures with size less than 2-3 nm.

Intermixing can be accounted for by taking the ratio of the integrated intensities of Si-Ge and Ge-Ge peaks as was shown above. Therefore the value of stress can be estimated using the expressions for Si-Ge and Ge-Ge peaks positions for $\text{Si}_{1-x}\text{Ge}_x$ alloys [34] only after the intermixing effect (or Ge content, x) is known

$$\omega_{\text{Si-Ge}} = 400.5 + 14.2x - 575\varepsilon \quad (5)$$

$$\omega_{\text{Ge-Ge}} = 282.5 + 16x - 384\varepsilon \quad (6)$$

where ε is strain (which is directly related to the biaxial stress σ). Based on these expressions the value of ε has been estimated for our samples, which are listed in Table 2. From these values and the frequency behaviour (see Figs. 6c and d) we can conclude that the stress is compressive and with the increase in the number of the layers the structure becomes more relaxed. For the samples with 10 and 21 layers the frequencies of both peaks are quite close to the calculated value of fully relaxed $\text{Si}_{0.5}\text{Ge}_{0.5}$ layers [34] shown by stars in Figs. 6 (c and d)

$$\omega_{\text{Si-Ge}} = 400.5 + 14.2x \quad (7)$$

$$\omega_{\text{Ge-Ge}} = 282.5 + 16x \quad (8)$$

The same analysis has been applied for the second set of samples with single layers of dots grown at different temperatures and with different thickness of the Si cap layer. As can be seen from Table 2 these growth conditions lead to a different shape, size and areal density of Ge dots. Their Raman spectra also show quite substantial difference in relative intensities of both peaks (Si-Ge and Ge-Ge) and their peak positions. For example the Ge-Ge peak position of uncapped layer of Ge dots is shifted from $\sim 304 \text{ cm}^{-1}$ for the sample grown at 460°C to 291 cm^{-1} for the sample grown at 800°C . The ratio of the integrated intensities allows us to conclude that the intermixing effect is negligible for samples grown at 460°C and 525°C (without capping layer) and it is $>50\%$ for samples grown at 800°C (see Table 2). Moreover, the comparison of Raman spectra of samples grown at the same temperature shows the influence the intermixing effect when Si cap layer is deposited on the top. It can be seen that the intermixing effect is higher for thicker Si cap layers (and higher growth temperatures, 700°C and 800°C).

From this analysis we can conclude that at high temperatures the intermixing effect is larger but stress is smaller, while for the samples grown at low temperature the effect of these two factors is opposite. The effect of the dots shape also plays an important role on stress as can be seen from Table 2.

4. Conclusion

In conclusion we have also analysed our results together with data published on Raman investigation of different Ge/Si QD layers. The results of this comparison are presented in Table 4. From this table it can be seen that the Ge peak is shifted substantially to the high frequency side ($>310 \text{ cm}^{-1}$) for Ge/Si QDs grown at low temperature, with high areal density and with typical size of dots (base/height=7-10/1-2). In such a case the subtraction

of Si peaks (related to the Si substrate) is not so critical. However, we believe that in all other cases, even when spectra were measured at the condition of the suppression of Si peaks (in VH polarization), the subtraction of Si two-phonon spectrum is necessary in order to obtain reliable data from Raman spectra.

The comparison with data obtained for thin (10 nm) SiGe layers shows that the Si-Ge and Ge-Ge peaks in the Raman spectrum of QDs are more pronounced despite the equality of the layer thickness for both samples. The stronger polarization of the Si-Ge Raman lines indicates an alignment of the Si-Ge bonds, most likely, on the surface of the Ge dots.

Table 4. Growth conditions and characteristics of different Ge/Si nanostructures

Reference	Growth technique, T°C	QDs base/height, nm	N of layers	Si cap thickness, nm	Peaks position, cm ⁻¹	
					V _{Si-Ge}	V _{Ge-Ge}
[35]	MBE (250 ⁰)	7-10/1.2	6	10	415	316
[36]	MBE (200-300 ⁰)	10/1.2-2.4		10	415	316
[18]	MBE (500 ⁰)	20/1	1	160	419	303
[37]	MBE (600 ⁰)	60/3	10	22.4	410	298
[25]	LPE (920°C) Ge islands	200/100	1		405.7	288
		160/20	1		408.7	291
[38]	MBE (600 ⁰)	h-1.2	30	200	403	301
[39]	MBE (650 ⁰)	42/4	20		403	301
[40]	MBE (600 ⁰)	Layers/15	25		410	296
		Layers/20	25		410	298
[13]	MBE (550 ⁰)	8/1-2			417	312
This work	UHV-CVD (460°-800°C)	45-100/5-7	1-21	~20-100	408-417	289-304

Thus we can conclude:

1. In order to obtain reliable information on the properties of Ge/Si QD heterostructures from Raman measurements, the data must be collected with different polarizations and properly referenced to Si substrate spectra measured under the same conditions.
2. Raman spectra of samples with Ge/Si quantum dots are more pronounced and strongly polarized, compared to SiGe alloys of the same thickness.
3. The intermixing effect from the substrate is negligible for samples grown at low temperature and without Si cap layer. This effect is >45% for samples grown at 800°C and 700°C (without cap layer). The presence of the cap layers will increase the intermixing effect by a factor of ~ 1.3-1.5 times in both cases. Such an enhancement of intermixing can be attributed to the strain field distributed over the dot surface. For multilayer structures the average intermixing effect is ~ 75% (for 21 layers of Ge dots), and layers are nearly 100% relaxed.
4. Different growth conditions result in totally different composition and stress distribution within Ge/Si quantum dots. In particular for the Ge dots grown at low temperatures (mainly hut clusters) the stress is larger and intermixing effect is smaller, compared to the surface on which domes and pyramids coexistent. Typically the Raman spectra of these samples are more pronounced. For the samples grown at high temperature, the average intermixing effect is >60%.

Acknowledgments

The authors thank Tim Grasby for the donation of samples with thin SiGe layers. The financial support from Enterprise Ireland and French Embassy in Ireland (Ulysses (FR/2003/016) Programme) and Enterprise Ireland Basic Research Grant Scheme (SC/01/209) are gratefully acknowledged. A.V.B. thanks the RFBR grant 02-02-17311 for partial financial support during this work.

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NANOSYSTEMS OF POLYMERIZED FULLERENES AND CARBON NANOTUBES

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Abstract

Nanosystems based on polymerized fullerenes and carbon-nanotubes begin to play an important role in the field of nanotechnology. Nanotubes can be used as molecular wires, and can even figure as building elements for molecular electronics. Furthermore nanotubes can be used as amplifiers in composite materials, as a result of their unique mechanical properties. Many other applications, as for example as electron emitters for flat screens, are currently under development. Fullerenes are known to be strong electron acceptors, which enables them to support the electron-hole pair separation in polymer based photovoltaic cells. The use of fullerene chains instead of fullerenes could improve the anisotropic electronic conductivity in the contained polymer layer, and therefore enhance their performance.

1. Introduction

Fullerenes and carbon-nanotubes represent two novel forms of carbon, which were discovered in 1985 and 1991, respectively. During the first years of fullerene research the main directions were related to the preparation and characterization of the diverse types of fullerene molecules, as well as to chemical derivatisations. Later it was found that individual fullerene molecules can build up covalent bonds to others and consequently form dimers, trimers, oligomers, or polymers. Depending on the reaction conditions, 1D-, 2D-, and 3D-phases can be obtained. Polymerised fullerenes proved to offer extremely interesting properties, such as extreme hardness (3D), ferromagnetism (2D), metallic or semi-metallic conductivity (1D, 2D) etc. The structure of carbon nanotubes can be either single walled or multi walled. For both types of tubes a broad variety of applications begins to show up: Nanotubes as storage for molecules or ions, electron emitters, electrical conductors, molecular electronics, amplifiers in polymers etc. For all these applications it is required to develop highly effective preparation and purification methods. With respect to a possible intercalation into the inner tube channel, the selective opening of closed tips can be performed by mild oxidation reactions. A very interesting C-nanotubes derivative was found in form of an intercalation compound with C₆₀, so called “peapods”. Handling of individual tubes as well as using self-assembly for obtaining aligned tubes are still a challenge.

2. Preparation of Fullerenes

There are various methods for fullerene preparation. In all of them, high temperatures are used to obtain carbon-vapour containing C_2 units. These molecules loose energy by colliding with noble gas atoms and form bigger units, such as graphitic particles, which are in principal thermodynamically preferred, however are destabilized in form of small aggregates, due to the presence of big numbers of dangling bonds in relation to the number of atoms. As a concurrence reaction, closed shell particles are formed. Therefore in all cases mixtures of fullerenes and soot are obtained. Depending on the reaction conditions, various portions of different fullerenes can be obtained, whereby C_{60} and C_{70} play a dominant role. In 2002 the synthesis of C_{60} via classical chemical reactions was first described [1], now offering the opportunity to prepare types of fullerenes, which cannot be obtained by the established methods.

2.1. KRÄTSCHMER-HUFFMAN METHOD [2]

In the Krätschmer-Huffman method high currents are passed through two contacting graphite rods, which leads to the evaporation of the graphite. The graphite rods are placed in a reaction chamber filled with He under reduced pressure (ca. 140 mbar). The fullerene yield is 5-10% [3].

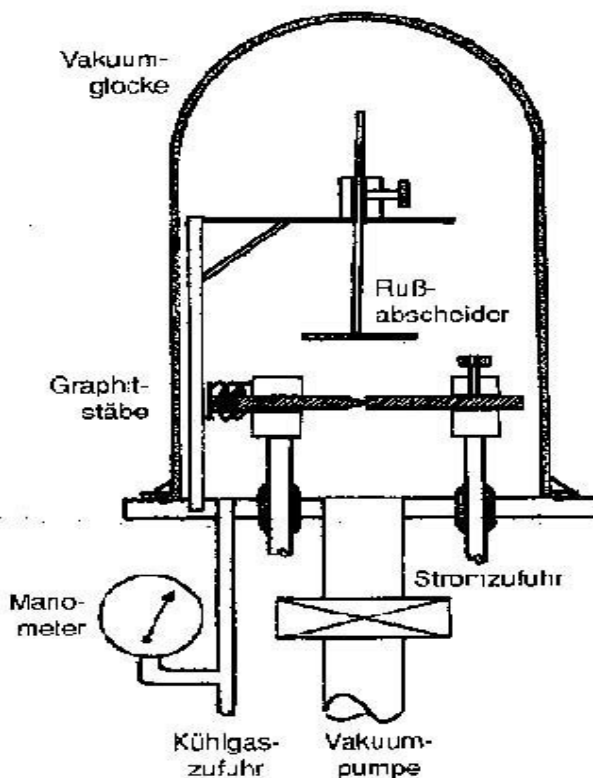


Figure 1: Fulleren-generator [2]

2.2. ARC EVAPORATION OF GRAPHITE [4]

This method, introduced by Smalley, is very similar to the Krätschmer-Huffman method, however the graphite rods are not in contact, which leads to the formation of an arc after the application of high voltage. The graphite is evaporated in the arc, giving a fullerene yield of up to 15%. Due to the UV radiation being emitted from the arc, the diameter of the graphite rods can not be enhanced very much, as in this case an increasing proportion of the formed fullerene molecules would be destroyed [5].

2.3. INDUCTION METHOD [6]

Fullerenes can also be prepared by inductive heating of carbon to temperatures of about 2700°C in a diluted He atmosphere. The fullerene yield is ca. 10%.

2.4. LASER-EVAPORATION OF CARBON [7]

The use of power lasers allows to evaporate nearly all kinds of carbons in a diluted inert gas atmosphere, the fullerene yield is reported to reach several %.

2.5. SOLAR ENERGY [8]

Focused sunlight can be used to evaporate carbon. This method offers the advantage that the starting carbon material must not necessarily be a good electrical conductor. Furthermore up-scaling is possible, as the UV radiation is much less intense compared to the arc method, however the fullerene yield proved to be comparatively low.

2.6. SOOTING FLAMES [9]

In the soot of flames polyaromatic hydrocarbons as well as fullerenes can be found. The fullerene yield is strongly dependent on the reaction conditions and reaches 0.003 – 9%.

3. Isolation of Fullerenes [10]

Fullerenes can be extracted from the other soot components by various organic solvents (benzene, toluene, CS₂ etc.).

As the most efficient method, Soxhlet extraction in combination with an ultrasonic treatment was established. By this method, soot particles, which contain fullerene material in their core, can be broken and the fullerenes can be solved.

4. Separation and Purification of Fullerenes [11]

The different fullerenes can be separated by column chromatography, using various stationary phases and eluents.

Also the use of preparative HPLC proved to be successful.

As the ultimative purification procedure, sublimation in vacuum is applied.

5. Properties of Fullerenes

Fullerenes are spherical carbon clusters. They contain $2(10 + M)$ carbon atoms, forming always 12 pentagonal and M hexagonal rings. This building principle follows from the Euler theorem. Therefore, the smallest imaginable fullerene is C_{20} . However, it was found that for the stability of the fullerenes the isolation of the contained pentagons by hexagons plays an important role ("Isolated Pentagon Rule", IPR). Hence the smallest stable fullerene is C_{60} , as the IPR can not be realized for a cluster with less than 60 atoms.

The double bonds between the six-membered rings are not completely delocalised, as in benzene, but behave chemically much more as do double bonds in electron deficient polyolefins.

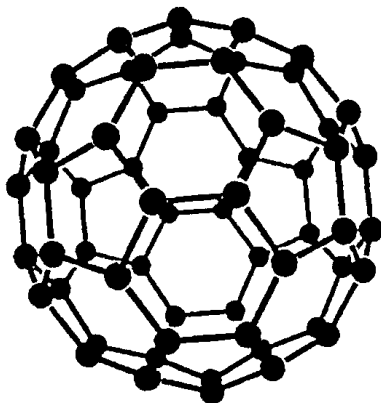


Figure 2: C_{60} -Fullerene

As a by-product of fullerene synthesis "bucky onions" are formed, consisting of different fullerenes, being interlocked (building principle of Russian doll).

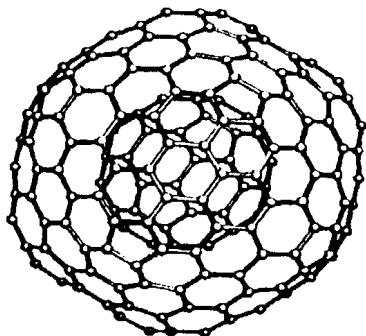


Figure 3: Bucky Onion

Fulleren derivatives can be divided into three groups:

- endohedral fullerenes
- exohedral compounds
- and heterofullerenes.

5.1. ENDOHEDRAL FULLERENES

Endohedral fullerenes contain at least one atom or ion inside the carbon cage. There are different preparation methods for endohedrals:

- co-evaporation of carbon and metals or metal oxides (laser, arc)
- heating of fullerenes in presence of a gas under enhanced pressure (window mechanism)
- defined opening and closing of the fullerene cage via chemical reactions
- bombardment of thin fullerene films with metal ions.

Beside endohedrals with noble gases, such with lanthanides and alkali metals have been prepared. Surprisingly the synthesis of $N@C_{60}$ was successful [12].

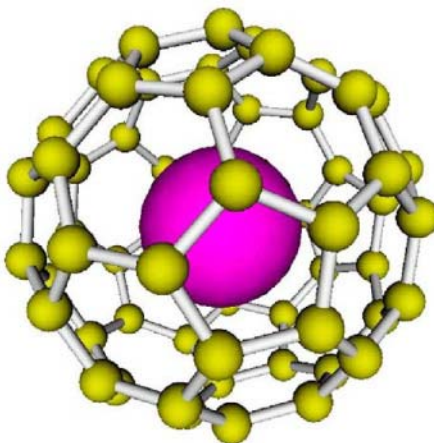


Figure 4: $He@C_{60}$

5.2. EXOHEDRAL COMPOUNDS

Functionalisations with a broad variety of organic addends have been carried out, opening up the wide field of fullerene side chain chemistry. Furthermore a big number of inorganic reagents, such as halogens, oxygen, strong Brönsted acids, sulphur, anhydrous nitrates etc., were found to form fullerene derivatives.

Alkali metals, iodine and interhalogen compounds can be intercalated into the fullerene lattice.

Under high pressure and enhanced temperature fullerenes can form dimers, oligomers and polymers. A T, P-phase diagram, comprising 3-membered rings, 4-membered rings, and 3D polymers, is reported [13].

Also 1D- and 2D-polymerisation was achieved. Some 2D-polymers were found to show ferromagnetic behaviour [14].

Furthermore fullerene molecules can be at least combined to form dimers by conversion with interhalogen compounds and subsequent reaction with ethanol, as well as by tribochemical reactions.

5.3. HETEROFULLERENES

In heterofullerenes at least one carbon atom is replaced by a heteroatom, as for example N, S, or B. In case the heteroatom has a number of valence electrons deviating from the number of valence electrons in carbon, a doping effect occurs. Up to now, only very few heterofullerenes could be obtained in preparative quantities, for example $C_{59}N^+$, which is, however, only stable in form of the dimer [15].

6. Preparation of Carbon Nanotubes

Hollow CVD carbon fibres were reported already in the eighties [16-18], however no one at that time was much interested in these materials.

In contrast, the discovery of carbon nanotubes („CNs“) by Iijima in 1991 [19] resulted in more than 6000 scientific papers up to now, and still an increase in scientific activities can be stated.

There are two types of carbon nanotubes: single wall carbon nanotubes (“SWNTs”) and multi wall carbon nanotubes (“MWNTs”). SWNTs consist of a single rolled up graphene sheet (fig. 5). The electronic properties of such tubes depend on the position of the tube axis with respect to the edges of the elementary cell of the graphene.

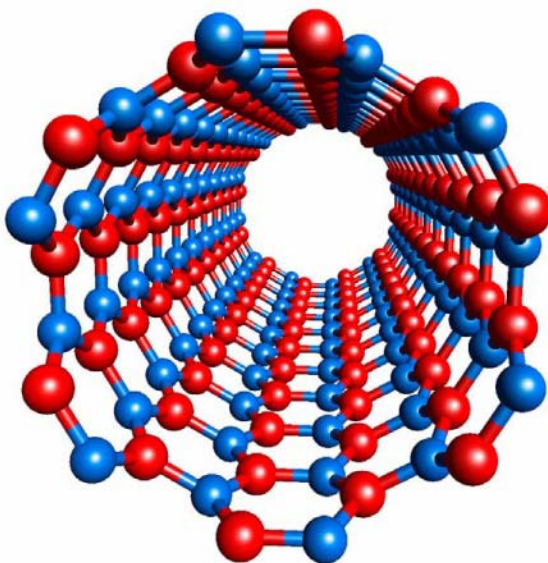


Figure 5: SWNT

MWNTs consist of concentrically interlocked nanotubes with increasing diameters (fig. 6).

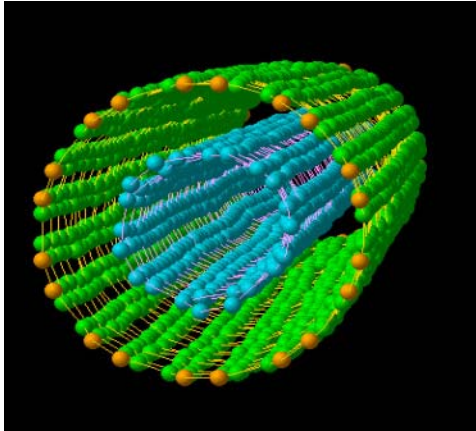
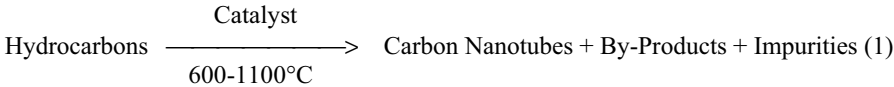


Figure 6: Double wall carbon nanotube

There are mainly four different methods for the production of carbon nanotubes:

6.1. CATALYTICAL DECOMPOSITION OF HYDROCARBONS [18, 20-24]



Using this method, SWNTs, MWNTs or arrays of aligned MWNTs (fig. 7) are obtained, depending on the reaction conditions.

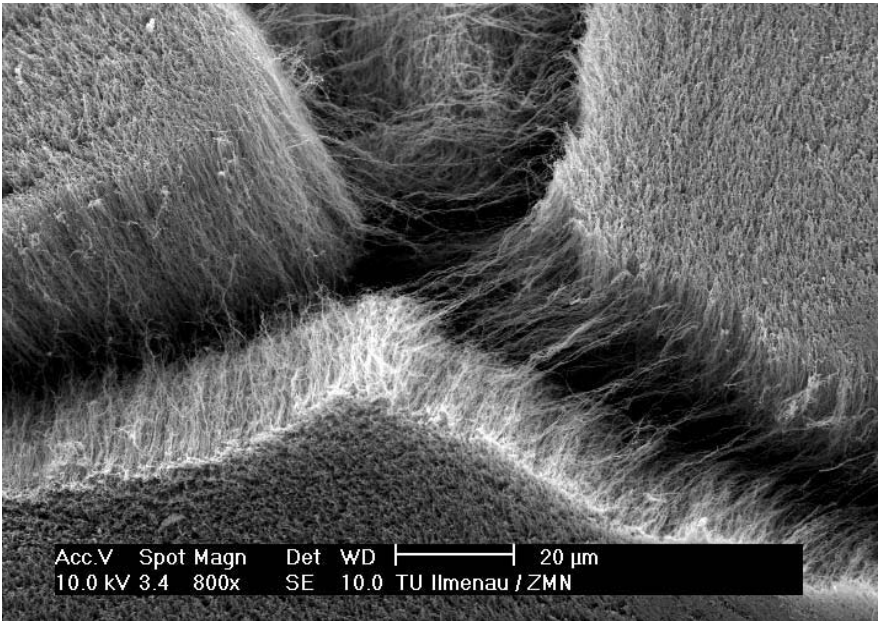


Figure 7: Aligned MWNTs obtained from catalytic decomposition of benzene at 800°C, forming a “lawn-like” structure on a quartz glass substrate

The yield can be as much as 40%, so that in a lab-scale apparatus some 100 g nanotubes can be produced per day.

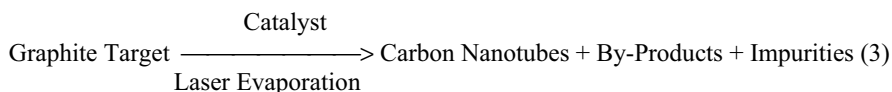
Beside aligned tubes, tubes being arranged in form of ropes, bundles or coils are also found.

As the biggest disadvantage of this preparation method, the often comparatively bad crystallinity of the tube walls can be regarded.

6.2. DC- OR AC-ARC BETWEEN GRAPHITE ELECTRODES [19, 25-29]



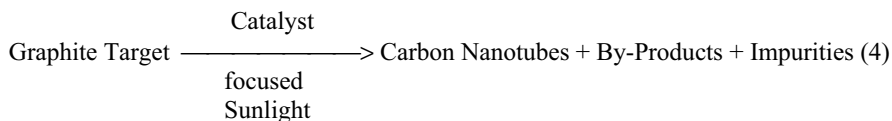
6.3. LASER EVAPORATION [30-33]



Using these preparation methods, SWNTs, MWNTs, and double wall nanotubes are obtained. The wall structures are close to being perfect. The tubes reach a length of up to one μm , and are mostly closed at the tube ends by bowl shaped carbon aggregates.

In conventional lab-scale apparatus some 10 g nanotubes can be produced.

6.4. SOLAR ENERGY [34]



The advantages of this method are the possibility of using isolators or powdered carbon catalyst mixtures as starting materials, and the broad variability of the reaction conditions.

The morphology of carbon nanotubes as well as the yield and possible forms of agglomeration are governed by many parameters, as for example type and composition of catalysts (often used: ferromagnetic transition metals as Fe, Co, Ni), composition of the gas phase, type of carbon source, temperature, pressure, flow rate etc. There are still challenges for the improvement of carbon nanotubes synthesis:

- Control of inner and outer tube diameter
- Control of tube length
- Control of chirality and wall structure
- Enhancement of yield
- Alignment of tubes or tubes bundles
- Production of wide area thin films consisting of nanotubes on various substrates

As can be seen from formulas (1) – (4), the carbon nanotubes products contain always by-products and impurities (C_{60} , bigger carbon molecules, soot particles,

graphite particles, catalyst particles etc.). Therefore for most applications a purification process is required

7. Purification of Carbon Nanotubes

In the literature, various methods (or combinations of them) for the purification of nanotubes are proposed:

- Oxidation in acids [35-38]
- Gas phase oxidation [39-43]
- Radiation [44,45]
- Filtration [46-48]
- Chromatography [49-56]
- Use of Graphite Intercalation Compounds [57]
- Use of tensides [58]
- Use of polymers [59]
- Hydrothermal treatment [60]
- High temperature treatment [61,62]
- Bromination [63]

8. Properties of Carbon Nanotubes

The outer and inner diameters of SWNTs are found to be 0.4 – 5 nm and 0.2 – 4.8 nm, respectively. The length can reach several micrometers.

MWNTs have outer diameters of 4 – 50 nm and inner diameters of 3 – 12 nm. The length of MWNTs can be up to several millimeters.

Therefore, very large aspect ratios are realizable.

Carbon nanotubes reveal many excellent chemical, physical, and mechanical properties. The electrical resistivity along the tube axis amounts to about $10^{-4} \Omega\text{cm}$, the maximum current density is found to be ca. 10^{13} Am^{-2} . The thermal conductivity amounts to ca. $2000 \text{ Wm}^{-1}\text{K}^{-1}$. The Young's Modulus is extremely high (ca. 1 Tpa). The specific surface area most often is found to be $80 - 600 \text{ m}^2\text{g}^{-1}$, however the highest experimentally found value exceeds $1000 \text{ m}^2\text{g}^{-1}$.

These properties can principally be tailored by variation of diameters, number of concentric tube walls, chirality [64], tube lengths, crystallinity etc.

9. Applications of Fullerenes and Carbon Nanotubes in Nanosystems

Fullerenes and carbon nanotubes reveal a very big potential of application, ranging from catalysts to microelectronic components. Some of the applications are already commercialised or are just standing at the threshold of commercialisation.

If we speak about the use of fullerenes and nanotubes in nanosystems, we focus on such properties of these nanocarbons, which are directly related to a functionality based on their specific structure.

A good example is the use of aligned nanotubes (see fig. 7) as field emitters in flat screen technology. Furthermore nanotubes can be used in molecular electronics, for example as molecular wires, single electron transistors, field effect transistors etc.

Currently, the principal possibility of such applications has been proved, however a lot of research and development has still to be done before the introduction to the market. A very promising application for fullerenes and, may be, also for carbon nanotubes, is the use in a polymer-based photovoltaic cell. From the MO diagram of C_{60} follows that three low energy LUMOs are present, whereby C_{60} acts preferably as an electron acceptor. A very important criterion for the efficiency of a photovoltaic cell is the velocity of electron/hole separation. The electron transition step to C_{60} fullerene (fig. 8) proved to be ultrafast (< 200 femtoseconds [65]). Therefore the addition of fullerenes enhances the efficiency of such polymer based photovoltaic cells. However, it is needed to create a conducting path for the electrons, as electron and hole have to be carried off as quick as possible, in order to avoid recombination of electron and hole. Whereas the holes are guided via the polymer chains, the electronic conduction path has to be formed from neighbouring C_{60} molecules (fig. 10), which explains, why about 50 weight % of C_{60} material has to be added to the polymer (percolation threshold). The overall construction of a polymer photovoltaic cell is shown in figure 11, the efficiency is reported to be about 2.5% [66]. On the surface of the fullerene molecules the electrons are partly delocalised, whereas between the molecules the electron transport comes off via a hopping mechanism. In order to enhance the solubility of C_{60} in an organic solvent, in which also the polymer component can be solved, often C_{60} derivatives with organic side chains are applied. There are now some ideas in order to reduce the necessary proportion of C_{60} (or C_{60} derivatives) in a polymer photovoltaic cell:

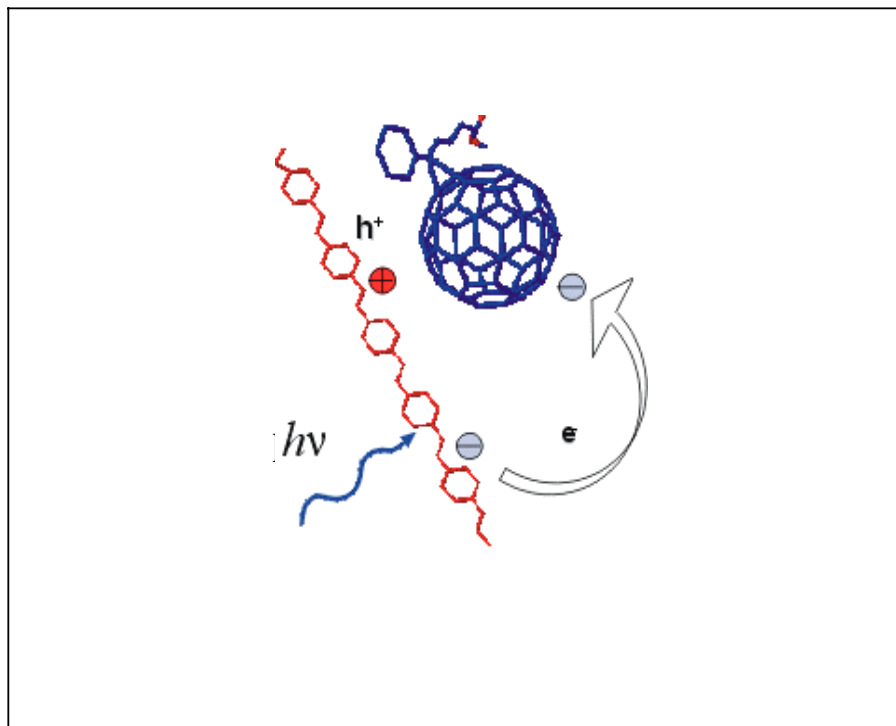


Figure 8: Electron/hole separation in polymer/fullerene matrix

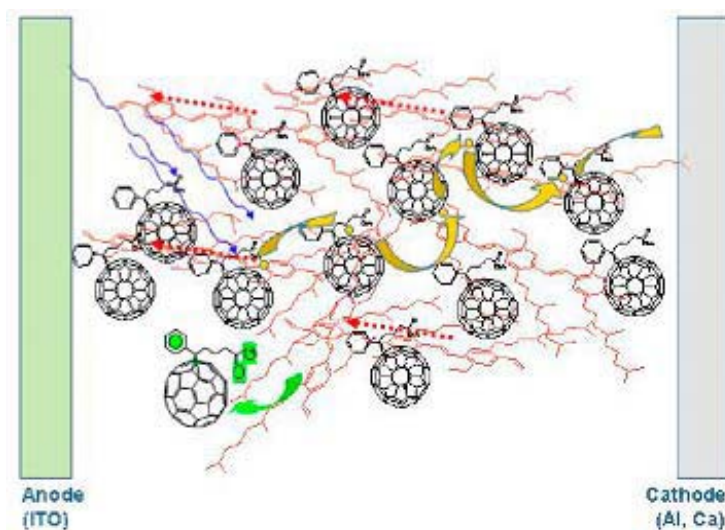


Figure 9: Electron and hole transport in a polymer photovoltaic cell

- Use of C₆₀ chains, which could be aligned in electric and/or magnetic fields; problems: can we achieve a uniform chain length? Can we find an organic solvent for short C₆₀ chains, which is compatible with the polymer matrix?
- Use of aligned carbon nanotubes (see fig. 7); problem: do nanotubes act in similar way as fullerenes, as concerns electron/hole separation?
- Use of aligned peapods with C₆₀ or C₇₀ (fig. 12); problem: which effect will have the peapods on the electron/hole separation?
- Use of aligned chains consisting of alternating nanotubes and fullerenes units; problems: how to prepare in uniform way? How to introduce into the polymer matrix?
- General use of endohedrals in order to optimise the electronic properties; problem: efficiency of preparation!
- General use of nanotubes (or nanotubes units) filled with clusters from ferromagnetic transition metals, in order to improve the possibility of alignment; problem: which effect will have the transition metal on electron/hole separation?

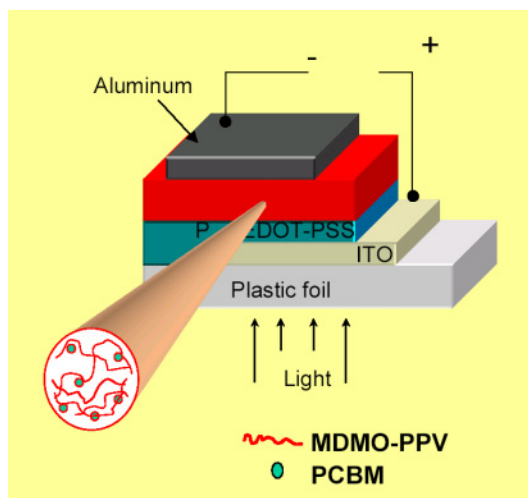


Figure 11: Polymer photovoltaic cell

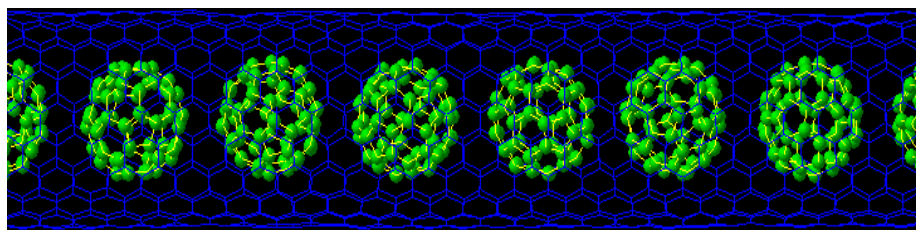


Figure 12: Peapod with C₆₀

Another idea is, to use a completely different concept of cell construction, comprising a separate fullerene/nanotube layer. In this case also a 2D fullerene polymer, or even a 3D fullerene polymer could be used. Furthermore the alignment of any chain structure could be much facilitated in this way.

Many other applications of (polymerized) fullerenes and nanotubes in nanosystems can be imagined, for example in biological and medical systems. However, as mentioned already, an improvement of preparation methods, in order to obtain well defined samples in large yields is necessary with respect to the requirements of a technical application.

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SYNTHESIS AND CHARACTERIZATION OF C₆₀-AND C₇₀ POLYMER PHASES

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Since their discovery fullerene-polymers have attracted much interest, due to their peculiar properties and potential applications in various fields [1-2]. By polymerization of fullerenes, a large increase in conductivity is observed, and 3D polymerized phases are reported to be harder than even diamond [3-5]. Also the 2D-C₆₀-Polymers have generated much attention after the discovery, that tetragonal phases showed to be ferromagnetic [6].

However, up to now the preparational methods for such materials comprise always high pressure and temperature treatment, which restricts the obtainable dimensions of samples to about one mm³. As for practical applications much larger samples are needed, another preparational route, using normal pressure and only moderately elevated temperatures, has to be found. As a first step in order to obtain polymerized C₆₀-phases, C₁₂₀ was received by tribochemical treatment using KCN or metallic Li powder as catalysts [7-8].

We succeeded in synthesizing C₁₂₀ through conversion of fulleren-60 with the interhalogen compound Iodinemonobromine at 80° C and normal pressure.

For this the obtained crystals of IBr, prepared from the elements by stirring I₂ powder and Br₂ at 45°C for five hours, were converted in a sealed double ampoule, containing C₆₀ on the one side and an excess amount of IBr on the other side, at 80°C for 2-4 weeks. The resulting product was purified by passing over N₂ at room temperature and then subsequently washed in ethanol in order to remove the excess IBr.

Thereby a black product was formed, which turned out to be C₁₂₀, a C₆₀-dimer, which can be considered as a subunit of C₆₀ polymers (Fig. 1).

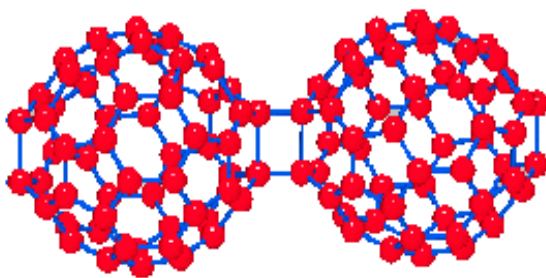


Figure. 1: C₁₂₀, a C₆₀ dimer

The characterization of the product was performed by Raman-measurements. Fig. 2 shows the Raman-spectrum of C_{120} , which shows all fundamental vibrations of C_{60} , but slightly shifted, and additional modes, which can be explained by a symmetry degradation ($I_h \rightarrow D_{2h}$) in C_{120} . The spectrum can be subdivided in 4 main sections: In the frequency range below 200 cm^{-1} the spectrum shows new bands which can be assigned to the vibrational torsion and stretching modes of the C_{60} units in C_{120} (Fig. 3).

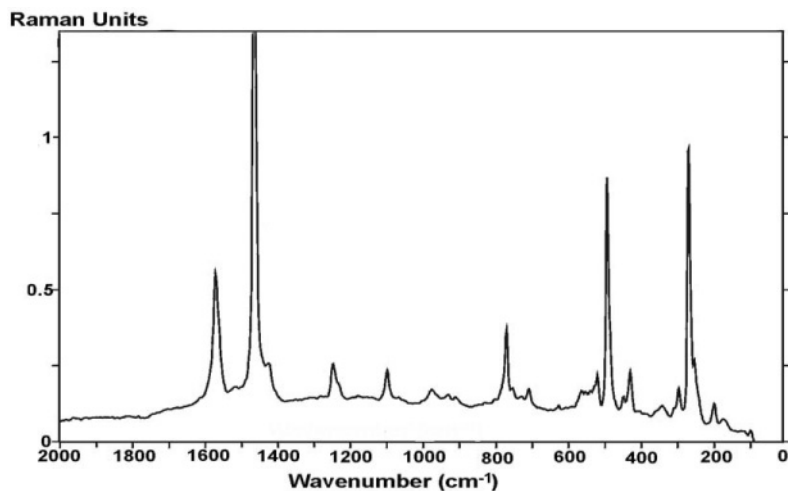


Figure 2: Raman spectrum of C_{120}

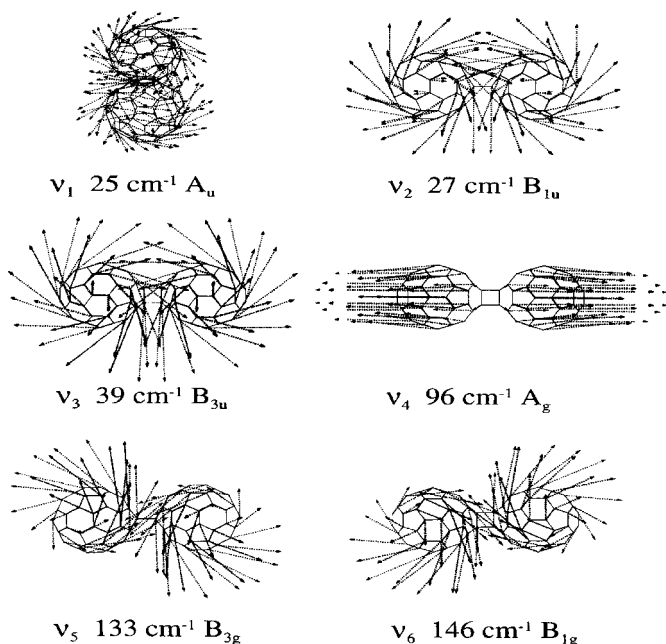


Figure 3: Raman modes of C_{120} in the low frequency range

The squashing modes of the dimeric fullerene can be found from 200 to 800 cm^{-1} . In the range 900-1000 cm^{-1} some additional Raman bands, corresponding to the stretching and breathing mode of a four membered ring, occur. This ring is formed between the two C_{60} spheres by covalent bonding upon dimerization. The occurrence of Raman bands at wavenumbers higher than 1000 cm^{-1} can be attributed to valence-vibrations of the C_{60} cages. The further reaction of the purified dimer with IBr under same conditions leads to the formation of short C_{60} -polymer-chains (Fig. 4)

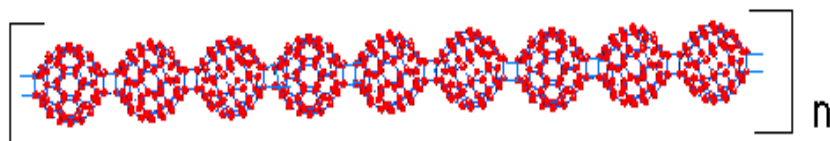


Figure. 4: One-dimensional C_{60} -polymer chains

A first characterization of the samples was performed by Raman scattering. The Raman spectra obtained (Fig. 5) is similar to that of the dimeric phase. Additional peaks are observed especially in the range of 200 to 20 cm^{-1} and 1000 to 700 cm^{-1} . In the spectrum the $\text{Ag}(2)$ mode, which is quite sensitive to the type and degree of polymerization, is shifted down to smaller wave numbers. All these results indicate a one-dimensional polymerization of C_{60} .

Conjugated C_{60} or C_{70} -chain-polymers with up to 12 connected monomer packages can also be produced by activation in an UV reactor under argon atmosphere. Therefore a C_{60} - or C_{70} -toluen-solution was filled into the reactor and irradiated for 60 minutes. For purification, the material was washed with acetone and dried by passing through N_2 .

Afterwards the materials were characterized by Raman scattering and ^{13}C -NMR spectroscopy.

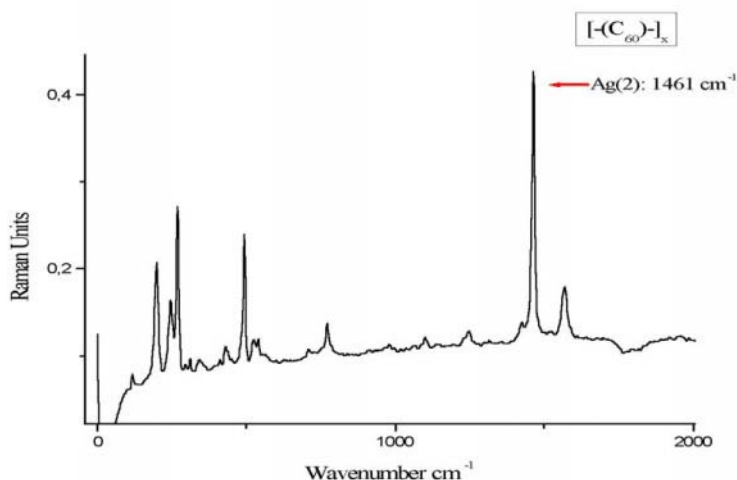


Figure. 5: Raman spectrum of $(\text{C}_{60})_n$, a C_{60} -1D polymer chain

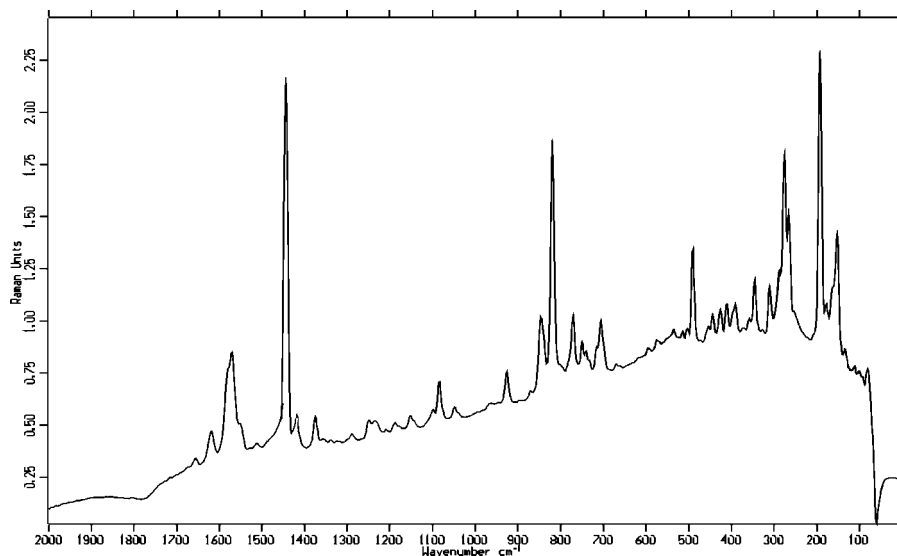


Figure. 6: Raman spectrum of the C_{60} -photopolymer

During the reaction of the fullerene C_{60} in the UV-reactor the violet toluene solution turned into a dark brown one. After removing the solvent and purifying the product, thin brown plates were obtained, which showed much less solubility in toluene. The obtained Raman spectra (Fig. 6) is very similar to that of $(C_{60})_x$. Due to the fact, that by photo-polymerisation more C_{60} molecules are connected to a one dimensional polymer chain, the pentagonal pinch mode is shifted to even smaller wavenumbers. In the range of $900 - 1000 \text{ cm}^{-1}$ the modes of the connecting “Cyclobutanring” can be observed.

As a conclusion it can be said that it is possible to produce one dimensional polymer chains using two different methods. The synthesis of one-dimensional C_{60} -chains can be done by photopolymerization using an UV-reactor under argon atmosphere.

We also showed that it is possible to polymerise C_{60} by another preparational route, using normal pressure and only moderately elevated temperatures by converting the monomer unit several times with the interhalogen compound IBr and treating the brominated product with polar organic solvents. Using this method C_{60} -polymers-chains with up to 6 connected C_{60} monomers can be obtained.

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THE NANOSPACE INSIDE SINGLE-WALL
CARBON NANOTUBES

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Abstract

The nanospace inside single wall carbon nanotubes was studied by Raman spectroscopy and high resolution transmission electron microscopy. To explore this space, C₆₀ molecules were filled into the tubes to create a peapod system. Upon doping with electron donors the cage of the tubes as well as the cages of the fullerenes received charge and eventually turned into C₆₀⁻⁶ molecules. These molecules react to a linear and single bonded polymeric phase. Alternatively, upon annealing at high temperatures the C₆₀ molecules serve as a carbon source to grow a second tube inside the primary tube. This tube exhibits extremely narrow Raman lines for the radial breathing mode indicating a highly defect free material. They thus apostrophe the inside of the tube cage as a nano clean room. The small size of the inner-shell tubes allows for a full assignment of the observed radial breathing modes to chiral vectors. The deviation of electronic and vibrational properties of the tubes from a tight binding behavior is demonstrated.

1. Introduction

The inside of closed molecular cages has been a challenge for researchers and engineers working in material science ever since interest in non conventional structures started. The fullerene cages, as discovered by Kroto *et al.* in 1985 [1], provided a realistic chance to set up a new field in material science, dealing with encapsulated structures. Immediately after the discovery of the fullerenes carbon cages with enclosed metal atoms or metal atom clusters were found [2]. First, only in the mass spectra of the materials but later on, at least some of them, also in small amounts of solid material [3]. The study of such systems revealed for the first time some insight into properties of the inside of the cages. Clusters or molecular groups were observed, which do not exist outside the cage or had a different electronic structure. Column 1 in Tab. 1 lists some examples where emphasis was laid on families of clusters with more than 2 atoms. Unfortunately, the preparation of all these compounds is very difficult and time consuming, since it is based on an incidental encapsulation of the cluster into the cage during the growth of the latter. Opening the carbon cages, filling them with atoms and reclosing has not been possible until now.

Table 1. Filling of carbon cages; Col. 1,2: fullerenes, Col. 3,4: single wall carbon nanotubes

Endohedral fullerenes	Ref.	Single wall carbon nanotubes	Ref.
X ₃ N@C ₈₂ , X = Y, Sc, Er	[4]	Metal halides ((Na, Al, ...) chlorides or fluorides)	[10]
Sc _x @C ₈₄ , x = 1, 2, 3, 4	[5]	metal wires	[11]
Sc ₂ C ₂ @C ₈₄	[6]	carbon phases (fullerenes, carbon nanotubes, carbynes)	[8,9,12]

In contrast to the case of the fullerenes, the caps of multi-wall and single-wall carbon nanotubes could be opened on purpose and subsequent filling was demonstrated in many cases. Early studies of the filling referred to multi-wall tubes [7] but recently filling of the single-wall carbon nanotubes (SWCNTs) was also possible [8,9,10]. It was demonstrated for a selected number of different materials such as metal halides, different carbon phases or even with metals in the form of thin metal wires. Selected examples are listed in Tab. 1, Col. 3,4.

The challenge to grow new materials inside the tubes and to react them to new compounds is evident. All materials in the tubes will exhibit quasi one-dimensional properties, they are highly shielded from the outside and they are located in a concave nanospace with a rather different electron orbital configuration as compared to e.g. the same material on the outside of the tubes. This can intuitively be recognized from the geometry and from the orbitals of a small SWCNT depicted in Fig. 1. The diameter of the tube shown is smaller than 1 nm. The smaller the tube diameter the stronger the deviation from a clean π -bonding of the valence π -orbitals.

The filling of SWCNTs can be used to learn about their interior. The following problems are relevant:

- On the preparative side it needs an opening of the tubes. After this, filling from the gas phase or from solution can be performed. Eventually, chemical reactions can be launched inside the tubes.
- One serious problem in the area is the reliable evidence for the effective encapsulation of the fillers. High resolution transmission electron microscopy (HRTEM) is a first candidate to document this but it operates very site selective and cannot provide average values. In the case of filling tubes with fullerenes, the case of the so called “peapods”, Raman spectroscopy has proven to be an excellent tool [9,13]. For this particular filler, x-ray analysis was also used successfully to evaluate the degree of filling [14]. Finally, quantitative determination of the filling was demonstrated from electron energy loss spectroscopy (EELS) [15].
- Eventually, the properties of the new materials must be explored. Very little is known today at this point. This holds in particular for the nanotubes grown inside a primary tube. This system has become known as “double wall carbon nanotubes” (DWCNTs). Transport, field emission, mechanical properties, functionalization, or compounding have to be studied and can be expected to yield superior properties as a consequence of the protected nature of the inner tubes.

In this contribution we report on new experiments and analyses referring to the exploration of the inside of SWCNTs. The report is limited to results from pure nanocarbon systems such as peapods and DWCNTs. Chemical reactions inside the tubes will be demonstrated as well as unusual properties of the inner-shell component of the DWCNTs, such as an extremely narrow line width of the radial breathing modes. A full assignment is given for the Raman response of this modes to the chiral vectors of the tubes.

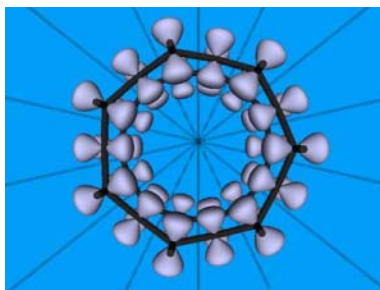


Figure 1. Geometry and π -orbitals for α (7,7) single-wall carbon nanotube.

2. Basic elements of single wall carbon nanotube description and analysis

Single wall carbon nanotubes are conveniently be considered as rolled up graphene sheets [16]. Any lattice vector $C_{n,m}$ of the sheet defines a SWCNT in the sense that the tube is generated by rolling up the graphene sheet. This is done in a way that the origin O and the top A of this lattice vector or “folding vector” coincide. The tubes generated in this way are truly one-dimensional systems with unit cell vector T . Figure 2 depicts the definitions. As immediately deduced from the figure the diameter d of the tubes is the length of $C_{n,m}$ divided by π . It is expressed as

$$d = (a_0 / \pi) \sqrt{3(n^2 + nm + m^2)} \quad (1)$$

where a_0 is the carbon-carbon distance in graphene, assumed 0.141 nm in our case. Equation 1 holds as long as changes in lengths as a consequence of up rolling are neglected. The components n, m of the folding vector determine whether a tube is metallic or semiconducting. A tube is metallic if $n-m$ is an integer multiple of 3.

As a consequence of the one-dimensionality the electronic states of the tubes are jammed into van Hove singularities where their density diverges. Within the tight binding approximation the van Hove singularities are symmetrically arranged around the Fermi level of the tubes. Optical transitions and resonance Raman excitations are dominated by transitions between pairs of such divergencies. Importantly, this transition energy depends inversely on the tube diameter, at least as long as the trigonal warping of the graphene bands is neglected. The transition energies are conveniently assigned as E_{jj}^s for the transition in the semiconducting tubes and E_{jj}^m for the transitions in the metallic tubes. In both cases the index j assigns the van Hove singularities in the valence band and in the conduction band which participate in the transition. The zone folding procedure allows to obtain all electronic states and thus to evaluate the electronic density of states (EDOS) for all tubes starting from the graphene lattice [17]. For SWCNTs with standard diameter of the order of 1.36 nm the first transition energies ($j = 1$) for semiconducting tubes are typically 0.65 eV whereas this transition for the metallic tubes is typically 1.9 eV or about a factor three higher. This is demonstrated in Fig. 3, where the possible transition energies for the various tubes are plotted versus the inverse tube diameter (Kataura plot [18]). The tube diameter range which provides resonance excitation in Raman experiments with standard SWCNTs and with visible light is highlighted. As one can see E_{33}^s becomes the relevant transition for the semiconducting tubes whereas for the metallic tubes E_{11}^m is in resonance. Deviations from the $1/d$ straight line originate from trigonal warping of the conduction and valence bands in the graphene band structure.

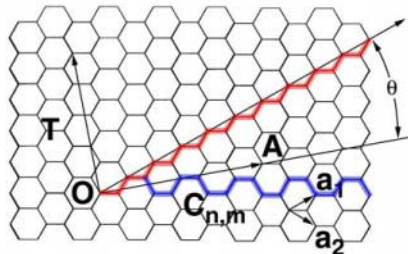


Figure 2. Description of SWCNTs by the graphene lattice vectors $C_{n,m}$. a_1 and a_2 are the unit cell vectors of the graphene sheet. T and θ are the unit-cell vector and the chiral angle of the tube, respectively. The marked directions refer to zigzag and armchair tubes.

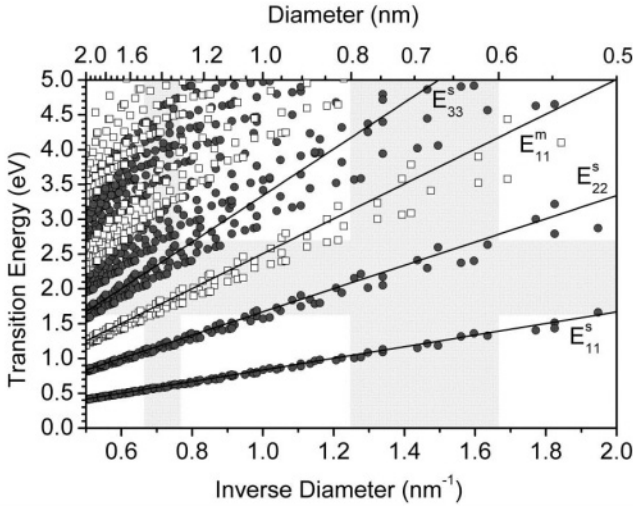


Figure 3. Transition energies between van Hove singularities versus inverse tube diameter. Each bullet or square represents one tube. Evaluation was for a value of 2.9 eV for the π -electron overlap integral γ_0 . Highlighted areas are for the visible spectral range (horizontal) and for standard and small tubes (vertical).

If the tube diameter becomes smaller, e.g. below 1 nm, the transition energies shift to the blue according to the $1/d$ law. Then, at least for the semiconducting tubes, the next lower electronic transition energy E_{22}^s may become relevant for the resonance process. Raman scattering is a key experimental technique for the analysis of SWCNTs. Three modes are relevant for diagnostics and are usually dominating the Raman spectra: the radial breathing mode line (RBM-line) around 180 cm^{-1} for standard tubes, the defect line (D-line) around 1400 cm^{-1} , and the graphitic line (G-line) around 1590 cm^{-1} . The names implicate the origin of the lines. The RBM characterizes the radial breathing of the tubes and scales as $1/d$. It is therefore of particular importance for the determination of the tube diameters. A widely used empirical - but theoretically confirmed - relation between the latter and the RBM frequency is

$$\nu_{\text{RBM}} = C_1/d + C_2 \quad (2)$$

where C_2 describes the contribution of a possible tube-tube interaction for e.g. SWCNTs in a nanotube bundle. It was reported to be of the order of 10 cm^{-1} . Values for C_1 were reported between $220 \text{ cm}^{-1}\text{nm}$ [19] and $248 \text{ cm}^{-1}\text{nm}$ [20], where in the latter case no constant term C_2 was used. *Ab initio* calculations revealed $239 \text{ cm}^{-1}\text{nm}$ for armchair and 235 cm^{-1} for zigzag tubes [21]. The D-line comes from a phonon at the K-point of the phonon dispersion and thus needs defects to establish momentum conservation in the light scattering process. A double resonance scattering process, or in the case of the tubes more precisely, a triple resonance scattering process is responsible for its visibility [22]. The mode frequency increases with the energy of the exciting laser as approximately $50 \text{ cm}^{-1}/\text{eV}$ and its intensity scales with the defect concentration. The G-line is derived from the E_{2g} mode in graphene or the corresponding mode in graphite. In the latter it is observed at 1582 cm^{-1} . For metallic tubes the G-line exhibits a Fano-Breit-Wigner line shape and appears downshifted by about 40 cm^{-1} . Since for standard tube diameters the metallic tubes resonate with red laser light on their E_{11}^m transition, Raman spectra excited in this spectral range are dominated by the asymmetric line shape with a downshifted peak position.

3. Filling with fullerenes (peapods)

Filling of SWCNTs with fullerenes, in particular with C_{60} , needs a special treatment. Following to a great extent the description reported by Kataura *et al.* [9] we had best experience with the following procedure:

- Opening of the tubes: reflux with 15% H_2O_2 at 370 K to open the tubes and remove carbon particles;
- Etching: with 37% HCl to remove metallic particles and to create defects on the side walls, drying at 380 K;
- Equilibration: heating in a fused quartz tube with stoichiometric amount of C_{60} at 920 K;
- Annealing: in dynamical vacuum at 1070 K to get rid of remaining C_{60} ;
- n-Doping: in situ equilibration of peapods with potassium vapor at 450 K sample temperature; weak doping after 2 hours equilibration, heavy doping after 6 hours exposure;

This procedure yields 85% to 100% filling for the part of the tubes with a diameter ≥ 1.2 nm, as determined from Raman and EELS analysis. Figure 4 depicts evidence for successful filling. Part (a) shows a HRTEM where the peas in the pods are clearly seen despite the strong bundling of the tubes. Part (b) of the figure depicts the Raman response as excited with a blue laser. The Raman lines from the encaged C_{60} are assigned by the symmetry species. The two component line around 374 cm^{-1} is the overtone from the RBM of the tube.

Several experiments have demonstrated the possibility to dope SWCNTs with electron donors such as alkali metals [23,24] and electron acceptors such as Br_2 or $FeCl_3$ [25,26]. In contrast, chemical doping of fullerenes was only possible with electron donors. It was certainly interesting to check the response of the peapods on n- and p-doping. Whereas in the latter case only the tubular cage accepted the holes, in the case of n-doping the tubes as well as the fullerenes received charge, at least after heavy doping. In the initial stage of the doping process only the Raman response of the tube modes responded which is a strong signature that charge transfer is only to the wall of the tubes. Only after heavy doping the response of the C_{60} modes changed. Besides a general weakening of the spectra the pentagonal pinch mode $A_g(2)$ started to shift downwards. Eventually, at saturation of the doping process, it is recorded at 1428 cm^{-1} . This means a downshift of 38 cm^{-1} from its initial value of 1466 cm^{-1} . The change of the line position of the pentagonal pinch mode is demonstrated in Fig. 5a. The figure depicts the tangential part of the Raman response of the peapod modes. The spectra

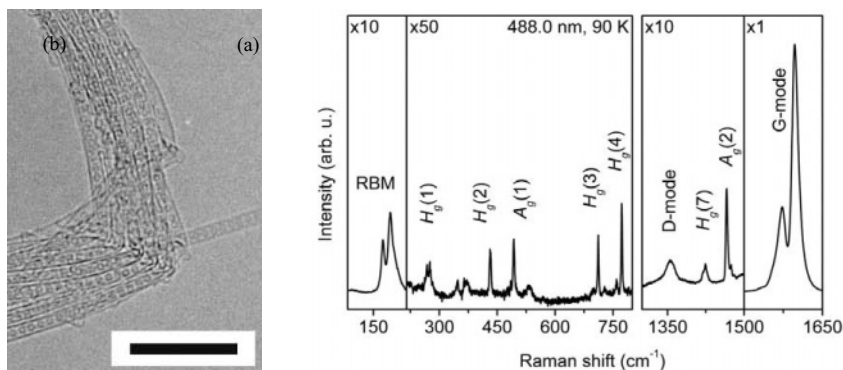


Figure 4. High resolution TEM of peapods with 10 nm scale bar (a) and Raman spectrum of a peapod sample as excited with 488 nm at 90 K (b). The indicated scaling factors demonstrate the dominance of the response from the tubes. The Mulliken symbols assign the response from C_{60} .

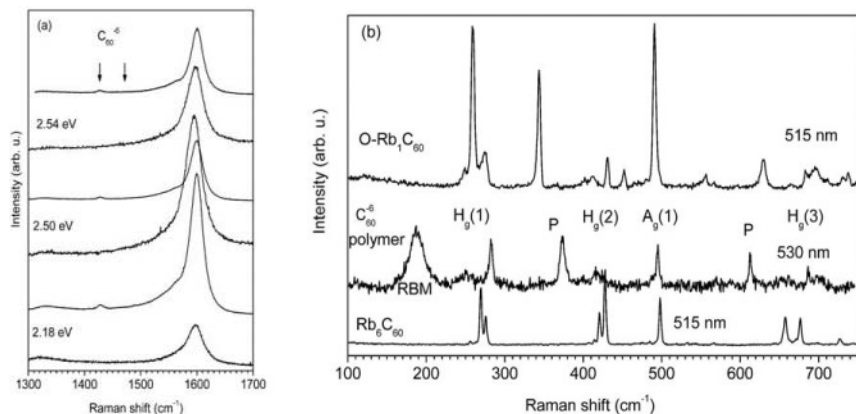


Figure 5. (a) Raman response of the tangential part of the peapod spectrum after heavy doping with potassium as excited with three different lasers (first, third and fifth spectrum from top). The second, fourth and sixth spectra are the response from simultaneously doped empty tubes. Arrows assign the position of the $A_g(2)$ mode of C_{60} before and after doping. (b) Radial part of the Raman response of the heavily doped sample (center) in comparison to the spectra from polycrystalline C_{60} (bottom) and polymeric orthorhombic C_{60} .

were recorded with three different lasers. In each case the response from a simultaneously doped sample without C_{60} filling is presented. In all three spectra for the filled tubes the response from the pentagonal pinch mode of the fullerene is clearly seen whereas it is missing in the spectra of the unfilled tubes. The downshift of the pentagonal pinch mode in C_{60} with doping is very well known and well calibrated with respect to the charge on the C_{60} cage [27]. For the observed strong shift the calibration has the value 6.5 cm^{-1} per elementary charge on the cage. For a downshift of 38 cm^{-1} this yields a charge of -5.8 or approximately -6 elementary charges per cage.

The radial part of the response provides even more information. It is shown in Fig. 5b, center. Again, the response from the encaged C_{60} is assigned by the Mulliken symbols. This spectrum is not a typical Raman response for a C_{60}^{-6} molecule shown for comparison at the bottom of the figure. Clearly two new lines appear at 350 and at 620 cm^{-1} , assigned as P. These lines were observed repeatedly for polymeric phases of C_{60} . As an example the top spectrum in Fig. 5b represents the response from orthorhombic $Rb_1C_{60}^{-1}$ which is known to exhibit a linear polymeric phase at low temperatures. Clearly, the response of the polymer is there, though slightly shifted. Thus, we conclude to have a polymeric C_{60}^{-6} phase inside the tubes. A polymeric phase of C_{60}^{-6} has not been observed so far for the C_{60} system. It is in this sense unique and can be stabilized only inside the cage of a SWCNT.

From calculations reported earlier by Pekker *et al.* [28] on the stability of fullerene polymers, one can even identify the type of the polymer. The calculation was performed on a tight binding basis. According to the latter the most stable phase for a C_{60}^{-6} cage is as single bonded two-dimensional polymer. Since this phase can not exist inside the tube one has to check the next candidate. This is a single bonded linear polymer which satisfies the geometrical constraints and is therefore the best choice. The charge from the potassium atoms is thus transferred to the cage of the tube as well as to the cage of the fullerene. The latter accepts about 6 electrons per cage and connects to a linear chain by covalent bonds. A completely new structure is established. The potassium ions are assumed to stay outside the two cages.

4. Double wall carbon nanotubes

Annealing the peapods at rather high temperatures in a dynamic vacuum transforms the C_{60} cages into a new SWCNT inside the primary tube [29]. In our case the annealing was performed at 1580 K for two hours with slow cooling. The result of this temperature treatment is depicted in Fig. 6. The HRTEM shows clearly the new structure consisting of the double wall tubes. Since the peapod sample was 100% filled the new material consists to a very large degree of double wall tubes. The distance between the two walls is rather uniform and scales between 0.34 and 0.38 nm [30]. Figure 7b compares the Raman response of the three carbon systems discussed here. The single wall nanotube response (bottom) exhibits the RBM, the overtone of the RBM, the D-line and the G-line. The peapod spectrum (center) shows in addition the response from the peas. The split structure for the $A_g(2)$ line located at 1466 and 1473 cm^{-1} and for the $A_g(1)$ line located at 495 and 502 cm^{-1} of the peas are characteristic features for the encaged C_{60} . The top spectrum in Fig. 6b represents the response from the DWCNTs. A new set of rather sharp lines in the high frequency region of the RBM appears which is safely assigned to the RBM response from the inner tubes. Also the G-line displays a more structured pattern as compared to the SWCNT spectrum, indicating again the response from both tubular cages.

The process which transforms the C_{60} cages into the extra tubes is not yet clear. Two types of reactions are imaginable. In the first model the C_{60} cages undergo a cyclo-addition reaction and transform to dimers. Subsequently the system undergoes successive Stone-Wales transformations and additional cyclo-additions until eventually the inner tube is formed [31]. The Stone-Wales transformations are not only responsible for the growth of the tubes but also for the adaptation of the diameter of the new tube to the diameter of the primary tube. An alternative model suggest that the cages break up to a high degree, forming e.g. a C_2 plasma which recondenses into the inner shell tube. Adaptation to the outer shell tube diameter is then immanent in the growth process. In both models tube growth occurs without support of a catalyst. There are some very recent and still unpublished results which favor of the plasma growth model rather than the Stone-Wales transformation model [32]. These results were obtained from a comparison of C_{60} and C_{70} grown DWCNTs and from a dynamical study of the growth process.

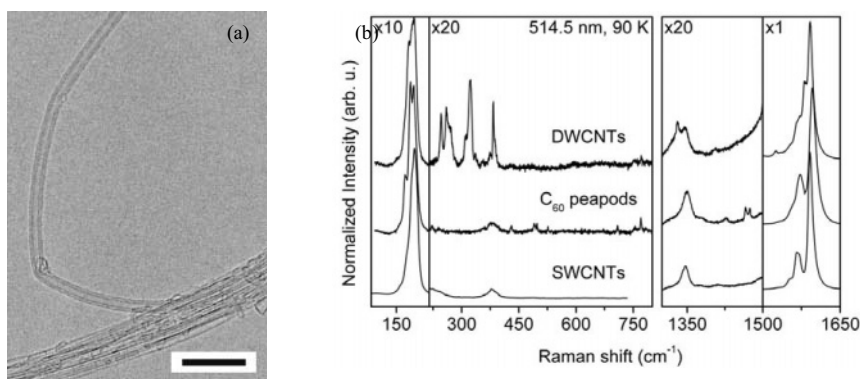


Figure 6. Transformation of peapods to DWCNTs. (a) High resolution TEM with scale bar 10 nm and (b) Raman spectra for the radial (left) and for the tangential (right) modes. The spectra were recorded for 514 nm excitation and represent the response from the unfilled tubes (bottom), peapods (center) and DWCNTs (top). Scaling of the intensity is as indicated.

The Raman characterization of the DWCNTs becomes even more exciting if yellow and red lasers are used for the excitation. An example is depicted in Fig. 7. Part (a) shows the response of the G-lines in a pristine material and in the related DWCNTs. As expected the spectrum for the pristine tubes is dominated by the Fano-Breit-Wigner response from the resonating metallic tubes. In contrast, the spectrum for the DWCNTs is dominated by the semiconducting tubes with the strong line at 1590 cm^{-1} . The enhancement of the line originates from the inner-shell tubes which are now resonating on the E_{22}^s transition due to the smaller tube diameter. The resonance conditions for the inner-shell tubes are elucidated in Fig. 3 in detail. Part (b) of the figure depicts the RBM of the outer-shell and of the inner shell tubes. Particularly for the excitation with 647 nm very strong and sharp lines are observed. The width of the lines is determined by the resolution of the spectrometer which was 1.4 cm^{-1} in the present case and for the red laser excitation.

Studying the Raman response with more than 20 different laser lines revealed the full set of lines for all geometrically allowed tubes. Each of the sharp lines in Fig. 8b represents a tube. Between 250 cm^{-1} and 460 cm^{-1} 39 different Raman lines were identified [33]. Two of them were assigned to overtones from the outer-shell RBM. The highest frequency was recorded at 460 cm^{-1} which corresponds to a tube diameter of 0.52 nm if the relation of Eq. 2 between RBM frequency and tube diameter is applied with constants C_1 and C_2 of $233\text{ cm}^{-1}\text{nm}$ and 14 cm^{-1} , respectively. The lowest observed RBM frequency from the inner shell tubes was at 245 cm^{-1} corresponding to 0.98 nm tube diameter. The two limiting values are determined by the smallest tube which can accept a C_{60} molecule and by the cut off of the distribution function. Assuming a wall to wall distance between the inner shell and the outer shell tube of 0.335 nm , equivalent to the inter plane distance in graphite, the diameter for the smallest tube which can accept a C_{60} molecule is 1.19 nm .

In a recent calculation Melle-Franco *et al.* [34] investigated the condition for filling SWCNTs with C_{60} . The calculation was based on Brenner potentials for the fullerene cage and on a MM3 based van der Waals potential for the interaction between tubes and C_{60} . If the tube is too small both the tube and the fullerene are subjected to some elastic deformation. The fullerene accepts a prolate form and the hosting tube expands at the location of the fullerene. If the tube is too large the C_{60} molecule should be oblate distorted. This effect could not be observed in the calculation, probably because it is too small. Some of the results from the calculation are presented in Fig. 8. The energy

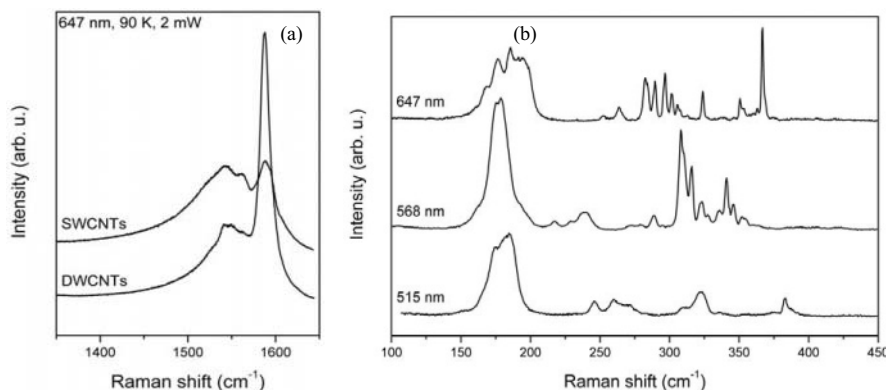


Figure 7. (a) Raman spectra of tangential modes for SWCNTs and DWCNTs originating from the same batch. Excitation was with a 647 nm laser at 90 K . (b) Raman response in the RBM frequency range excited with three different lasers as indicated. The broad peak at 180 cm^{-1} is the response from the outer-shell tubes, the narrow lines are from the inner-shell tubes.

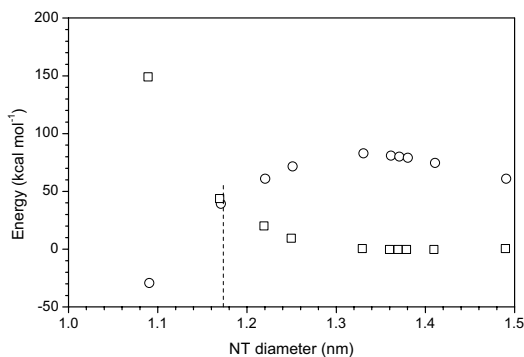


Figure 8. Distortion energy (open squares) and binding energy (open circles) versus tube diameter for SWCNT filled with C_{60} . The dashed line marks the cross over.

Versus diameter diagram shows that for tubes smaller than 1.3 nm a deformation energy is required. This energy increases rapidly as the tube diameters become smaller. The binding energy increases on the other hand with increasing tube diameter and reaches a maximum value for 1.34 nm. For larger tubes the binding energy starts to decrease slowly. This reduction of binding energy is due to the lack of optimum interaction between C_{60} and tube. The fullerene starts to move to the side of the tube wall and the number of interacting carbon atoms is decreasing. This result should be helpful for the search of other possible fillers. What is obviously needed is a molecule with a three-dimensional shape and a size which fits right into the tube.

The fact that in the experiments all geometrically allowed tubes were observed suggests to go for an full assignment of chiral vectors to the observed RBMs. As it turned out this is possible but it was not enough to simply use Eq. 1 for the calculation of the tube diameters and Eq. 2 for its relation to the RBM frequencies. Since the inner-shell tubes are so small deviation from the results for the graphene sheet are noticeable and can not be neglected.

The shortcomings of the simple graphene model is clearly demonstrated in Fig. 9a. The figure depicts the deviation between calculated and observed RBM frequencies for the case of the graphene diameters. The systematic deviation is evident. The strong scattering of the plot points is only partly due to experimental error. It an additional root from neglecting the influence of the chiral angle θ on the RBM frequencies.

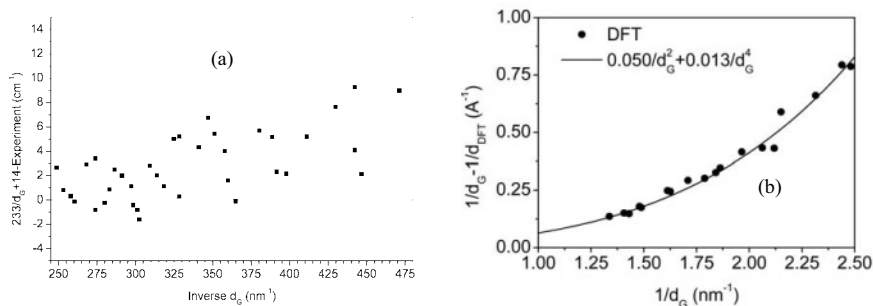


Figure 9. Difference between calculated and observed RBM frequencies (a) and influence of curvature on the geometry as represented by the difference between inverse tube diameters (b). The full drawn line in (b) is a polynomial fit according to the relation indicated in the figure.

Fortunately, at least some of the inner-shell tubes have small enough unit cells, so that *ab initio* density functional theory (DFT) can be applied for the evaluation of the geometry of the curved graphene sheets and for RBM frequencies. Such calculations were performed using the *Vienna Ab Initio Simulation Package* (VASP) [35]. The deviations between analyses using the simple graphene sheet derived values and DFT values are depicted in Fig. 9b. It shows the differences between inverse tube diameters $1/d_G$ evaluated from the graphene lattice and $1/d_{DFT}$ evaluated from the VASP calculation as a function of $1/d_G$. Bullets represent the evaluated differences, the full drawn line is a polynomial fit as indicated in the figure. The largest chiral tube which could be analyzed by DFT was a (7,4) tube with a DFT diameter of 0.756 nm ($d_G=0.748$ nm). The simplest way to consider the influence of the curvature as evaluated from DFT is to use d_{DFT} in the denominator of Eq. 2 instead of d_G . For the selected assignment the values for C_1 and C_2 were $233 \text{ cm}^{-1}\text{nm}$ and 14 cm^{-1} , respectively, as determined from a minimum deviation between calculated and observed frequencies.

The final assignment of the chiral vectors to the observed RBM frequencies are depicted in Fig. 10. Three lasers were selected to present the result. The given assignment is strongly related but refined with respect to the assignment reported by Pfeiffer *et al.* [36]. There is a one to one mapping between the Raman lines and the geometrically allowed modes.

The assignment given above is the first correlation between the full set of RBM Raman lines and geometrically allowed tubes. It deviates from previous assignments reported for semiconducting tubes [37] by about 5% in frequency for equal (n,m) . The large number of Raman lines used for the assignment provides an enhanced reliability as compared to the previous results. It is in good agreement with an assignment obtained for individual tubes [20] if in the latter case the tube-substrate interaction is considered and included in the C_1 constant.

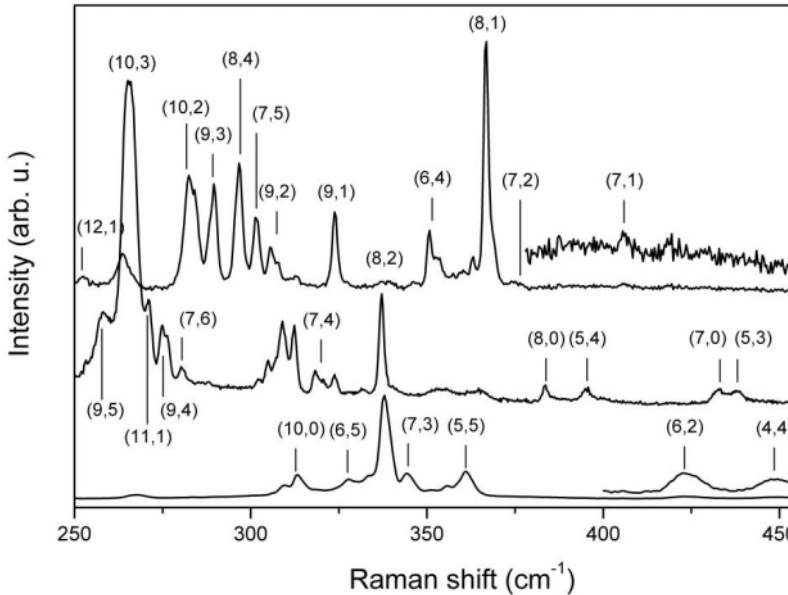


Figure 10. Assignment of chiral vectors to RBMs of inner-shell tubes. The assignment is represented by three selected lasers as indicated.

The deviations from the simple graphene derived frequencies and electronic structure for the narrow tube is not only evident from the tube geometry. Some tubes, e.g. (7,0) and (5,3) exhibit the same diameter and therefore degenerate RBM frequencies if evaluated from the graphene sheet. Experimentally and according to the assignment given above they appear at two different frequencies, separated by 6 cm^{-1} . VASP calculations revealed two different frequencies separated by 9 cm^{-1} in reasonable agreement with the experiment [36]. The observation of metallic tubes is surprising on a first glance. According to the tight binding based plot in Fig. 3 resonance enhancement for such tubes should only be activated for excitation with ultraviolet light. However, VASP calculations [36] and density functional tight binding calculations [38] show that for very small tube diameters deviation from tight binding EDOS become important. Additional states appear between the main van Hove singularities. This holds in particular for the energies below the first van Hove singularity and gives rise to transition energies below E_{11}^m . In full agreement with this result metallic tubes are not observed for the (five) largest tubes but become visible for the smaller tubes.

One of the most striking results with respect to the Raman response of the RBMs from the inner-shell tubes is their small line width. To explore this property in more detail we recorded the Raman response at 20 K in the high resolution mode of the spectrometer. In this mode the resolution for red laser light is 0.5 cm^{-1} or a factor three higher than for the normal resolution mode. Spectra recorded in this mode are depicted in Fig. 11 for three different laser excitations. The figure not only demonstrates that the Raman response of the inner-shell tubes is almost a factor of ten larger than the response from the outer-shell tubes, at least for the deep red laser. It also reveals that line pattern for the response from the tubes grown inside the primary tubes (high frequency part of the spectra) is highly structured whereas the response from the normally grown tubes is broad and unstructured. Line widths are still dominated by the resolution of the spectrometer. To obtain a good value for the intrinsic line width of the

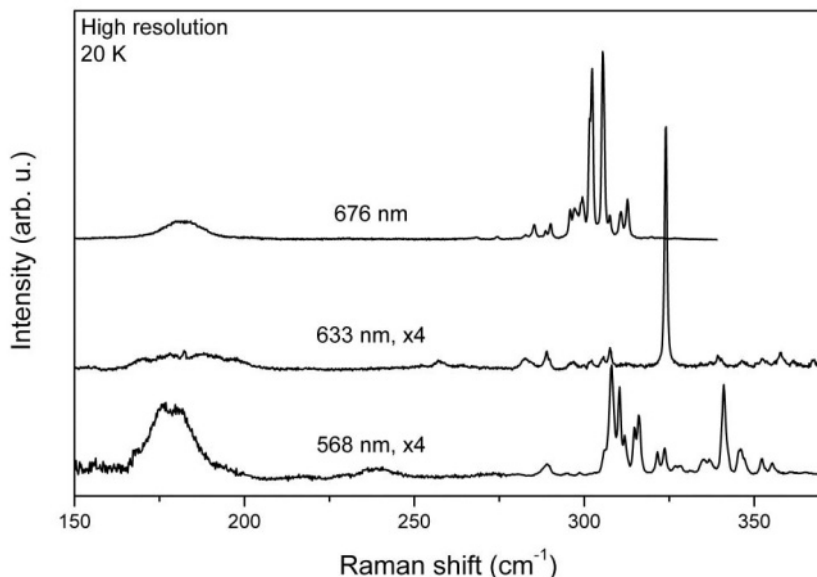


Figure 11. RBM spectra from DWCNTs as recorded in high resolution at 20 K with three different lasers as indicated.

RBM from the inner-shell tubes in each case the shape of the laser line was recorded simultaneously with the recording of the RBM spectra. The individual Raman lines of the RBMs were then fitted with a Voigtian line profile where the Gaussian part was kept constant at the value of the laser line. The width of the Lorentzian component was used as a fitting parameter. This is a self consistent procedure similar to a deconvolution of the Raman lines. In this way intrinsic Lorentzian line widths down to 0.35 cm^{-1} were obtained. This is an order of magnitude lower than the line widths reported so far for the RBM response.

The unexpectedly narrow lines indicate a high degree of perfectness of the inner-shell tubes and a homogeneous and perturbation free environment. The evaluated line widths are probably close to the intrinsic line widths originating from phonon-phonon coupling. The concave interior of the nanotubes may therefore be regarded as a clean room of nanosize. Certainly, this is another argument for the possibility to grow new and unconventional materials in the nano laboratory inside the primary tubes.

The high resolution analysis also revealed a characteristic line splitting for most of the tubes. This splitting is not yet well understood but may be traced back to the fact that one type of inner tube may grow inside at least two outer tubes with different diameters [36]. From a difference in the resulting tube-tube interaction an apparent splitting of the lines is possible.

5. Conclusion

The interior of SWCNTs is demonstrated to be a concave nanospace for the growth of new materials with unusual properties. Examples are given in the form of nanotubes filled with C_{60} . These peapods represent an other new form of all carbon systems. Upon doping this system with an alkali metal (potassium) charge transfer is observed to the cage of the tubes as well as to the cage of the fullerenes. As a consequence of the charging the fullerenes react to a polymeric phase which has not been observed previously.

Alternatively to doping, the fullerenes inside the nanotube can react to build a new tube inside the original tube. The new tube exhibits very narrow Raman lines which is an indication of highly defect free growth and homogeneous environment. The space inside the primary tubes is therefore considered to provide clean room conditions with nano scale dimensions. The small diameter of the inner-shell tubes allows for the first time to provide an assignment for all geometrically allowed SWCNTs in the diameter range between 0.52 and 0.98 nm.

The presented experiments and their analysis give first evidence for the use of the interior of SWCNTs as a nano scale laboratory. The results are promising examples for the growth of new materials which will exhibit quasi one-dimensional structure and properties.

Acknowledgement

This work was supported by the Fonds zur Förderung der Wissenschaftlichen Forschung in Austria, project P 14386 and by the EU network NANOTEMP (HPRN-CT-2002-00192) The receipt of peapod samples and the supply of the HRTEM figures prior to publication by Prof. H. Kataura, Tokyo Metropolitan University, Tokyo, JP is highly appreciated. We thank O. Dubay for supplying Fig. 2.

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MECHANICAL PROPERTIES OF CARBON THIN FILMS

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Abstract

Thin film – substrate interaction, residual stress and elastic properties in the disperse and films of nanometric size are of great importance in the development of microsystems, nanostructures and nanomaterials when working with atoms, molecules or supramolecule structures. Scaling down of geometrical dimensions of the structures, devices and systems is accompanied by control of matter on the micro and nano-meter length scale.

Physical principles of the conventional method for the internal stress measuring - the cantilever technique and electronic speckle pattern interferometry are discussed and related to the stress control in thin film – semiconductor substrate system. Stress kinetics of the thin film structure can be monitored in – situ allowing to control this process at the nucleation stage of the film. The main advantage of the electronic speckle pattern interferometry as compared to the classical interferometry and holographic methods is ability to measure strain of the real diffusive surfaces. Development of the electronic speckle pattern interferometry allows to apply it to the small size (hundreds of micrometers) objects (microelectromechanical devices, microstructures etc.) to monitor and control variations of geometrical dimensions of the different components. Development of the new analysis method is prospective for the new type of structures – freestanding films. Technology of producing of such form film (metallic, diamond like carbon, multilayer structures) combines advantages of plasma based technologies of deposition and combinations of different type of etching. Application of the newly developed optical method with the microtensile machine allows defining elastic properties of such thin film and influence of different technological conditions during deposition.

Carbon nanofibers have been grown by direct ion beam deposition from the acetylene gas (C_2H_2) and hexane-hydrogen vapor ($C_6H_{14}+H_2$) on Si<100> substrates at 500°C and 750°C temperature. In all cases SiO_2 overlayer with catalytic Ni film has been used. Features of the nanofiber structures and relation with the residual stress were defined.

Optimization of the technology of the diamond like carbon films enabled to apply this film in the mold used for the nanoimprint lithography (NIL). Equipment and the technology of the NIL was created and applied in our institute for the replication of the photonic structures in the semiconductor substrate. Preparation of the diamond mold for the NIL let to avoid polymer – mold sticking problems during mold separation and raise mold durability as well.

1. Introduction

The developments of miniaturized tests are vital task in materials science and is currently important problem in many domains in science and technology. In addition to the microelectronics or optoelectronics, traditional technologies like microlithography and microfabrication are rapidly finding applications in many areas, from sensors and actuators to biomedical devices. Wide range of materials and structures can be found in such applications. Metallic, insulator, semiconductor materials in form of thin films, shells, micro-beams etc. are employed. Advanced carbon materials such as diamond-like carbon, microcrystalline and nanocrystalline diamond films, carbon nanotubes are under intensive investigations due to their unique and very promising properties [1, 2]. Diamond and related carbon materials have been widely investigated for diverse applications such as hard coatings, optical windows, surface acoustic wave devices and electron field emitters.[1,2]. A wide array of techniques has been developed for the deposition of those novel carbon materials. Particularly, direct ion beam deposition is a versatile tool of formation of many materials in thin film form [3-12]. Many process parameters such as ion beam energy, plasma power, substrate temperature, angle of ion beam incidence, system pressure, gas composition and flow rate, can be autonomously controlled over a wide range of process conditions [3]. In such a way ultra hard, wear resistant, low friction diamond-like coatings can be grown at room temperature [4-10]. Therefore ion beam deposition of diamond-like carbon (DLC) films is already used for protection of the magnetic media, metal, ceramic, and, especially, glass and plastic. In particularly the problem of intrinsic stress has received much attention, since these films typically possess high average stress after growth [10-17].

Film testing requires that one differentiates between the properties of the film, which are adherent to the substrates and those that are free standing, that is, they have been separated from their substrates. The high internal stress limits the thickness of the film and affects the adhesion of the coating [14]. It hinders wide spread applications of carbon coatings [15]. Intrinsic tensile residual stress has been shown to be due to the presence of a high grain boundaries density [16]. The coalescence of grain boundary(17) and attractive atomic forces across grain boundaries [17] is believed to be the origin of tensile stress as well. The existence of a non-diamond phase was found to be beneficial to the relaxation of intrinsic tensile stress in the films [17] and compressive stress has been shown to be due to non-diamond carbon impurities at the grains boundaries [16].

The use of optical probe techniques for the real - time monitoring of different processes is favored because of their nondestructive character and their potential use in real time feedback control. Depending on the properties of the object to be investigated (opaque or transparent) and problems to be solved, the different experimental techniques can be applied: laser reflective interferometry, laser spot scanning interferometry, optical leverage with a laser beam [19-24] etc. A common feature for all the mentioned techniques is a registration of strain during bending, tension or compression of freestanding films (stress- strain experiments) or registration of the strain of the film-substrate structure due to residual stress that is related to technological steps of thin film formation.

In this article we report some mechanical properties of the carbon films produced by direct ion beam using optical interferometry. Some applications of such films for micro- and nanostructures formation are presented. In particularly the use of diamond like carbon film as a lithographic ion-etching mask and imprint lithography mold is reported.

2. Experimental

2.1 ION BEAM SYNTHESIS OF NANOSTRUCTURED CARBON FILMS

In all experiments crystalline n-Si <100> wafers have been used as substrates. In some cases 300 nm thermal SiO₂ film onto the wafers was deposited.

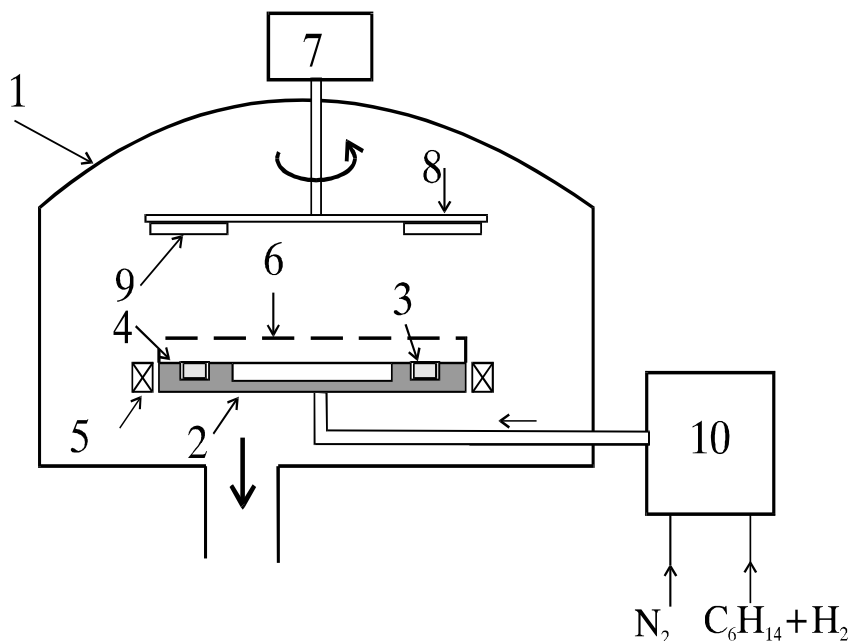


Figure 1. Schematic diagram of the α -CN_x-H ion beam deposition system:

1 - vacuum chamber; 2 - electrostatic ion source; 3 - ion source anode; 4 - ion source cathode; 5 - solenoid; 6 - grid; 7 - rotating sample holder unit; 8 - sample holder; 9 - samples; 10 - gas flow controller

Carbon films growth was performed using an Ion beam etching unit URM3.279.053 (Figure1) equipped with the autonomous electrostatic ion source and substrate resistive heater (deposition temperature can be reached up to 800°C). After the stabilization of the substrate temperature, C₆H₁₄+H₂ vapor has been introduced into electrostatic ion source and 15 min ion beam deposition was performed. C₆H₁₄+H₂ vapor mixture has been used as a hydrocarbon source. The pure H₂ transport gas flowed into the chamber through a special thermostatic mixer, containing liquid C₆H₁₄ reagent. For studies of the nitrogen doping effects, through the other channel the N₂ gas flowed only. The C₆H₁₄+H₂ vapors were mixed with the N₂ gas before reaching the ion source. The C₆H₁₄+H₂ and N₂ vapor flux was regulated by a needle valve. While applying nitrogen, concentration of N₂ in the C₆H₁₄+H₂+N₂ gas mixture was changed from 0 to 40%.

Conditions of the deposition process are shortly presented in the Table 1.

Table 1. Conditions of the carbon films deposition process

Substrate	n-Si <100>
Reagents	C ₆ H ₁₄ +H ₂ , N ₂
Gas pressure	(2·10 ⁻²) Pa
N ₂ concentration	0-40 %
Ion beam energy	(0.8±0.1) keV
Deposition temperature	20-750°C
Ion beam current density	(0.12±0.01) mA/cm ²

2.2 ANALYTICAL TECHNIQUES

Chemical composition of the films was evaluated by X-ray photoelectron spectroscopy. Measurements were carried out using a KRATOS Analytical XSAM800 spectrometer operating at constant pass energy. An Al K_α line was used as X-ray source. The measurements were performed at normal incidence to the sample surface. The C/N ratio in the film was obtained from the ratio of the integrated net intensities of the N1s and C1s XPS lines.

The thickness and refractive index of α-CN_x:H films were measured by a laser ellipsometer Gaertner L115 (λ=632,8 nm).

Surface morphology of the films was investigated by an atomic force microscope NANOTOP-206. V-shaped “ULTRASHARP” Si cantilever (force constant 1.5 N/m) has been used. The measurements were performed using a contact-static constant force mode.

He-Ne laser (wavelength – 632.8 nm, output power - 15 mW) was used for the Raman spectroscopy. Light was analyzed with an f/5.3 double monochromator with 1200 lines/mm gratings and detected by photomultiplier (cooled to 283 K) and a photon counting system.

Identification of different phases (Figure 2) was based on well known regularities presented in⁽¹⁾. It is known that carbon forms a variety of crystalline and disordered forms due to its possibility to exist in three hybridizations sp³ (diamond), sp² (graphite), sp¹. Diamond has a single RAMAN active mode at 1332 cm⁻¹. Single crystal graphite has single RAMAN active mode at 1580 cm⁻¹. Disordered graphite has a second mode at around 1350 cm⁻¹ labeled D (disorder induced peak). RAMAN spectra even of the most disordered carbons remains dominated by the G and D modes of the graphite. It is valid even when the carbons have not particular graphitic ordering.

As one of the low-cost methods for determining film stress, an optically levered laser technique was used to measure a radius of substrate curvature induced by a deposited film. The sensitivity of the cantilever technique in the strain measurements can reach up 10⁻⁶ and this fact allows applying this method for control of the nucleation and coalescence of thin films that can be provided both in –situ or ex-situ. Stoney's equation for a film whose thickness is small as compared to the substrate thickness, relates average stress in the film and variation of the curvature of film – substrate system:

$$\sigma_f = \frac{1}{6} \frac{E_s h_s^2}{(1-\nu) h_f} \left(\frac{1}{R_2} - \frac{1}{R_1} \right) \quad (1)$$

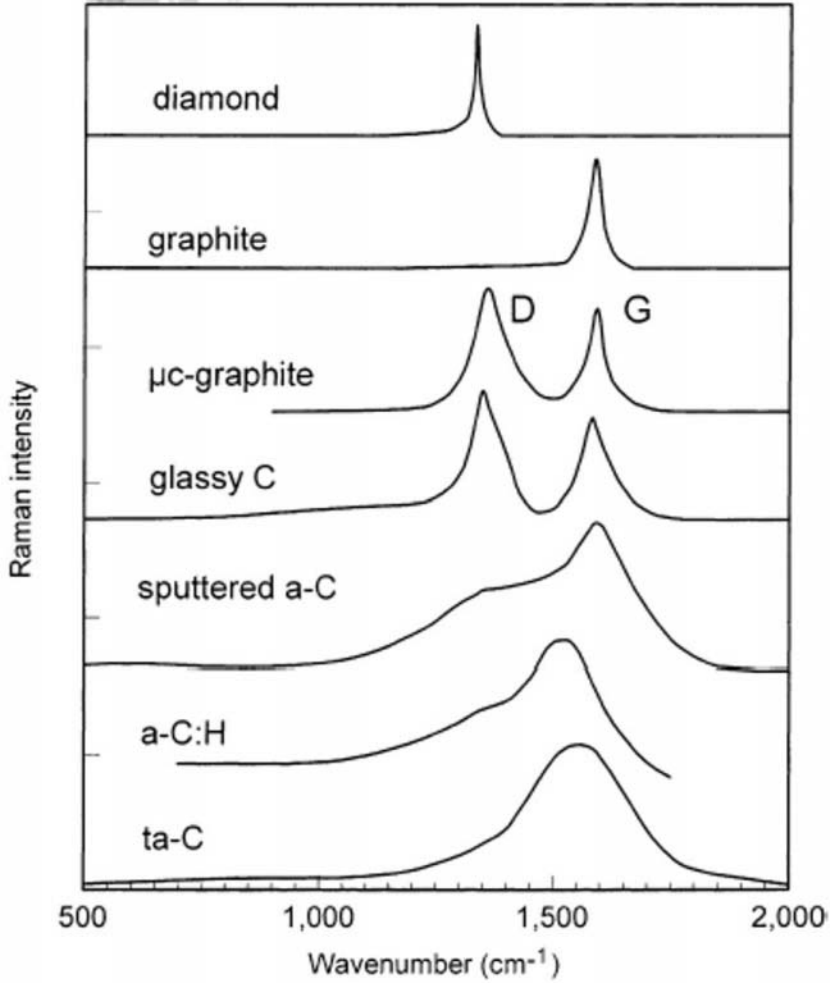


Figure 2. Typical RAMAN spectra of the different carbons (after [1]).

Where E_s is Young's modulus of the substrate, h_s is the thickness of the substrate, ν is Poisson's ratio of the substrate, h_f is the thickness of film, R_2 and R_1 are the radii of the substrate after and before thin film deposition respectively.

In the present study the prism interferometer including He-Ne laser (wavelength 632.8 nm, output power 10 mW) was used to measure curvature of the substrate [19].

Applying extra thermal heating of the formed structure within a small temperature region (tens of degrees) one can differentiate between the intrinsic stress (that is constant within a narrow region of temperatures) and change of thermal stress, that is a linear function of the applied temperature:

$$d\sigma_{th} = E_f (\alpha_s - \alpha_f) dT \quad (2)$$

where $d\sigma_{th}$ is the change of thermal stress (due to extra heating), α_s and α_f are the thermal expansion coefficients of the substrate and thin film, and dT is the incremental temperature.

Knowing the rate of change ($d\sigma/dT$ due to extra heating), one can define thermal stress component of the residual stress in thin films (assuming that linear dependence is valid for the investigated region of temperatures):

$$\sigma_{th} = \frac{d\sigma}{dT}(T_2 - T_1) \quad (3)$$

where T_1 is the deposition temperature and T_2 is the room temperature.

These measurements were performed using a Michelson interferometer [19] supplied with the noncontact heater and temperature control system mounted to the thermostabilized vacuum chamber.

3. Experimental results and discussions

3.1 EFFECTS OF CATALYTICALLY-ASSISTED DEPOSITION AND TEMPERATURE ON DIRECT ION BEAM DEPOSITED CARBON FILMS AND NANOSTRUCTURES

The dependence of stress in α -C:H thin films on deposition temperature is presented in Fig. 3. Monotonous tensile stress increase with the temperature can be seen. These changes can be explained taking into account changes of the structure of α -C:H films investigated using RAMAN scattering spectroscopy. It can be seen in Fig. 3b, that in the case of the film deposited at 130°C temperature, a peak at $\sim 1490 \text{ cm}^{-1}$ can be seen. This peak (G-band) can be designated as the stretching vibration mode of graphite crystals [1]. From the other hand only a negligible shoulder (disorder induced peak) in $1330\text{-}1350 \text{ cm}^{-1}$ range can be seen. Such spectra are typical for diamond-like carbon films [1]. (Nearly identical spectra were observed in the case of room temperature deposited films.) Further increase of the deposition temperature results in substantial changes of the structure of α -C:H films. A wide and very intensive ID peak at the $\sim 1300 \text{ cm}^{-1}$ can be seen in the case of the thin films deposited directly onto the SiO_2 layer at 200°C and 450°C temperatures. Similar approach of the RAMAN spectra has been reported for polymer-like carbon films deposited by plasma enhanced CVD without the negative substrate bias, while negative substrate bias resulted in formation of the diamond like films [25]. Increase of the stress with the deposition temperature can be explained by worsening of the thermodynamic conditions of the C-C bond formation. Polymer-like films deposited in this study were relatively soft. Therefore, increased stress level reported for these films in present research is rather controversial, because in other studies decrease of the stress level with the decreased hardness was reported. However, value of compressive stress of polymer-like carbon film reported in [26] was similar to value of tensile stress in ours study (0.7 GPa and 0.4 GPa respectively).

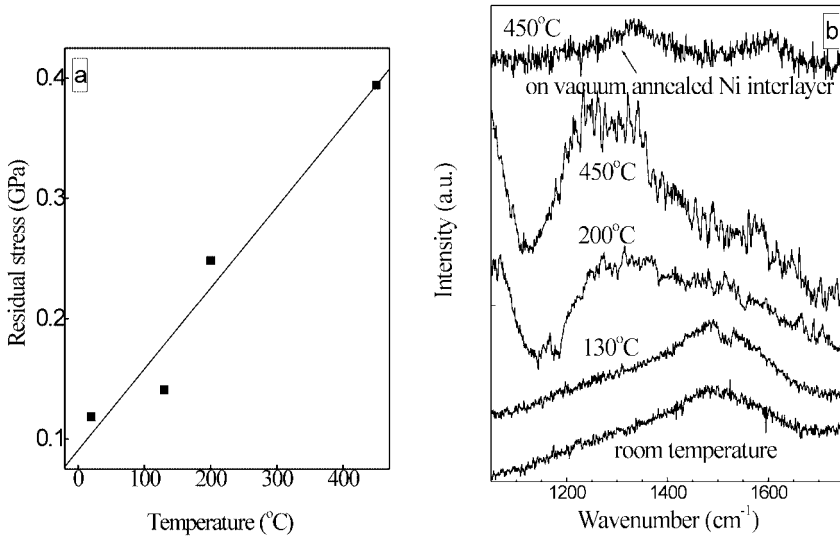


Figure 3. The residual stress (a) and RAMAN spectra (b) of the carbon films deposited at different substrate temperatures.

3.2 EFFECTS OF DOPING BY NITROGEN ON DIRECT ION BEAM DEPOSITED CARBON FILMS

Introduction of the nitrogen resulted in the decrease of the internal stress of α -C:H films (Fig. 4a). It can be explained by decrease of the sp^3/sp^2 bond ratio and formation of the more graphite-like films. Wide I_G peak at the 1520 cm^{-1} dominated in Raman spectra of the all investigated α -CN_x:H films (Fig. 4b). Wide I_D peak at 1350 cm^{-1} wavelength can be seen as well. The disorder in sp^3 atom bond matrix increased (sp^3/sp^2 ratio decreased) when N_2 concentration increased. As a result films became more graphite-like.

Increase of N_2 concentration results in decrease of wear resistance. It means, that carbon nitride films deposited at higher nitrogen fluxes are softer as a result of the higher ratio between the graphite and diamond phases and lower density. The observed decrease of wear resistance (Fig. 5a) is relatively small, in maximum it is less than 20 %, (for N_2 concentrations 20% or less). However further increase of nitrogen concentration up to 30% resulted in significant decrease of the film wear resistance (more than 3 times for shorter interaction length and more than twice for longer interaction length).

Dynamics of the stress at the 20°C temperature range close to the room temperature was investigated using thermostabilized vacuum chamber with the laser interferometer. While applying extra heating to the samples up to the 60°C, the decrease of the stress by 60-70 MPa was observed for all investigated samples. The typical dependence of the stress changes on the temperature due to extra heating for the film deposited at 130°C (film thickness 400 nm) is presented in Fig. 5b. Extrapolating the dependence of Fig. 5b by a line, rate of change of the stress was defined $d\sigma/dT = -2.9\text{ MPa/deg}$. Evaluation of the tensile thermal stress in accordance to (3)

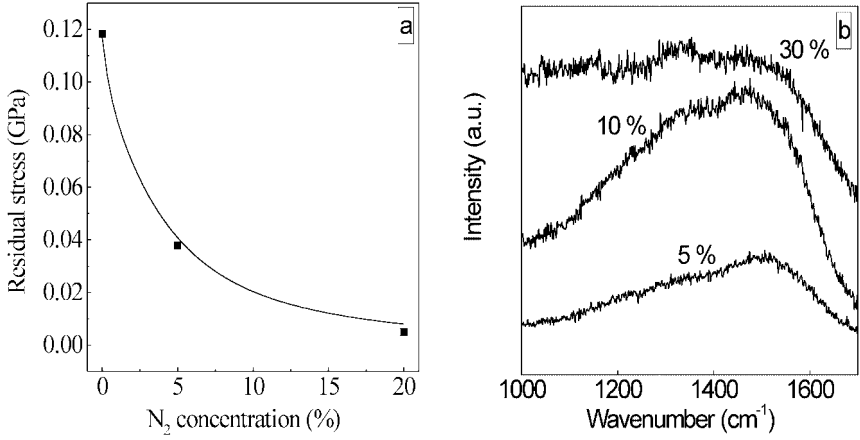


Figure 4 The Internal stress (a) and Raman spectra (b) of $\alpha-CN_x:H$ films, deposited at different N_2 concentrations (Raman spectra after (4)).

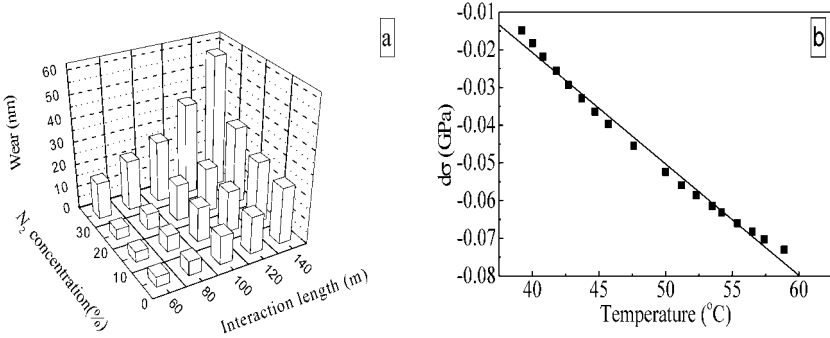


Figure 5. The wear resistance of $\alpha-CN_x:H$ films, deposited at different N_2 concentrations (a) (after⁽⁴⁾) and stress changes with the temperature of carbon film deposited at $130^{\circ}C$ temperature due to extra thermal heating after the deposition (b).

gives $\sigma_{th}=0.32$ GPa for the films deposited at $130^{\circ}C$, i.e. this value exceeds the total residual stress (0.14 GPa) presented in Fig. 3a.

Even more controversial results were obtained for the polymer-like carbon film deposited at $450^{\circ}C$ temperature. In this case $d\sigma/dT = -11.9$ MPa/deg and tensile thermal stress as high as 5.117 GPa was obtained.

On the other hand, there were not observed any definitive dependence of the stress on measurement temperature when carbon film was deposited at $300^{\circ}C$ onto the 5 nm thickness vacuum annealed Ni layer (clustered Ni, Fe, Co films are used as a catalytic layers for deposition of the carbon nanotubes).

Despite that stress tendency due to extra heating corresponds to the experimentally known values of thermal expansion coefficients, absolute values of the stress illustrate

that stress relaxation processes take place. The stress reduce is higher for the films deposited at high temperatures where polymer like carbon films are produced. During the cooling of the system substrate-film from deposition to room temperature thermal stress exceeds limits of the elastic deformation of thin film and stress relaxation due to the plastic deformation takes place. These considerations are in good agreement with the structure analysis.

Tensile stress was usually reported in diamond films containing no significant amount of non-diamond carbon phases [16]. Stress changed its sign from compressive to tensile with increase of the film thickness for CVD deposited DLC coatings [17, 27, 28]. On the other hand, tensile stress was reported for lower fluence and lower pressure DLC films deposited by laser ablation [29] and CVD [28]. While ion beam fluence and film deposition rate was the same [11] or even lower [10] than in our study. It can be mentioned, that with the increase of the ion energy stress changed its sign from compressive to tensile for ion beam assisted deposition synthesized carbon nitride films [30]. Intrinsic tensile residual stress has been shown to be due to the presence of a high grain boundaries density [16]. The coalescence of grain boundary [17] and attractive atomic forces across grain boundaries [18] is believed to be the origin of tensile stress. The existence of a non-diamond phase was found to be beneficial to the relaxation of intrinsic tensile stress in the films [17] and compressive stress has been shown to be due to non-diamond carbon impurities at the grains boundaries [16]. These facts are in good agreement with decreased tensile stress with deposition temperature observed in our study. In addition tensile stress (values similar to our study - 0.2-0.4 GPa) was observed in MWCVD DLC films produced at 825°C temperature while negative bias assisted deposition resulted in appearance of the compressive stress [18]. However, in cited study many more higher work pressure was used. Tensile stress similar to ours was reported for bias assisted DC plasma DLC coatings [31] as well. In that study similarly to ours tensile residual stress increased with increase of annealing temperature. Polymer-like carbon films were relaxed in comparison with the diamond like carbon films [26]. However, value of its compressive stress was similar to ours study (0.7 GPa and 0.4 GPa respectively).

Therefore, decrease of the compressive internal stress with increased nitrogen doping can be explained by increased amount of a non-diamond phase [17] beneficial to the relaxation of intrinsic tensile stress [17] and by appearance of the compressive stress due to non-diamond carbon impurities at the grains boundaries [16]. It can be mentioned, that tensile stress was observed in carbon nitride coatings deposited by laser ablation at lower fluence and lower pressure [29]. Tensile stress of coatings with 8% nitrogen was slightly higher than in present study (0.14-0.47 GPa). While compressive stress decreased with the increase of the N/C ratio in [12].

3.3 APPLICATIONS OF DIAMOND LIKE CARBON COATINGS FOR THE NANOIMPRINT LITHOGRAPHY

Developed diamond carbon films were used for nanoimprint lithography. Patterning and silicon reactive ion etching was applied to fabricate deep structures in the silicon ($n\text{-Si} < 100$) substrates. Diamond like carbon film was synthesized on the surface of patterned silicon substrate at room temperature.

Commercial photoresist (Shipley Microposit S1805, thickness about 500 nm) was spun and cured at a 110°C temperature. Furthermore photoresist layer was used as thermosetting polymer for the hot imprint using silicon – diamond like carbon mold. Hot imprint was performed at a pressure 1.2 MPa using a simple home-built press. The

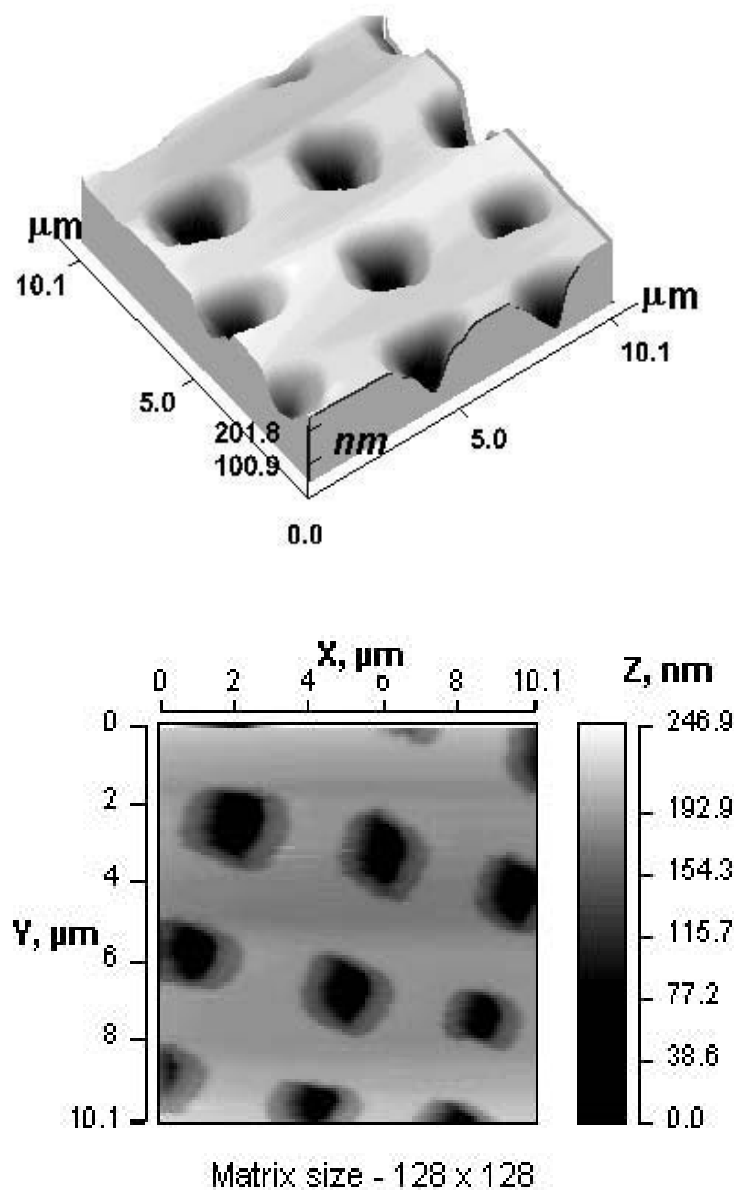


Figure 6. AFM image (3D and 2D) of silicon pits (horizontal mark size – 5 μm , vertical mark size – 125 nm).

stamp was heated to the imprint temperature (130°C), then pressure was applied and held during 1 min under imprint temperature. Separation of the stamp and the sample was performed after the cool down to room temperature. The residual layer of photoresist was removed in a vacuum chamber by O_2^+ ion beam (ion energy $E = 500$ eV) using multicell ion source. Photoresist mask was applied to the reactive ion etching of the structures in the silicon substrate, which geometry was controlled by atomic force microscope. Fig. 6 shows the AFM image of the silicon pits fabricated using silicon – diamond like carbon mold.

Acknowledgements

This work was partially supported by the Lithuanian State and Studies Foundation.

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THIN CARBON LAYERS ON NANOSTRUCTURED SILICON – PROPERTIES AND APPLICATIONS

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Abstract

Thin carbon layers such as silicon carbide (SiC) and diamond like carbon (DLC) layers on silicon, or on nanostructured silicon substrats were obtained by different methods. This paper is a review of our results in the areas of carbon layer microfabrication technologies and their properties related to different microsystem applications. So, silicon membranes using a-SiC or DLC layers as etching mask, as well as silicon carbide membranes using a combined porous silicon - DLC structure were fabricated for sensor applications. A detailed evaluation of the field emission (FE) properties of these films was done to demonstrate their capability to be used in field emission devices. Carbon thin layers on nanostructured silicon samples were also investigated with respect to the living cell adhesion on these structures. The experiments indicate that the cell attachment on the surface of carbon coatings can be controlled by deposition parameters during the technological process.

1. Introduction

The aim of this paper is to evaluate the properties and the applications of carbon layers such as silicon carbide and diamond-like carbon thin films deposited on nanostructured silicon or on silicon, by different methods. Generally, the carbon film properties relieve their capability to be used for applications, such as: blue light emissive sources (due to PL properties), adherent layer between two metals (due to their reactive interface with metals), coatings or protective layers (due to their high chemical resistance), or decorative layers (due to the high refractive/absorption coefficients), and as mask in etching and diffusion processes. The field emission from different carbon films was intensively studied. In most of the cases, the field emission is due to the field enhancement by film morphology and structure. Recently, carbon thin layers on nanostructured silicon samples were also investigated with respect to the living cell adhesion on these structures, with biomedical applications. In this paper we present a review of the results of our reserch team, in the domain of thin carbon layers on nanostructured silicon.

2. Experimental

2.1. SAMPLE PREPARATION

Si-p, and Si-p+ type wafers with (100) and (111) orientation were used as substrates for nanostructured silicon layers. Porous silicon (PS) layers were realised by silicon electrochemical dissolution in 25% HF ethanoic solution, the current density being $10\text{mA}/\text{cm}^2$. For biomedical applications, 35-40% porosity PS layers were obtained in an anodisation process with $20\text{mA}/\text{cm}^2$ current density, and 35% HF ethanoic solution. Different technological processes (table 1) were used to obtain thin carbon layers for various applications.

Table 1

Carbon layers	Substrate	Deposition method	Experimental conditions	Film thickness (nm)
a-SiC	silicon	LPCVD by liquid hexamethyldisilane precursor	$T_{\text{dep}} = 720\text{-}950^\circ\text{C}$; precursor flow rate = 5-8 sccm; $P = 0.5$ torr	60-100
a-C	porous silicon	Electron gun evaporation method	$P = 6 \times 10^{-5} - 1 \times 10^{-4}$ mbar; $I = 180\text{mA}$; $U = 7\text{kV}$	20-40
Poly-SiC	porous silicon	PECVD method	$T = 800^\circ\text{C}$; $t_{\text{dep}} = 1\text{h}$; $P = 200$ W; $D_{\text{precursor}} = 0.8$ ml/h; $H_2 = 2\text{-}3$ l/min; $P_i = 2\text{-}2,5$ Torr	40-60
DLC-layers	scratched silicon , or porous silicon	PECVD method from methane or methanol precursor	$T = 800^\circ\text{C}$; $t_{\text{dep}} = 8\text{h}$; $P = 750$ W, $D_{\text{CH}_3\text{OH}}$ or $\text{CH}_4 = 0.015$ l/min, $H_2 = 6\text{-}13$ l/min, $P_i = 30$ Torr.	100

The film thickness and uniformity were determined by a laser profilometer.

2.2. THIN CARBON LAYER CHARACTERIZATION

The film morphology was investigated by Scanning Force Microscopy (SFM) using a TMX 2000 Explorer instrument with scanning ranges from $50\text{ }\mu\text{m}$ to 300 nm . The scanning rate was about 3 Hz. The cantilevers used were made of silicon nitride with "V" shape, with constant force of 0.032 N/m . Almost the same cluster size of approx. 50 nm on X/Y axes was determined for both DLC (Fig. 1) and high temperature SiC (Fig.2b) films.

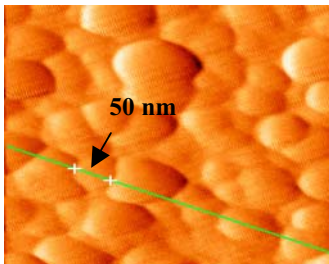


Figure 1. SFM image of the PECVD-DLC film. Deposition conditions: $t = 800^\circ\text{C}$, $t_{\text{dep}} = 7\text{h } 30'$, $P_{\text{plasma}} = 750$ W, $\text{CH}_3\text{OH} = 12,8$ ml/min, $H_2 = 13$ l/min, $P_i = 30$ Torr, $P_f = 33$ Torr.

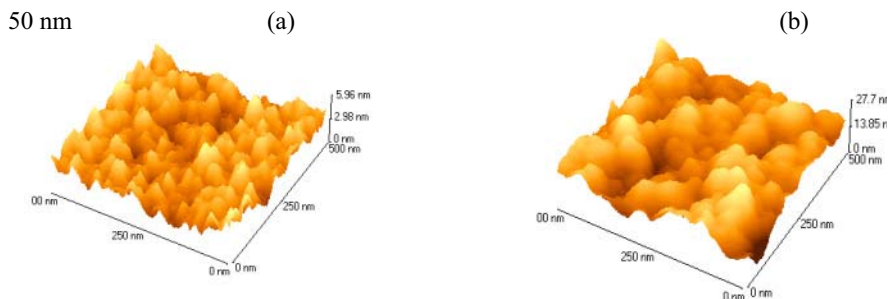


Figure 2. SFM image of silicon carbide films deposited at different temperatures: (a) $T=770^{\circ}\text{C}$; (b) $T=950^{\circ}\text{C}$

SiC-PECVD layers realised by hexametildisilane decomposition on porous silicon substrate present a polycrystalline structure (Fig. 3), and the structure of carbon layers obtained by electron gun evaporator is amorphous (Fig. 4).

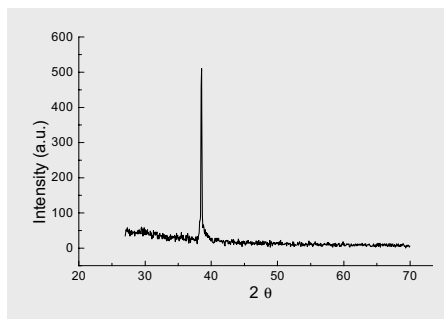


Figure 3. XRD spectra of polycrystalline SiC.

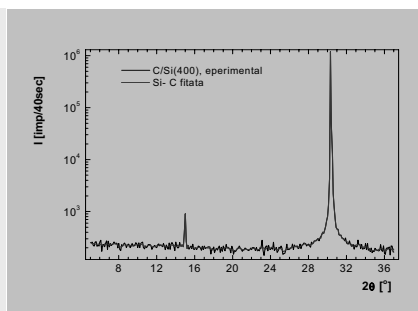


Figure 4. XRD spectra of carbon layers obtained by electron gun evaporator

DLC/PS Raman spectrum indicated as seen in figure 5, that the carbon coatings consist of both amorphous carbon and disordered graphite structure. Raman spectrum presents two peaks, one broad peak at about 1360cm^{-1} , indicating the presence of disordered graphite induced by sp^3 carbon atoms, and the another at 1530cm^{-1} corresponding to that the carbon films are principally amorphous carbon.

The DLC layers are characterised by good photo-luminescence properties (Fig. 6).

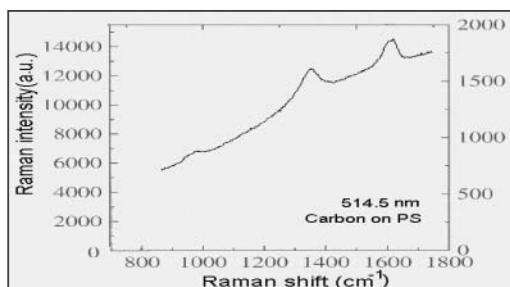


Figure 5. DLC layer Raman spectrum. Deposition conditions are: precursors, $\text{CH}_4 + \text{H}_2$; $\text{CH}_4 = 0,05\text{ l/min}$; $\text{H}_2 = 5\text{ l/min}$; $T=850^{\circ}\text{C}$; $p=19\text{-}20\text{Torr}$; $t_{\text{dep}}=6\text{h}$

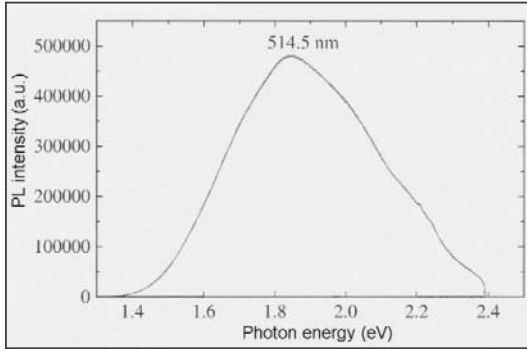


Figure 6. PL spectrum of DLC layer

Structure, composition and electrical properties of a-SiC-LPCVD films were previously reported [1-2].

Ellipsometric measurements relieve high refractive and absorption film coefficients for the investigated films.

3. Applications

3.1. SENSOR MEMBRANE FABRICATION

10-50 μm Si membranes for gas or pressure sensors were realised by selective etching of $\langle 100 \rangle$ Si in alkaline solutions, using different carbon layers as mask: LPCVD-aSiC; PECVD SiC or DLC. The Si membranes were realised either by plasma etching of a-SiC layer in $\text{CF}_4 + 5\% \text{O}_2$ feed gas or by a-SiC layer thermal oxidation at temperature between 900-1000 $^\circ\text{C}$.

SiC layers can be easily structured by dry etching in gaseous mixture of CF_4 and O_2 [3]. DLC layers, due to their strong resistance in chemicals, were selectively deposited on different substrates, such as Mo, silicon scratched, and porous silicon [4;5]. (Fig. 7).

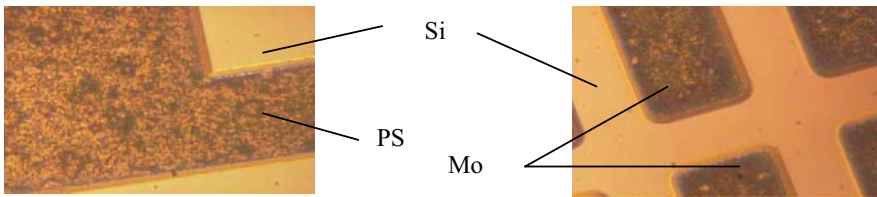


Figure 7. DLC selective deposition on different substrates: Si; PS; Mo

Carbon layers can not be etched in wet solutions. Based on the very good resistance of the carbon layers to the alkaline solution attack, SiC or DLC membranes can be obtained by carbon layer deposition on PS/silicon structures (Fig. 8). The experiments were realised on 50% porosity PS layers. The carbon film was deposited after the precursor (hexamethyldisilane) infiltration in the substrate pores, at the temperature 20-100 $^\circ\text{C}$. This can be realised in the following conditions: (i) the porous substrate was maintained 1 h in vacuum chamber; (ii) the precursor must be introduced in the cool CVD reactor, before heating at the deposition temperature (720-750 $^\circ\text{C}$). After Si etching, carbon based membranes of different thickness (1-20 μm) were obtained [6]. The technological process for carbon membrane realisation is presented in figure 9.

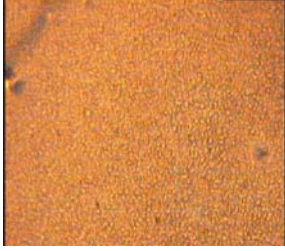


Figure 8. DLC layers on PS substrate obtained from $\text{CH}_4 + \text{H}_2$ at $T = 850^\circ\text{C}$; $P = 20\text{Torr}$; $t_{\text{dep}} = 2\text{h}$; $\text{CH}_4 = 0,015\text{ l/min}$; $\text{H}_2 = 5\text{-}6\text{ l/min}$; PS (60% porosity, and $3\mu\text{m}$ thickness) on Si

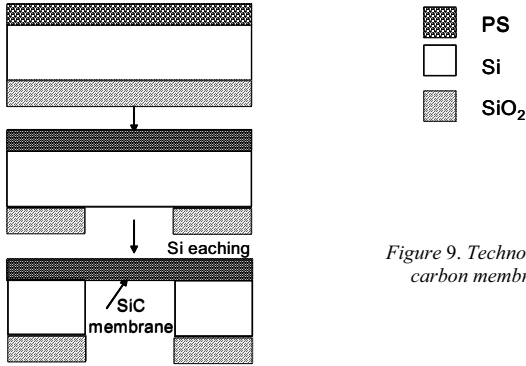


Figure 9. Technological process for carbon membrane fabrication

3.2. FIELD EMISSION PROPERTIES OF THE A-SIC AND DLC FILMS

The field emission properties of a-SiC and DLC layers were evaluated for field emission device applications. The main advantages of such films used for electron emission are: (i) simple deposition method; (ii) the film thickness can be as small as desired; (iii) no tips or special structures are necessary (Fig. 10).

Electrical field emission measurements were carried out in a high vacuum chamber at a pressure of 10^{-8} Torr, on 0.1 cm^2 emitting area using a metallic anode at $75\mu\text{m}$ distance to cathode.

The Fowler -Nordheim (F-N) characteristics of the investigated films are presented in figure 11.

The limits of the FE current densities were 0.12 and 2.4 mA/cm^2 , at electric fields values of $6\text{ V}/\mu\text{m}$ and $25\text{ V}/\mu\text{m}$ for SiC layers, and 0.12 and 0.8 mA/cm^2 , at electric fields values of $28\text{ V}/\mu\text{m}$ and $42\text{ V}/\mu\text{m}$ for DLC films.

The a-SiC/Si in comparison with DLC/Si structures are characterised by higher current emission at lower external fields. So, more electrons were emitted from SiC films comparatively with DLC films. In the investigated structures the field emission is due to

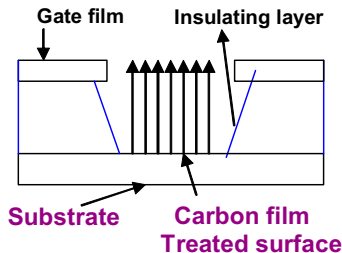


Figure 10. Field emission structure with carbon film.

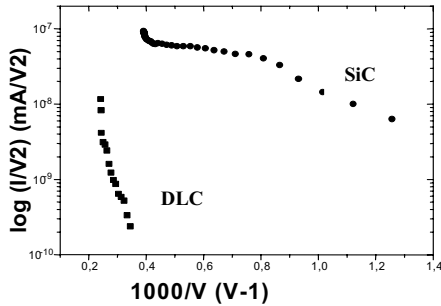


Figure 11. *F-N characteristics of DLC and SiC layers deposited on p-Si*

field enhancement by carbon film morphology and structure and not to the NEA phenomenon [7].

3.3. CARBON LAYERS ON POROUS SILICON MATRIX FOR APPLICATIONS IN BIOLOGY

Bulk crystalline silicon is not a biocompatible material. By partial electrochemical dissolution in HF based solutions, the obtained porous silicon layers have a very complex, anisotropic, nanocrystalline architecture of high surface area, and hydrophobic surfaces by hydride bonds (SiH_x). The nature of the surface bonds can be modulated to provide: stable PS surfaces, modifiable surface characteristics, the potential to interface organic/anorganic materials. So, different PS surface treatments, like: (i) thermal treatments in O_2 , (ii) thin carbon, or silicon carbide layer deposition, (iii) thin gold layers, (iv) surface derivatization by an electrochemical method, have been reported to produce a PS hydrophilic and stable; by these treatments the modified surface acquires biomaterial properties. For the biological applications we developed technologies to obtain different PS layers with 35-50% porosity on Si-p+ (100) and Si-p+(111), $\rho = 0.01 - 0.018 \, \Omega\text{cm}$, followed by different treatments for surface structure modification/stabilisation [8].

In Table 2 the technologies used to modify the porous silicon surface in order to ensure its biocompatibility are presented

Table 2

No.	Treatment	Temperature ($^{\circ}\text{C}$)	Time (min)	Pressure (mbar)	Thickness (nm)
T1	Thermal treatment in N_2	300 800	60 30	-	200
T2	a-SiC layer by hexamethyldisilane	770	5	0,3	50
C1-C5	Carbon layer deposition		10	6×10^{-5} – 1×10^{-4}	20-40
T3	Hexamethyldisilazane treatment	Temperat. heated up 90-150 $^{\circ}\text{C}$	-	-	-
T4	Carbon monolayer deposition		2	5×10^{-6}	5

In this paper we discuss about the samples with carbon layers on porous silicon, C1-C5. The difference between them is only the orientation of Si substrate: C1-C2-C5 – carbon layer on PS/ Si(100), and C3-C4 - carbon layer on PS / Si (111).

PS layers are obtained in the same technological conditions.

To demonstrate the biocompatibility of porous silicon covered with different carbon layers we have cultivated B16F1 mouse melanocytes in normal conditions (at 37°C in 5% CO₂ atmosphere in RPMI 1640 medium supplemented with 10% fetal calf serum) using these biomaterials as substrates. Usually, these cells are cultivated in special conditions on plastic materials pretreated with polyllysine, a compound that stimulates cell adesion.

After 48 hours the cells were visualized by immunofluorescence technique, the chased protein being calnexin, an endoplasmic reticulum resident lectin-like chaperone, present in all eukariotic cells. The technique involves the formation of antigen-primary antibody complex that is visualised using a secondary antibody coupled with a fluorofor. The final complex, including the fluorescently labelled antigen was visualized using a Nikon Eclipse E600W fluorescence microscope.

In order to visualize the cells we performed the following steps. First the cells were fixed on silicon by chemical cross-linking using formaldehyde when formation of methylene bridges between a variety of side groups (including amino, amido, guanidino, thiol, phenolic, imidazolyl and indolyl) occurs. In order for primary antibody to have access to intracellular structures (eg, ER) a permeabilization step is required. Therefore, we have used PBS-Triton X 100 0.2% solution as permeabilizing agent. Once the antigen-primary antibody complex is formed, it can interact with the secondary antibody rising the final complex that can be visualized. As primary antibody we used rabbit anti-calnexin IgG and as secondary antibody Alexa Fluor 488 goat anti-rabbit IgG with absorbtion at 488 nm and emission at 520 nm.

The experimental data show that porous silicon covered with carbon layers is a good biomaterial with no citotoxicity (figure 12). The pattern for calnexin distribution in the

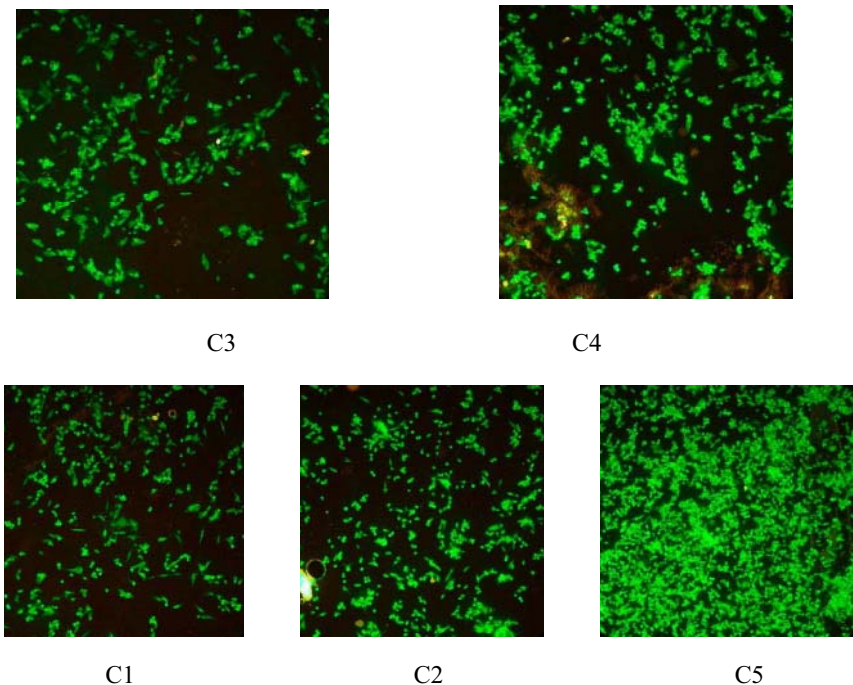


Figure 12. B16F1 cells on different substrates: C1, C2, C5- carbon layers on PS/ Si(100), and C3- C4 - carbon layers on PS / Si (111)

cell is normal; in live cells calnexin is seen only in the ER (the more intense dots) but, because of the fluorescent background we can visualize the entire cell. Based on visual observation we can say that the morphology of cells is normal as we previously noticed on B16F1 cells grown on special substrates used in immunofluorescence technique (data not shown).

The number of the adherent cells varies among the different PS substrates indicating a variation between the biological properties of the substrates. The same type of substrate (eg C2 and C5 prepared on different silicon wafers) presents different number of adherent cells; this might be due to the differences in the surface chemistry and topology. Interestingly, melanocytes grown on some PS substrates (eg. C5 and C2) were found clustered, which is an unusual feature for these cells and this may be due to a lack of uniformity of the modified surface.

4. Conclusions

Thin carbon based films properties in correlation with their main application in microsystems were presented. Thus, carbon based films due to their high resistance in alkaline solutions are used to obtain Si membranes or even carbon based membranes for different sensor applications. Another important application of these films is as FE material for vacuum microelectronic devices.

Also, the PS substrates are biocompatible materials, appropriate for cultivating adherent cells *in vivo* and without noticeable toxicity. Moreover, morphologically, the melanocytes cultivated on PS are similar with the control cells. It is also important to emphasize that no further coating with polylysine or collagen was required, which further recommends these materials as suitable bioactive substrate.

Acknowledgements

The authors would like to thank dr. J.M.Albella- ICM Madrid, and dr. I.Stamatin, University of Bucharest for some experimental processes; this work was part of the Romanian National Programms.

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1D PERIODIC STRUCTURES OBTAINED BY DEEP ANISOTROPIC ETCHING OF SILICON

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Abstract

The potentialities of the vertical anisotropic etching of (110) silicon for fabrication of one-dimensional photonic crystals have been studied. It has been shown that the technique allows to form structures with wide photonic band gaps in the middle IR spectral range suitable for microphotonic elements in a silicon chip. Besides the technique enables to fabricate highly birefringent artificial media. This media behaves as a negative uniaxial crystal with the optical axis parallel to the wafer plane and exhibits an extremely high IR birefringence $\Delta n=1.5$.

1. Introduction

Photonic crystals (PC) are materials with a regular change in the refractive index, n , with periodicity of the order of the wavelength [1]. PC can have periodicity in one, two or three dimensions. The forbidden gap for photons of certain frequency range, similar to that for electrons in atomic crystals, arises for the structures with the proper values of refractive index, symmetry and period. This is called a photonic band gap (PBG) which leads to the appearance of the stop bands in reflection or transmission spectra.

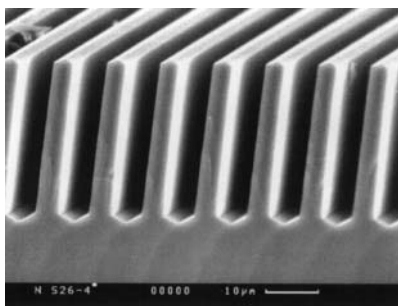


Figure.1 SEM image of the periodically grooved silicon (cross section view).

It is known that the refractive index contrast plays an important role in optical properties of periodic structures. The larger the ratio of n_H/n_L , the wider is PBG and the lower is the number of layers. From this point of view, the choice of the pair “Si-air” is very promising, since such a medium has high contrast ratio (3.42/1) in the IR range. There are a few different technological methods for preparation of 1D PC. The most common way is thin film coating or microporous etching resulting in the multilayered structures with altering sheets of high (n_H) and low (n_L) refractive indices [2,3]. Another approach to fabricate 1D PC is anisotropic etching of deep and narrow

grooves in (110) Si using an alkaline solution [4]. The periodical structures obtained in this way we call grooved silicon (gr-Si). Fig.1 shows the SEM image of a grooved Si structure obtained by this method. It consists of thin silicon walls and air gaps between them. Contrary to the multilayer structures where the refractive index periodically varies along the vertical axis, the refractive index of gr-Si varies in the horizontal direction, so it acts as 1D PC for the light propagating in the wafer plane. This property makes gr-Si as an attractive material for silicon integrated optics. The technique of deep anisotropic etching is compatible with silicon processing and allows to form a number of different microphotonic elements. Among them are micro-cavities, coplanar wave-guides, optical filters, modulators, etc. The air space of the grooves combined with the high index contrast enables to fabricate composite PCs by filling the grooves with various substances.

Apart from the PBG structures, gr-Si forms optically anisotropic media for the light propagating in the vertical direction. Previously it has been shown that the effective media of macroporous silicon with a regular pattern of deep channels (2D PC) acts as a positive uniaxial crystal with the optical axis oriented along the channels [5]. This is an example of the so-called anisotropy of shape [6]. According to the theoretical prediction gr-Si should work as a negative uniaxial crystal in the spectral range where $\lambda \gg A$ (A is the "lattice" constant of the periodic structure). Its optical axis is perpendicular to the Si ribs, i.e. lies in the wafer plane.

The present work has been focused on the studies of the periodic structures of gr-Si. The goal was to develop PBG structures and birefringence media in the middle IR range. The PBG was detected experimentally under the side illumination of the wafers, and the birefringence was measured under the normal incidence of polarized light.

2. Sample fabrication

Anisotropic etching of (110) silicon wafers with resistivity of 100 Ohm cm has been performed in 44% aqueous solution of KOH at 70°C for 1-4 hours, depending on the required depth.

The thermal oxide of 0.8-0.9 μm thick was served as a mask during the etching of the grooves. Standard photolithography was used to form the patterns. The photomask included the device structures consisting of alternating bright and dark stripes of equal width D_0 . To provide a precise alignment of the stripes with $\langle 111 \rangle$ direction on (110)

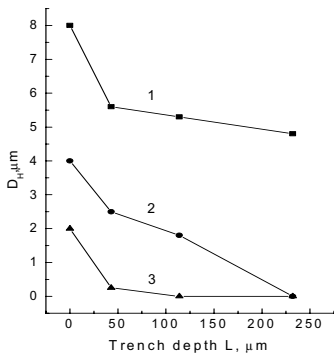


Figure 2. Thickness of silicon walls, D_s , vs depth L of anisotropic etching for device structures of different types. D_0 : (1) 8, (2) 4, and (3) 2 μm .

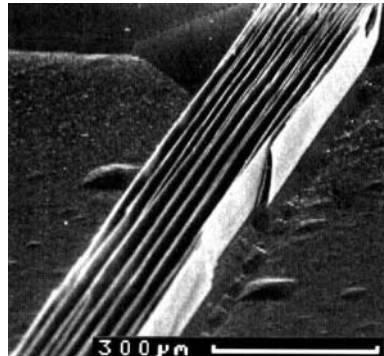


Figure 3. SEM image of 4 μm period structure with deep grooves.

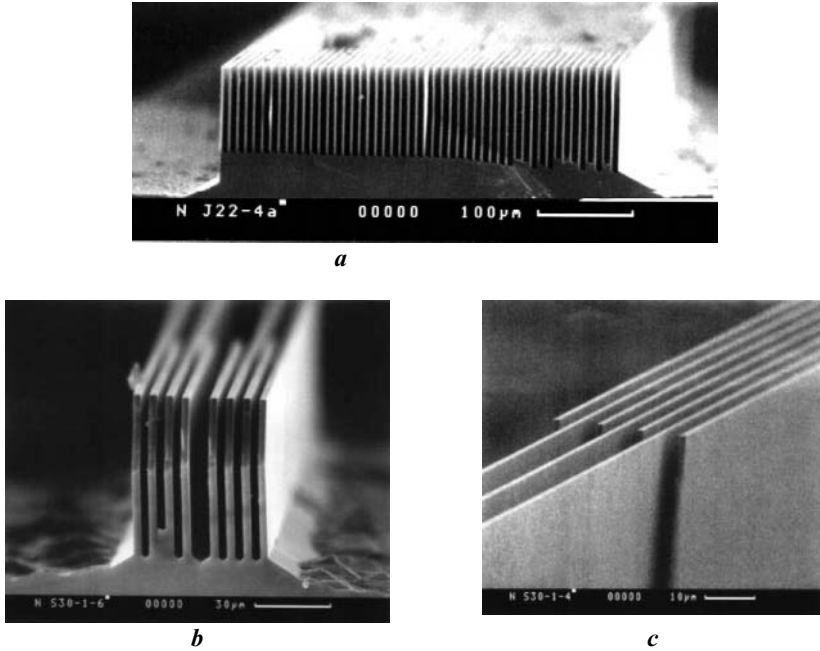


Figure 4. Examples of 1D periodic structures obtained by wet anisotropic etching: a bar of 50 period grooves (a), micro-cavity (b) and inter-digital (c) structures.

wafer plane, a preliminary deep etching of special alignment marks has been used [7]. It should be noted that the fabrication of structures with small-period is constrained by the lateral etching ("undercutting") and by the mechanical strength of the silicon walls. The walls are thinned both through the undercutting of the photoresist in the buffer etchant (at the stage of window opening in the oxide) and due to the certain deviation from verticality during deep etching of silicon. As a result, Si walls were retained only upon the etching to the depth of $<50\mu\text{m}$ for the structures with $D_0=2\mu\text{m}$ (period $A=4\mu\text{m}$), and to the depth of $<150\mu\text{m}$ for $D_0=4\mu\text{m}$ ($8\mu\text{m}$ periodicity). This is seen in Fig. 2, which demonstrates how the thickness of silicon wall depends on the initial width D_0 of the dark stripes in the photomask. For the structures with the thinnest walls, we observed the partial wall destruction and the flexure, leading to the adhesion of adjacent planes (Fig. 3). We were able to fabricate structures with small periods (up to $3\mu\text{m}$) and various number of periods as well as the micro-cavities and the inter-digital structures (see Fig. 4a,b, c).

3. Gap Map

The PBG position and width depend on the ratio of the optical thicknesses of layers with high and low refractive indices, which is the filling factor D_{Si}/A in our case. Constructive information can be derived from the so called "gap maps".

In order to draw this map the calculations of PBGs were performed by the characteristic-matrix method [8] using the following values of the refractive indices: $n_{\text{Si}}=3.42$ and $n_{\text{air}}=1$. The PBG regions for 7 period structures were determined as the values of λ with reflection $R>99\%$. The gap map of 1D PC based on gr-Si in unit-less coordinates is shown in Fig.5. The analysis shows that the largest relative width of

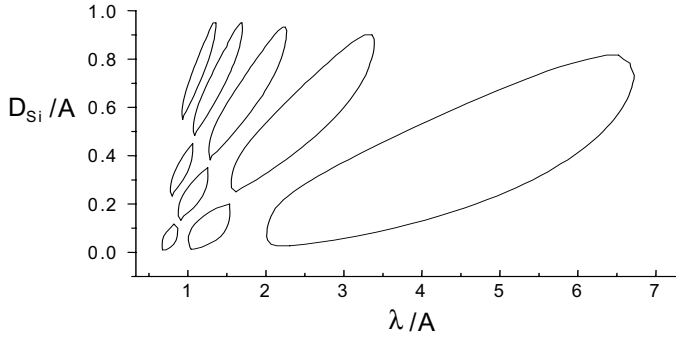


Figure 5. Gap map calculated for 1D PC based on periodically grooved silicon.

PBG, $\Delta\lambda/\lambda_0=0.73$, can be obtained at filling factor of $D_{Si}/A=(n_{Si}/n_{air}+1)^{-1}$ which corresponds to the optical thickness of $n_{Si}D_{Si}=\lambda/4=0.226$. Here $\Delta\lambda$ is the width of the stop band and λ_0 is the centre of its wavelength region.

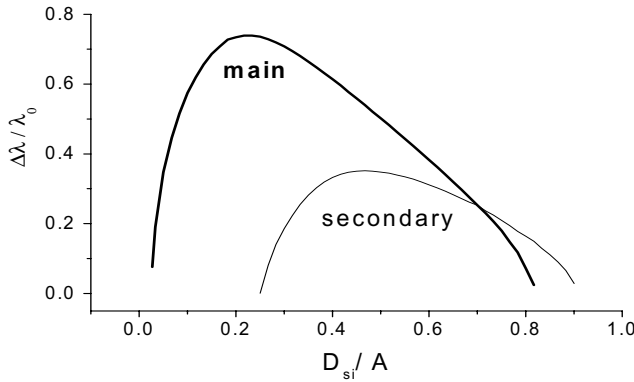


Figure 6. The dependence of the stop band width versus the filling factor for two lowest PBGs.

Apart from the main PBG, the PC has several wide secondary stop bands. It should be noted that the maximum width of the second gap corresponds to the larger relative thickness of Si walls D_{Si}/A , compared to the main PBG (Fig. 6). The wide secondary band gaps obtained are of particular interest since they allow to use an additional shorter wavelength range without changing the lattice constant A .

4. FTIR measurements

The optical properties of the grooved Si structures were studied with a Digilab FTS-60 A and Digilab FTS 6000 Fourier spectrometers in the spectral range of 450-6000 cm^{-1} and 700-7000 cm^{-1} with 8 cm^{-1} resolution. FTIR measurements of PBG in reflection mode have been performed in conjunction with a UMA 500 infrared microscope. IR measurements of grooved Si are critical to the direction of the light propagation through the whole structure. The IR beam should not be shaded by other parts of the structure (see [9] for details). The geometry of the latter experiment is presented in Fig.7.

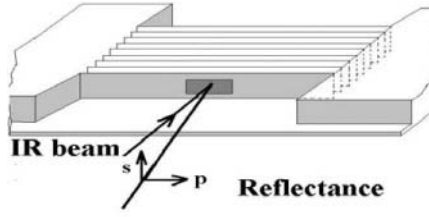


Figure 7. Schematic of FTIR reflection measurements of PBG.

The single beam reflection signal from the gold-coated glass has been used as a background. The example of spectrum obtained in such a manner is shown in Fig. 8a. This spectrum demonstrates the wide stop bands of high reflection and the corresponding regions of low transmission. The spectrum is in a good agreement with the simulation (Fig.8b)

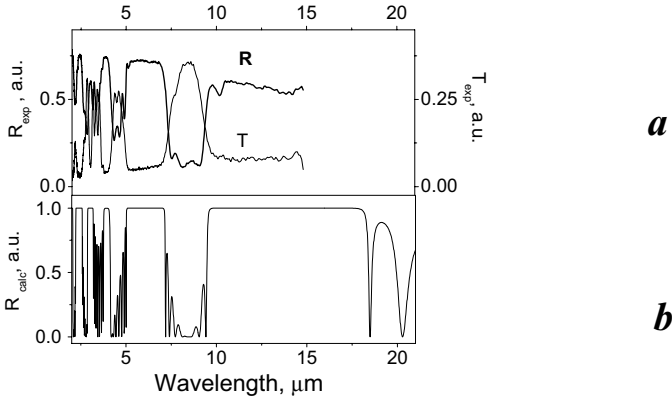


Figure 8. Experimental (a) and calculated (b) spectra of 1D PC based on grooved Si (period of structure $A=3\mu\text{m}$, number of periods $m=7$).

5. Birefringence

The anisotropy of shape in optically isotropic crystal is caused by the presence of cavities with the preferential orientation along one of the directions. The optical axis of macroporous 2D photonic crystal is perpendicular to the wafer plane, and this does not suit for discrete devices. A more convenient structure, based on mesoporous Si produced by anodizing of (110) Si was proposed in [10]. The optical axis of this artificial crystal lies in the wafer plane, which is more relevant to the practical purposes, although the anisotropy of such a crystal is relatively small.

To study birefringence in gr-Si a special structures with large grooved area were designed and fabricated. The grooves with the period $A=4, 5$ and $6\mu\text{m}$ for different samples had vertical walls of the thickness $D_{\text{Si}} = 1.0, 1.2$ and $1.4\mu\text{m}$, respectively, alternated with air gaps of $30\mu\text{m}$ depth. To enhance the mechanical strength of thin Si walls, solid Si strips with width of $20\mu\text{m}$ were left between the $400\mu\text{m}$ long grooves. Owing to the specifics of anisotropic etching, the width of these strips increased with depth, and reached the value of $120\mu\text{m}$ near the interface with the Si substrate.

The schematic of the experiment and the sample structure are shown in Fig.9. The electric vector of the incident light was oriented either parallel $E_{\parallel}$ or perpendicular $E_{\perp}$ with respect to the grooves. This corresponds to the propagation inside the crystal of the ordinary (o) and the extraordinary (e) waves, respectively.

In Fig.11 one can see the reflection spectra of one of the samples. These spectra differ significantly for $E_{\parallel}$ and $E_{\perp}$ polarisations, manifesting that $n_e < n_o$. The effective refractive indices for o and e waves were found from the neighboring extremes

$$n_{o,e} = \frac{10^4}{4l(\nu_1 - \nu_2)}$$

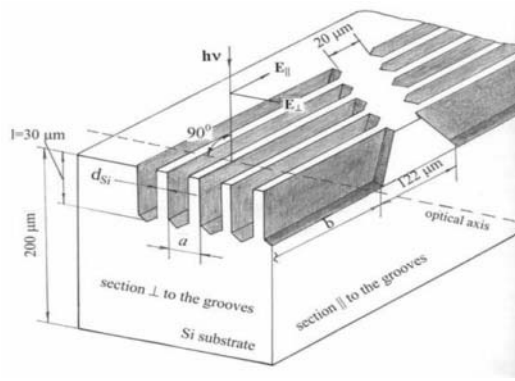


Figure 9. The sample structure and the scheme of optical measurements in polarized light.

To find the anisotropy of the refractive indices, Δn , the classic geometry with a diagonal polarisation was used: polarizer P before the sample has been rotated by 45° to the optical axis of the crystal, and the analyzer A , situated after the sample, was oriented either parallel $A \parallel P$ or perpendicular $A \perp P$ to the polarizer (Fig.10).

The transmission spectra, obtained in diagonal geometry for the same sample, are shown in Fig.12. The spectral position of the maxima for $A \perp P$ coincides with positions of minima for $A \parallel P$. This is due to the phase shift by π for e and o waves at the exit from the grooved layer, which enables to find $\Delta n = \frac{10^4}{2l(\nu_1 - \nu_2)}$.

The values of n_o , n_e and Δn found for the samples with various A are summarized in the Table. The values calculated with simple expressions for the effective dielectric

constants [6]: $\epsilon_{\perp} = \frac{\epsilon_1 \epsilon_2}{f_1 \epsilon_2 + f_2 \epsilon_1}$ and $\epsilon_{\parallel} = f_1 \epsilon_1 + f_2 \epsilon_2$ are also listed in this

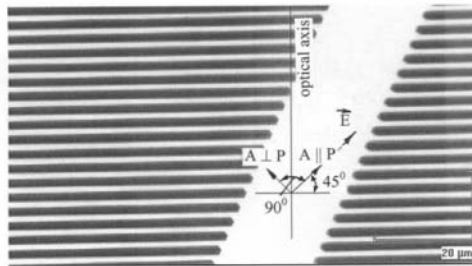


Figure 10. Top view of the sample and orientation of polarizer and analyzer with respect to the grooves under anisotropy characterization

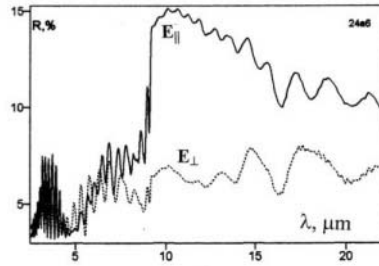


Figure 11. The reflection spectra of sample with $A=6\mu\text{m}$ for two polarizations $E_{||}$ and $E_{\perp}$.

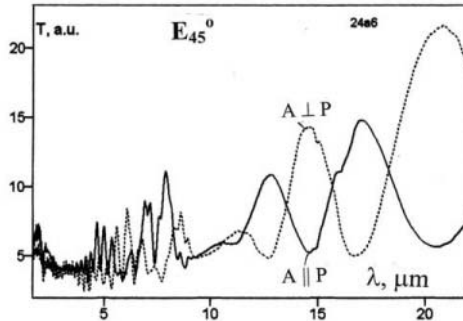


Figure 12. Transmission spectra of sample with $A=6\mu\text{m}$ for diagonal polarization geometry.

Table. Here $f_1 = 1 - p = \frac{D_{Si}}{A}$, $f_2 = \frac{D_{air}}{A} = p$ and ϵ_1, ϵ_2 are the dielectric constants

for Si and air, respectively. The analysis of these formulas shows that our structures with high porosity $p = D_{air}/A = 0.75-0.77$ are not the best for obtaining the largest value of Δn . Though, these structures demonstrate a very large $\Delta n \approx 1.5$, which is practically independent from λ in the spectral range of $\lambda > 12 \mu\text{m}$. The experimental values of the refractive indices and an anisotropy are larger than the calculated data. The reason for that arise probably from the fact that the approximation $\lambda \gg A$ is not valid for the spectral range under investigation. The infiltration of the grooves with a nematic liquid crystal with an average refractive index $n_{LC} = 1.6$ reduces Δn of the composite down to ≈ 1 .

Table. Geometric parameters of grooved Si samples, their effective refractive indices and anisotropy

Sample №	$A, \mu\text{m}$	$D_{Si}, \mu\text{m}$	p	calculated			experimental			
				n_o	n_e	$n_o - n_e$	n_o	n_e	$n_o - n_e$	Δn
24a4	4	1	0.75	1.92	1.14	0.78	2.9	1.4	1.5	1.4
24a5	5	1.2	0.76	1.89	1.13	0.76	2.8	1.3	1.4	1.5
24a6	6	1.4	0.77	1.86	1.12	0.74	3.0	1.5	1.5	1.6
24a6LC*	6	1.4		2.16	1.77	0.39	-	-	-	1.0

It should be noted that the effective Δn of gr-Si samples is larger than that found for macroporous silicon ($\Delta n = 0.366$ [5]) and substantially larger than Δn for the well known natural crystal CaCO_3 $\Delta n = 0.172$. The important advantage of the grooved Si, compared to the macroporous Si, is in-plane position of the optical axis. A proper choice of the grooved Si porosity ($p = 0.325$) should increase Δn even more.

6. Conclusion

Periodically grooved Si structures with different lattice constants (3-16 μm) and different geometry were designed and fabricated. These structures can serve as 1D photonic crystals. The possibility to obtain the main PBG in the middle IR range (centred at $\lambda \approx 13 \mu\text{m}$) has been demonstrated both experimentally and theoretically. The shift of PBG position toward the near-IR spectral range is limited by the mechanical strength of thin silicon walls. The solution to this problem can be found from the exploitation of the wide secondary band gaps.

Moreover, gr-Si exhibits optical anisotropy of shape. The experimental studies of birefringence have demonstrated that periodically grooved Si structures possess an extremely large difference in the effective refractive indices for the ordinary and the extraordinary rays. This might be of a great interest for fabrication of different IR optical elements.

Acknowledgments

The authors acknowledge the INTAS project 01-0642 and Russian Programms "Physics of Solid State Nanostructures" and "Optics and Laser Physics" for the financial support of this work.

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DIODE SHOTTKY SYSTEMS ON Al – NANOSILICON INTERFACE LAYER - Si

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Abstract

The peculiarities of formation of an intermediate nanolayer between metal and semiconductor in Al–(SiO₂)–n-Si, Al–p⁺–n-Si, Al–silicide–Si structures and its influence on parameters and characteristics of Schottky diodes (SD) are analyzed. It is shown, that pulse laser irradiation of the SD transformed interface layer in the Al–nanostructured layer–Si structures and corrected the SD characteristics.

1. Introduction

The Al-n-Si, Al- silicide-Si metal - semiconductor contacts (MES) with Schottky barrier (SD) and ohmic contacts Al-n⁺-Si are basic building blocks of modern silicon superlarge integrated circuits (SLIC). In real contacts due to the diffusion processes and solid state reactions between metal and semiconductor on the MES structured intermediate nanolayer is formed, parameters of which can considerably differ from those of materials in contact. Therefore, the electrophysical characteristics of SD and ohmic contacts are determined by physicochemical properties of the interface and depend on constructive and technological factors.

The urgency of the issues of experimental investigation of the electronic processes occurring in nanodimensional structures with SD, of development of theoretical quantum-mechanical models of charge transport in such structures is stipulated by a transition to submicron technology of SLIC, and by application of radial methods (ionic implantation, laser treatment, MBE) to technological processes [1-6].

In the given paper a review of the peculiarities of formation of a phase composition and of the interface structures at thermal treatment, laser irradiation and other technological processes is made. The influence of the phase composition and interface structure on parameters of the interface (e.g. surface electronic states (SES), contact potential difference), current-voltage (I-V) and the C-V characteristics of MES is analyzed. Mechanisms of charge transition in the classical structure of MES with Schottky barrier and development of dimensional quantum-mechanical effects at charge carrier transfer through nanodimensional interface are also considered.

2. Peculiarities of formation of the interface in the Al-Si, Al-silicide-Si contacts

2.1. LOW TEMPERATURE PROCESSES OF THE INTERFACE FORMATION

The thickness of the interface d_0 depends on preprocessing of silicon surface, a deposition technique and properties of metal [7, 8]. The investigation of the Si subsurface layer structure by slow electron diffraction (SED) in the Au-Si contacts during the metal deposition shows, that amorphousation of the metal-Si interface is already observed at room temperatures. The change of the Si Auger peaks points out the formation of a chemical bonding of the Si atoms with those of metal. This process is accompanied with a rupture of the Si-Si covalent bondings ($E_b \sim 2$ eV) and makes catalytic effect on the process of the Si oxidation. The experimental results reported in [9, 10] indicate, that for considerable blending of metal atoms and those of Si on the interface, the minimum critical thickness of metal layer amounts to 3-4 monolayers. The thickness of the amorphous metastable interface d_0 is of the order of 1.5 nm. The similar d_0 values are obtained for the Al (Ni, W) - Si MES using standard technological methods of surface preparation before the deposition of metal: d_0 ranges from 0.3 up to 3 nm with the interface dielectric permeability (ϵ) being equal $2 \div 3.5$.

The doping of a surface with metal (Cu, Sn, Ni) originating from etching and rinsing solutions results in the d_0 varying from 1.8 to 4.5 nm, while ϵ changes from 1.5 to 3.7.

Low temperature formation of the silicide interface in the Pt-Si structures was investigated by photoelectronic spectroscopy (PES) [10]. An increase of the Pt film thickness from 0.14 to 5 monolayers on the Si surface (111) is followed by the shift of a 3s-line of silicon approximately by 1 eV towards a Fermi level E_F . It also confirms the rupture of the Si - Si bondings and reaction of Si with Pt. The lines of the Si internal atomic level of 2p and that of Pt (4f) are shifted towards larger and smaller values of a bonding energy, respectively. The fraction of silicon appears to be present in platinum even when the grade of platinum covering of a silicon surface is greater than 40 [8, 10].

The interface parameters for the most metal-silicon contacts, determined from the SD (C-V)- characteristics vary in limits from 5 to 30 nm.

2.2. THE INTERFACE FORMATION AT ELEVATED TEMPERATURES

The formation of nanostructural (nsSi) interface in the Al-Si contacts at elevated temperatures ($T \sim 400\text{--}550^\circ\text{C}$) occurs owing to floatable penetration of the components and due to solid state epitaxial growth of the p^+ -Si layer, doped with aluminum, from a supersaturated solid solution of Si in Al at the MES cooling [7, 11]. Floatable penetration of Si into Al takes place at $T \geq 400^\circ\text{C}$. On the initial stage silicon locally diffuses into Al through local defects in the layer of residual SiO_2 , thickness of which d_{SiO_2} is of 10-15 Å, and mainly through the grain boundaries of the Al polycrystalline film. Aluminum interacting with SiO_2 recovers silicon. Due to baking between Si and Al formation of the 2-20 nm thick transition oxide of complex composition of $\text{Al}_2\text{O}_3 + \text{SiO}_2$ becomes possible. Moreover, a number of the Al inclusions in a shape of needles can penetrate the substrate.

In order to restrict floatable penetration up to $T \sim 550^\circ\text{C}$ into the Al film Si is introduced at simultaneous deposition of Al and Si, selecting the Si content Si in Al to be at a level of 1%.

Solid state epitaxy of nsSi arises at a temperature cycling in the technological process and is caused by diminution of the Si solubility in Al at temperature decrease after the MES baking.

The thickness of the p^+ -Si layer is of about 20-40 nm. The concentration of Al as of acceptor impurity in p^+ -Si at fast cooling can correspond to a limit of the Al solubility in Si at $T = 500^\circ\text{C}$ and amounts to 10^{18} - 10^{19} cm^{-3} [11]. At a repeated temperature cycling of MES up to the temperatures of 200-300°C the thickness of nsSi increases approximately by 4 nm, and the acceptor density in p^+ -Si decreases down to $7 \times 10^{17}\text{ cm}^{-3}$.

Introduction of Si in high concentration (0.6 g/mole) into the Al film stabilizes thickness of p^+ -Si at a level 20 nm, which is preserved at a low temperature cycling [7].

The Auger-analysis of the typical profiles of Al, Si, O, B and C at a level-by-level etching with the Ar^+ ions Al (70 nm) - p^+ -Si reveals the presence of interaction between Si and Al, remained sections of SiO_2 , and also the possibility of autodiffusion of boron from silicon into the interface.

The investigations of the phase formation processes in the Al-silicide-Si interfaces at high temperatures ($T \sim 200$ - 300°C) points the presence of no more than three phases of silicide, formed between metal (Me) and silicon: Me_2Si , MeSi , MeSi_2 in MES [11, 12]. The phase enriched with metal (Ni, Pt, Pd) is formed at $T \sim 200^\circ\text{C}$, (for Co - $T \sim 350^\circ\text{C}$). The kinetics of the Me_2Si and MeSi phase growth is described by the parabolic law with an activation energies of about 1.5 eV and 1.6 ± 2.5 eV, respectively. The transition from the Me_2Si phase to that of MeSi takes place at $T > 350^\circ\text{C}$ (for PdSi $T > 700^\circ\text{C}$). This process is accompanied with variation of mechanical tensions at the Me-Si interface. In the Ni-Si structures of tensions of stress in Ni_2Si transform into those of strain in NiSi. For Pt and Pd monosilicide is a final phase formed at the interface for Ti, Ro, Gf - first.

Dissilicide phase of MeSi_2 is formed at $T \geq 600^\circ\text{C}$ (CrSi_2 at 450°C) and is characterized by activation energy of the process from 1.7 to 3.2 eV. It is the first and the one growing phase on MES for refractory metals (Cr, Mo, V, Ta). Silicides of VSi_2 , WSi_2 at the early stage of reaction show a linear dependence of the interface thickness on the process duration. Nickel, cobalt and iron silicides grow epitaxially on the Si substrates, which allows for good agreement of the crystalline lattice parameters of the adjoining phases.

In the Al (1500 nm) -PtSi (140 nm) -Si contacts an intermetallic compound of PtAl_2 is formed owing to the interaction of an aluminum film of metal padding of an integrated circuit with silicide [11]. At protracted storage the initial MES is transformed into the Al-PtAl₂-Al-Si structure. To prevent this process one uses multilayer structures such as Al (150 nm) -W (100 nm) -Ti (50 nm) -PtSi (60 nm) -n-Si. The heat treatment of the given structure at $T=450^\circ\text{C}$ during 30 minutes promotes interaction of Al and W over the contact area and the one of Al and Ti is stimulated on the MES perimeter due to tensions nearby the Si- SiO_2 interface. At $T \sim 500^\circ\text{C}$ there is a local penetration and point interaction between Al and PtSi on the edge of the contact. As the result of the diffusion of aluminum in silicide and of silicon through W_xAl_y , Ti_xAl_y layers on the MES perimeter the $\text{Al}_x\text{Pt}_y\text{Si}_z$ ternary compound is formed, while in Al a solid solution of Si:Al exists. The formation of the Si precipitates and local sections of Al, containing Si follows the decomposition of the ternary compound. Such MES is characterized by structural inhomogeneity over its area and nonuniformity of the corresponding electrical parameters.

2.3. FORMATION OF THE INTERFACE AT LASER IRRADIATION OF MES.

The effect of a laser radiation on MES has thermal character [13]. A metallographic research of morphology of the surface of structures Al - Si at their level-by-level etching display, that the physicochemical processes in MES at an pulse laser irradiation (PLI) are similar to processes at a thermal bakeout. For structures Al-n-Si, Al-p⁺-n-Si, Al-SiO₂-n-

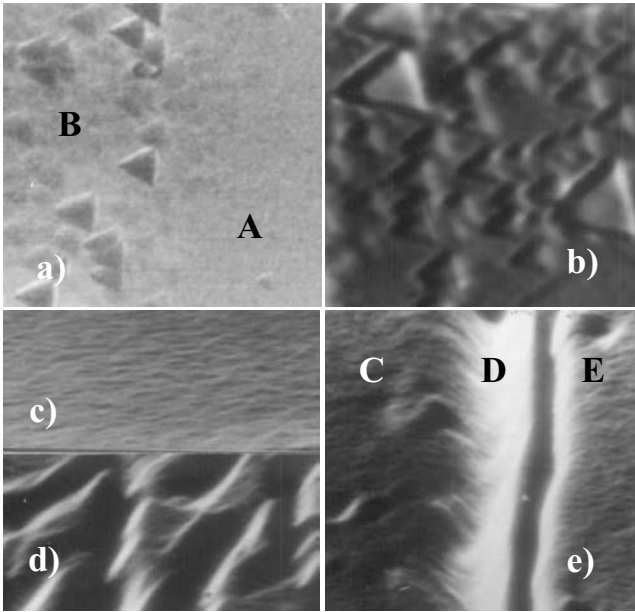


Figure.1. The silicon surface morphology after etching of aluminium in MES Al-SiO₂-n-Si (a, b) and Al-p⁺-n-Si (c, d, e). a, c, e) $I_0=85 \text{ kW/cm}^2$; b, d) $I_0>95 \text{ kW/cm}^2$. The image in raster electronic microscope; c, d, e - at a mode of y-modulation. Magnification: a, b) - $\times 4500$; c, d, e) - $\times 15000$.

contacts Al-SiO₂-n-Si the density of the packaging defects outside SD (fig.1a, B) increases. In integrated structures formed in windows SiO₂, there are separate defects (fig. 1e, c) on perimeter of contact. A preferred direction interdiffusion Al and Si is the area D at the Al - Si interfaces near SiO₂ (fig.1e, e).

At optimal conditions PLI $I_0 \sim 80-95 \text{ kW/cm}^2$ the surface Si is homogeneous, and defects of packaging it do not detect. At $I_0 \sim 95-115 \text{ kW/cm}^2$ the processes of the diffusion Si on borders of aluminium grains (fig.1d) are boosted. Preferred directions of the diffusion are the points of linking of three and more blocks Al. At $I_0 \sim 105-120 \text{ kW/cm}^2$ the processes of the Si diffusion on all area of grains Al with a consequent deposition of an epilayer Si from a supersaturated solution Si-Al are made active. In a fig. 2a the presence of an acting epilayer Si (F) of micron thickness in structures Al-p⁺-n-Si is shown in the area of aluminium contact (H - demarcation Al-SiO₂) after an etching of aluminium, and its absence outside SD (J). At $I_0 > I_c$ PLI of an interface Si-SiO₂ in subsurface layer Si the system of spatially oriented photoinduced point defects (J) is formed, and in contacts Al-

Si, Al-TiW-Pt_xSi_y-Si there is a threshold value of intensity PLI $I_c \approx 95-105 \text{ kW/cm}^2$ [14, 18].

In subsurface layers Si after etching Al reference are watched triangular etch pits, for orientation of a plate (111), which are stipulated by of the structures defects of a substrate (fig.1a, b). Dominant are the defects of packaging and exits of lines of a dislocation pile-up (fig.2c). PLI of contacts Al - Si at magnification I_0 from 60 up to 95 kW/cm^2 reduces in complete vanishing of defects in subsurface layers Si under a Al film on a demarcation metal - semiconductor as in MES with a thin layer of a dielectric SiO₂ (fig.1a, section A), and with p⁺-Si by a transition layer (fig.1c). However in

SiO_2 -n-Si defects outside SD fade, but transition nanolayer of defects on Si (fig.1b) under aluminium contact occurs. Thus the interaction between metal and semiconductor is implemented in a solid phase.

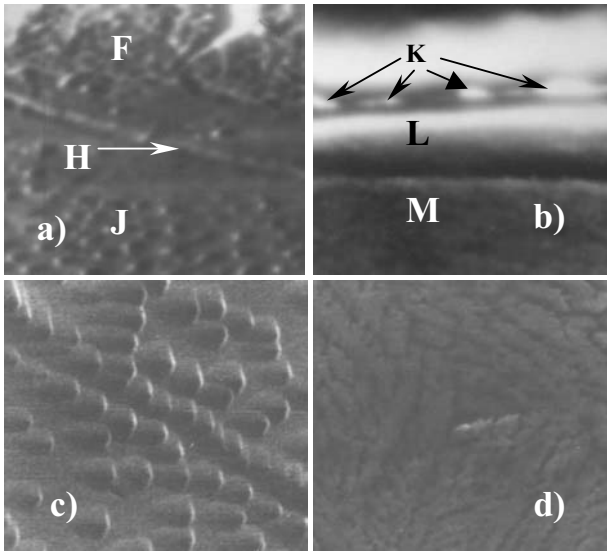


Figure 2. The image of an intermediate layer (a, b) and structural defects (c) on a surface Si in MES Al-Si (a, b, c), and structured intermediate silicide layer in MES Al-TiW-Pt_xSi_y-Si. a, b) $I_0 < I_c$; c, d) $I_0 > I_c$. The image in raster electronic microscope. Magnification: a) $\times 1000$; b) $\times 10000$; c, d) $\times 4500$.

irradiation of contacts Al-TiW-Pt_xSi_y-Si stipulated the formation of a structured layer silicide (fig.2d) on an acting epilayer n-Si on a silicon substrate.

Research transversal having chopped off structures Al-p⁺-n-Si (fig.2b) has shown presence of the transition layer of a solid solution Al-Si (L) between Al (K) and Si (M), formed owing to thermal handling of investigated structures and consequent PLI. Depending on a condition PLI the thickness of a transition layer varies in limits from 200 up to 1200 nm, that is compounded with results of an electroetching of structures Al-Si [18]. At $I_0 > 120\text{-}130 \text{ kW/cm}^2$ in the transition layer MES Al-Si dislocations pile-up and structured systems of defects oriented according to a crystallographic orientation of a silicon substrate are formed (fig.2c). The similar

2.4. PHYSICAL PATTERNS OF THE MES INTERFACE FORMATION.

At the elevated temperatures of the Si substrate ($T > 400 \text{ }^\circ\text{C}$) the formation of two-dimensional (2D) structures consisting of metastable interface is observed. At large surface coverings the 3D-islands of metal are formed [8]. The structured arranged 3D-phase passivates the Si surface to the interaction with oxygen.

A few mechanisms of a low temperature reaction accompanied with a formation of an amorphous or silicide-like membrane between metal and silicon are considered to be theoretically possible. In Ref. [11] it is supposed, that the rupture of the Si-Si covalent bondings is caused by interstitial atoms of metal. Confirmation of the given hypothesis is the experimentally detected formation of silicide in the reactions with metals, atoms of which are capable to diffuse on the interstices of Si. But, in this case, a necessity of critical thickness of a metal layer for activation of the interphase interaction becomes unclear.

The model of the metal free electron screening of the valence bonds of semiconductor atoms partially solves the given conflict. The authors [19] assume, that low temperature

formation of the intermediate nanolayer is typical of all semiconductors with the band gap $E_g \leq 2.5$ eV or with $\epsilon \geq 8$.

On the basis of the investigations of solid state interaction of a chromium film of different thickness, deposited on atomically pure surface of Si, with the layer of natural oxide, the hypothesis on influence made by the tension on the MES interface on interphase blending of Si and metal is proposed [20]. By SED and electronic Auger-spectroscopy (EAS) it is established, that the beginning of interaction between Cr and Si occurs simultaneously with formation of the Cr film with the thickness d_0 of 0.3 ± 0.6 nm and volume-like electronic structure. At $d > 0.6$ nm a metal film exhibit elastic properties, with $d_0 \sim 1, 5-1, 8$ nm being achieved, silicide formation is completed and further the amorphous film of metal is formed.

It is possible to explain the formation of the transition layer in MES at PLI in structures Al–Si and Al–silicide–Si with the help of a physical analog of diffusion processes in a solid phase boosted by thermoelastic tension in contact layers of structure (fig.2c,d) [17, 18].

According to estimates, optimal condition of a heating of a demarcation Al–Si (up to temperature $T \approx 550$ °C, that does not exceed temperature of an eutectic of the Al–Si system $T_e = 577$ °C) is carried out at a radiant intensity $I_0 = 95$ kW/cm². In the contact layer of silicon by thickness 5 microns the temperature gradient is about $1.6 \cdot 10^4$ K/cm, and near unirradiated surface of silicon - 10^3 K/cm. As the linear expansion coefficients Al and Si differ in 10 times ($\alpha_{Al} = 23.1 \cdot 10^{-6}$ K⁻¹, $\alpha_{Si} = 2.33 \cdot 10^{-6}$ K⁻¹), at PLI on the surface Al and in a contact layer Si there are elastic tension of widening, and in Al contact area - tension of squeezing. In effect the crystalline lattices Al and Si on boundary MES are deformed, that reduces in boost of the diffusion of boundary atoms Al in Si, and also atoms Si from depth of a chip in contact field Si. Thus it is necessary to expect magnification of a diffusivity Al in Si at PLI at the expense of increase of deformation potential of a crystalline lattice. Such processes promote a relaxation of dot crystal defects Si (vacancies and interstitial atoms), defects of packaging, detrusion of lines of dislocations, diminution of the sizes of clusters in Si contact area. As is known, the effective thermal bakeout of imperfections in chips is carried out at temperatures much below than temperature of a melting (T_m): vacancies - $T = 0.2T_m$, interstitial atoms - $0.05T_m$, dislocations - $0.5T_m$.

3. Electrophysical properties of the contacts and characteristics of SD with the intermediate layer between metal and semiconductor

3.1. PHYSICAL MODEL OF A CHARGE TRANSPORT IN SD SYSTEMS ON Al - NANOSILICON INTERFACE LAYER – Si

Correlation between electrophysical and physical properties of the contact with parameters of metal, interface and semiconductor as well as computational methods of the interface parameters on the basis of experimentally measured (I-V) and C-V characteristics were fundamentally surveyed in [7, 21]. The current transfer through the interface (fig.3a) can be determined by emission of charge carriers over the barrier of space charge region (SCR) (1⁰, 1), carrier tunneling through thin enough SCR (2), the generation-recombination processes with participation of levels in SCR (3, 4), tunnel-resonance transition of carriers through local levels in SCR, and also generation-recombination of carriers in quasineutral region of semiconductor (5). At the presence of a tunnel-transparent dielectric transition

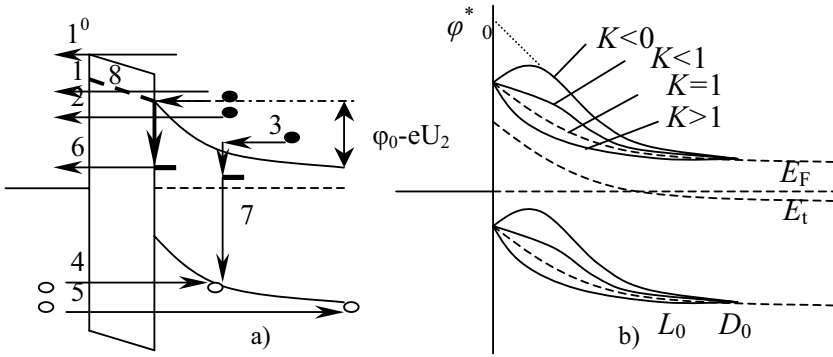


Figure 3. The mechanisms of charge transfer in MES Al-SiO₂-n-Si (a), and band diagram of the MES with intermediate p⁺-layer (b).

layer a current through surface levels, i.e. electronic states at the SiO₂-Si interface (6), becomes essential. While for the extended interface diffuse-drift current transfer over the energy barrier of a transition layer, and a current brought about by "uneven" mechanism, namely by multistage resonance tunneling through a spatial network of levels at the interface play the major role.

According to the theory [7], the Schottky layer is implemented on a metal-semiconductor in limits

$$2,3kT < \phi_0 < E_g - 2\mu + (3/2)kT \ln(m_n^* / m_p^*), \quad (1)$$

where E_g is the forbidden gap of the semiconductor, μ is distance from Fermi level to the bottom conduction bands, m_n^* and m_p^* are effective masses of electrons and vacant holes electron sites accordingly.

The potential distribution $\phi(x)$ and electric field strength $E(x)$ in the field of a space charge of the semiconductor is determined as a result of the solution of a Poisson equation and for a random distribution of impurities in a semiconductor looks like:

$$\phi(x) = (e^2 n_0 / 2\epsilon\epsilon_0)(L_0 - x)^2, \quad (2)$$

$$E(x) = -(en_0 / \epsilon\epsilon_0)(L - x). \quad (3)$$

At $x=0$ we shall receive

$$\phi_0 = (e^2 n_0 / 2\epsilon\epsilon_0)L_0^2; E_0 = -(en_0 / \epsilon\epsilon_0)L_0; L_0 = (2\epsilon\epsilon_0 / e^2 n_0)^{1/2}. \quad (4)$$

If the density of the active carries charge is equal Kn_0 in the area from $x=0$ up to l (where $K=p^+/n_0$, p^+ - impurity concentration in p⁺-Si layer), and it is equal n in the area from $x=l$ up to D_0 , for such contact to a transition layer we shall receive effective values of parameters:

$$\begin{aligned} \phi_0^* &= \phi_0 + (e^2 n_0 / \epsilon_2)l^2(1-K); D_0 = \sqrt{L_0^2 - l^2(1-K)}; \\ E_0 &= -(en_0 / \epsilon_2)[D_0 - l(1-K)]. \end{aligned} \quad (5)$$

Parameter K receives a value $K < 0$ if the sign of charges in areas from $x=0$ up to l and from $x=l$ up to D_0 will be different. Physically it means shaping a potential quantum hole of width l in a transition layer between metal and semiconductor (fig.3b). Height of a potential hill at $U=0$ is determined by a maximal value of potential

$$\phi_{\max}^0 = (2\pi e^2 n_0 / \epsilon_2)(D_0 - l)^2(1-K^{-1}) = (1-K^{-1})\{[l + (l^2/L^2)(1-K)]^{1/2} - l/L_0\}^2. \quad (6)$$

The external voltage applied to MES, is redistributed between a transition layer (U_1), region of the space charge (U_2) and in the volume of the semiconductor (U_b). It reduces in change φ_0 or φ^*_0 up to $\varphi_0 - eU_2$ or $\varphi^*_0 - eU_2$ and respective alteration of SCR width in the semiconductor.

The complete analysis of probable mechanisms of charge transfer in MES in view of currents through surface electronic states on contact and deep levels in the transition layer and SCR of the semiconductor is carried in [4, 7]. Let's mark, that for development of size effects in structures Al – nanosilicon transition layer - Si most essential are the tunnelly-resonance currents, and also currents of majority carriers through discrete levels in the extended transition layer.

The current-voltage characteristic MES at small direct and reverse voltages stipulated by currents of majority carriers of the charge in an allowed band of a dielectric extended transition layer looks like:

$$I = I_s \exp[(e/kT)\sqrt{(U_1^0 - U_1)/\varepsilon_1 d}] \{1 + [dv_n / 4u_n (U_1^0 - U_1)] + \exp[e(U_1^0 - U_1)/kT] \exp[(e/kT)\sqrt{e(U_1^0 - U_1)/\varepsilon_1 d}]\} [\exp(eU/kT) - 1]. \quad (7)$$

Here $I_s = SeAT^2 / [1 - dv_n / 4u_n (U_1^0 - U_1)]$; A is Richardson constant for metal; d is thickness of a transition stratum; u_n - movability of electrons in a dielectric stratum; U_1^0 is voltage drop in the transition stratum at $U=0$. Direct and the back current at major displacements restricted to a space charge.

The charge transfer through discrete levels in the transition layer depends on the degree of a level occupation. At feeble filling the equation at a current-voltage characteristic record as [7]:

$$I = I_s \exp[(eU_1/kT)(2\Delta/d)] [\exp(eU_1/kT) - \exp(-eU_2/kT)]. \quad (8)$$

At considerable filling of a level:

$$I = I_s \exp[(-eU_1/kT)(\Delta/d)] [\exp(eU_2/kT) - \exp(-eU_1/kT)]. \quad (9)$$

The saturation current I_s is determined by expression

$$I_s = Sf(U) \{ \exp[e(U_1^0 - U_1)/kT(\Delta/d)] - 1 \} \times \times \{ \exp[e(U_1^0 - U_1)/kT(1 - 2\Delta/kT)] - 1 \}^{-1}, \quad (10)$$

where $\Delta = N^{-1/3}$ is the medial distance between levels; the function $f(U)$ for the tunnel mechanism of the carriers emission between centres receives a value

$$f(U) = \exp\{-(4/3)(2m^*/\hbar^2)^{1/2} d / (U_1^0 - U_1)\} \times \times [E_t^{3/2} - (E_t - e(U_1^0 - U_1)\Delta/d)^{3/2}]. \quad (11)$$

At resonance tunneling of electrons through a system of barriers the joint current should take into account energy reflected E and transiting E' of an electron [4]:

$$I = \frac{e}{4\pi^3 \hbar} \int_0^\infty dk_l \int_0^\infty dk_t [f(E) - f(E')] T^* T \frac{\partial E}{\partial k_l}. \quad (12)$$

The transparency factor T^*T is the function of a kinetic energy of an electron E_x . Taking into account a distribution function of electrons the Fermi $f(E, E')$, the expression for a current is possible to integrate for transversal in relation to a barrier of a direction:

$$I = \frac{em^*kT}{2\pi^2\hbar^3} \int_0^\infty T^* T \ln \left(\frac{1 + \exp[(E_F - E_l)/kT]}{1 + \exp[(E_F - E_l - eU)/kT]} \right) dE_l. \quad (13)$$

At $T \rightarrow 0$ this expression becomes

$$I = (em^* / 2\pi^2\hbar^3) \int_0^{E_l} (E_F - E_l) T^* T dE_l, \text{ for } U \geq E_F, \quad (14)$$

$$I = (em^* / 2\pi^2\hbar^3) \left[U \int_0^{E_F - U} T^* T dE_l + \int_{E_F - U}^{E_F} (E_F - E_l) T^* T dE_l \right], \text{ for } U \leq E_F. \quad (15)$$

According to the relations (13-15), feature of structures with two and more barriers is the stage increase of a current at magnification of voltage, presence of extremums and sections with negative differential resistance on a current-voltage characteristic.

3.2. EXPERIMENTAL INVESTIGATIONS OF INTERFACE LAYER PARAMETERS AND OF THE SCHOTTKY DIODES CHARACTERISTICS

The energy parameters of the SiO₂ nanolayer differ drastically from those of protective passivating thick oxide layers. At $d_0 < 50$ nm the Si potential barrier of Si - tunnel thin SiO₂ equals $\phi_b \sim 1.5$ eV. The barrier transparency for carrier tunneling varies from $T^*T = 1$ at $d_0 \sim 0.5$ -0.8 nm to $T^*T = 10^{-3}$ at $d_0 \sim 3$ -4 nm.

The SES spectra at the Al deposition on the Si surface cleaved in vacuum were studied by the X-ray photoelectric spectroscopy (XRES) [9, 10, 19]. The formation of the 0.25 nm thick layer of Al practically leads to the vanishing of the SES spectrum of the Si free surface, whereas at $d_{Al} = 0.8$ nm metal spectrum formation comes to its end. The SES spectrum depends on a kind of metal and a character of its interaction with semiconductor. The chemical responses cause formation of silicide on the interphase boundary of MES. The formation of the Si-Me (Pt, Pd) bondings changes an electronic spectrum of valence band. The diffusive penetration of Me in Si is accompanied with formation of point defects in the nsSi interface and appearance of several additional shallow and deep levels in the Si band gap.

The presence of the Si-F bonding on the Si surface and two levels of SES with the ionization energies of $E_i = 0.3$ -0.4 eV and 0.78-0.86 eV result from the electrochemical deposition of Ni on the n-n⁺-Si. The adsorption of metals on the Si surface can be followed by formation of the bonding of the metal atom with the Si structural defect. The levels with the energies of $E_i = 0.66$ -0.71 eV and 0.74 eV arise correspondingly to this process for Ag, Cr, Na. The level $E_i = 0.59$ eV can be ascribed to the formation of the oxide hydrated layer with the Si-O-Si-OH bondings.

Laser irradiation of the Al-TiW-Pt_xSi_y-n-Si structures with intensity of $I_0 \sim 60$ -105 W/cm² can promote an annealing of the deep levels assigned to structural defects in SCR of silicon and change significantly a spectrum of levels connected with impurities of Pt, S, O, Ni [21-24]. The radiative irradiation of the Al-n-Si contacts is accompanied with formation of the level at $E_l = E_c - 0.42$ eV with concentration of $N_l = 3 \times 10^{16}$ cm⁻³. In the Al-n-S initial MES in the p⁺-Si interface and diffusive layer the levels with density comparable to a value for a basic dopant were not detected. The systematized results of the investigations of the deep levels in Si are reported in [25].

The investigation of the potential barrier height ϕ_b in the Al-n-Si contacts on the method of the Si surface treatment shows, that the minimal value of $\phi_b=0.5$ eV is obtained at the presence of the tunnel thin SiO₂ layer in MES. For contacts obtained by the deposition of Al on the Si surface cleaved in vacuum ϕ_b equals 0.72 eV. The formation of the p⁺-Si layer resulting from thermal annealing calls forth the ϕ_b increase up to 0.76-0.78 eV. The transformation of MES into the typical of the contacts the Al-p-p⁺-n-Si type is accompanied with reduction of ϕ_b by 0.03-0.05 eV.

Table 1

I_0 , kW/cm ²	Al-p ⁺ -n-Si		Al-SiO ₂ -n-Si	
	ϕ_b , eV	n	ϕ_b , eV	n
0	0,73	1,08	0,55	1,66
85	0,76	1,06	0,59	1,58
96	0,78	1,01	0,61	1,56
106	0,80	1,05	0,64	1,47
117	0,75	1,18	0,66	1,41

The similar changes of ϕ_b and ideality coefficient of the current-voltage characteristic n take place at a subthreshold pulse laser irradiation of MES (Table. 1) [17, 18]. The relevant transformation of the current-voltage characteristic and C-V one of the Al-n-Si SD depending on PLI intensity is shown in a fig. 4, 5. Calculation of parameters of the transition p⁺-layer [7, 18] for the Al-n-Si structures points out its existence on MES at optimum modes of irradiation. Thus ϕ_0^* increases up to 0.85 eV, and the sizes of p⁺-layer are comparable to a shielding length in the semiconductor at $N_d = 10^{16}$ cm⁻³ and equal $l \approx 130$ nm. The increase ϕ_b at $I_0=I_c$ is well explained by the formation of a p⁺-layer and is in agreement with the data on a thermal annealing. However, at heat treatment such process is accompanied by increase of n up to 1.07, and at photon correction - the decrease down to 1.01.

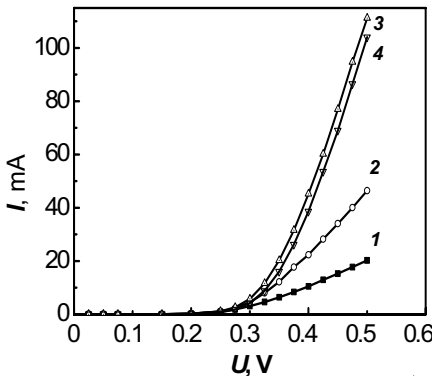


Figure 4. Current-voltage dependence of Al -p⁺-n-Si SD after pulse laser irradiation. 1 – $I_0 = 0$ kW/cm², 2 – $I_0 = 85$ kW/cm², 3 – $I_0 = 105$ kW/cm², 4 – $I_0 = 125$ kW/cm².

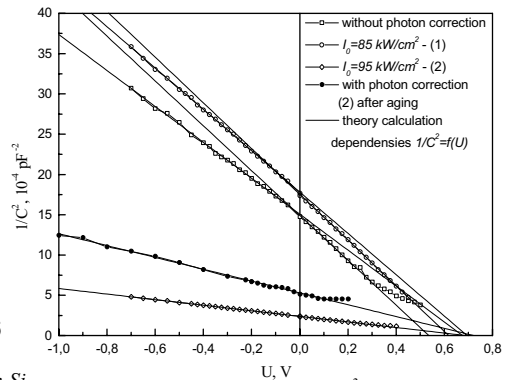


Figure 5. The dependencies $1/C^2=f(U)$ for the structures Al-p⁺-n-Si formed on free from SiO₂ the silicon surface.

For the MES with the silicide interface the dependence of ϕ_b on a work function of carriers from silicide is insignificant. It confirms an assumption on presence of a large density of SES of the contact or on the formation of a glass-like layer of semiconductor with the thickness of 0.5-1 nm at the interface, which stabilizes ϕ_b .

The laser irradiation of the $\text{Pt}_x\text{Si}_y\text{-Si}$ contacts with the area of $S \sim 400 \div 10000 \text{ } \mu\text{m}^2$ [18, 25], after different conditions of a preliminary thermal treatment, causes ϕ_b increase from 0.74-0.78 eV up to 0.8-0.86 eV.

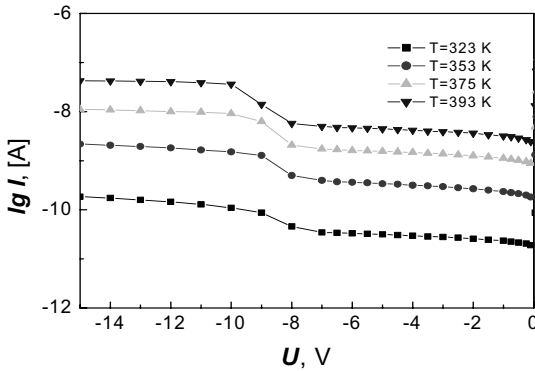


Figure 6. A current-voltage characteristic of structures Al-TiW-PtSi-Si after PLI.

Correspondingly n diminishes from 1.05-1.11 down to 1.01-1.06. For some PtSi-Si SD of small area ($S \sim 100 \text{ } \mu\text{m}^2$) ϕ_b decreases from 0.78 eV to 0.74 eV with the n increase up to 1.19-1.27.

In the Al-silicide-Si contacts thermoemission and tunnel-resonance currents and those through SES are considered to be basic. The embodying of the specific mechanism is defined by electronic properties of the silicide-Si interface and by its thickness.

The thermoemission current is observed exclusively for MES with the small SES density and (or) with thin interface. The tunnel-resonance mechanism of current transition with participation of deep levels in the SCR of Si is characteristic of the $\text{Pt}_2\text{Si-n-Si}$ contacts.

Main features of the reverse current-voltage characteristics of the Al-TiW-PtSi-Si contacts of the small area (fig.6) can be explained by means of multistage resonance charge transfer through two networks levels in the interface layer with consequent tunneling of carriers through SCR in Si [7]. Whereas energy barrier on the MES boundary is modeled by two serial sections - extended interface and the SCR layer, on which the reverse bias applied to the system distributes. The shift of the intermediate section of the current-voltage characteristic by voltage can be attributed to decrease of the Si band gap at elevated temperatures. The simulation of charge transfer through nanosize two-barrier structure [3, 4] yields dependence of a log of a current on applied voltage, which qualitatively overlaps in the first approximation with the experimentally obtained current-voltage characteristic. But in experiment the parts with negative differential resistance are don't observed.

4. Conclusion

The processes of self-diffusion occurring in MES at the absence of chemical reactions between metal and semiconductor bring about appearance of amorphous or nanostructural intermediate layer of a solid solution at the interface. In the Al-n-Si, (Al+Si)-n-Si, Al-the SiO_2 thin layer-Si contacts in the process of thermal treatment the following junction is alternatively formed: 1) Al- $\text{p}^+\text{-n-Si}$, 2) Al- $\text{p-p}^+\text{-n-Si}$, 3) Al- p-n-Si . In a MES, where the chemical interaction of metal with Si takes place, silicides and intermetallic compounds, generally exhibiting metal properties, can be formed at the interface. Where as relation of work functions of the materials in contact varies, causing additional alteration of electrical parameters of the aluminum - silicide - silicon SD. It should be mentioned, that the thickness of the interface between Al and Si of the order of 1.5 - 40 nm is much less than

the SCR field penetration depth in the Si structures with Schottky barrier. The presence of the interface and structural defects in the Si SCR essentially influences on the physical properties of SD and the mechanisms of charge transfer in MES. The pulse laser irradiation of the SD transformed interface layer in the Al–nanostructured layer–Si structures and corrects the SD characteristics. A special interest now is represented by questions of mathematical simulation and experimental researches of performances of structures Al – nanosilicon intermediate layer – Si, in view of development in them of different charge transfer mechanisms, and also embodying on their basis of functional devices for the generation of high-frequency oscillations, commutators of a current, transformers of a signal level, optoelectronic devices.

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NANO-BIO ELECTRONIC DEVICES BASED ON DNA BASES AND PROTEINS.

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Abstract

A key challenge of the current research in nanoelectronics is the realization of biomolecular devices. The biomolecules have specific functionalities that can be exploited for the implementation of electronic and optoelectronic devices. Different nanotechnological strategies have been pursued to implement the biomolecular devices, following a bottom-up or a topdown approach depending on the used biomolecule and on its functionality. In this paper we present our results on the implementation of nano-biomolecular devices based on modified DNA nucleosides and metalloproteins.

The first kind of devices is based on a DNA base, the guanosine, which is engineered in two different modified forms: the lipophilic deoxyguanosine derivative I, and the lipophilic 8-oxodeoxyguanosine.

These biomolecules show strong electron-donor properties and internal dipole. Moreover these modified nucleosides exhibit self-assembly and self-recognition properties, resulting in the formation of two-dimensional ordered supramolecular structures in the solid state. The aggregates show a clear semiconductor behaviour with blue band-gap and coherent band transport. These are used, in combination with nanopatterned metallic contacts separated by narrow gaps between 200nm and 30 nm, to fabricate novel biomolecular electronic devices with excellent photodiode behaviour and metal/semiconductor/metal characteristics at room temperature. A three terminal device, like field effect transistor based on a deoxyguanosine derivative (a DNA base), is demonstrated.

A totally different approach is followed for the implementation of devices based on proteins. The use of electron-transfer proteins, such as the blue copper protein azurin (Az), is particularly attractive because of its natural redox properties and their self assembly capabilities. Our results about the fabrication, characterization and modelling of devices based on this redox protein are presented. The charge transfer process in protein devices depends on their redox centers (the metal atom) and their orientation in the solid state, achieved through different immobilization methods. A biomolecular electron rectifier is demonstrated by interconnecting two gold nanoelectrodes with an azurin monolayer immobilized on SiO₂. The device exhibits a clear rectifying behavior with discrete current steps in the positive wing of the current-voltage curve, which are ascribed to resonant tunnelling through the redox active center. The basic properties of Azurin-based three terminal devices are also reported. A prototype of biomolecular transistor in the solid state and operating in air, based on such class of proteins is presented.

1. Introduction: Bio-self-assembly and motivation.

The Moore's Law, the 1965 prediction by Intel co-founder Gordon Moore that manufacturers would double the number of transistors on a chip every 18 months, with resulting declining prices and increasing performance, has been fulfilled for four decades by the semiconductor industry. But the latest edition of the annual International Technology Roadmap for Semiconductors--a joint effort of semiconductor industry associations in Europe, Japan, Korea, Taiwan, and the United States—lists reasons for thinking that this may soon change. The Roadmap explores "technology nodes"—advances needed to keep shrinking the so-called DRAM half-pitch, half the spacing between cells in memory chips. Currently, the industry is moving to a DRAM half-pitch of 130 nanometers, about three-thousandths the width of the proverbial human hair. The Roadmap forecasts that researchers must lower that figure to 35 nanometers by 2014, simply to continue doubling the number of transistors. In the year 2000 update (available online at public.itrs.net), 12 working groups representing various aspects of chipmaking

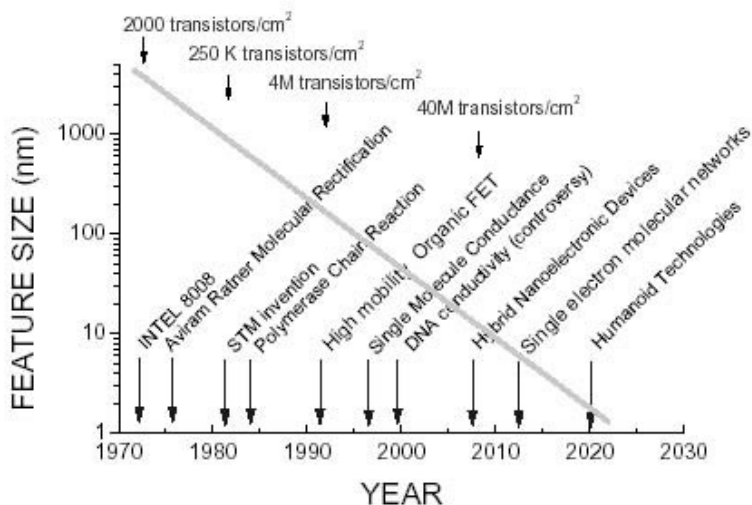


Figure 1 : Minimum feature size of electronic components during the years. The straight line represents the trend predicted by the Moore's law. The arrows indicate the number of transistors integrated in a chip and some milestones (accomplished or expected) of modern chemistry, biology and physics.

assess whether those “technology node targets” can be achieved. In figure 1 we exemplify the linear trend of the Moore Law, and the concomitant occurrence of some milestones of modern chemistry, physics and biology. Possible future scenarios are indicated just to envisage how the progress of nano-bio-electronics may impact the future of electronic technologies.

In various laboratories worldwide, minimum features sizes which are a factor of 10 smaller (or more) than the 130nm node have been demonstrated. However the SIA (Semiconductor Industry Association) road map projects that even though the miniaturization trend will continue for another 15-20 years, it is becoming increasingly difficult to continue to down-

scale because of real physical limitations including size of atoms, wavelengths of radiation used for lithography, interconnect scheme ,etc.. No known solutions currently exist for these problems.

One of the potential roadblock to continue the scaling beyond the 50nm node is the molecular electronics. While engineers and scientists have been long aspiring to manipulate structures controllably and specifically at the micro- and nanometer scale, nature has been performing these tasks with great accuracy and high efficiency using highly specific biological molecules such as DNA and proteins. In the last decade there have been dramatic advances toward the realization of molecular scale devices and integrated computers at the molecular scale [1]. First pioneering experiments were performed demonstrating that individual molecules can serve as nano-rectifiers feature size (nm)

[2], and switches [3,4] one thousand times smaller than those on conventional microchips. Very recently the assembly of tiny computer logic circuits built from such molecular scale devices has been demonstrated [5].

Researchers are working to join biology and nanotechnology, fusing useful biomolecules to chemically synthesized nanoclusters in arrangements that do everything from emitting light to storing tiny bits of magnetic data. The result is a merger that attempts to blend biology's ability to assemble complex structures with nanoscientists' capacity to build useful devices. One of the biggest drivers behind nanotechnology's enthusiasm for biological systems revolves around the organism's impressive ability to manufacture complex molecules such as DNA and proteins with atomic precision. Chemists create molecules up to hundreds of atoms in size without too much trouble, controlling the position of every atom. But beyond that, traditional synthetic schemes become unwieldy and too inefficient to be practical. Computer chip engineers--the most advanced materials makers--do much better. They can craft chips with 200 millions transistors, each with features on the order of 100 nanometers. "Bottom-up" fabrication together with organic and biological synthesis techniques provide new solutions to these problems. A variety of extremely sophisticated molecular systems exists in nature that vary in density , sense and relay information, perform complex computational tasks, and selfassemble into complex shapes and structures, namely : DNA, proteins and the human brain.

The strongest motivation to use biomolecules as building blocks for the construction of artificial computational systems lies in their self-assembly properties.

The self-assembly properties of biological units can be defined as “ the process of self-organization of one or more entities as the total energy of the system is minimized to result in a more stable state”. This process of self-assembly inherently implies: a) some mechanism where movement of entities takes place using diffusion, electric fields, etc.; b) the concept of “recognition” between -linkers”, that drives the self assembly ; c) the “recognition” results in binding of elements dictated by forces (electrical, covalent, ionic, hydrogen bonding, van der Waals, etc..), such that the final physical placement of the entities originates a state of lowest energy [6].

2. Interconnection, self-assembly and device implementation

To date a fully biological device, presumably operating in a living (liquid) environment, is far from being realistic. An intermediate and necessary step is to fabricate hybrid devices in which the functionality of the biological molecules is exploited through the interconnection

with a more conventional solid-state inorganic device. This is the case, for instance, of a field effect transistor whose gate channel consists of a self-assembled biomolecular layer. Though at the early stage, such technology is very fundamental for the understanding of the biomolecular systems and for the exploration of their potentialities.

The bio-device implementation processes are based on two fundamental steps:

- i) The nanofabrication of a pattern which interconnects the bio-entity to the external world (load, power supply, circuit etc...), following a typical “top-down” lithographic approach
- ii) the self-assembling of the bio-molecules (“bottom-up” fabrication) to immobilize the biosystem in the pattern.

Nanocontacts can be fabricated with advanced nano lithography methods. By using standard EBL we are able to fabricate electrodes with separation in the range of 40nm. In order to reduce the tip separation down to about 20nm, we have developed a modified EBL process by brushing the PMMA resist for a precisely determined short time before the e-beam writing. In this way the resist is partially exposed and the subsequent EBL writing, the tails of the Gaussian e-beam allow us to reach the right dose also in the areas near the edges of the tips resulting in a final gap smaller than the nominal one (50 nm). In the plot of figure 2 we show the reduction of the inter-electrode gap as a function of brushing time Dt . When Dt ranges from 20s to 50s, the separation is reduced almost linearly well below 40nm.

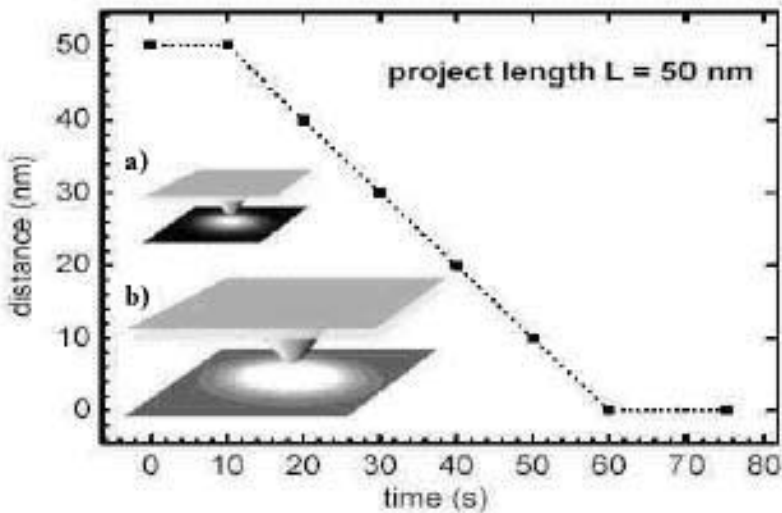


Figure 2: Reduction of separation between electrodes as function of the brushing time Dt of PMMA resist by a defocused e-beam. When Dt ranges from 20 to 40 s, the separation is reduced almost linearly from 40 to 20 nm; for $Dt = 60$ s, the tip separation becomes zero. The insets outline our technique. (a) Gaussian shape of e-beam. (b) First, the resist is partially exposed with the defocused e-beam (gray background instead of the previous black one). Then the tails of the focused Gaussian e-beam allow the resist near to the edges of the tips to reach the right dose, resulting in a final inter-electrodes distance smaller than the nominal one (50nm).

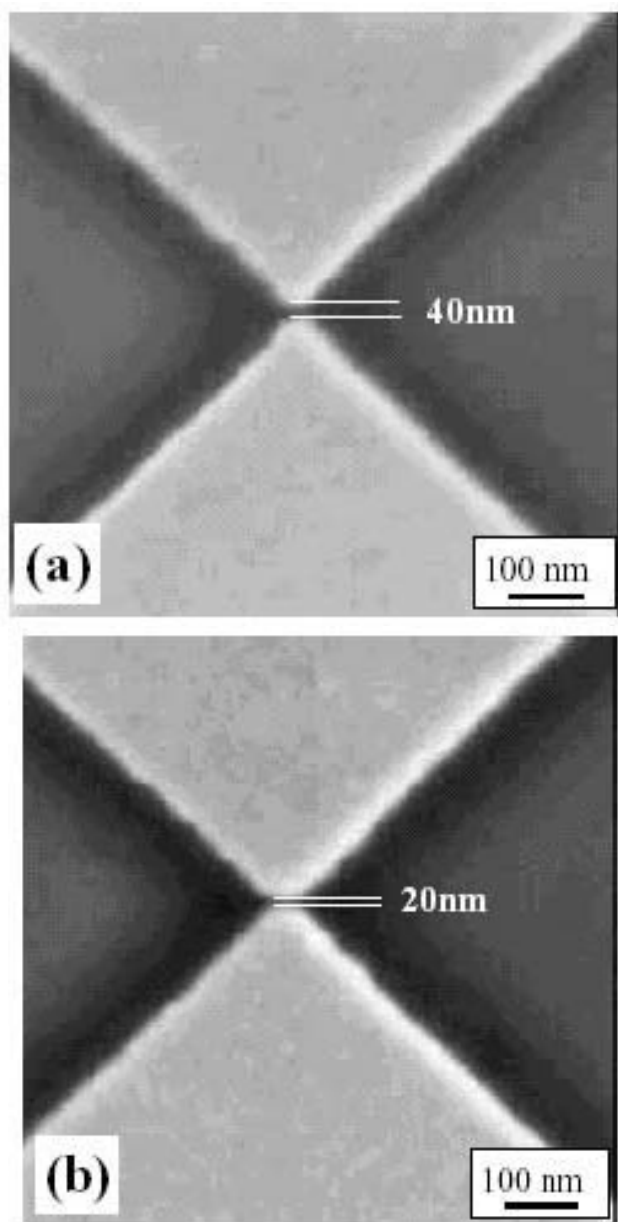


Figure 3: Plan-view SEM images of Cr-Au nanotips after lift-off using brushing of PMMA resist before EBL process in order to reduce the inter-electrode separation: (a) electrodes with

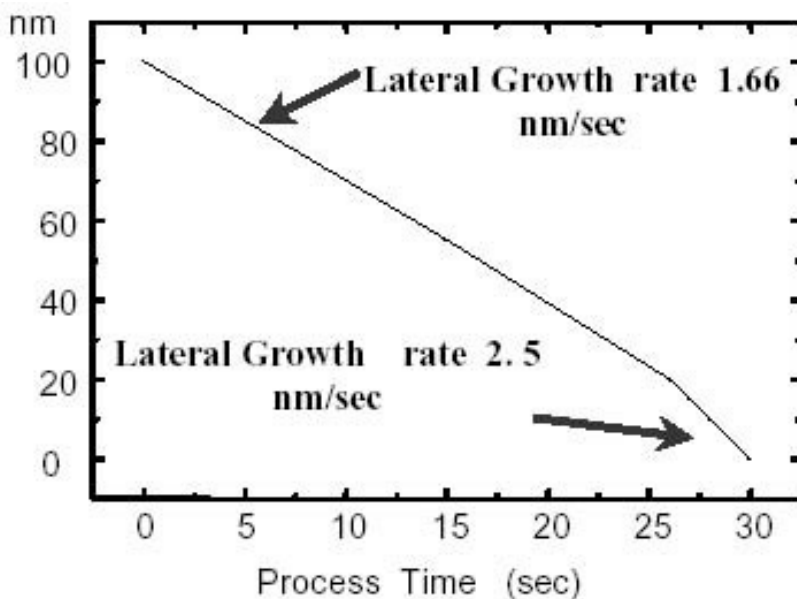


Figure 4: Calibration curve of the Au electroplating process. separation of 40 nm (brushing time $Dt = 20s$) and (b) of 20 nm ($Dt = 40s$).

In figure 3 we show the SEM images of Cr/Au nanotips after the lift-off process with separation of 40nm (fig. 3a) and 20nm (fig. 3b) obtained by EBL with the additional brushing of PMMA for a time of 20s and 40s respectively.

However, the implementation of single molecule devices requires the availability of electrodes with sub-10nm separation. For this purpose, we have developed a two-step process consisting of standard EBL and lift-off, to fabricate 100nm separated electrodes, followed by Au electroplating deposition to reach the 10nm separation. The calibration curve of the Au electroplating process (fig. 4) shows the reduction of inter-electrode gap as a function of the electrodeposition duration. The lateral growth rate varies from 1.66 nm/s, at the beginning when the Au vertical growth is more significant, to 2.5 nm/s when the gap is reduced below 20nm.

In figure 5 we show the high magnification (HM) SEM images of tips obtained with EBL and liftoff followed by Au electro-deposition. By carefully adjusting the process parameters and duration, from a initial gap of 100nm, we were able to achieve a minimum gap of only 7 ± 2 nm (fig. 5d).

A possible systematic approach to build complex biomolecular devices is to start from wellcharacterised clean substrates (such as Si(100), SiO₂ or Au(111) single crystal surfaces) to deposit submonolayers of spatially isolated molecules or biomolecular functional units. The self assembling of the biological units on the substrate can follow different pathways like: a) the bulk (polymer) entrapment, i.e. absorption; b) surface absorption (physisorption); c) non-directed covalent binding to the surface (chemisorption); d) electrostatic adsorption; e) covalent binding at defined (molecularly engineered) sites of the biocompound; f) binding by bio specific interactions (Fig.6) [8].

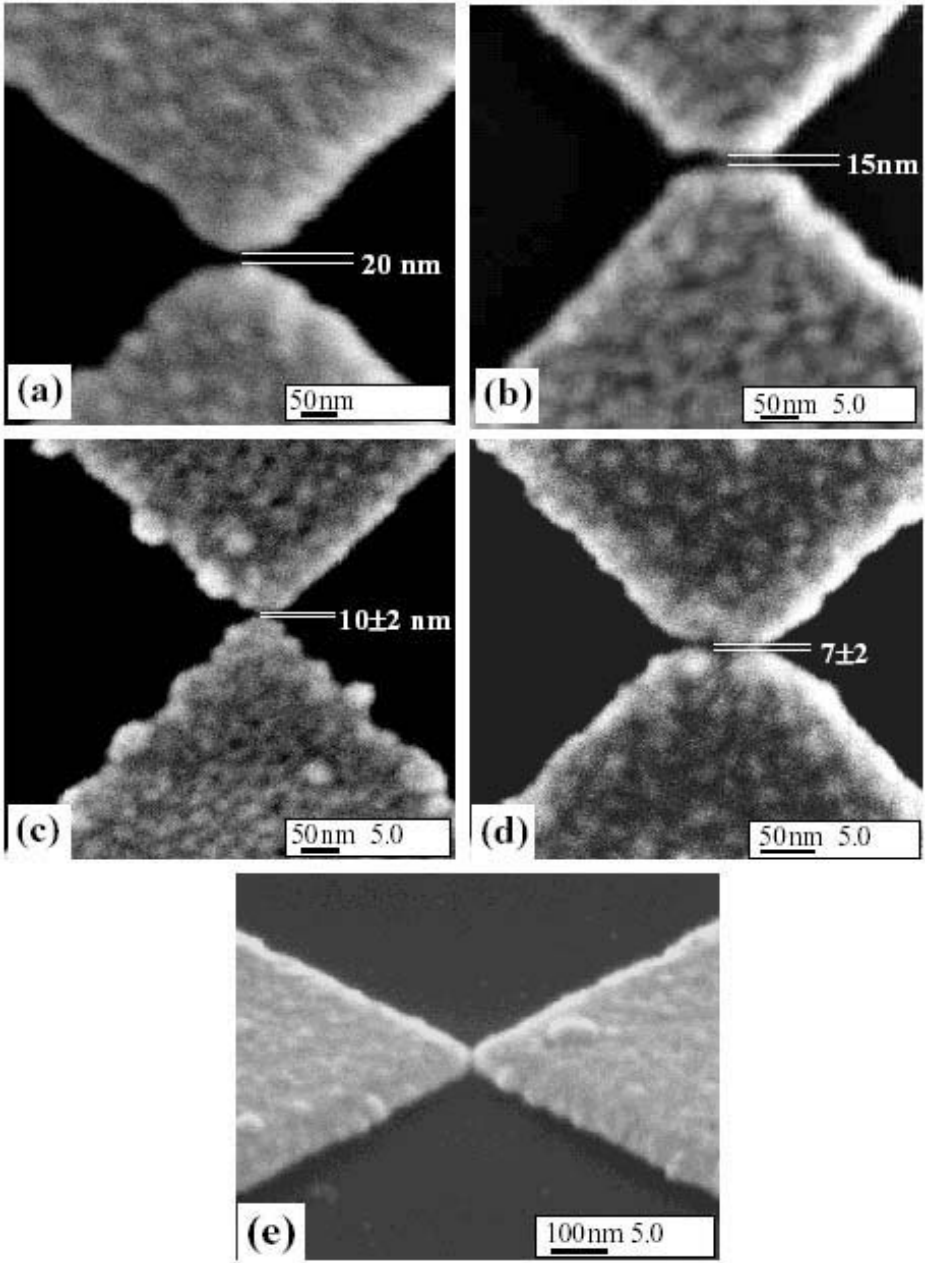


Figure 5 : HM SEM images of electrodes obtained with EBL and lift-off followed by Au electroplating deposition (process time Dt) (for all samples, the initial separation before the electro-deposition was 100 nm). (a) Cr/Au tips with separation of 20 nm ($Dt = 25$ sec); (b) Cr/Au tips with separation of 15 nm ($Dt = 26$ sec); (c) electrodes with separation of 10 ± 2 nm ($Dt = 27$ sec) and of only 7 ± 2 nm ($Dt = 28$ sec). (d) Cross-section SEM micrograph of electrodes with separation of 20 nm (sample tilting » 60°). (e) Cross-section SEM micrograph of electrodes with separation of 20 nm (sample tilting » 60°).

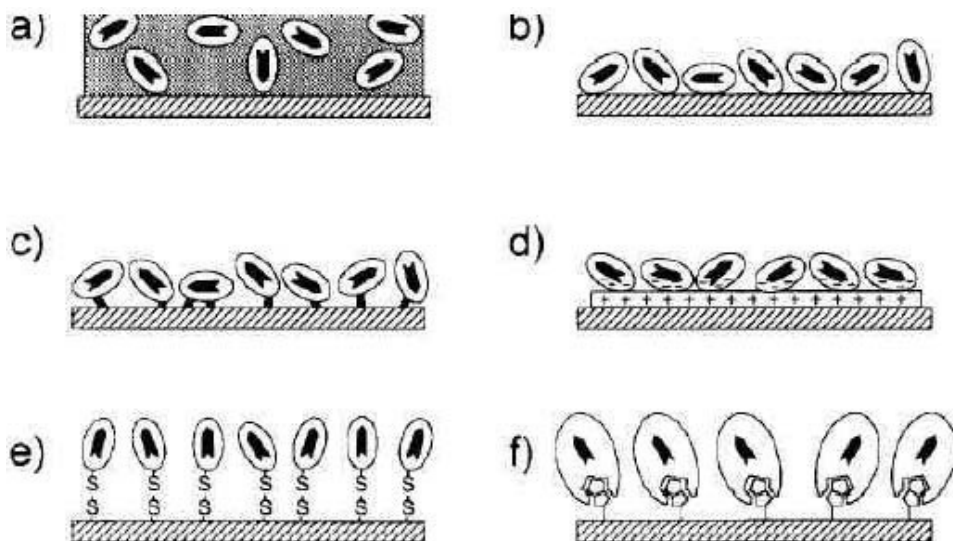


Figure 6: Schematic of the different self assembling mechanisms of the biological units onto a substrate

3. Nano-devices based on deoxyguanosines.

The choice of guanine as the basic molecular constituent of hybrid nano electronic devices was dictated by the low oxidation potential, that favors charge transport, by the intrinsic dipole moment due to charge displacement towards the Oxygen atom (of the order of 7 D), and by the spontaneous self-assembling properties both in solution and in the solid state [9]. The base was modified, in the lipophilic deoxyguanosine derivative form [10] (Fig.7), to favor the formation of supramolecular ordered structures in the solid state. The guanosine

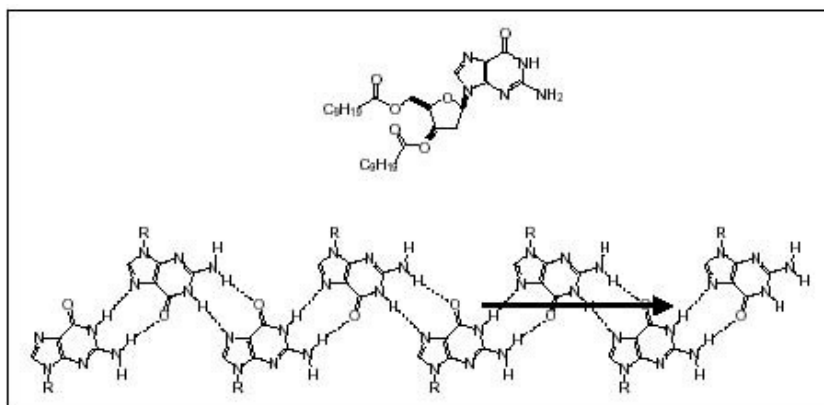


Figure 7: Geometry of an individual guanine molecule, and a guanine hydrogen-banded ribbon-like aggregate. The arrow indicates the total dipole along the ribbon backbone.

exhibits striking self-assembling properties in the solid state, resulting in the formation of ordered clusters that behave like wide band gap semiconductors [11]. These molecular layers were used to interconnect planar metallic nanopatterns separated by gaps between 30 nm and 800 nm, to fabricate biomolecular electronic devices with clear diode and metal/semiconductor/metal (MSM) characteristics at room temperature. The starting molecules were synthesized and purified according to the procedure described in Ref.[9], and a deoxyguanosine solution in CHCl_3 was prepared at low concentration (between 10^{-1} and 10^{-4} M). A drop of constant volume (2 ml) was deposited by a Hamilton syringe in the gap of two metallic contacts and gently dried in low-vacuum (10^{-3} bar), until the deoxyguanosine film spontaneously formed. The metallic electrodes were prepared by electron beam lithography in a 35nm/6nm Au/Cr film deposited on a SiO_2 substrate (roughness below 0.2 nm). Upon controlled evaporation of the deoxyguanosine solution, the molecules were found to aggregate spontaneously to form ordered self-assembled guanosine crystals (SAGCs). For molar concentrations of the solution in the range of 10^{-3} M, and for the evaporation rate fixed by the base pressure of 10^{-3} bar, the deoxyguanosine molecules form ribbon-like structures; these are stacked to form a uniform layered film of thickness comparable to the thickness of the Au/Cr contacts. The morphology of the SAGCs was studied in detail by contact Atomic Force Microscopy (AFM) experiments within the contact gap (Fig.8). The ribbons form an ordered supramolecular structure, laying parallel to each other with a periodicity of 2.5 nm and a length up to $\gg 100$ nm. Over such a length scale, the packed lamellar structure of the SAGC, physisorbed on the surface between the electrodes, gives rise to an orthorhombic unit cell of size $a=1.3\pm0.1$ nm and $b=2.5\pm0.2$ nm. For distances longer than 100 nm, that ordering is lost, and the ribbons form randomly oriented SAGCs.

The SAGCs were deposited onto planar devices with gaps $L = 60, 120$ and 800 nm. The narrowest gap was small enough to probe transport within an individual SAGC. The 120 nm gap was used to probe few SAGCs, whereas the widest gap was used to probe an ensemble of randomly oriented SAGCs. The current-voltage (I-V) characteristics measured at room temperature in the dark (Fig. 9) show a striking dependence on L . For wide gaps

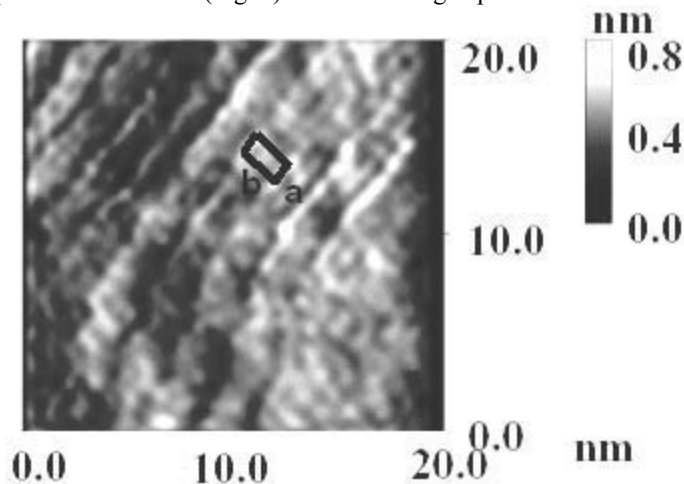


Figure 8 : AFM image of the molecular layer deposited in the gap ($L=60$ nm) between the two electrodes. The AFM measurements were performed in contact mode in air.

($L=800$ nm, Fig. 9), a symmetric non-ohmic behavior and a clear hysteresis loop in the downward-upward sweeps was found. This behavior was reproduced and confirmed for wide contact gaps (down to $L=200$ nm). The same I-V characteristics were measured in all the disordered SAGCs obtained at different molar concentrations or on different substrates (e.g. glass), regardless of the width of the contact gap. This indicated that the disordered guanosine films behave like a rectifying barrier and induce a capacitor effect in the planar device, regardless of the film morphology and device size. The situation changed dramatically in the 120 nm device (Fig.9), where only few SAGCs were present between the electrodes. The I-V characteristics show a non-linear symmetric behavior with a zero current region in the voltage range between -2 V and $+2$ V. For bias higher than 2 V the current increases to a sub-mA level, with a dynamic resistance of the order of a fraction of MW, and then it saturates. The shape of the I-V curve in this case is similar to that of a MSM device with a very high light sensitivity (about 1 W/A) [12]. The hysteresis is considerably reduced, consistent with the reduction of the capacity due to the smaller amount of SAGCs probed in the gap. A further change of the I-V curves occurs for contact gaps of 60 nm (or less), where only one SAGC is probed. Under this condition the device exhibits a clear diode-like characteristic, with currents of the order of few mA for positive bias (at 10 V) and nA for negative bias, without hysteresis. The onset of the diode occurs around 0.8 V. The observation of an asymmetric I-V characteristic in devices where a single nanocrystal is probed suggests that a strong dipole is formed in each SAGC. As shown later, this originates from the total dipole of the molecules ordered in the ribbon-like structure of the SAGC's. These results suggest that different conduction mechanisms concur to charge transport in the SAGC layers, depending on the relative variation of the gap width (L) versus the self-assembling length (l). Since the SAGCs spontaneously form on a length scale $l < 100$ nm, it is necessary to distinguish between the coherent transport phenomena within a single SAGC in the 60 nm device, and the incoherent transport phenomena involving neighboring SAGCs in the wider devices. These can be distinguished by the temperature-dependence of the DC conductivity σ_{DC} . The results of these experiments clearly indicated that in the narrow gap contact the conduction occurs through band like charge transport while for the $L=120$ nm device hopping and incoherent transport. The semiconductor behavior observed in the individual SAGC is supported by the observation of a photocurrent spectrum similar to the absorption spectrum of inorganic semiconductors, revealing an absorption onset around 3 eV in the device with $L=60$ nm (Fig. 10). In addition, the calculations reveal that the diode-like behavior of the devices formed by a single SAGC is due to the strong dipole within the nanocrystal. For wider contact gaps many SAGCs with random orientations are probed by the gold electrodes, so that the total dipole averages to zero, and the asymmetry induced by the spontaneous polarization is lost. In this case the I-V characteristics of the device becomes symmetric. Consequently, for length scales larger than the self-assembling length, the transport is primarily governed by incoherent tunneling or hopping processes among neighboring SAGCs. This description is supported by the observation of a Mott-like conductivity for devices with $L > 100$ nm.

To check the dependence of the device characteristics on the electronic properties of the molecule and on the self assembling and physisorption processes devices with different molecules ($\text{dG}(\text{C}10)_2$ and $\text{8oxodG}(\text{C}10)_2$) and solvents (chloroform and 1, 2, 4-trichlorobenzene) were produced. The results of these experiments showed that the mechanisms predominate.

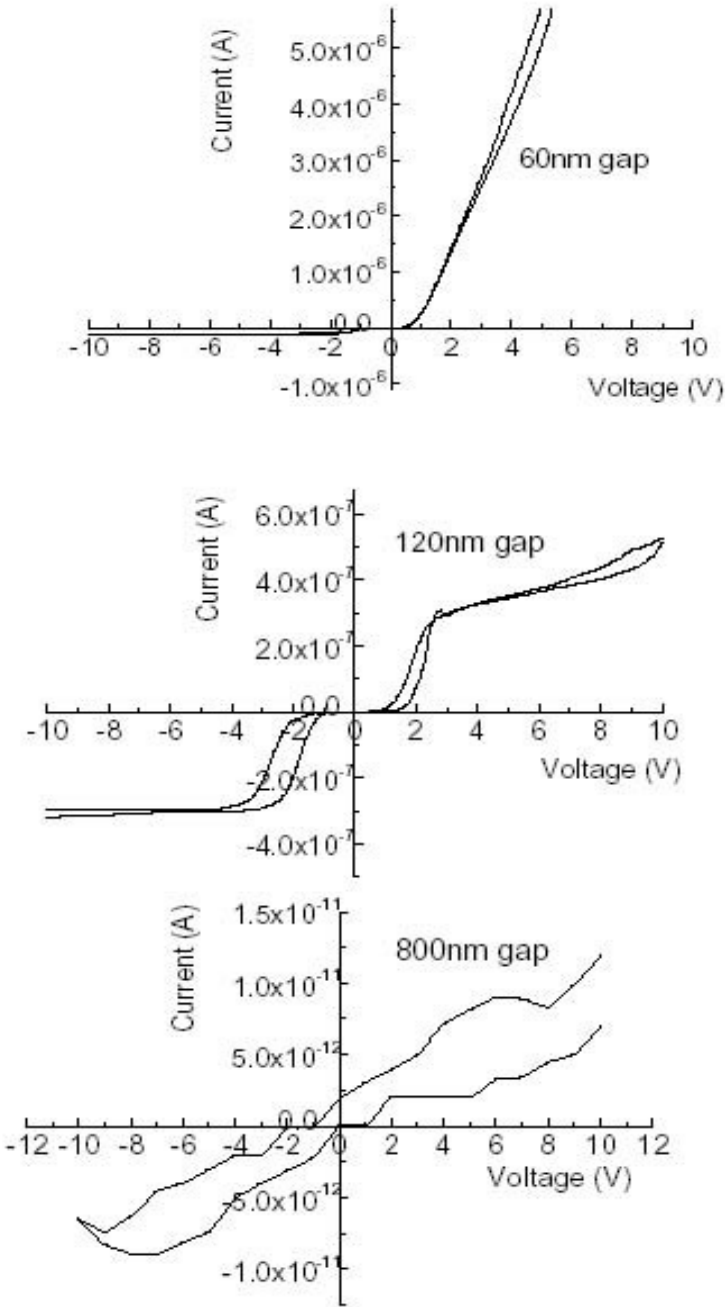


Figure 9 : Current-voltage characteristics measured in three hybrid devices with gaps of 60, 120 and 800 nm at room temperature and in air.

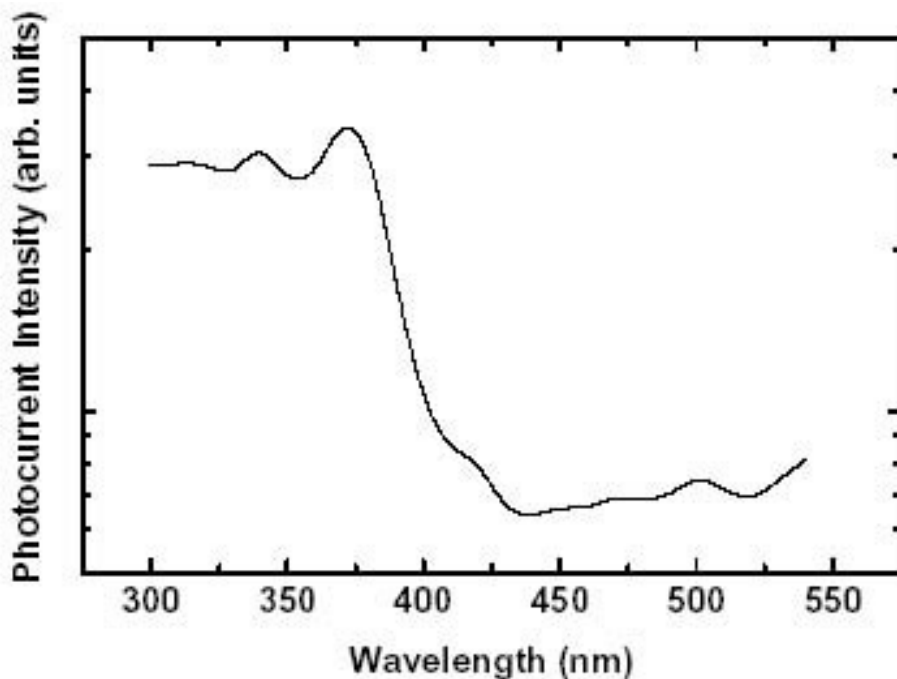


Figure 10: Photocurrent spectrum of the self assembled gunosine crystals as measured by biasing the device with -1 V.

reduction of the oxidation potential in the 8-oxodeoxiguanosine favors conduction with a visible reduction of the zero current region in the I-V curves. However, the different supramolecular arrangement in the layer partially cancels the intrinsic dipole effect, thus reducing the curve asymmetry (low rectification ratio) and the current density in the device. If 1, 2, 4-trichlorobenzene was used as solvent, no macroscopic ordering was observed in the molecular layer in the solid state with a consequent reduction of the device performance [13]. This again confirms the crucial role of the self assembling process in these biomolecular devices.

By using the same modified DG base a field effect transistor, behaving like a p-channel MOSFETs was demonstrated [14]. The prototype structure investigated was a planar metal-insulator-metal nanojunction, consisting of two arrow-shaped metallic electrodes facing each other and connected by the molecules. A third electrode (gate) was deposited on the back of the device to produce a field-effect transistor (see Fig. 11)

Typical I-V curves under forward bias at different gate bias are reported in Fig. 12. The entire current-voltage characteristics on log scale are displayed in the inset of Fig.12. They are asymmetric, with a rectification ratio (RR), defined at a fixed source-drain voltage V_{ds} :

$$RR(V_{ds}) = I(V_{ds})/I(-V_{ds}) \gg 3. \quad (1)$$

This is the typical value obtained in most samples, suggesting that the intrinsic dipole

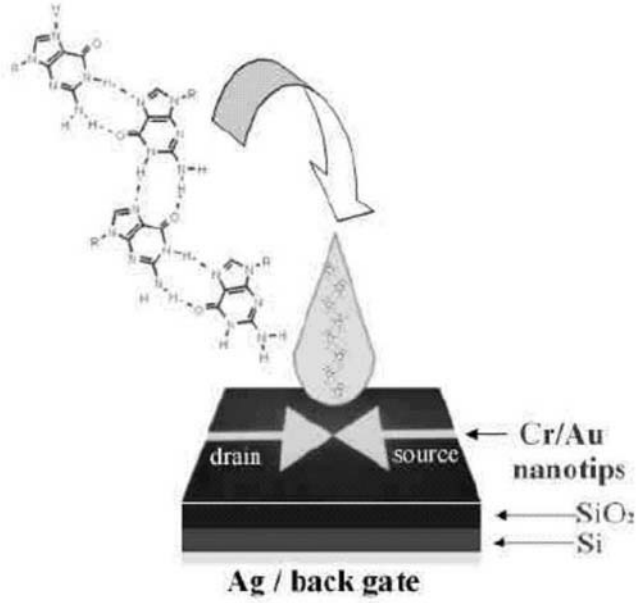


Figure 11: Scheme of the Self-organized ribbon of dG(C10)2 and the nanodevice structure . (a) Self assembly and cast deposition of dG(C10)2 on the three-terminal device, consisting of two arrowshaped Cr/Au (6nm/35nm thick) electrodes on a SiO₂ substrate and a third Ag back electrode (not on scale). Samples were obtained by depositing a 2ml drop of a 3.5×10^{-4} M solution of dG(C10)2 in chloroform.

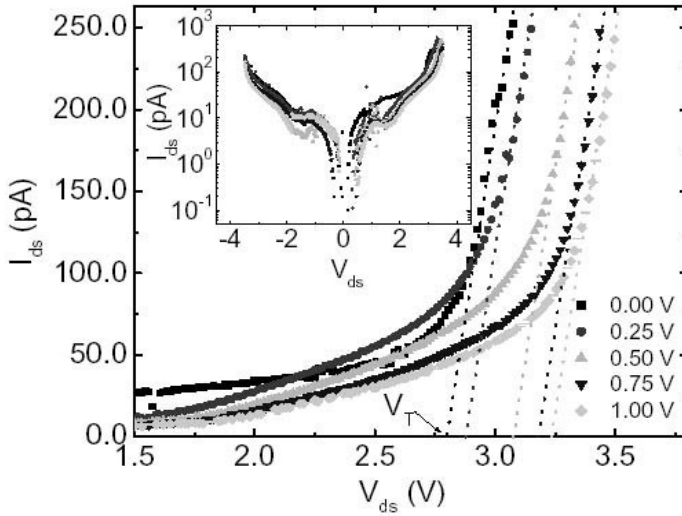


Figure 12: I - V characteristics of the three terminal deoxyguanosine device with electrode separation of 40 nm. Dependence of the source-drain current (I_{ds}) on the voltage (V_{ds}) at different gate voltages (V_G). The voltage threshold (V_T), indicating the onset of conduction, can be modulated by tuning the control gate-voltage V_G . The dashed lines extrapolate V_T for any V_G value. Inset: Log plot of the full current-voltage curves at different V_G .

moment is partially preserved in the supramolecular layer connecting the electrodes and induces an asymmetry in the charge pathway resulting in a preferred direction for the current flow. A low-current plateau is present at low bias in the current-voltage characteristics (resistance of tens of GW, indicating that these systems behave like insulators at low voltages). The current rises steeply above a threshold voltage (V_T) of the order of 3V following an exponential dependence. The extent of the lowconductivity region observed in the voltage range between -3V and 3V increases with increasing the gate bias (V_G). V_T can be extrapolated by fitting the different I-V characteristics for each gate voltage, by means of a straight line of constant resistance (dotted lines in Fig.12). Figure 13 (right hand scale) displays the threshold voltage (V_T) as a function of the gate voltage, showing a linear dependence on V_G .

The current at fixed drain-source voltage decreases with V_G (Fig. 13a, left hand scale) just like in a p-channel MOSFET. Using the small signal equivalent circuit for a MOS it was possible to evaluate the maximum voltage gain AV_{max} of the transistor, given by the product of the transconductance g_m times the output resistance r_o , which resulted:

$$\left| A_{V_{max}} \right| = g_m r_o = 0.76$$

Such a value represents a reasonably good result, when compared to other small-channel molecular devices which normally exhibit gain in the range between 0.3 and 0.5 (see Table 1). It is important to notice that the difficulty in creating an ideal Ohmic molecule-metal contact and the resulting potential barriers at the interface determines the device performances. Molecular engineering and the improvement of injection using different metals and/or other device geometries thus leave large room to improvement of the device, to accomplish gain values greater than one. Another crucial issue is the perfect control of the self-assembly of the molecular layer: in fact local changes in the self-organization of the molecules might behave like defects in conventional semiconductor devices, which limit the device performance. Under this point of view, an interesting strategy appears to exploit covalent bonding of molecules in order to chemically control the self-assembly step.

The hybrid molecular p-channel MOSFET [14] exhibits some differences with respect to the standard silicon counterpart. In fact, despite these devices show an almost constant mobility as expected in the standard MOS transistor model, resulting in linear dependence (see Fig. 13a) of I_{ds} on V_G for a given V_{ds} , the expected saturation of I_{ds} does not occur in the guanosine devices. This suggests a description of these devices in terms of band alignment and resonant transport in the molecular layer, where the shift of V_T is due to the modification of the molecular bands induced by the gate potential. Figure 14 sketches this mechanism: at $V_G=0$, when V_{ds} reaches V_T (Fig. 14a) resonant tunnelling due to level alignment occurs. If V_G is increased by DVG (Fig 14b), a shift in the molecular band is induced, resulting in a different alignment condition. In this case an additional DVT is needed to activate transport across the structure, consistent with the results of Fig.13a.

The interest in such molecular devices derives mainly from the following features: (i) the voltage threshold for the conduction can be modulated by means of a control gate-voltage V_G ; (ii) the very small size of the device and the perspective of large integration at low cost.

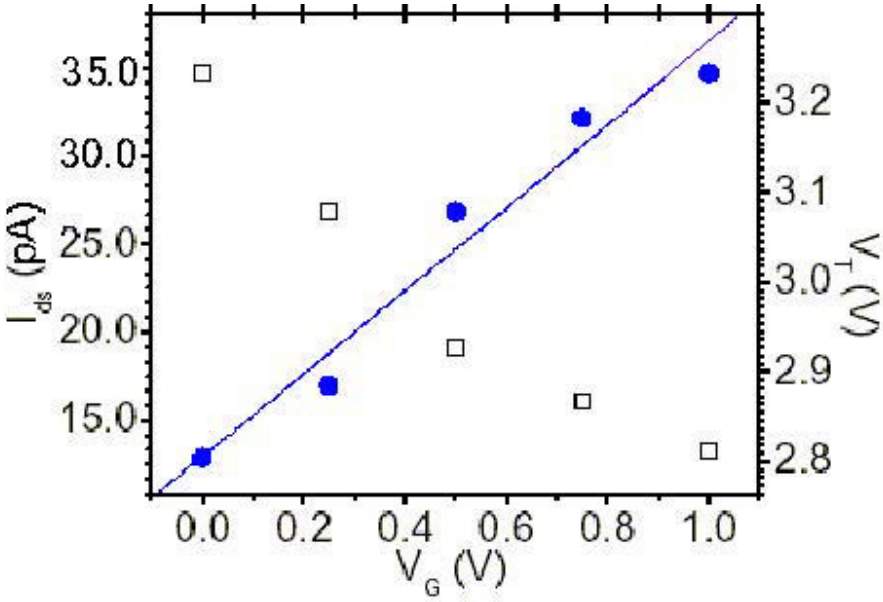


Figure 13: (a) Left scale: dependence of the source-drain current (I_{ds} , hollow squares) on the gate voltage V_G at $V_{ds}=2.0V$. Right scale: dependence of V_T (circles) on the gate voltage V_G .

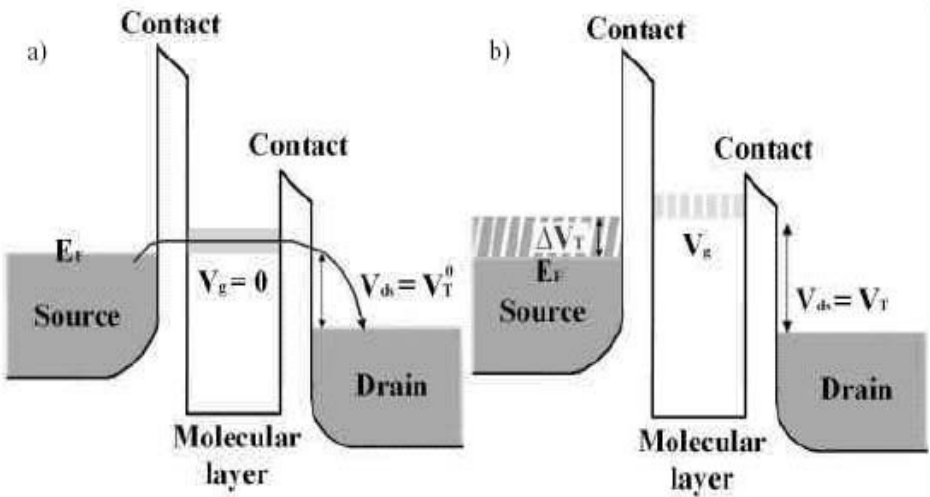


Figure 14: (a) Resonant tunneling due to level alignment at $V_{ds} = V_T^0$. The yellow bar represents the molecular electronic band at $V_g=0$. (b) The application of a gate bias V_g induces a shift of the energy bands resulting in a different alignment condition. Therefore an additional DVT between source and drain has to be provided to activate the conduction process.

Table 1: Voltage gain of state of the art nanodevices and conventional semiconductor transistors. The active molecule or the device technology is quoted in the central column. For conventional MOSFET, gain is quoted in the weak inversion regime.

Ref	Molecule/ Technology	Av
Dekker et. al, Nature 393, 49	Carbon Nanotubes (CNTs)	0.35
Avouris et. al, Phys. Rev. Lett. 89, 126801	CNTs	0.5
	DNA nucleosides	0.76
Typical devices data-sheet	CMOS 0.35 μm	50
	CMOS 0.18 μm	31
	CMOS 0.13 μm	15
		Weak Invers.

4. Nano-electronic devices based on metalloproteins.

Besides all those devices based on proteins and enzymes which belong to the family of biosensors, having typical size of hundreds of microns or more, a novel example of protein-based active electronic device has been recently demonstrated [15]. The natural electron transfer activity of blue-copper metalloproteins (like azurin) is exploited for the realization of molecular switches whose conduction state can be controlled by tuning their redox state through an external voltage source (gate). In order to realize a real biomolecular device in the solid state operating in air, a comprehensive study of the redox, electronic and electrical properties of the metalloproteins linked to an inorganic substrate under non-physiological environments has been conducted [15]. Azurin [16] from *Pseudomonas aeruginosa* is a small (molecular mass 14.6 kDa, Fig. 15 (a)) and soluble metalloprotein involved in the respiratory phosphorylation of its hosting bacterium. Structural and electronic studies have shown that the Az capability to function as a one-electron carrier, in the biological environment, is due the equilibrium between the two stable oxidation states of the Cu ion, Cu+1 (reduced) and Cu+2 (oxidised), and to the structural stability of the active site. The redox active centre of azurin contains a copper ion liganded to 5 aminoacid atoms in a peculiar ligand-field symmetry, which endows the protein with unusual spectroscopic and electrochemical properties such as an intense electron absorption band at 628 nm, a small hyperfine splitting in the electron paramagnetic spectrum, and an unusually large equilibrium potential (+116 mV vs SCE) in comparison to the Cu(II/I) aqua couple (-89 mV vs SCE) The absorption spectrum of an azurin solution is reported in Fig. 15(b). The broad band centred at 628 nm is related to S(Cys)®Cu charge-transfer transitions, while the peak centred at 275 nm is due to electronic transitions originated from UV light absorption of aromatic residues of the protein.

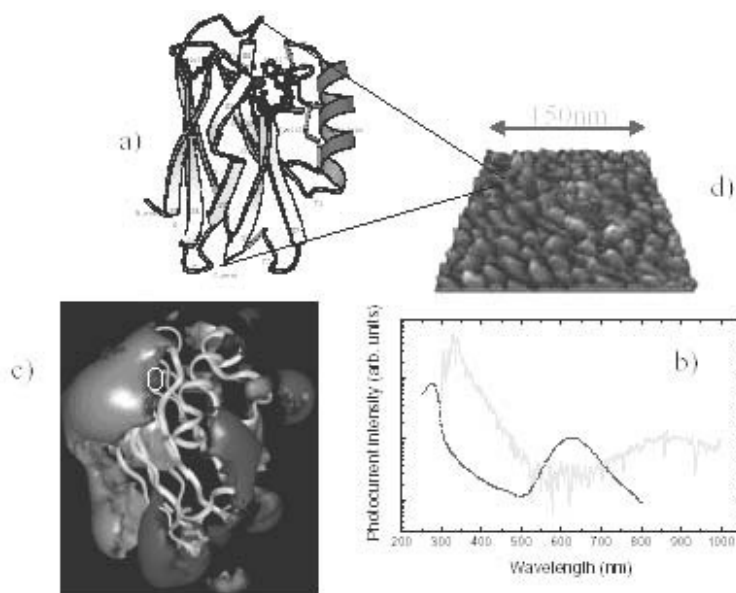


Figure 15: a) Structure of azurin from *Pseudomonas Aeruginosa*. Note the S-S bridge (yellow) used for oriented immobilization, and the amino-groups (Tj) , used for random immobilization (blue) -b) Absorption spectrum of azurin in solution (dashed line) and photocurrent spectrum (continuous line) from an immobilized solid state film of azurin on Si/SiO₂ interconnecting two Au nanocontacts. The photocurrent measurements were carried out under a bias voltage of 5V. c) MEP of the oxidized azurin. Iso-potential surfaces are shown at -0.5 (red) and 0.5 kcal/mol/e (blue). Note the spatial separation of the positive (blue) and negative (red) charge clouds giving rise to the molecular dipole. The Cu site is identified with a white circle. The yellow frame indicates the Cys3-Cys26 disulfide bridge.— d) AFM image of an azurin monolayer. The AFM measurements were performed in non-contact mode and in air on a working device.

While the redox properties of azurin can be exploited for obtaining a current flux, its peculiar structural properties can be exploited for immobilizing the protein onto the metallic substrate. The surface disulfide bridge Cys3-Cys26 (Fig. 15(a)) may be used to bind the protein to gold (or other electronically soft metals), thus envisaging the possibility to deposit oriented layers on gold substrates. The achievement of oriented immobilization is extremely crucial for electronic applications in which the charge transport benefits of the long range order of the transporting material. Orientation can in principle affect conduction in two ways: (i) it allows increased protein coverage, thus favoring electron transfer among neighbouring molecules, and (ii) it enhances, for a given coverage, the intermolecular electron transfer (due to the fact that the positions of the Cu-sites are approximately coplanar, thus offering more favorable pathways for conduction).

In addition, the molecular electrostatic potential (MEP) of the protein in solution is known to be important in protein interaction properties at medium and long-range distances in solution, and plays a fundamental role in the recognition processes of biomolecules. It is therefore expected that electrostatics will influence both the deposition kinetics of the proteins in solution, and their selfassembly. The charge distribution on the azurin surface gives origin to an electric dipole, as clearly shown in Fig.15(c). The occurrence of such a strong intrinsic dipole (150 Debye) suggests that twoterminal circuits, interconnecting solid

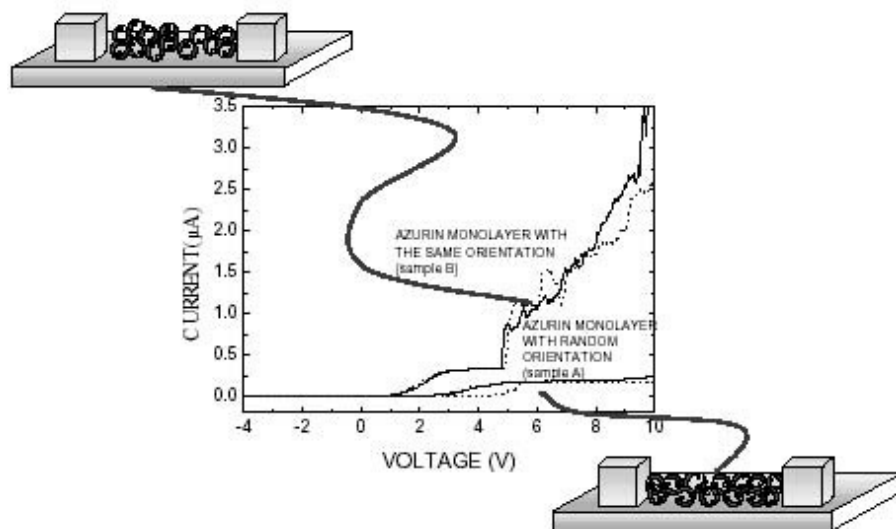


Figure 16: Current voltage curves of oriented (B) and non-oriented (A) proteins films. The gap between the gold electrodes was 70 nm. The possible arrangement of proteins between the electrodes in the oriented (top-left) and randomly oriented (bottom-right) layers are illustrated schematically. The positive and negative potential regions, the Cu site and the disulfide bridge are indicated by the same color code as in Fig.15(c).

state films of immobilized azurin molecules, should have an intrinsic polarity which depends on the value and on the orientation of the molecular dipoles. Both oriented and non oriented azurin films should exhibit a macroscopic polarization. However, the total dipole is enhanced by depositing oriented self-assembled films with parallel dipoles. If the dipole distribution is preserved in the devices after drying, we expect that it will induce a macroscopic electric field favoring conduction. The planar biomolecular devices consisted of two Au nanoelectrodes separated by a small gap, where a solid state azurin monolayer was immobilized. Random and oriented immobilizations were attained by following two different chemical modification of the SiO₂ surface. Randomly oriented layer are obtained by immobilizing the proteins through the 12 amino-groups (blue-stripes in Fig.15a)), resulting in 12 possible orientations of equal probability for the molecule. A different functionalization of the SiO₂ surface, instead, results in a covalent binding through the unique Cys3-Cys26 disulphide bridge (yellow stripes at the bottom of the Az molecule in Fig.15a). The use of such a unique sticky site results in a perfectly ordered array of Az molecule, whose Cu redox center is located about 4 nm above the SiO₂ surface. Fig.15(d) shows a non-contact AFM topographical image of an Az film deposited onto a SiO₂ substrate. The lateral size of the imaged proteins ranges around 12 nm, due to tip-sample convolution (the actual size of Az from X-ray crystallography is about 4 nm). The quality of the pictures is further influenced by the substrate roughness, improving a lot on atomically flat substrates. The height of the visible features is instead about 4 nm, consistent with the single protein size. In Fig. 15(b), the photocurrent spectrum measured on a solid state Az layer by biasing the sample at 5V is compared to the absorption spectrum of Az in solution. The photocurrent exhibits a strong absorption onset for wavelengths shorter than 400nm, consistent with the absorption spectrum. In addition, the

absorption band around 628 nm, observed in the azurin solution, corresponds to a clear current minimum in the photocurrent spectrum. This indicates that no charge transfer occurs through the Cu atom when it is reduced, suggesting that the electron transfer mechanism through the Az redox site can be exploited to implement functional electronic and optoelectronic devices.

The comparison between the current-voltage curves measured in the oriented (sample B) and randomly oriented (sample A) azurin layers is reported in Fig.16. The continuous and dotted lines represent the downward and upward sweeps, respectively. Three important effects can be deduced from this comparison. Both curves are asymmetric, with a strong rectifying behavior. The value of the current measured under forward bias between the nanoelectrodes suggests that the electron transfer mechanisms in the protein, between the Cu site and the edges, is quite effective in determining the conduction processes. The difference between the positive and negative wings of the current curve of both sample A and B may be attributed to the presence of the dipole in the azurin molecules which sets the polarization of the planar devices.

The current flowing through the device with the oriented layer is about ten times larger than that flowing through the device with the non-oriented layer. In fact, the regular orientation of the Az molecules in sample B, determined by the unique sticking site on the protein (the Cys3-Cys26 bridge) exploited for the layer formation, drives the self-assembly on the substrate, resulting in a distribution of parallel dipoles, as schematically depicted in Fig. 16. This induces a macroscopic electric field favoring conduction. In sample A, although the electrostatic long range interaction may favour some dipole alignment on the surface, a complete parallel orientation of the molecular dipoles cannot be achieved as a consequence of the many possible sticking sites on the protein surface used in the immobilization procedure.

In the oriented protein layer under forward bias the current is step-like with a smooth exponential rise in the region between 1.9 and 2.3V, and a steep rise around 4.9 V (Fig.16). The step centered around 2.1V corresponds to the energy required by the protein molecule to reduce the Cu atom by means of the electronic transition involving the S(Cys)⁺Cu charge-transfer. This corresponds to the 627 nm band in the absorption spectrum shown in Fig.15(b). The step around 4.9 V corresponds to the energy required to perform resonant tunneling via the redox levels of azurin. Such a process occurs through a coherent two-step tunneling in which the electrons go from the negative to the positive electrode via the molecular redox level. This is consistent with the electrochemical STM measurements and in situ cyclic voltammetry curves, showing a maximum at -4.96eV (measured with respect to the vacuum level). This step is also observable in the I-V curve of sample A, though less pronounced and with a small hysteresis

In order to further elucidate the role of the metal ion and the effects of purity of the protein sample on the device performances, three different types of high-purity of engineered azurins were used for implementing oriented layer devices as shown in Fig.17 [17]:

- i) a highly-purified synthetic-azurin, referred to as “recombinant azurin”, in sample (A) of Fig.17. These proteins are identical to the natural proteins (Fig.15a), through with a higher degree of purity;
- ii) a modified synthetic azurin with the Cu atom replaced by a Zn atom (Zn-Az), in sample (B) of Fig.17;
- iii) a modified azurin without metal atom (called APO-Az), in sample (C) of Fig.17.

Sample (A) shows the same rectification and step-like character observed in the devices fabricated with oriented commercial (non-purified) Az layers, reported in Fig.16. However, the current flowing through device (A) with recombinant proteins is two orders of magnitude larger. This suggests that highly purified proteins are best suited for molecular electronic applications. Reasonably, a high degree of purification favors a closer packing of the proteins onto the device substrate and avoids passivation phenomena of the substrate.

Sample (B) shows a less pronounced rectifying behavior, without the redox-induced steps characteristic of the Cu atom, and a current intensity about one order of magnitude lower than sample A. This is ascribed to the electronic properties of Zn, which are different from those of Cu. Zn has in fact only one stable redox state, Zn^{2+} , which is redox inert, thus preventing Zn-Az molecules from being efficient redox species-mediated electron carriers.

The importance of a metal atom in the protein structure is demonstrated by device (C), which was built using APO-proteins obtained from recombinant Az. In the absence of metal redox center in the protein structure, the bio-device does not show any measurable conduction. This indicates that the metal in the protein is responsible for the electron transfer as reflected in the transport characteristics of Az biomolecular diodes.

The natural electron transfer activity of the azurin can be exploited for the realization of molecular switches whose conduction state can be controlled by tuning their redox state through an external voltage source (gate).

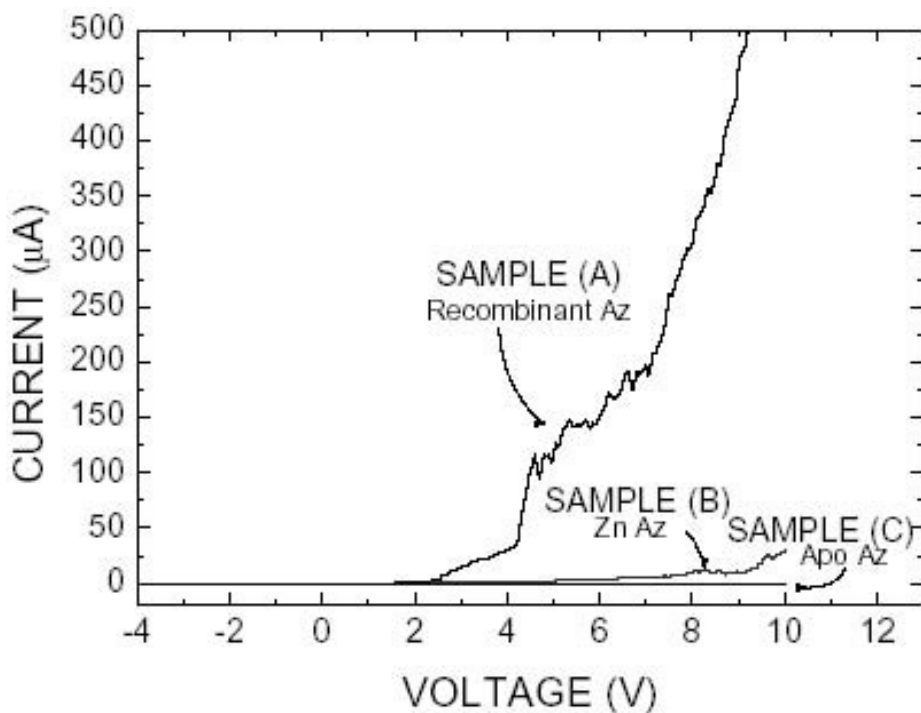


Figure 17: Current voltage curves of (A) recombinant Az (black), (B) Zn-Az (red), and (C) APO-Az (blue). The gap between the gold electrodes was 70nm.

The natural electron transfer activity of the azurin can be exploited for the realization of molecular switches whose conduction state can be controlled by tuning their redox state through an external voltage source (gate).

The molecular devices were made on thermally oxidized (SiO_2 thickness 100nm) silicon wafers. In the first step of the technological process, photolithography followed by lift-off was used to define the contact pads (Cr/Au, Ti/Au or Ti/Pt, thickness 6/60nm) on SiO_2 and the Ag gate (50 nm-thick) on the back of Si-substrate. Then we performed electron beam lithography (EBL) on polymethyl-methacrylate (PMMA) resist to define the electrodes with separation in the range between 20 and 100 nm. The molecular film was then deposited by room temperature cast deposition between the metal electrodes. The azurin monolayer is immobilized onto the channel by means of surface functionalization and chemisorption. Both commercial natural azurin and synthetic and purified azurin were used to implement the devices.

All the fabricated devices were tested at room temperature and ambient pressure. Prior to protein deposition, a control on the empty devices (without molecules between the electrodes) was performed to check the effective insulation between the source(S) drain (D) and gate (G) terminals along the different current pathways. All these tests revealed IDS and ISG values lower than 20 pA and typical open circuit resistance larger than 100GW.

In Fig. 18a we show the current voltage characteristics of a protein device for a source-drain voltage (V_{DS}) >0 as a function of the gate bias (V_G) in the range between 0V and 4V (first active region). As a general feature the IDS current remains low ($<20\text{pA}$) up to a V_{DS} bias voltage of about 2.3V and then increases reaching 100pA intensity at 6V. A clear

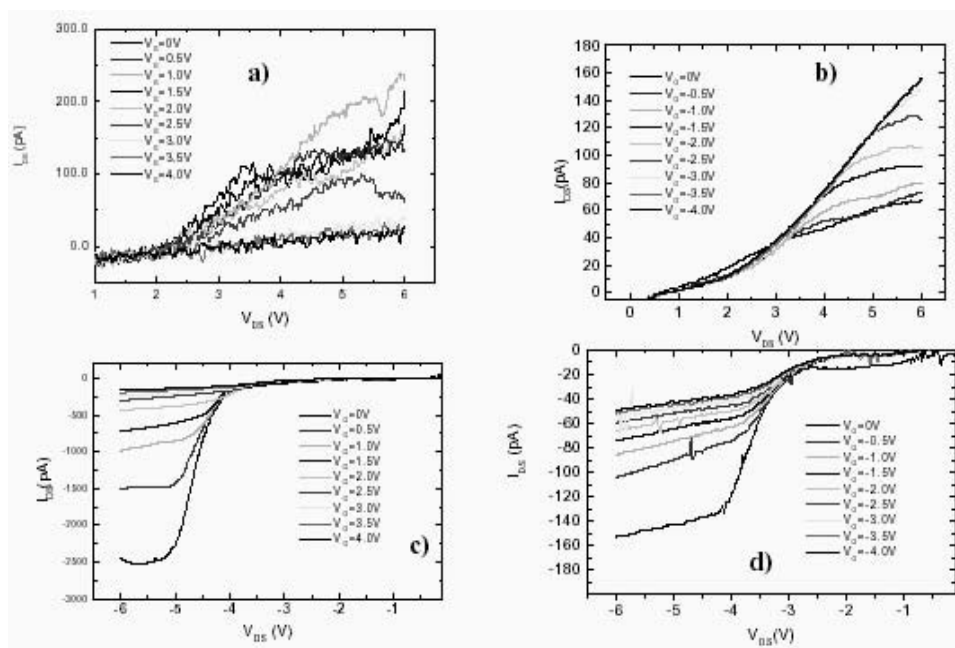


Figure 18 : I-V characteristics of the protein transistor in the four different active regions : a) $V_{DS} > 0$, $V_G > 0$; b) $V_{DS} > 0$, $V_G < 0$; c) $V_{DS} < 0$, $V_G > 0$; d) $V_{DS} < 0$, $V_G < 0$.

modulation effect is visible as a function of V_G . The dependence of the I_{DS} current as a function of the V_G intensity is reported in Fig.19a for a fixed value of V_{DS} ($V_{DS}=4.5V$). The current increases up to a maximum value of 200 pA at $V_G=1.1V$, then it decreases to the 100pA level at $V_G =2V$, and finally falls down to the open circuit value for higher applied gate voltages.

Similar set of measurements were performed under positive and negative V_{DS} with positive (Figs. 18a and 18c, respectively) and negative (Figs. 18b and 18d, respectively) gate bias namely: $V_{DS}>0$, $V_G>0$ (18a); $V_{DS}>0$, $V_G<0$ (18b) ; $V_{DS}<0$, $V_G>0$ (18c) ; $V_{DS}<0$, $V_G<0$ (18d). In Fig. 18b by decreasing the gate potential the current increases up to 160pA at $V_{DS}= 6V$. The corresponding dependence of the I_{DS} current as a function of V_G is reported in Fig. 19b for a V_{DS} value of 5V. In this case we did not observe the resonance of Fig.19a, but only a smooth increase and a saturation at 115pA in the range between -2.5 and $-4V$. For $V_{DS}<0$, $V_G>0$ (Fig. 18c) and $V_{DS}<0$, $V_G<0$ (Fig. 18d) we observed a decrease and an increase (in absolute values) of the I_{DS} negative currents in the two cases, respectively, with increasing the gate voltage, respectively. As a general trend the current increases linearly for V_{DS} voltages higher than 3V and then saturates in the range between 4.5 and 6V. In this voltage range the operation of the protein transistor resembles that of an inorganic MOSFET in the saturation region, with constant I_{DS} current value for each curve.

The room-temperature drain-source current as a function of the gate potential, for $V_{ds} = 5.5$ V, is further investigated in figure 20a. The transfer characteristic exhibits a pronounced resonance with a gaussian-like shape centered at $V_g=1.25V$. In this region, the transconductance changes from positive to negative values. The peak to valley ratio and the FWHM are 2 and 0.3V, respectively. This feature gradually disappears after some cycles of measurements due to the ageing of the molecular layer, which is not encapsulated.

From an electronic viewpoint, the device switches from a n-MOS FET behaviour before resonance to a p-MOS FET after resonance. This is a key result because it allows us to exploit the advantages of a complementary logic, fabricating both p-type and n-type devices on the same chip. For the implementation of an inverter, the unipolar technology would require a load resistance (Fig. 20b), whereas a complementary logic (Fig. 20c) - incorporating both p-type and n-type transistor – would overcome such limitation. This results in **(i)** a decrease of the logic gate occupation area (reduced to the transistor-size scale); **(ii)** a reduction of the fabrication complexity, since in integrated circuits technology,

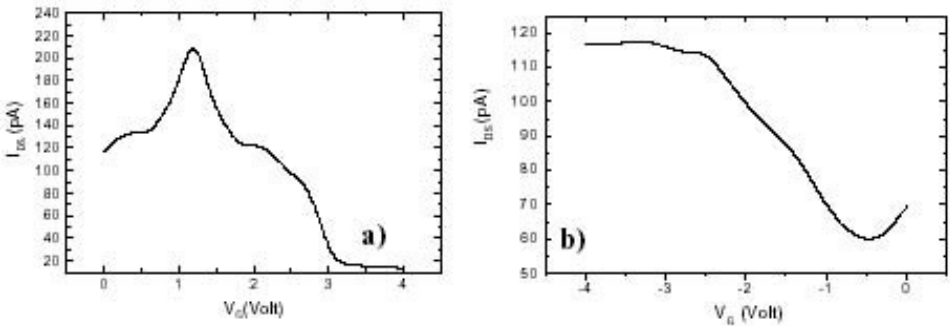


Figure 19 : I_{DS} current intensities as a function of V_G at fixed V_{DS} values for the four active region reported in figures 5 : a) $V_{DS}=4.5V$; b) $V_{DS}=-5V$; c) $V_{DS}=5V$; d) $V_{DS}=-5V$.

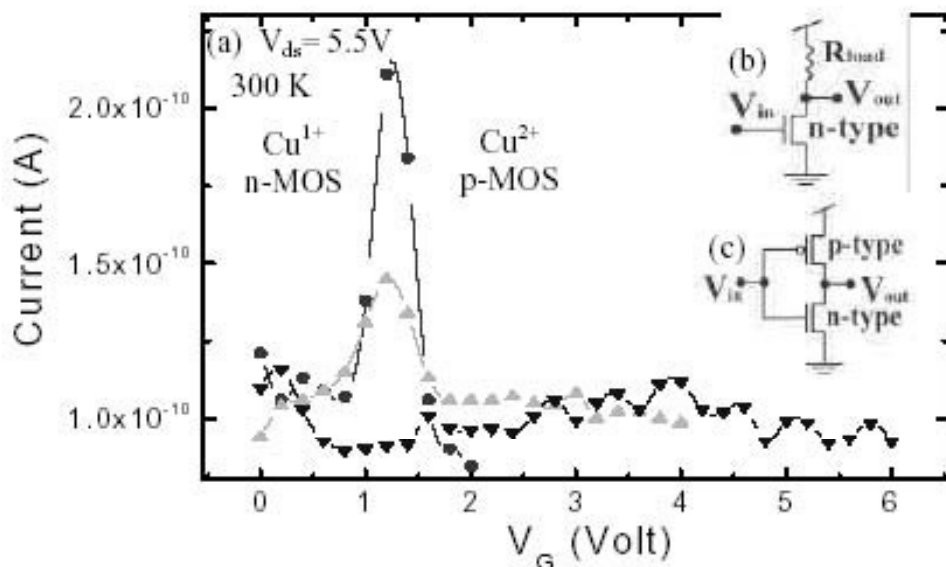


Figure 20: (a) Transfer characteristic of protein FET. A pronounced resonance with a gaussianlike shape centered at $V_G = 1.25V$ is present. In this region, the transconductance changes from positive to negative values. The peak to valley ratio and the FWHM are 2 and 0.3V, respectively. This feature gradually disappears after some cycle of measurement due to the aging of the molecular layer (the red, green and blue curves are recorded in sequence). Insets: Electronic applications of such azurin device (b) A standard n-MOS inverter using a resistive load; (c) a CMOS inverting amplifier made with the protein FET and having the advantage of consuming power only during the switch.

accurate resistors are harder to make than capacitance and transistor and (iii) reduction of power consumption because, as opposed to unipolar inverters which consume power in the low state, CMOS consume power only when switching.

Our redox proteins devices are very different from standard inorganic semiconductors and conventional organic devices. Silicon MOSFETs and thin-film transistors (TFTs) are based on a gate field modulating the width and the conductance of a semiconducting channel, whereas the accepted mechanism for carbon nanotube FETs is the Schottky-barrier dominated transport. In proteins, the long range electron transfer (ET), which represents one of the key processes of living systems involved in photosynthesis and respiration, occurs between a donor (D) and an acceptor (A) site. Two different models for ET have been proposed, i.e. a superexchange mechanism (consisting of direct quantum tunneling between the donor and acceptor) or a sequential (incoherent) hopping between adjacent sites. The main factors influencing the ET rate are: (1) the distance between the two redox centers (electron tunneling has an exponential decrease of the ET rate with distance, whereas hopping leads to a slowly decay as the inverse of the distance); (2) the nature of the microenvironment separating the donor and acceptor (which mediates the virtual state or provides intermediate states, respectively), (3) the reorganization energy λ , i.e. the energy required for all structural adjustments (in the reactants and in the surrounding molecules) which are needed to assume the configuration required for the transfer of the electron and (4) the driving force. In particular, in the case of Azurin, the essentially unchanged copper

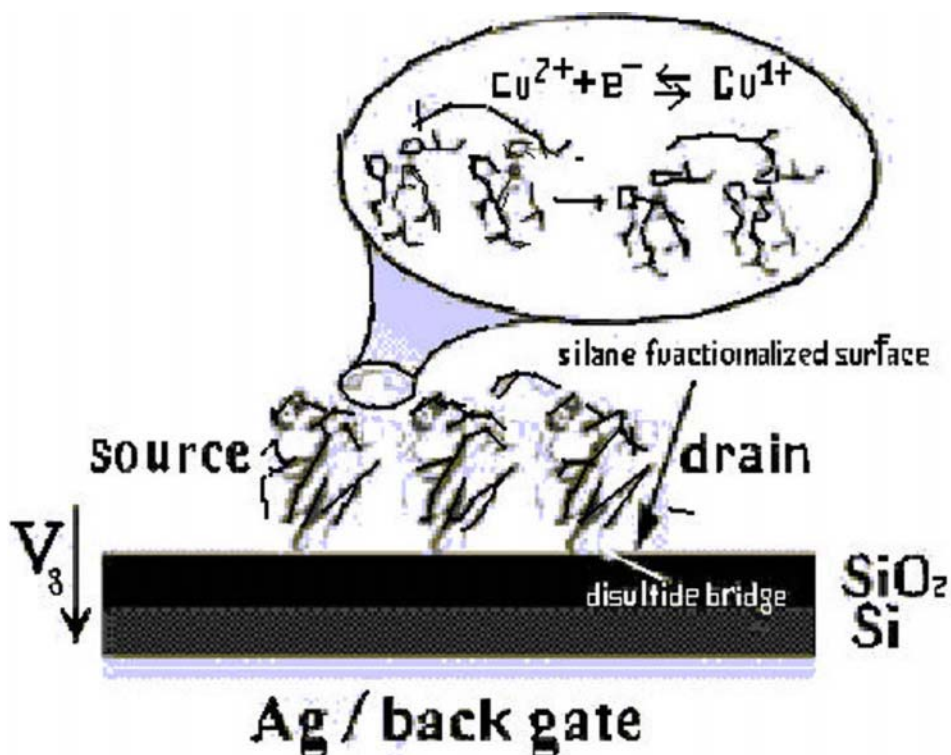


Figure 21: Three-dimensional crystal structure of the blue-copper protein Azurin containing the central Cu ion as redox site; cross section (not to scale) and transport mechanism of the protein FET. The site geometry of the copper site (the blue sphere at the top) is a distorted trigonal bipyramid one. The disulfide bridge (Cys-3 – Cys-26, indicated in yellow at the bottom) opposite to the copper atom, is exploited to induce chemisorptions of Azurins on silane-functionilazed substrates. The field effect transistor consists of a protein monolayer connecting two arrowshaped Cr/Au electrodes on a SiO₂ substrate. An Ag back-electrode acts as the gate. As a consequence of chemisorption, proteins sits on the surface with the electron transfer pathway - coupling the copper atom and the disulfide bridge- perpendicular to the substrate. In our model, transport is based on sequential electron hopping between one reduced azurin (blue copper ion in the inset) to an adjacent oxidized one (red ion in the inset). The gate (vertical) field influences the oxidation state of the redox site, originating the resonance.

site geometry in the Cu(II) and Cu(I) state minimizes the reorganization energy λ and favours the fast electron transfer.

The transport of electrons through systems containing redox sites occurs via electron hopping from one reduced (Cu(I)) molecule to an adjacent oxidized (Cu(II)) molecule, see Figure 21. Therefore, the presence of two adjacent Az molecules in the Cu(I) and Cu(II) redox states is required to have current flux between two planar electrodes.

Let us indicate by k_{im} the inter-molecules transfer rate. In analogy to solid-state physics, we introduce two functions f_{Cu}^{+1} and f_{Cu}^{+2} which provide the probabilities that a copper site is in the Cu(I) and Cu(II) state, respectively (or the population of reduced and oxidized azurins in the layer). Obviously, it results $f_{Cu}^{+1} = 1 - f_{Cu}^{+2}$. Consequently, the overall electron transfer rate WET takes the form:

$$W_{ET}(V_{ds}, V_g) - k_{im}(V_{ds})G(V_g) - k_{im}(V_{ds})f_{Cu^{2+}}(V_g)f_{Cu^{1+}}(V_g) - k_{im}f_{Cu^{2+}}(V_g)[1 - f_{Cu^{1+}}(V_g)]$$

where we have assumed that V_{ds} and V_g influence k_{im} and $dG = f_{Cu^{2+}}(1 - f_{Cu^{2+}})$ respectively. In $f_{Cu^{2+}}^2$ If we assume that at $V_g=0$ most molecules are in the reduced state (Cu(I)), with increasing V_g the number of oxidized molecules increases, other words, given the proteins and their arrangement in the layer, the inter-molecule transfer rate k_{im} only depends on the in-plane driving force, which is related to the bias applied between drain and source electrodes (hopping mechanism). On the contrary, the gate voltage only affects the electronic properties of the redox site. As a consequence of the covalent bonding on the silanized surface, the protein is chemisorbed onto the SiO_2 surface with the natural electron transfer route – which joins the copper site to the disulfide-bridge – almost perpendicular to the surface. The vertical field applied along this direction (due to V_g) modifies the oxidation state and induces a change in the equilibrium of the redox reaction, thus modifying the balance between the two populations, i.e. the probability density function also. Therefore $\frac{df_{Cu^{2+}}}{dV_g} > 0$ and the relation $\frac{dG}{dV_g} = \frac{dG}{df_{Cu^{2+}}} \frac{df_{Cu^{2+}}}{dV_g} = 0$ is fulfilled provided

$$\frac{dG}{df_{Cu^{2+}}} = 1 - f_{Cu^{2+}} = 0, \text{ i.e. if } f_{Cu^{2+}}(V_g) = \frac{1}{2}$$

Therefore, hopping mediated electron transfer (and consequently the current as a function of V_g) is maximum when the populations of protein in the Cu(II) and Cu(I) state are equals, otherwise the current is lower. This phenomenological model explains the presence of the resonance in the transfer characteristics shown in Fig. 20. Moreover, this model is consistent with the interpretation of the redox peak in cyclic voltammetry curves and in electrochemical STM experiments performed on azurins chemisorbed on Au(111) substrates.

Acknowledgements

We are thankful for the invaluable support and exciting collaboration with various colleagues. We would like to thank Elisa Molinari, Rosa Di Felice, Francesca De Rienzo, Paolo Facci at S3-INFM research center in Modena (Italy), Gerard Canters and Martin Verbeet at Leiden University (NL), Salvatore Masiero, Tatiana Giorgi, Gianpiero Spada and Giovanni Gottarelli at University of Bologna (Italy).

Financial support by NNL-INFM, by the Italian Ministry of University and Research (MIUR) through the FIRB project “molecular nanodevices” and by EC through SAMBA project is gratefully FIRB acknowledged.

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DNA, DNA/METAL NANOPARTICLES, DNA/NANOCARBON AND MACROCYCLIC METAL COMPLEX/FULLERENE MOLECULAR BUILDING BLOCKS FOR NANOSYSTEMS: ELECTRONICS AND SENSING

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Abstract

The article presents the latest results on electronic properties and sensing of many nearly-discovered nanosystems such as DNA polymerized molecules (DNA polymer), DNA/metal nanoparticles, DNA/Fullerene (C₆₀), DNA/SWCTs (single wall carbon nanotubes) and DNA/MWCTs (multi wall carbon nanotubes), DNA/carbyne fibers, Macrocyclic metal complex (metaphthalocyanine - MPc)/C₆₀. It demonstrates the synergy between electronics and sensing nanosystems. Also, an in depth discussion of the route towards DNA/gold nanoparticle, DNA/nanocarbon, MPc/fullerene nanosystems is presented (concepts and realization).

1. Introduction

The synthesis, characterization and manipulation of macromolecules in nanosystems – systems that have features or characteristic lengths between 1 and 100 nm – bring together chemistry, physics and biology in an unprecedented way.

Phenomena occurring in such systems are fundamental to the working of synthesized molecular devices, systems but also to living organisms. The ability of nanosystems creation is essential to introduce a wide range of chemical and materials flexibility into these structures to build up more complex nanostructures that can ultimately rival with biological nanosystems.

In this respect, DNA molecules, DNA polymerized molecules and nanocarbons (fullerenes, heterofullerenes, nanotubes, carbolite, carbyne) [1] and MPc/fullerene are potentially ideal nanoscale building blocks because of their length scale, well-defined architecture, controlled technologies, ease of processing and wide range of chemical functionality that can be incorporated.

In this review on the basis of our own work and known investigations we will have a look at a number of promising DNA polymer, DNA/nanocarbon and MPc/C₆₀ electronic, photonic applications that have been developed recently in the first years of the 21st century.

In the sections we compared DNA molecules and DNA polymerized molecules (DNA polymer) as building blocks: molecular and electronic structures, charge transport. Sensing of DNA conjugated polymer films to UV-Visible light observing from a conductivity changing have been analyzed.

For DNA-linked gold nanoparticles assemblies in networks we viewed an interrelation for electronic structure, charge transport and resistance behavior under temperature and microwave power changing.

The changes in electronic structure of DNA/C₆₀ molecular complex under increasing of C₆₀ contents are revealed by optical and tunneling current spectroscopy [4].

The characteristics of carbon nanotube, DNA/carbon nanotubes and carbyne-like fibers building blocks such as: chemical bonds, electronic structure, charge transport and sensing to the temperature changing are estimated.

Electronic structures of CuPc, C₆₀ molecules and CuPc/C₆₀ molecular complexes in toluene have been compared. Model of the sensing of CuPc/C₆₀ fullerene molecular complex to UV-Vis light have been characterized.

The section on the conclusion and future are presented.

2. DNA molecules and DNA polymerized molecules as building blocks

DNA molecules as building blocks in nanotechnology of nanosystems has probably only just begun, but already produced some striking results [2-8] as in electronic, optic nanosystems engineering such as in tissue engineering [9-26].

The first step on this way is the study of DNA on the molecular level, which may point to new directions in nanosystems design and construction – not just mimicking biomolecular systems, but actually using DNA biomolecules themselves to construct novel nanosystems [4, 27-28].

In addition to its well-known importance to biology, deoxyribonucleic acid (DNA), as a one – dimensional macromolecule, has attracted interest as a material for use in functional mesoscopic electronic devices [29, 30] and molecular computing [31, 32].

2.1. DNA MOLECULAR STRUCTURE

Physical properties of DNA are originated not only from the very complicated multiscale structure of an individual DNA molecule but also from the active influence of DNA molecules on their environment and vice versa. The building blocks of a DNA molecule are nucleotides which consist of nitrous nucleotide base, sugar and phosphate radicals. There are four kinds of nucleotides constituting DNA: adenine, guanine, cytosine, and thymine (for RNA thymine is replaced with uracil). The so called primary structure of DNA is the polymer chain (the strand) of nucleotides connected via the oxygen atom at the 3' end and 5' end. Secondary structure of DNA is due to the complimentary nature of nucleotides. Two strands of nucleotides are connected into the single DNA molecule by hydrogen bonds in such a way that guanine is always paired with cytosine and adenine – with thymine. Additional bonding arises between nucleotide bases mainly by virtue of π -electrons of aromatic-like rings. This double stranded ribbon-like structure twists into a helix. There are major and minor grooves. The protruding parts are two phosphate-sugar strands with the phosphate radicals forming the outer layer. It should be emphasized that the double stranded DNA helix can exist in different modifications depending on the temperature and environment: A, B, Z, λ and other forms. The tertiary structure is determined by the macroconformations of DNA molecule.

2.2. DNA ELECTRONIC STRUCTURE

Electronic structure of DNA and computing methods are reviewed in paper [15]. BLYP and similar DFT exchange-correlation potentials are suitable for the ground state calculations. As was mentioned above the electronic properties of DNA depend drastically on the structural form of DNA and its environment. Moreover there is a large variety of artificial polymerized structures consisting of nucleotide bases which can be fabricated by manipulating of individual molecules.

Considering electronic structure, DNA molecule can be decomposed into simple structural units mentioned above: nucleotide base, sugar radical, and phosphate radical. This can be done because the molecular orbitals close to HOMO and LUMO are well localized on these atomic groups, that is provided by the single sp^3 -hybridized linear bonds connecting the groups: N-C bond connecting base and sugar, and oxygen atoms connecting phosphorus and sugar. Electronic structure calculations confirm this (Fig. 1). Hydrogen bonds and interbase electronic coupling are weak sufficiently to be considered within the tight binding approximation.

The sugar ring has HOMO substantially lower and LUMO substantially higher than respectively HOMO and LUMO of the base and the phosphate group (Fig. 1).

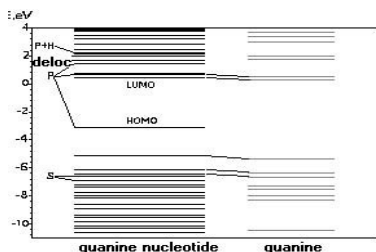


Figure 1. Molecular orbitals (MOs) of hydrogen passivated guanine nucleotide (left) and guanine (right) obtained by DFT calculations with hybrid exchange-correlation potential Becke97 and with double-zeta basis set (without structure optimization). "P" means localization on phosphate group and "S" – on sugar. Lines connecting nucleotide's and base's MOs mean localization on guanine. All MOs above 4 eV and below -11 eV and also two orbitals marked on the figure are delocalized on the whole nucleotide molecule. MOs localized on phosphate group should be considered with care because of their environment-dependent character.

Therefore it can be considered as an "insulator". HOMO and LUMO of nucleotide bases correspond to π -electrons states of aromatic-like rings, thus making them not very sensitive to the environment. It should be noted also that the bases are partially hidden inside the DNA helix. The phosphate group is the opposite case. Its electronic states are very sensitive to the environment. This is especially pronounced because the phosphate groups form the outer layer of the DNA molecule. Being hydrogen passivated the phosphate group of atoms has substantial negative charge in the ground state (sub-electronvolts). Thus the electronic states localized on phosphate group must be considered only with specifying the environment of the DNA molecule. These states play an important role in electronic properties of DNA because they lie within the LUMO - HOMO gap of nucleotide bases as indicated in Fig. 1 and shown in the papers [16,17]. Typically DNA exists in or is prepared from the solutions. Under such conditions cations from the solution adsorb on the strands and also in the minor groove as was modeled in [19] changing the electronic structure of the DNA. The major groove formed by nucleotide bases is chemically less active [18]. In this context it should be noted that the charge density of a hydrogen passivated nucleotide is distributed in such a way that the base and the phosphate group are negatively charged and sugar is positively charged. The influence of environment (via counterions) on the electronic properties of DNA is studied in details in the paper [16]. The individual electronic structures of nucleotide bases are quite well understood. Molecular orbitals are shown schematically in Fig. 2 indicating similar electronic structures for different bases that appears e.g. in the absorption spectra shown in Fig. 3. The electronic structure of a polynucleotide chain consisting of identical base pairs was considered in the papers [8,9,11] for DNA and in the paper [12] for some artificial

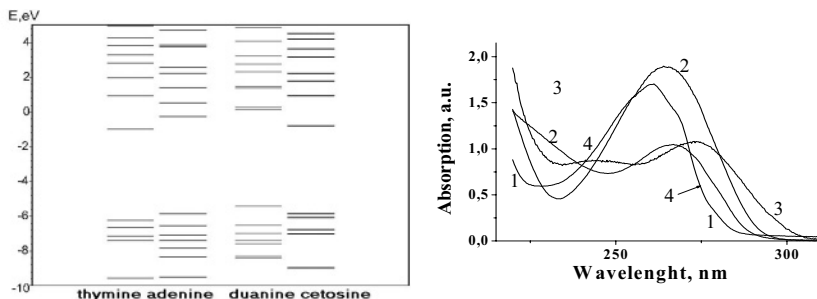


Figure 2. (left) Molecular orbitals (MOs) of DNA bases obtained by DFT calculations with hybrid exchange-correlation potential Becke97 (B3LYP produces the same results) and with 6-31G* basis set (without structure optimization). The exchange-correlation potentials HCTH98, PBE96, PW91 get similar electronic structure but with 1.5 eV smaller LUMO-HOMO gap.

Figure 3. (right) Absorption spectra of nucleotide bases: 1 – adenine, 2 – thymine, 3 – guanine, 4 – cytosine.

UMO conduction bands of DNA as a one-dimensional crystal is of the order of 0.3 eV [11], top valence bands are much narrower, their width is of the order of 40 meV [11]. The tight binding approach (see e.g. [12]) is based on well defined localized states of individual nucleotide base and small nearest neighbors' interbase couplings via π -orbitals between stacked bases and hydrogen bonds between complimentary bases in a pair. Computational methods on electron structure calculation have been used in [16,17].

2.3 DNA MOLECULE IN DIFFERENT FORMS. DNA POLYMERIZED MOLECULES

Absorption spectra of DNA have wide bands in UV range at 240-270 nm which is result of absorption band laying of separate nucleic bases. These bands response to the excitation of π -electrons in aromatic rings.

The absorption spectra of DNA in water solution with various concentrations of DNA molecules. The absorption spectra of DNA molecules in water solutions are presented in the wavelength range of 200-350 nm (Fig.4) and 400-700 nm (Fig.5), with various concentrations of DNA molecules in water. Two more intensive lines of absorption with maxima at 202 nm and 258 nm are in UV region (Fig.4) and are characterized electron transition between inside levels of double helix of DNA. Weak shift of the line absorption at 202 nm, with the changing of concentration of DNA in water (till 10 nm), is caused by DNA molecule hydrate in water.

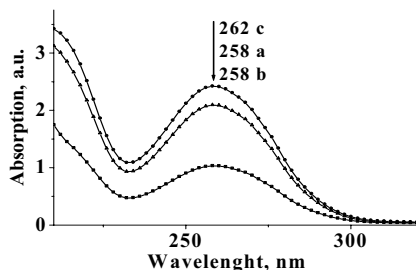


Figure 4. Absorption spectra of DNA water solution with various ratio between DNA gel and water: a - 1:1; b - 1:40; c - 1:50

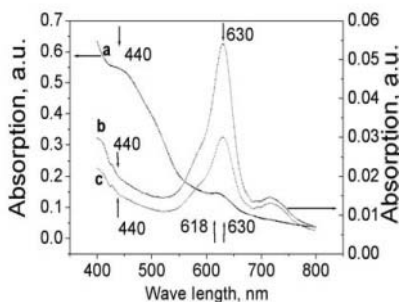


Figure 5. Vis absorption spectra of DNA gel in water with various concentration of water (DNA:H₂O): a - 1:1; b - 1:40; c - 1:50.

One of the principal directions of the bioelectronics must be the DNA carrier systems development due to the possibility of long-range carrier transport in DNA molecules showed semiconductor or insulator behavior DNA to carrier out charges to change DNA / metal electrode conductivity by light illumination for charge injection in DNA [4,29]. For the DNA polymerized gel in water solution in the Vis range DNA absorption spectra (Fig.5), can have selective absorption at 440, 618, 630, 720 nm [4,29]. Then the experimental evidence of DNA polymerized layer resistance change by light illumination in 440 nm wave length was obtained in this work. The model of these changes was discussed.

3. Charge transport in DNA polymerized molecules networks

3.1. CHARGE TRANSPORT IN DNA MOLECULE

There are two distinct mechanisms of charge transport in real systems containing DNA molecules: ion conduction of DNA solution as an polyelectrolyte and excitation transfer between nucleotide bases. There are some problems with distinguishing of these two kinds of conductivity experimentally because of comparable value of the charge mobility and possible charge transfer between nucleotide bases and environment through the grooves.

Charge transport through polynucleotide chain was studied experimentally [15-20, 34, 35] and theoretically either by Green function method [21-24] or by tight binding hamiltonian [12,25-27]. Polynucleotide chains show nonlinear voltage-current characteristics and Arrhenius temperature dependence with crossover to weak dependence at room or lower temperatures.

Because of the narrow conduction and valence bands of a polynucleotide chain the disorder effects are crucial for excitation transfer along the chain. The main disorder factors which shift the electronic energy levels of a unit cell are: 1) Difference of adenine and guanine LUMO (0.4 eV) and HOMO (0.45 eV) in adenine-guanine junction (in the case of natural chains), the same for thymine-cytosine junction. Adenine-thymine and similar junctions are almost insulating. 2) The environment dependence of molecular and thus electronic structure mainly via phosphate group modification and also by other adsorption centers, this influence is suggested to be greater than 0.1 eV or comparable with it as follows from Fig. 2 Fig. 4. Moreover additional levels available for excitation transfer can arise within the LUMO-HOMO gap. 3) The geometrical effects like non uniform bending of DNA helix. 4) Temperature induced disorder which destroys the valence bands at room temperatures. Therefore in solution prepared DNA all the electronic states are localized and the charge transport is of the hopping nature. True band conductivity is possible only for specially fabricated polynucleotide chains where the disorder effects are reduced to minimum.

Another problem of natural polynucleotide chains is the absence of intrinsic charge carriers. There are different mechanisms to get the carriers. One of them is carriers injection into the open ends of polynucleotide chain. Another way is doping of nucleotide bases probably via solution-based process. The modification of phosphate group (as kind of doping) is easy to make via the solution-based process though the charge transfer between phosphate-sugar group and base is rather weak (but possible as shown in [10]). The last mechanism is charge transfer from the electrolyte solution to polynucleotide chain through the major and minor grooves by adsorption of ions.

It should be noted also that geometrical bending of DNA molecule obstructs the efficient field induced current through DNA polynucleotide chain.

The main conclusions are as follows: 1) high charge mobilities can be achieved for specially fabricated polynucleotide chains with regular stacking of bases and good overlap

of π -orbitals which depends on stacking geometry; 2) to obtain high conductivity the problem of absence of intrinsic charge carriers must be additionally solved.

3.2 CHARGE TRANSPORT IN DNA POLYMERIZED MOLECULES IN NETWORKS

For the experimental study of DNA's type conductivity and to obtain electron density of states tunneling spectroscopy with Pt/Ir tip was used. On I-V characteristics of the Pt/Ir tip-tunnel gap-DNA hydrogel layer-tunnel gap-Pt/Ir structure we found out the following features (Fig.6): the non-linear behavior; the negative differential resistance with the width of this region changing from 0.06 to 0.23 V that is typical for resonance tunneling through double barrier; the approach to the heterostructure with zero irregularity in increasing of the current with the steps that are typical for Coulomb blockade and for jumping transport of charge carriers [36].

The part of these features can be conditioned by the electronic structure of this layer and the interface in the heterostructure. In order to study the electronic structure of the layer we investigated the shape of the normalized differential resistance of the layer. It can be seen from the normalized differential conductance - voltage curves that there is a voltage gap at the low applied bias.

The widest range with negative differential resistance, which determines a voltage gap, equals 0.7 V with offset to positive voltage of 0.1 V and current at 0.07 nA.

The I-V characteristics and differential resistance for metal strip (Pt/Ir or Cu) -tunnel gap - DNA polymerized molecules layer - tunnel gap - metal strip (Pt/Ir or Cu) structures have features also, which have been defined by charge transport through local states in this layer.

These I-V curves are nonlinear and asymmetrical. From $(dV/dI)(V/I)$ curves we estimated the band gap of these new material are $E_g=0,98$ eV; and $E_g=1,33$ eV

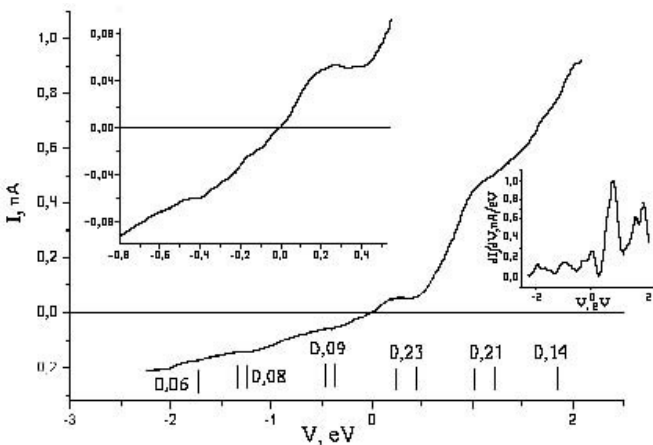


Figure 6. Typical tunnel I-V characteristic of the Pt/Ir tip-tunnel gap- DNA polymerized molecules in layer-tunnel gap-Pt/Ir and Density of States versus energy for the DNA polymerized molecules in networks in the layer on Si surface obtained from these characteristics.

4. UV-Visible light illumination sensing of DNA polymerized molecules film: the changes in the conductivity

The most intensive absorption peaks of DNA in UV range are caused by the excitation of π -bonds in aerosol rings (240-280 nm). The absorption features in the UV spectral range represents nearly all the spectral weight associated with the electronic excitations of the base pairs of DNA helix. These excitations can not be associated with the

bandgap in the usual sense. For DNA duplex the optical transition corresponds to the transition between energy levels of the various single bases, i.e. intra-base excitations, while the transition matrix element involving energy levels of different bases (such as Adenine to Thymine or Cytosine to Guanine optical transitions) is vanishingly small. The bandgap corresponds to the energy difference between the top of the HOMO band and the bottom of the LUMO band, with these bands in general corresponding to different bases [37].

The UV absorption spectra of DNA molecular gel in water (with value ratio between DNA gel and water: 1:1) and separate nucleoside bases computer simulation are represented in Fig. 3-4, respectively. These spectra shows that the most essential contribution to the UV absorption of DNA molecule is caused by thymine and adenine (purine) that mainly determines the conductivity of DNA molecule. The additional exciting of nucleoside bases that occurs under UV impact can lead to the changes of DNA conductivity. Thus, the measurement of the DNA conductivity under UV-irradiation may be used as the detection method of the nucleoside bases states.

Therefore, the effect of UV irradiation on the conductivity of the polymerized DNA experientially realized in this work.

The films of DNA polymerized molecule gel were placed on the insulator between two golden strips. The samples were exposed to UV-Vis irradiation of a standard mercurial lamp (200-800 nm) and the current through the film as the function of the applied voltage was measured for different moments of the irradiation time.

The dependence of the DNA film conductivity on the irradiation is shown in Fig.9. The effect of the irradiation appears in decreasing of the DNA film conductivity. Furthermore, in the conductivity the saturation effect is observed: after the relaxation time of the conductivity changes DNA film doesn't react on the absorbed irradiation.

When the irradiation is switched off the current increases to its initial value before the irradiation. A small opposite effect is observed at 50-100 seconds just after each switching on or off the irradiation. The changes of the DNA film conductivity under the irradiation are reversible.

A possible explanation of the conductivity changes in the range of 10-15 nS could be a modification of the single DNA configuration in the film caused by the excitation of the base pairs in the DNA helix. The observed saturation effect is associated with an accumulation of charges in the limited number of excited base states.

Thus, the sensing of the DNA polymerized molecules film to the UV-Vis irradiation could be detected by the conductivity changes.

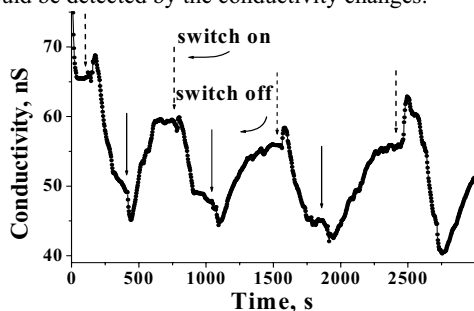


Figure 9. The dependence of DNA film conductivity on UV – vis irradiation. Dash line –the irradiation is switched on. Solid line – the irradiation is switched off.

5. Visible light illumination sensing of DNA polymerized molecules: resistive photosensor in 440 nm wavelength

The idea on the driving of the resistance of DNA polymerized molecules layer by light illumination on the wavelength, when it is no possible to warm of this layer, is

experimental examined. The wavelength 440 nm was choused from absorption spectra of DNA gel: the maximum of the absorption at this wavelength in spectra was revealed. The typical changes of a resistance of DNA polymerized molecules layer between two probe from Au strip by four probe method was obtained: a resistance increase in $(2.5 \div 5.5) \cdot 10^6$ Ohm range under the voltage $0.25 \div 0.55$ V (the current through DNA polymerized molecules layer is 10nA) in the $15 \div 328$ sec range and decrease in $(5.5 \div 4) \cdot 10^6$ Ohm range under the light illumination and the voltage $5.5 \div 3.8$ V (the current through DNA polymerized molecules layer is 10 nA) in the $634 \div 1012$ sec range (the time of light illumination). The model of the carrier transport in DNA polymerized molecules layer, what has been adapted account for intrinsic and boundary DNA molecular properties is discussed.

The investigations are carried out in the four probes in a "cross" channel structure with the DNA layer on the Au probes (the distance is 2 mm) and the dielectric surface A with the voltage between two middle Au probes 0.1 - 1 V range, the current through the intermediate DNA polymerized layer is 10 nA (the DNA layer area is $5 \times 16 \text{ mm}^2$). The change of the voltage between two middle Au probe without and with light illumination, was measured and the resistance was calculated. The wave length of the light illumination (440 nm) was selected from the Vis absorption spectra of DNA gel in water with various concentration of water. The concentrated DNA gel from Amicon a GRACE company has been used.

In Fig.10 the typical time change of the DNA layer resistance under the voltage and light illumination ($h\nu = 440$ nm) after the two applying of the voltage without and with light illumination, and after the following applying in the air. In the result of the analysis of these curves for the DNA layers exposed in the air for 28 hours, (curves a) and 52 hours (curves b) it has been have determined after applying of the voltage between Au electrodes and the current flow across the DNA layer that the resistance increases up to 2,91 and 0,856 MOhm and times of the resistance increasing are 151 and 328 s for the curves a and b, respectively. Under illumination of DNA layers, their resistance decrease up to 1,23 and 0,624 MOhm and these times are 634, 1012 s for the curves a and b, correspondently. After two illumination of the DNA layer, its resistance decrease on 1,67 MOhm. The time of the resistance decreasing is 587 s (curve a). The time change of the DNA layers resistance has exponential behavior. The time constants in this law have been calculated: $327 \pm 6 \text{ s}^{-1}$ and $275 \pm 12 \text{ s}^{-1}$ for the DNA layer after 28 and 52 hours exposing, respectively.

If we suppose that the resistance change of the layer is maximal after 28 hours in the air, when the layer of polymerized DNA consists of non separate DNA, and DNA molecules have contacts, which value decreases after 52 hours, then in the model of the resistance changes of this layer it is necessary to take into account the influence of light illumination on the resistance of these contacts.

The typical changes of the resistance of the polymerized DNA layer on four Au probes and the dielectric surface by four probe method were obtained: the resistances increase in $(2.5 \div 5.5) \cdot 10^6$ Om range under the voltage of $0.25 \div 0.55$ V (the current through polymerized DNA layer is 10 nA) in the $151 \div 328$ s range and decrease in $(5.5 \div 4) \times 10^6$ Om range under the light illumination and the voltage of $5.5 \div 3.8$ V (the current

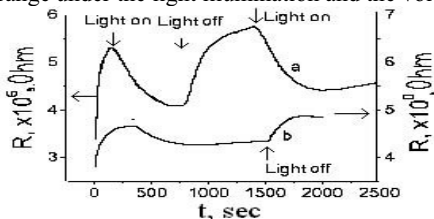


Figure 10. The typical time change of the DNA layer resistance under the voltage and light illumination ($h\nu = 440$ nm): a – after two applying of the voltage, b – after the following applying of the voltage in the air

through polymerized DNA layer is 10 nA) in the 634÷1012 s range (the time of light illumination). The model of the carrier transport in the polymerized DNA layer, which account for the intrinsic and boundary DNA molecular properties can be used for these changes of the DNA layer resistance.

6. DNA-bound to gold plates

6.1 IMAGE OF DNA- BOUND GOLD PLATES ASSEMBLIES

Image of surface morphology the DNA-linked gold nanoparticles assemblies on the Si surface Fig.11 illustrates that the nanoparticles with size that changes from 8.7 to 51.5 nm (white space in Fig.11, right image) in clean Si surface without DNA, are observed. DNA-linked gold nanoparticles assemblies with size from 51.5 to 200 nm form networks. Thus formation of assemblies is result of linking gold nanoparticles by DNA molecules (gray area that fill space between Au nanoparticles in Fig.11, right image).

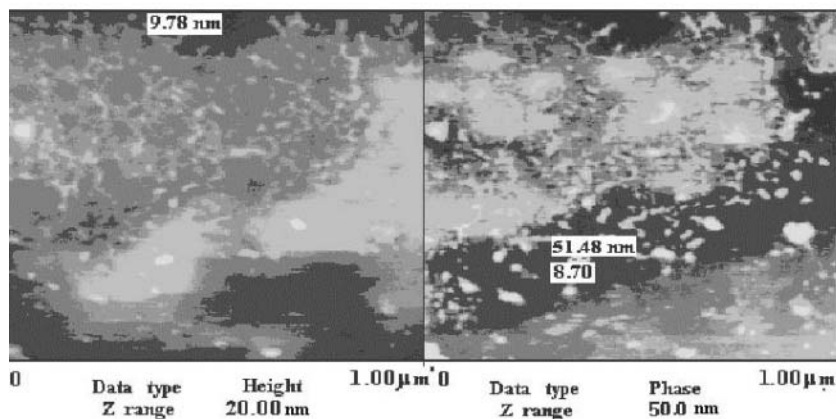


Figure. 11. The images of the DNA-linked gold nanoparticles assemblies on the Si surface: the regime of tapping mode is for right image (the area is $1 \times 1 \mu\text{m}^2$, z range is 50 nm; the regime of contact mode is for left image (the area is $1 \times 1 \mu\text{m}^2$, z range is 20 nm).

6.2 OPTICAL SPECTRA OF DNA-LINKED GOLD PLATES ASSEMBLIES IN GEL.

In absorption spectra of DNA polymerized molecules in gel with gold plates the maxima of absorption at 260 nm (for DNA polymerized molecules in gel with gold plates that have 300-350 microns, less then 150 and mixture from less than 150 and 300 – 350 microns in lateral size) were evaluated. These plates formed by DNA-linked Au nanoparticles assemblies. The addition absorption maximum at 428 nm wavelengths was common for DNA-linked gold nanoparticles assemblies. The absorption maximum at 440 nm for DNA polymerised molecules in gel without gold plates was obtained (Fig.14, curve a). Then we supposed that shifting of the position of these maximum was caused by the absorption at the DNA-Gold plate interface. Therefore, the absorption maximums at 332 nm wavelengths in spectra with gold plates that have

lateral size less than 150 microns and mixture from less than 150 and 300–350 microns can correspond to gold plates with the lateral size less than 150 microns. Only in absorption spectra with gold plates with the lateral size 300–350 microns the absorption maxima at 368 nm are revealed.

The color change from red to blue in absorption spectra of Au nanoparticles linked by DNA is associated with forming a aggregates of thousands of gold particles, with dimension in the hundreds of nanometers that shifts from the single particle absorption peak at 520 nm to the aggregates peak at 580 nm. The red shift associated with coupling between two particles is very small (a few nm) [38].

Then we can assume that in these spectra absorption on interface DNA-Gold plate as main was observed.

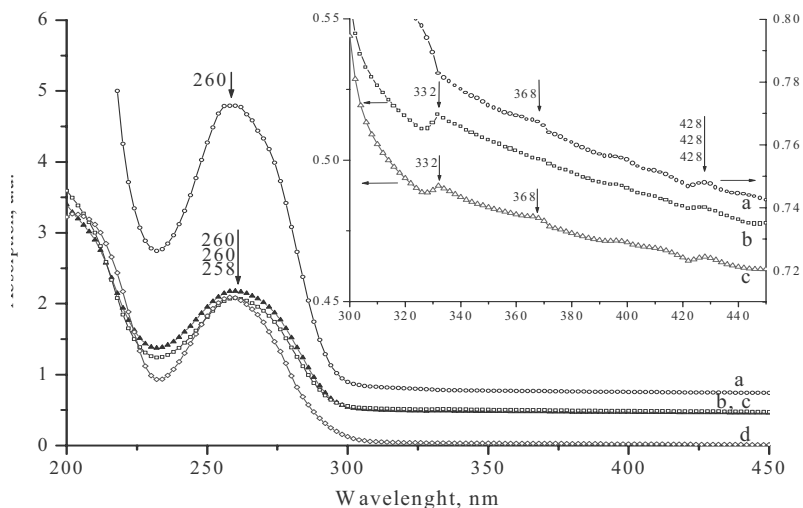


Figure 14. Absorption spectra of: a - DNA polymerized molecules in gel with gold plates having 300 - 350 microns in lateral size; b - DNA polymerized molecules in gel with gold plates having less than 150 microns in lateral size; c - DNA polymerized molecules in gel with gold plates having less than 150 and 300 - 350 microns in lateral size (the contents of bigger plates is less than in DNA polymerized molecules in gel with 300 - 350 microns only); d - DNA polymerized molecules in gel without gold plates

6.3 INFRARED SPECTRA OF DNA-LINKED GOLD PLATES ASSEMBLIES IN GEL

From the comparison of IR-spectra of DNA polymerised molecules in gel and DNA-linked gold nanoparticles assemblies in gel it is visible that the main part of DNA transmission spectra doesn't efficiently change after addition of Au nanoparticles to DNA polymerised molecules in gel [29]. The general view of the spectra remains the same. The wavenumbers of some vibration modes shift and the formation of new lines of absorption at 524, 860, 948, 1072, 1136, 1284, 1380, 2972 cm^{-1} are observed.

The presence of new absorption lines with wave numbers 1072 and 1136 (cm^{-1}) are conforming on the vibration mode of $\text{CH}_2\text{-O-S}$ bond allows making a deduction, that the golden plates are attached to DNA molecules through the sulfur, because the most used technique in such a way [40,41]. We obtained the disappearance of C-H mode (620 cm^{-1}), which is destroyed by the replacement of hydrogen. Note, that adsorption of ions on DNA was simulated in [28], where it was found that the dominant adsorbents are cations which are concentrated mainly near the phosphate groups and also in the minor groove. Hybrid DNA-gold nanostructures is considered in [10].

7. Charge transport in DNA-linked gold plates assemblies

The typical I-V characteristics of structures such as Pt/Ir tip-tunnel gap-Au nanoparticle hosted in DNA hydrogel layer-Si substrate/Cu plate, which are presented in Fig. 15, were used for the calculation of the energy distribution of DOS (density of states) in Au nanoparticles, hosted in DNA hydrogel on Si surface.

The DOS curves versus energy for the Au nanoparticles with various sizes on Si are shown in Fig.15. These experimental obtained DOS versus energy curves correspond to the electronic level structure of Au clusters on the conducting surface. In order to understand these richly structured DOS spectra, we checked whether the small size of Au clusters might lead to the concomitant appearance of the nonmetallic properties.

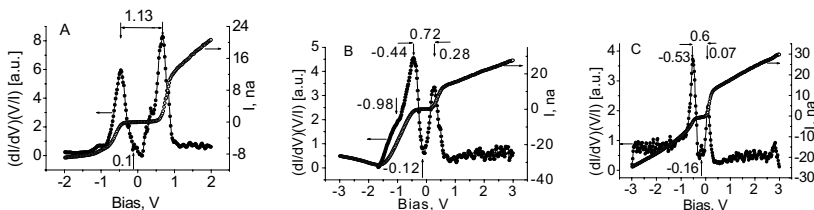


Figure 15. Density of states for Au(DNA) nanoparticles and (I-V) characteristics of the Pt/Ir tip-Au(DNA) nanoparticle-Si/Cu structure for different Au nanoparticles sizes (A,B,C).

Islands with two layers of gold and the band gap of 0.3 eV are found to be the most effective for catalysing of the reaction of CO. These results suggest that supported clusters, in general, may have unusual catalytic properties as one dimension of the clusters becomes smaller than three atomic spacing. Thus small metal clusters will likely be quite useful in the design of nanostructured materials for catalytic applications.

The value of the energy gap for the Au clusters was estimated by us from the voltage range with minimum of DOS near the Fermi level (in Fig. 15 near the point $V=0$). It is turned out that $E_g=1.13$, 0.72 , 0.6 eV. Using the data [30], the band gap of Au clusters versus the cluster diameter, we obtained that Au clusters in Fig. 15:

- $E_g=1.13$ eV are two dimensional (2D) clusters (cluster diameter is 1.8 nm)
- $E_g=0.72$ eV are two dimensional (2D) clusters (cluster diameter is 2.1 nm)
- $E_g=0.6$ eV are two dimensional (2D) clusters (cluster diameter is 2.8 nm) or 3D clusters, two atoms layer in height (cluster diameter is also 2.8 nm).

It is necessary also to take into account an influence of DNA molecular environment (as a dielectric medium) on I-V characteristics and DOS spectra, shown in Fig. 15. These show as the presence of the region with the negative resistance on I-V characteristic and corresponding increase DOS (Fig.15, B under $V=-0.98$ eV)

The direct confirmation of influence of DNA hydrogel environmental on Electronic Level Structure of Au clusters (as and on view of I-V characteristic structures Pt/Ir tip-tunnel air gap-Au nanoparticle hosted in DNA hydrogel layer-Si substrate/Cu plate), namely: a) DNA layer (Fig.15); b) Au without DNA (Fig.16) has been obtained in the result of studies of I-V characteristics of structures.

For comparison the DOS of DNA-linked Gold nanoparticles with the DOS of Gold nanoparticles we carry out the next investigations.

The typical I-V characteristics of Pt/Ir tip-tunnel gap-Au nanoparticle - tunnel gap-Au nanoparticle- Pt/Ir tip structure, which are presented in Fig. 16, were used for the calculation of the energy distribution of DOS (density of states and to estimate the size of Au nanoparticles on Si surface. This characteristic has the following features: a non-linearity and asymmetrical behavior. The voltage dependence of the differential

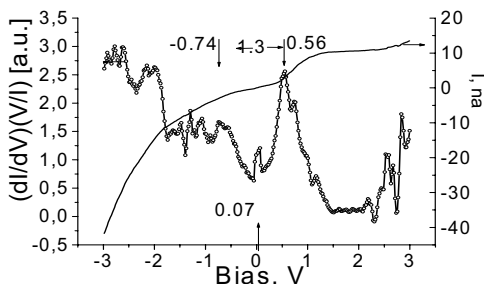


Figure 16. Density of States versus energy for the Au nanoparticles in the Au nanoparticles layer on Si surface. This curve is obtained from typical (I - V) characteristic of the Pt/Ir tip-tunnel gap-Au nanoparticle - tunnel gap-Au nanoparticle- Pt/Ir tip structure, which is also included into the Figure

conductance as well as normalized conductance exhibits a clear peak structure, which represent a local levels of energy, that is typical in the DOS for nanoparticles of Au which have nonmetallic properties.

The value of energy gap for the Au clusters was estimated from the range with minimum of DOS near the Fermi level (in Fig.16 near the point $V=0$). It is turned out that $E_g=1.3$ eV. Using the data of the band gap of Au clusters was estimate the cluster diameter: $E_g=1.3$ eV are two dimensional (2D) clusters (the cluster diameter is approximately 1.8 nm).

In the result we have actually shown that these molecular cluster layers on Si substrates have the electronic structure, which is typical for: unwrapped DNA [29] with the energy gap near the Fermi level, for the Pt/Ir tip-tunnel gap-DNA hydrogel layer-tunnel gap-Pt/Ir structure $E_g=0.7$ eV and periodical gaps 1.1 – 1.2 eV at distance from Fermi level; Au nanoclusters [36] with energy gaps for Pt/Ir tip-tunnel gap-Au nanoparticle - tunnel gap-Au nanoparticle- Pt/Ir tip structure. The gap could be interpreted, as being due to the electron confinement and thus the electronic structure of the Au nanoparticles, which formed on DNA, are Au clusters.

8. Sensing of DNA polymerised molecules and DNA-linked gold nanoparticles in networks on the temperature and microwave power changing

The variety of alive organisms has appeared, evolutionary and now exists due to persistent interaction with various factors of environment, adapting to their influence and changes, using them in the vital functions.

The majority of these factors has electromagnetic nature. For the spectrum range, where $h\nu > kT$, all the kinds of the biological activity to a certain degree have been already found. The case is somewhat different with the rest of wide range of electromagnetic spectrum, where $h\nu < kT$. This range includes diapasons from the superhigh frequency (SHF) to infralow frequency (ILF). For a long time ILF range is considered not to influence on alive organisms. The simple physical considerations led for such conclusions: as energy quantum in the spectrum range considerably less, from than the average kinetic energy of molecules ($h\nu \ll kT$), then ILF absorption in alive tissue may be associated only with the amplification of a molecule rotation, i.e. with the transformation of electromagnetic energy into thermal one.

So the energy absorption of the steady and slow changed electric and magnetic fields are associated with the molecule orientation. The calculations show that the considerable ILF thermal effects for organism may be expected only at the high intensity, namely at 10^2 V/m for SHF and 10^6 V/m for ILF,

The ILF SHF energy absorption is supposed to be associated with the rotation of intermolecular structures regarding to C-C bonds with the transmission junction of hydroxyl groups from one position with the hydrogen bond into another with the rotation levels of metastable states and so on. The possibility of ionization effects of ILF SHF leading to the formation of O_2 and OH radicals at the high impulse power is also considered.

The resistance (R) versus temperature (T) change has exponential decrease at the temperature increase (Fig. 17). Such a behaviour of the resistance of the layer from DNA polymerized molecules networks on Si or Al_2O_3 under the temperature increase is typical for a semiconductor. The rectified type of I-V characteristic for the structure metal (Pt/Ir or Cu) - the layer from DNA polymerised molecules networks on Si has been confirmed. (Fig. 18) Similar results for the layer from DNA-linked gold nanoparticles in networks have been obtained in [38-39]. But both the resistance of this layer of and its change were less.

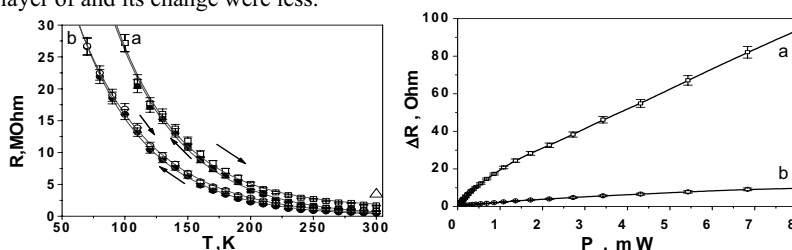


Figure 17.(left) The resistance (R) versus temperature (T) curves of the layer from DNA polymerised molecules networks on Si (■ and □- points) and on Al_2O_3 (▽ and ◇ points) surfaces (a and b, respectively). These curves correspond to measurements at one temperature cycling (temperature decreases from 300 K to 70 K and increases from 70 K to 300 K). The value of the resistance of this layer on Si (Δ- point) after temperature cycling is indicated.

Figure. 18 (right) The change of the resistance (ΔR) of the layer from DNA polymerised molecules networks on Si (□- points) under microwave power (P) and $T=300$ K [41]. The measurements after temperature cycling (the ΔR versus P, curve a) and after UV-vis spectroscopy (the ΔR versus P, curve b) have been carried out.

The change of the resistance (ΔR) of the layers from DNA polymerised molecules networks (Fig.18) and from DNA-linked gold nanoparticles in networks [5] on Si under rise of the microwave power (P) was increased. Resistance of the layer of DNA polymerised molecules networks on Si increases on $\Delta R=80 \Omega$ in the range from 0 to 9 mW (Fig.18). These changes decrease for this layer after ageing under UV-vis illumination. Resistance of the layer from DNA-linked gold nanoparticles in networks on Si in the same range increases on $\Delta R=96 \text{ Ohm}$. These changes decrease for this layer after ageing under UV-vis illumination [5]. Such a behaviour of the resistance of these layers could be defined by partially breaking part district or changing of the bonds in DNA polymerised molecules.

9. DNA polymerized molecules/ C_{60} building blocks: bonds

The organization of DNA/ C_{60} blocks in DNA hydrogel with C_{60} in water solutions (the contents of C_{60} is 4 mg/10ml) has been studied by IR spectroscopy. All the changes in IR spectra of DNA/ C_{60} testify about the transformation (partially unwrapped DNA molecule) of double helix of DNA molecule. DNA molecule is change by C_{60} molecules, as it was observed, it is capable to change the crystal structure of DNA.

The changing intensity and shape of absorption spectra respectively vibration modes are at wave numbers of 488 and 564 cm^{-1} , which correspond to oscillations of N-H...N and δ N-H bonds in bases of DNA molecule. In the IR spectra has been also revealed

the changing of the intensity of absorption spectrum at wave number of 1656 cm^{-1} respectively vibration mode oscillation of C=O bonds, which relating to groups under the C_{60} molecules inculcated in grooves double helix. Then one can assume that DNA: C_{60} block is self formatted.

10. Carbon nanotubes as building blocks for nanosystems: bonds, electronic structure and sensing

Carbon nanotubes (CNT) have unique electrical and mechanical properties, with the potential for revolutionary applications [41-42]. The immobilization of DNA, proteins and enzymes onto CNT, the helical crystallization and the interaction of proteins with CNT may be used for the development of new biosensors [43]. The biological molecules can be adsorbed onto the surface of CNT without losing overall biological shape, form and/or function. The CNT surface, because of its nanostructured topology, allows the enzyme to be adsorbed and the electrode to be positioned close to the electroactive prosthetic group of the enzyme. This will allow the direct electron transfer. Such access is not generally accorded to the smooth, polished surfaces of traditional electrodes. CNT with combined physico-chemical characteristics allow elaborating a new approach to the direct electrical communication with redox active biomolecules and construction of reagentless biosensors and nanobiosensors. Potentially enzymes bound to nanotubes represents a selective binding agent that in the presence of a substrate would cause a chemical reaction to act as a signal. The biosensors with CNT may be used as the microelectrodes.

The first direct experimental evidences for the organization of DNA/CNT molecular and nanocrystalline-Si networks, consisting of DNA double helix, CNT and nanocrystalline-Si building blocks, due to DNA molecules have been obtained in 5-7. The electronic structure self-formation and charge transfer for the network systems from building blocks by tunnel and photoluminescence spectroscopy have been studied in [14, 44-46].

For the application of MWCNT in optical systems and to construct simple logic circuits, it is necessary to create their layers. These layers have been created by DNA technology on Au, Si substrates [4]. For experiment we used MWCNT/(Si or Au) and MWCNT/DNA layers.

10.1. CARBON BONDS

10.1.1 XPS spectra of DNA polymerized molecules in gel, SWCNT, DNA gel/SWCNT. XPS equipment was made on the spectrometer of Series 800 XPS "Kratos Analytical" with AlK_{α} -ray ($h\nu=1486.6\text{ eV}$, analysed window is $2\text{X}2\text{mm}$). The interpretation of XPS core levels shift of Si, Al and O electrons were performed using standard samples and results.

Fig.19 is presented for a comparison of the layers from DNA polymerized molecules in

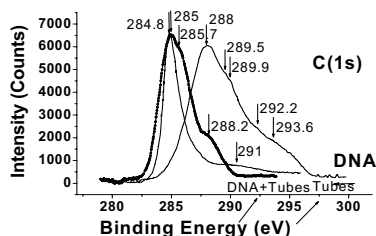


Figure 24. $\text{C}(1s)$ core levels for DNA, SWCNT, DNA / SWCNT layers at $T=300\text{K}$

gel, SWCNT, DNA gel/SWCNT mixture obtained by coating from DNA gel and mixture with DNA/SWCN nanoblocks as measured with C 1s XPS spectra. These spectra reveal that carbon bonds can be formed in DNA networks by adding of carbon tubes. This fact is observed also from IR spectra of DNA/SWCNT layer.

10.1.2. IR-spectroscopy of MWCNT and DNA/MWCNT layers. In the experimental IR-spectra the vibration modes at 360, 450, 650, 864, 1231, 1400, 1444, 1575 cm^{-1} , which have been theoretically predicted for MWCNT with diameter of 10-40 nm, we evaluated for DNA/MWCNT composite layer on these substrates. In these spectra the presence of additional DNA base groups were identified.

10.1.3 The Raman spectroscopy of MWCNT and DNA/MWCNT layers. Raman spectra [4, 48] was recorded by Raman spectrometer and 514.5 nm line of Ar laser was used for the excitation. Investigation of the Stokes, anti-Stokes processes, D- and G-bands by Raman spectroscopy (1000-2000 cm^{-1}) was made. The received Raman spectra of the MWCNT samples in the high frequency range are measured on the MWCNT/Si, MWCNT/Au, (MWCNT/DNA)/Au samples for the same excitation laser power densities and the same accumulation times. The D- and G- bands are observed between 1300 -1340 cm^{-1} and 1500-1600 cm^{-1} . Insets of results show that intensity of the G-band does not depend on Si or Au substrate, on the other hand the intensity of the D-band shows some dependence on the substrate. The additional bands at 1094, 1216, 1777 cm^{-1} were observed on (MWCNT/DNA)/Au layers.

10.2 ELECTRONIC STRUCTURE

Optical reflectance spectroscopy measurements were used for the detection of the electron transition in MWCNT and MWCNT/DNA structures. The normal-incidence reflectance spectra in the range of 300-1000 nm are recorded by the spectrometer with the high-sensitive registration of reflective signal. We have investigated electronic reflectance spectra of layers (Fig. 20). From reflectance spectra obtained for MWCNT and DNA/MWCNT layers the principal electronic absorption bands have been evaluated (2.95, 3.06, 3.95 3.33, 3.38 eV).

The role of the DNA in the optical absorption at the DNA/MWCNT interface is revealed by the existence of the 2.5-3eV and 2 eV bands (curves MWCNT/DNA/Au) and shifting of the minima at 2.96 eV, 3.05, 3.34 eV.

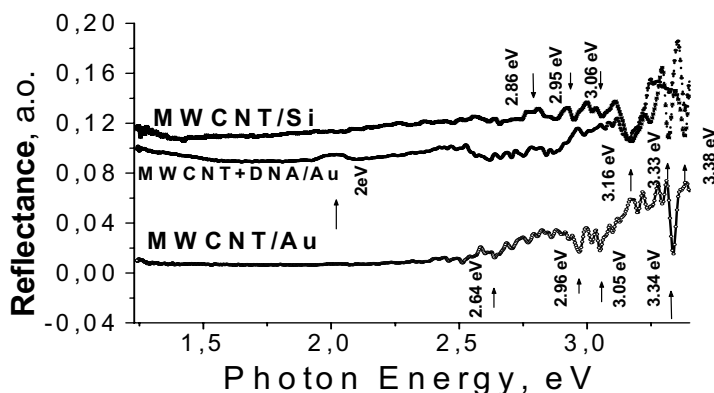


Figure 20. Reflectance spectra from MWCNT/Si, MWCNT/Au, MWCNT/DNA/Au structures

Using these results we assert that system of electron levels is self-formed at the (DNA/MWCNT)/ Si interface as a result of DNA-MWCNT interaction and optical absorption at 2.5 ± 3 eV is due to the MWCNT.

10.3 CARBON NANOTUBE/BIOMOLECULE SYSTEM

The aim is modifying of the ends of nanotubes and other types of nanowires with biomolecules and then using the nanotube as an electrical probe of biological interactions. The using of the nanotube at the interface between a single molecule and the macroscopic world gives the possibility to use electrical signals to study the behaviour of individual biomolecules [49].

It is widely recognized that the electrical properties of two-dimensional surfaces change in response to biological binding events. It is also known that it is possible to measure the electrical properties of single molecules. These nanotube/nanowire ideas are combining them to develop nanoscale electrical probes of biological binding events that ideally should permit measurements on individual biomolecules. The basic thrust of this project is to chemically modify carbon nanotubes and/or metallic nanowires with biological molecules and then measure the electrical properties of single nanotubes and how they change in response to biological binding events. Through a proper choice of geometry and other experimental conditions, it should be possible to selectively functionalize just the ends of the nanotubes/nanowires, and ideally to do this in such a way that each nanotube/nanowire is linked to just *one* biomolecule.

The second way is using of DNA-nanotube hybrids as architectural elements, using the chemical selectivity of DNA to control the assembly of nanotubes, nanowires, and other nano-objects.

The area of nanotube research involves the use of biomolecules as a way of controlling the *assembly* of nanotubes and other nanoscale objects into larger functional structures. Biomolecules exhibit an extraordinary degree of chemical selectivity; by linking of biomolecules to nanotubes, the goal is to use this chemical selectivity to control how nanotubes link to surfaces, to other nanotubes, and to a broad variety of nanoscale and macroscale objects.

Carbon nanotubes, when used as scanning probe microscope tips, have shown superior imaging capability compared to conventional tips. Chemically modified nanotube tips may be useful in chemical force microscopy. The non-toxic character of carbon nanotubes makes them a good candidate for biological applications, such as biosensors and membranes for controlled drug release.

11 Structure models, electronic structure of carbyne-like fibers

11.1 STRUCTURE MODEL

The aim of the investigation of carbyne-like fibers with metals doped and their systems is to determine structure, physical and chemical properties (sizes of carbyne fibers, element contents, chemical bonds, type of conductivity, the distribution of the electronic state in conduction band) and sensing on the environment conditions: temperature changes and place into DNA polymerized molecular gel.

The name "carbyne" denotes a hypothetical carbon allotrope based on a linear polymeric chain of sp-hybridized carbon atoms [50-53]. Carbyne can be derived either from polyynes (Fig.21) $[-(-C\equiv C-)]_n$ (chain of alternating single and triple bonds), or less stable polycumulene, $[=(C=)]_n$ (chain of only double bonds). Short chain (C_4 - C_8) polyynes lengths ranged from 119 to 121 pm while C=C bond of polycumulene lengths ranged from 132 to 138 pm.

Molecular orbital calculations indicate that cyclo C-18 carbyne (Fig. 21) should be also relatively stable and experimental evidence for cyclocarbynes has been found [18].

Carbyne structure, which would correspond to Fig. 21 was never obtained in the pure form, despite of continuing works on its synthesis. These studies support the idea that carbyne is realistic concept of crystalline carbon, in spite of notorious lack of convincing X-ray or other structural evidence made on macroscopic signal crystal. But chains construction with polyynes and polycumulene may be stable in structures, which introduce spatial separation between the chains, which can be obtained by including of impurities such as Cu, Fe, Na, I₂, H, O and N. The element model of carbyne structure in Fig. 21 with the kinked polyynes/polycumulenes is with impurity-stabilized kinks (points are unpaired electrons on carbon for impurity connections).

If carbyne structure exists, it is formed as a result of aggregations of kinked carbon chains. Atoms of carbon on kinks have unpaired electrons, which may be used for connection with atoms of the impurity or for interchains association of atoms in the polymer.

For polymeric carbon chains in that condition is the most probable structure with parallel kinked polycumulene and with their intermolecular connection between chains.

For kinked chains, which have about 10 atoms in the length, intermolecular interaction may be realized in packing presented on Fig. 21.

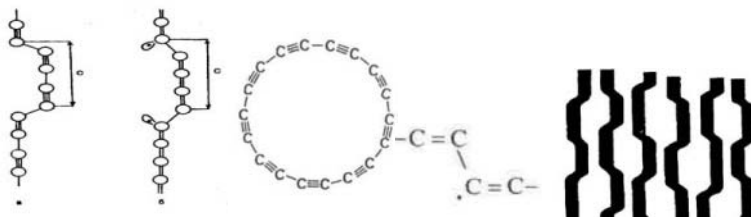


Figure 21. Geometrical model: a) kinked carbon chains construction with polyynes (a) and polycumulenes (b) types of connection; b) Cyclo C-18 carbyne, as one of the form of carbon chains; c) zigzag carbon chains packing into fiber.

11.3 ELECTRON STRUCTURE AND CARBON BONDS

Electron Energy Loss (the low energy loss region, <50 eV) from carbyne, as has been assumed, HOPG and diamond consist of main plasmon ($\sigma+\pi$ or σ) peak positions of carbyne; HOPG and diamond are at 19.5 eV, 23.6 eV and 34 eV, respectively [54-56].

The main peak of carbyne is broadened, because here the carbyne-containing material is surrounded by the graphite matrix. There are two stronger, compared with that from HOPG and diamond, peaks at 4.85 eV and 9.35 eV in the spectrum from carbyne; they are characterized as π -subband and π -subsubband transitions.

In the characterization of Raman spectra of carbyne (Fig. 22) structure in addition to

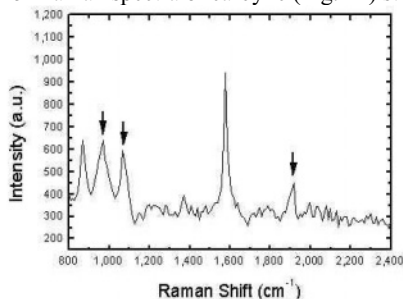


Figure 22. Raman spectra of carbyne structure [32].

the normal Raman peaks of highly oriented pyrolytic graphite at 1580cm^{-1} and 867cm^{-1} two peaks at 970cm^{-1} and 1070cm^{-1} must exist. According to the theory of Raman spectroscopy [57], these two peaks correspond to the stretching frequency of =C=C= , what corresponds to polycumulene. And also small peak at about 1910 cm^{-1} shows on the polyne form of carbyne [58].

11.3 FEATURES OF CARBYNE STUDY

Due to its unique geometrical structure, carbyne is expected to have many properties, as do fullerenes and carbon nanotubes [59]. However, in contrast to the discovery of fullerenes and carbon nanotubes, the existence of carbyne (chains construction with polynes and polycumulene) has been continuously disputed [60, 61]. Despite of many publications on carbyne, its existence has not been universally accepted and the literature has been characterized by conflicting claims and counter claims [28,33,37]. As a result, the studies on carbyne are far less than those on fullerenes and carbon nanotubes. In that case more researches are needed to learn whether or not a new carbon allotrope is, eventually, accessible and also for the study of its electronic properties.

11.4 EXPERIMENTAL INVESTIGATIONS OF CARBYNE-LIKE FIBERS AND SYSTEMS PROPERTIES.

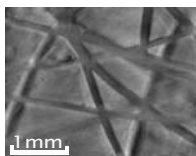


Figure 23. The optical image of carbone fibers.

Samples of carbon fibers, which were synthesized in Institute of Adsorption, NASU, Kiev, as carbyne-like materials with metals inclusions are used for investigations [61]. The optical image of these fibers (Fig.23) was obtained by the Laser-scanning profilometer (differential phase microscope - LSP).

12.4.1 Carbon bonds IR-spectra of samples measured by Specord M-80 Care Zeiss Jena spectrometer are presented in the Fig.24. The vibration modes under wavelength of 796, 1092, 1109 and $1525\text{-}1624\text{ cm}^{-1}$, which correspond to C-C and C=C bonds respectively were revealed. These modes have been theoretically predicted for carbyne [20].

The bonds of C=C and C-C confirm that the carbon fibers consists of polymeric chains of carbon with polycumulene type of the connection. Also C-C bond confirms existence of kinked model of carbon chains.

Comparison IR-spectra of carbon fibers and fullerenes, tubes gives the reason to approve that carbone fibers structure have the principal difference with the structure of

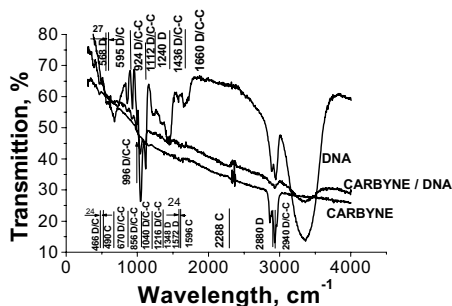


Figure 29. IR transmission spectra of layers on KRS-5 (42% TlBr - 58% TlI): carbon fibers (Fig. 26), carbon fibers /DNA gel mixture, DNA gel

fullerenes and tubes: vibration modes of 5 and 6 carbon atoms rings, which are typical for fullerenes and tubes, are not observed [62].

Raman spectra According to the theory of Raman spectroscopy of nanocarbon [32, 63, 64] in Raman spectra of carbyne fibers two small peaks at 975 cm^{-1} and 1068 cm^{-1} (514.5 nm line of Ar laser was used for the excitation) were revealed. These two peaks associated with the stretching frequency of =C=C= , what associated corresponds to polycumulene. In addition, two Raman active modes at 1340 cm^{-1} (diamond: D-line) and 1580 cm^{-1} (graphite: G-line) were also observed. These lines are typical for all forms of amorphous carbon. In polycrystalline graphite, both D and G lines appear, while their relative intensity (I_G/I_D) depends on the in-plane size of graphite crystallites, L_a :

$$L_a \approx 4.4 * I_G/I_D.$$

And in this case the intensity ratio equals $I_G/I_D \approx 1.45$, from which the in-plane graphite crystallite size in the sample can be about 6 nm in carbyne fibers.

11.4.2 Element contents Near with the basic part, which consists of carbon atoms, the carbon fibers also can contain impurity atoms [26,27] The impurities N, O, Mg, Al, K, Ti, Fe, Zn, Na were revealed in carbon fibers by the laser mass-spectroscopy method. The values of atom percents are: carbon 46 %, metal 15.5% oxygen -31.8%, and nitrogen atoms 8.4 % in carbyne fibers. These results confirm that carbon fibers contain carbyne chains, which are stabilized by impurities. Then we can identify carbon fibers as carbyne-like material. Note that the ratio between atom concentrations between carbon and oxygen atoms is 1.45. Also the vibration modes of C-O bonds at wavelength of 2288 cm^{-1} were observed in IR spectrum (Fig.24). These results evident that carbon fibers contain carbyne-like and carbon oxides parts.

11.4.3 The structure model Based on the experiments described in 9.4.1-9.4.2 and theoretical statements we assumed that ‘carbyne’ is formed from short kinked carbon chains association with simultaneous packing of a small amount of impurities in voids of the carbon matrix (Fig. 25). In this case the polycumulene chains are stabilized by these impurities.

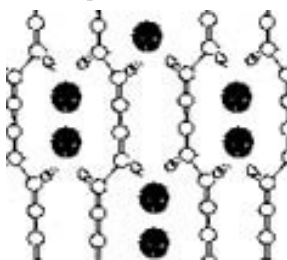


Figure 25. Structure model of a carbyne chains with metal atoms inclusions.

The metal atoms association in linear chains can be viewed in structure model (Fig. 25): Atoms of metal are placed on the ends of kinked chains and connect metal atoms with carbon ones. This model provides metal atoms association in voids of the carbon matrix, which is formed because the carbon chains are kinked and carbon atoms have unpaired electrons on kinks. The sizes of the created carbon matrix cells with metal inclusions depend on the size of the metal volumes. Different lengths of linear chains of =C=C= bonds (Fig.21; 25) are defined by sizes of included metals.

11.4.4. Conductivity Ampere-voltage (I-V) characteristics of structures metal (Pt/Ir or Cu tip) / carbon fiber or carbon fibers layer (the charge carrier along carbon fiber) are measured by tunneling spectroscopy and four-probe method. The conductivity was calculated from I-V characteristics of single carbon fibers. I-V were measured in the temperature range $20 \leq T \leq 300\text{ K}$. The voltage changed in the range of $\pm 2\text{ V}$, the current through the fiber was 0.5 mA . The linear behavior of I - V characteristics was observed at the current up to 0.1 mA and asymmetric behavior at the greater current [65]. The energy of activation of the charge carriers was 0.4 eV . The resistance of carbon fiber was 4 kOhm and resistivity was $0.025\text{ Ohm}\cdot\text{m}$. Dependence of the normalized conductivity $(V/I)dI/dV$ versus V for carbyne fiber is shown in Fig.26. The energy

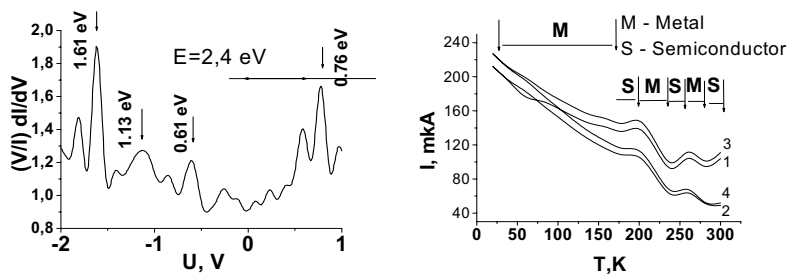


Figure 26. (left) Dependence of the normalized conductivity $(V/I) dI/dV$ versus V for carbon fiber.

Figure 27 (right). Behavior of the conductivity versus the temperature for 1 – fiber 1 (cooling), 2 – fiber 2 (heating), 3 – fiber 2 (cooling), 4 – fiber 2 (heating).

band gap of carbon fiber is near 2.4 eV (Fig. 26).

It is necessary to note, that $I-V$ characteristics of fibers 1 and 2 have different behavior in a thermal cycle. The fibers 1 and 2 at the stage of cooling and heating have the metal type or semiconductor type of the conductivity for different temperature ranges. It is a good correlation for different fibers. The metallic behavior at 20-175, 197-240, 260-280 K and semiconductor behavior were observed at 175-197, 240-260, 280-325 K temperature ranges (Fig. 27). The different type of the conductivity of the fiber at different thermal cycles was revealed and explained by non-homogenous structure of carbon fiber, which contains impurity of metals and surface oxides on carbon (10.4.2, 10.4.3). The dependence of the fiber conductivity versus the temperature can be used for the design of the temperature sensor.

11.4.5. DNA/Carbon fibers From IR-spectra of the layers of carbon fibers linking by DNA gel mixture and DNA gel (Fig.26) the role of DNA addition (such as the appearance of the absorption bands at 1049, 1420, 3345 cm^{-1} and the shift of the absorption minima at 1595, 2902 cm^{-1}) was determined. These IR-spectrum changes were connected with the chemical interaction of DNA bases. This was confirmed by the control of the conductivity of the single fiber after dropping of DNA gel in the centre of the fiber. The fiber conductivity increased in the time and was interminable.

12 Electronic structures of CuPc, C_{60} molecules and CuPc/ C_{60} molecular complexes in toluene

Absorption spectra of CuPc molecules in toluene for two concentrations (for 0.2 and 2 mg of CuPc nanocrystals dissolved in 10 ml of toluene - n_1 and n_2 , respectively) are given in Fig. 28. As can be seen, two intensive absorption bands (B- and Q-bands) with peaks at $E_1 = 1.7 \text{ eV}$, $E_2 = 1.85 \text{ eV}$, and $E_3 = 1.93 \text{ eV}$ for Q-band, and $E_4 = 3.36 \text{ eV}$ for B-band are observed for the CuPc molecules concentration n_1 in toluene.

For the concentration n_2 the peaks are observed at $E_1 = 1.7 \text{ eV}$ and $E_2 = 1.93 \text{ eV}$ for Q-band, and $E_3 = 3.34 \text{ eV}$ for B-band. So, the peak at 1.85 eV disappeared for higher concentration of CuPc in toluene, and a broader peak with maximum at $E_3 = 1.93 \text{ eV}$ was obtained. This peak is splitted into the two subbands with peaks at E_1 , E_2 for lower concentration. The energy edge of the B absorption band is uncertain in both the spectra. The values of the energy edge of Q-absorption bands (the edges of fundamental absorption of CuPc molecules) were found to be: $E_{01} = 1.49 \text{ eV}$, $E_{02} = 1.52 \text{ eV}$ for n_1 , n_2 concentrations, respectively.

For both spectra the minimum of the absorption is the X-band between Q and B absorption bands. The width of this band is $E_X = 0.75$ and 0.7 eV for n_1 and n_2 CuPc

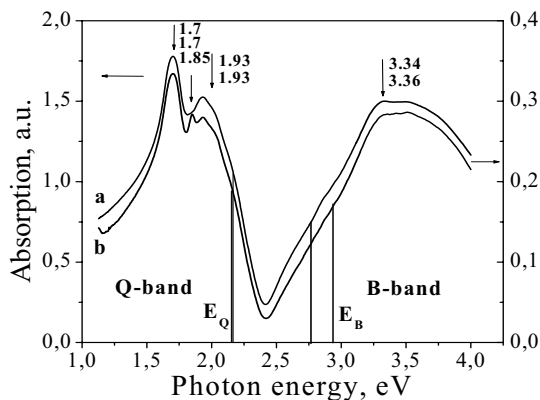


Figure 28. Absorption spectra of CuPc molecules in toluene for n_1 and n_2 concentrations (weigh CuPc nanocrystals/volume of toluene): a - 2 mg/10 ml (n_2) and b - 0.2 mg/10 ml (n_1)

concentrations, respectively. The width of the Q-bands for the same CuPc concentrations are: $E_Q = 0.59$ and 0.62 eV. The energy values associated with maxima in Q- and B-bands for CuPc in chloroform (in which the solubility of CuPc nanocrystals is higher) in accordance with [66-71] are higher than those in toluene: $E_1 = 1.78$ eV, $E_2 = 1.82$ eV, $E_3 = 2.03$ eV, $E_4 = 3.59$ eV. This result demonstrates that the solvent controls the absorption spectra. The difference in absorption of toluene or chloroform affects the absorption of CuPc molecules.

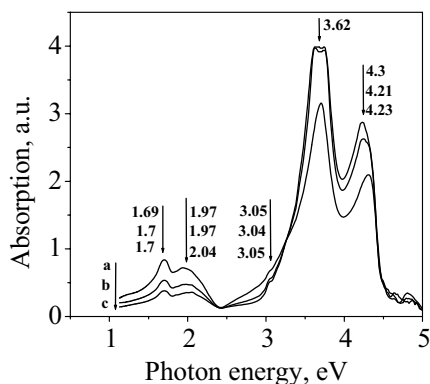


Figure 29. Absorption spectra of CuPc and C_{60} molecular mixture in toluene: a - 5/2 volume ratio of CuPc/ C_{60} molecules in toluene ("high" concentration of CuPc molecules in the mixture), b - 1/2 volume ratio of CuPc/ C_{60} molecules in toluene ("low" concentration of CuPc molecules in the mixture), c - 1/5 volume ratio of CuPc/ C_{60} molecules in toluene ("low" concentration of CuPc molecules in the mixture)

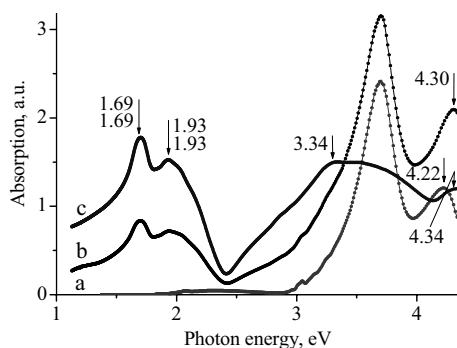


Figure 30. Absorption spectra of: a - C_{60} molecules in toluene with contents 2 mg/10 ml; b - CuPc and C_{60} molecular mixture in toluene(5/2 volume ratio of CuPc/ C_{60} molecules in toluene); c - CuPc molecules in toluene with contents 2 mg/10 ml

By comparing the energies E_1 , E_2 , E_3 , and E_4 , found experimentally, together with the experimental width of Q and X-bands with the electronic spectrum of the CuPc molecule obtained by modeling, we can determine the next electron transitions in CuPc molecules in toluene: X absorption bands ($E_X = 0.75$ eV and 0.7 eV); Q absorption bands with the energies of 0.59 and 0.62 eV for n_1 and n_2 concentrations, respectively. In Fig. 30 we can see for the curve **b** two broad absorption bands: the Q-band with the width of $E_Q = 0.58$ eV at the photon energy $E_1 = 1.69$ eV, and B-band with the width $E_B = 1.17$ eV at the photon energy of $E_4 = 3.62$ eV for contents of CuPc molecules (2mg/10ml) in the mixture from CuPc and C_{60} molecules in toluene.

Comparing the values of these photon energies with the corresponding ones for spectra of “low” concentrations of CuPc molecules (0.2mg/10ml) in toluene ($E_Q = 0.56$, 0.55 eV and $E_B = 1.26$, 1.27 eV), we can see that the addition of C_{60} molecules into the CuPc molecular solution in toluene causes the decrease of the Q-band width and the increase of the B-band width. These variations of widths can be associated with the formation of CuPc/ C_{60} molecular donor-acceptor heterojunctions and the electron transfer from CuPc molecule to C_{60} molecule after photoexcitation. The observed changes in the absorption spectra of the CuPc/ C_{60} molecular mixture in the photon energy range of 2.5-3.1 eV under increasing of the concentration of C_{60} molecules in the mixture (Fig. 30) confirms it.

Absorption maxima in the B-band which can be caused by the direct allowed transitions in the C_{60} molecule are: $g_g+h_g \leftrightarrow t_{1u}$ ($E = 3.62$ eV), $h_u \leftrightarrow h_g$ ($E = 4.23$, 4.3, 4.21 eV), $g_g+h_g \leftrightarrow t_{2u}$ ($E = 4.84$, 4.82, 4.9 eV). From the comparison of these values with similar values in the spectrum of C_{60} molecules in toluene — $g_g+h_g \leftrightarrow t_{1u}$ ($E = 3.73$ eV), $h_u \leftrightarrow h_g$ ($E = 4.38$ eV), $g_g+h_g \leftrightarrow t_{2u}$ ($E = 4.88$ eV) — we have concluded that only at the high concentration of C_{60} molecules in the mixture (1/5 ratio of volumes of CuPc/ C_{60} molecules in toluene and “low” concentration of CuPc molecules in mixture) the transition $g_g+h_g \leftrightarrow t_{2u}$ ($E = 4.88$ eV) is permanent.

In these spectra the widths of the band with minimum absorption (Fig. 29) does not change ($E_g = 0.67$, 0.66, 0.67 eV) when the concentration of CuPc molecules in the mixture increases. These widths are smaller than the respective ones in the spectra of CuPc molecules in toluene ($E_g = 0.7$, 0.75 eV).

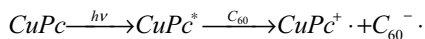
The decrease of the X-band width from $\Delta E = 0.70$ and 0.75 eV (CuPc nanoparticles in toluene solution) to $\Delta E = 0.39$ and 0.32 eV (mixture, consisting of CuPc crystals and nanoparticles in toluene) is revealed. The value of ΔE corresponds to separate nanoparticles in the first case and to molecular crystals in the second case.

13. Model of the sensing of CuPc/ C_{60} fullerene molecular complex to UV-Vis light

In metalphthalocyanine (MPc) films in order to efficiently separate the charges a strong electron acceptor such as C_{60} molecules can be used (Fig. 31).

The fullerene C_{60} is an ideal candidate for this purpose since it is able to gather at least six electrons as in alkali- C_{60} compounds (C_{60} nanocrystal is n-semiconductor) [69].

The scheme of charge-carrier photogeneration process for the CuPc and C_{60} in the composite is the following:



where: $CuPc^*$ designates photoexcited CuPc; $CuPc^{*+}$ is the charged $CuPc^*$ molecule after electron transfer from $CuPc^*$ to C_{60} ; $C_{60}^{-\cdot}$ is the charged C_{60} molecule after capturing an electron from $CuPc^*$.

In this paper the idea to form a CuPc/ C_{60} molecular heterojunction in a liquid solution with the overall objective to use this system as functional building block for novel

devices has been realized.

The selection of these molecules was driven by the need to obtain a molecular junction with high photoconductivity and efficiency for charge-carriers (this is typical for CuPc p-semiconductor) and by the need to get efficient separation of charges by C_{60} molecules [69].

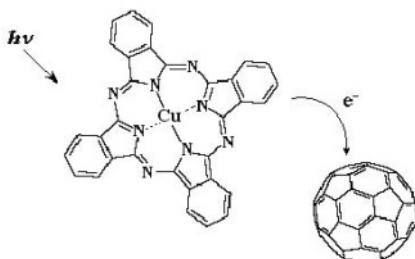


Figure 31. The model for electron transfer from CuPc molecule to C_{60} molecule under UV-vis photoexcitation.

14. Conclusion and future

Research on bioorganic (DNA)/organic (nanocarbon) molecules and organic (macrocylic metal complex)/organic (fullerene) solutions and molecular solids in the first years of the 21st century has been motivated by fundamental as well as practical questions.

Fundamental questions pertain to the complex nature of the constituents of these molecular solutions and films, namely the large neutral molecular moieties, to their electronic and vibrational excitations, to correlation effects and excitonic properties, and to random disorder due to structure fluctuations.

In spite of extensive research, basic phenomena that are central to the performance of devices, such as charge carrier injection into and transport through single DNA, DNA/fullerene, DNA/carbon nanotube or carbyne, macrocylic metal complex/fullerene C_{60} molecules and thin films are not understood to the same degree as they are for inorganic solids.

The complexity of relaxation and polarization phenomena that take place in the presence of molecular charges complicates the assignment of the energy levels of charge carriers.

Concepts such as molecular localization and polarization, electron-electron correlation, electron phonon (vibronic) coupling have long been applied to charged excitation and transport in these organic molecular systems. Substantial charge separation energies data is essential for constructing more reliable energy diagrams for carrier injection and transport phenomena in these organic molecular systems.

The next step in using of DNA molecules, DNA conjugated polymer, their complex with nanocarbons and metallophthalocyanine/fullerene molecules as building blocks in nanotechnology of nanosystems will be to incorporate these nanosystems in integrated devices, which will require a further optimization of methods currently available and new strategies that will allow the generation of arbitrary patterns via non-lithographic means. Regular arrays of nanosized features in DNA coatings can be produced now on a relatively large scale and we will see applications exploiting the intrinsic properties of such coatings.

The interaction of nanopatterned DNA molecular nanosystems with nanocarbon systems remains largely unexplored and this could be very fruitful research area where

biological molecular systems meet synthesized carbon nanosystems. Indicate that some polymer nanosystems techniques can be used in DNA nanotechnology nanosystems.

Acknowledgements

We are greatly indebted to Prof. L. Kavan for invaluable help in permanent discussion of results on carbyne systems and experimental measurements of Raman spectra of carbyne fibers and Dr. N. Naguib from Laboratory Prof. Y. Gogotsi for the Raman spectra of single carbyne fiber the measurement.

This work was partly supported by Greece-Ukrainian Bilateral Grant "Nanostructured films based on oxides, intermetalides and polymers on silicon surface for chemical sensors", №2M\192-2001 and by German Academic Exchange Service for Master Degree Student practice.

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SILICON NANOCRYSTALS IN SiO₂ FOR MEMORY DEVICES

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Abstract.

Charging phenomena in silicon nanocrystal MOS capacitors, which constitute the basic building blocks of silicon nanocrystal memories, will be reviewed in this paper. It will be shown that chemical vapor deposition of very thin silicon layers on oxidized silicon substrates, followed by high temperature thermal oxidation, constitutes a promising technique for the fabrication of two-dimensional arrays of silicon quantum dots in SiO₂.

1. Introduction

Silicon nanocrystals, also called quantum dots (QDs), show interesting properties, which make them suitable for use in novel devices [1,2]. Compared to bulk silicon, their electronic structure is different and it is determined by the size and the chemical environment of the nanocrystals. It consists of discrete energy levels into the conduction and valence band of the bulk material. By decreasing the size of the nanocrystals, the electronic bandgap of the material increases due to a shift of the confined states to higher values [3-5]. Another interesting property of QDs is that of controlled charging, due to the Coulomb blockade effect [6]. When a single charge is injected into a QD, it will occupy a confined state in the nanocrystal. The presence of this charge into the nanocrystal modifies the electrostatic potential within it so as injection of a second charge is blocked under the same external electric field. This second effect is used in single electron tunneling (SET) devices in order to control carrier injection and storage. Their basic operation (see fig.1) requires an island of electrons with a capacitance C which is small enough that a charging energy for the island (e^2/C) is much larger than the thermal fluctuations in the system ($k_B T$). Electrons may only flow through the circuit by tunneling onto the first unoccupied level, μ_{N+1} . Therefore, electrons will only flow one by one if the bias voltage V is increased such that $\mu_l > \mu_{N+1} > \mu_r$, where μ_l and μ_r are the chemical potentials of the highest filled electron states in the left (μ_l) and right (μ_r) electrodes respectively and μ_{N+1} is the chemical potential of the first available empty state for an electron in the QD.

Numerous SET based memory devices were proposed in the literature and their operation has been demonstrated [7-12]. A promising structure is the one using Si or Ge nanocrystals embedded in the gate oxide of a field-effect transistor (FET) and located at a tunneling distance from the transistor channel [13-18]. Compared to conventional non-volatile memories which use a continuous polycrystalline silicon layer as floating gate, in the case

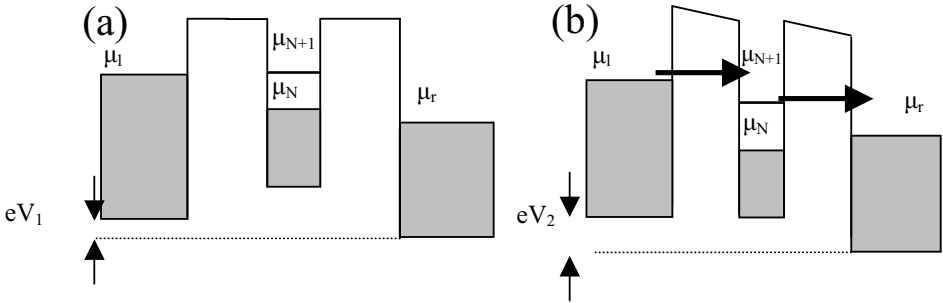


Figure 1. a) Coulomb blockade effect. If an island or QD has N electrons (μ_N being the chemical potential of the highest filled electron state) and another electron ($N+1$) is introduced by applying a voltage V_1 the chemical potential of this state is modified due to charging so as $\mu_{N+1} > \mu_l$. A larger voltage V_2 (b) is necessary in order to inject an electron from the left electrode to the state μ_{N+1} and then to the right electrode (single electron tunneling).

of silicon nanocrystal memories the charge storage medium is discrete and each QD acts as nano-floating gate [16]. The main advantage in this case lies in the fact that the floating gate is not electrically continuous, but it is distributed into nanocrystals so as charge loss through lateral paths is suppressed. As a consequence, very small tunneling oxide thicknesses may be used, resulting in faster write-erase times, much smaller degradation, compatibility with ultralarge scale integration scaling, lower operating voltages and lower power consumption [13].

For memory operation at room temperature, the charging energy of the nanocrystals (e^2/C) should exceed the thermal energy $K_B T$ by at least a factor of 10. This suggests that the nanocrystals must have at least sizes of the order of 10 nm and below. Sizes in the range of 3-5 nm are much more appropriate.

Different techniques were used to fabricate two-dimensional (2-D) arrays of silicon nanocrystals in SiO_2 at a tunneling distance from the silicon substrate. Low energy ion implantation of Si into a very thin SiO_2 layer followed by annealing at high temperature is one such technique extensively investigated [19,20]. Another technique, which is used in this paper, consists in depositing by Low Pressure Chemical Vapor Deposition (LPCVD) a very thin layer of amorphous silicon on a tunneling silicon oxide layer, which is then crystallized at high temperature and oxidized in order to produce an array of Si QDs in a layer in-between SiO_2 [22-28]. The charging properties of such a structure will be discussed below.

2. Silicon nanocrystal memory structure

The active part of a silicon nanocrystal memory is a metal-oxide-semiconductor (MOS) capacitor, in which the oxide film contains a 2-D layer of silicon nanocrystals at a tunneling distance from the silicon substrate (see fig. 2a).

The top oxide is relatively thicker than the tunneling oxide, in order to prevent carrier injection from the gate electrode. The silicon nanocrystal memory uses two more electrodes (source and drain) and it operates as a three terminal device (fig.2b).

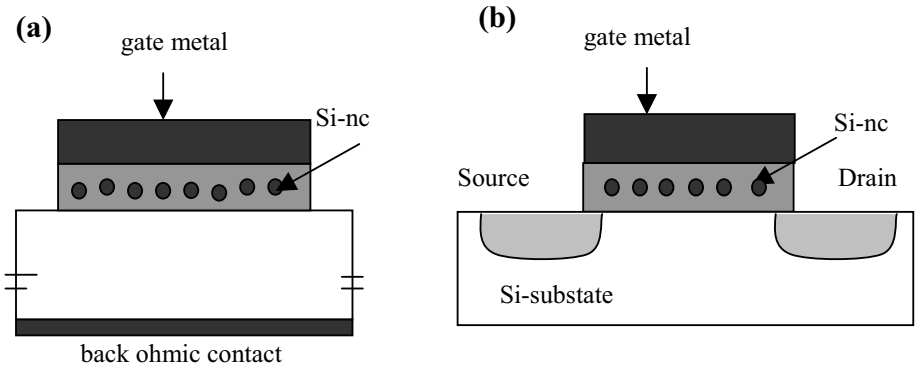


Figure 2. Schematic representation of MOS capacitor with Si-nc (a) and transistor (b)

The MOS structure may be used to evaluate the quality of the nanocrystals and their charging properties

3. Silicon nanocrystal growth and structural characterization.

As mentioned before, silicon nanocrystals were fabricated in this work by using LPCVD deposition of very thin silicon layers on SiO₂ and subsequent high temperature thermal oxidation. The initial SiO₂ tunneling oxides (thickness 3-4.5 nm) were grown by thermal oxidation on a p-type substrate. LPCVD silicon was deposited on top at 580°C, 300 mTorr for 2 min and oxidized at 900°C for 25 min. A final annealing step was performed at 900 or 1100°C for one hour. By this fabrication sequence, an array of silicon nanocrystals of diameter in the range of 1-2 nm, embedded in SiO₂, was obtained before the final annealing step. After annealing at 1100°C for one hour, the nanocrystals were larger, in the range of 2-3.5 nm, while no change was observed by annealing at 900°C. The bottom tunneling oxide was 3-4.5 nm thick, while the top oxide was 11-12 nm thick. Transmission electron microscopy (TEM) was used to characterize the nanocrystals [25, 29]. Plan view TEM images (see fig.3) revealed the size and size distribution of the nanocrystals, while cross sectional TEM images were used to characterize the SiO₂/Silicon nanocrystals/ SiO₂ structure. Fig. 4 shows a cross sectional TEM image from a sample annealed at 1100°C for 1 hour. We see that the silicon nanocrystal layer in-between SiO₂ is almost continuous, while the shape and size of the nanocrystals is not uniform. Some nanocrystals are almost spherical, (see high resolution TEM image of fig. 5a), while others are elongated, as the one shown in fig. 5b. By more careful observation, the elongated nanocrystal was found to consist of three spherical nanocrystals in contact to each other. Their average diameter was in the range of 2 nm. The average distance between the silicon substrate and the silicon nanocrystal layer was approximately equal to 4.5 nm, slightly higher than in the as-prepared sample and the sample annealed at 900°C.

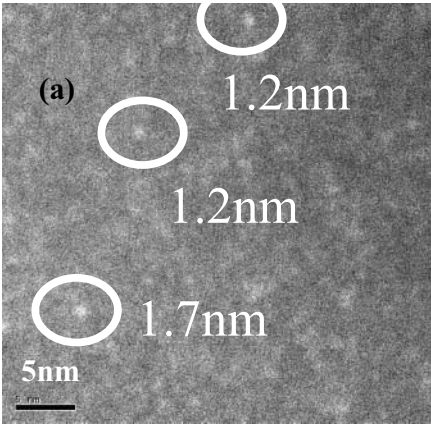


Figure 3. Plan-view, TEM micrographs of a sample oxidized for 25min and annealed at 900°C for 1 hour. The encircled bright spots are Si nanocrystals. The estimated diameter is also indicated.

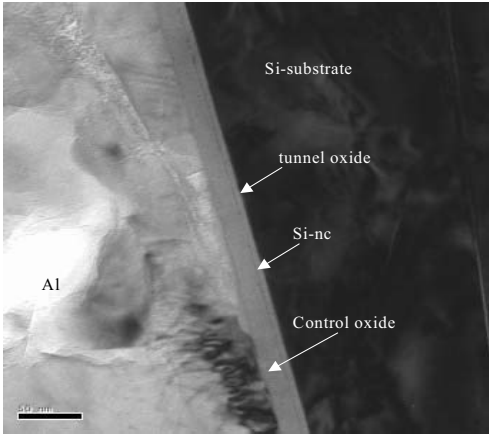


Figure 4. Cross-section, bright-field TEM micrograph, of a sample oxidized for 25 min and annealed at 900°C for 1 hour.

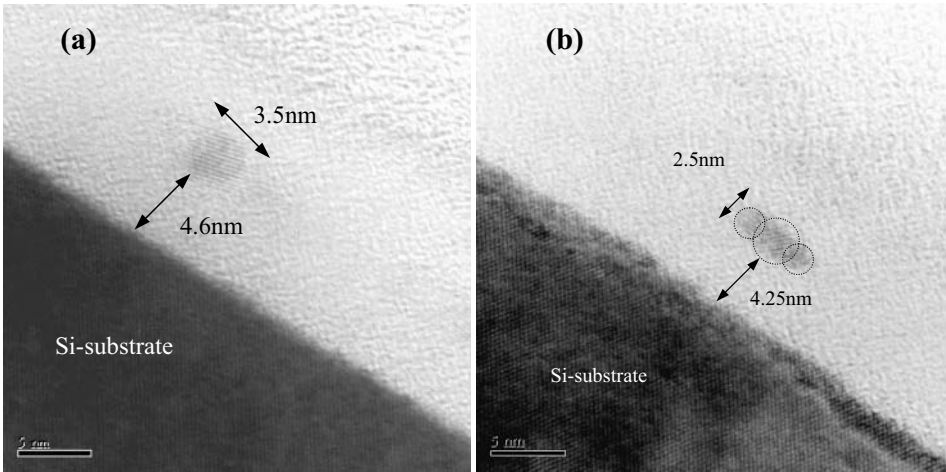


Figure 5. Cross-section bright field HRTEM micrographs of a sample oxidized at 900°C for 25min and annealed at 1100°C for 1 hour. (a) Spherical nanocrystal. (b) Cluster consisting of three nanocrystals in close proximity.

4. Charge trapping effects in silicon nanocrystal memories

Despite the significant progress towards reliable and reproducible nanocrystal memory operation, several issues still remain open. One of the problems still under discussion is the distinction between defects and silicon nanocrystal states and their contribution to the

charging of the structure [20, 29-33].

Charge trapping in the MOS capacitor structure may occur a) at interface states between the silicon substrate and SiO_2 , b) at different traps inside the SiO_2 layer (structural defects, compositional disorder), c) at silicon nanocrystal confined states and d) at interface states between silicon nanocrystals and the surrounding SiO_2 layer. States in SiO_2 and at the interface of SiO_2 with the silicon substrate are minimized by controlling the quality of the oxidation process. High quality thermal tunneling oxides with low density of interface states and states within the oxide were used in this work. The quality of the oxide was tested separately using capacitors without silicon nanocrystals embedded in the oxide.

I-V measurements

a) Samples annealed at 900°C for 1 hour

MOS capacitors with silicon nanocrystals within the gate oxide, using the SiO_2 /Silicon nanocrystals/ SiO_2 structure described above, were fabricated by using photolithography to define the gate area (mesa structure, Al gate metal) and by forming an ohmic contact on the backside of the wafer.

I-V characteristics were recorded in two different modes: a) using staircase voltage variation with fixed voltage step and step delay time and b) using continuous ramp voltage variation at constant ramp rate dV/dt . From the ramp I-V curves the corresponding C-V curves are deduced by dividing the current by the ramp rate dV/dt .

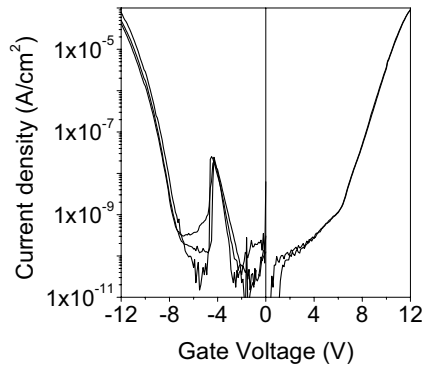


Figure 6. Staircase current density-voltage characteristics of the MOS capacitors of fig.1, obtained with a voltage step of 0.1V and a step delay time of 1sec. The voltage was swept from 0 to positive or negative values until breakdown. Different virgin diodes were used for each measurement.

Typical results obtained using staircase voltage sweep from samples annealed at 900°C for 1 hour are shown in figs. 6, 7. Fig. 6 shows I-V curves obtained by sweeping the voltage from zero to negative and from zero to positive values with a voltage step of 0.1V and a step delay time of 1 sec. A characteristic N-shaped peak is observed at negative values, while at gate voltages larger than -8V Fowler-Nordheim (F-N) tunneling of gate electrons initiates. At positive voltages the knee in the I-V curves shows the transition from low to high field conduction. Fig. 6 shows the I-V curves restricted to low voltages (before the initiation of high field conduction) for the capacitor in accumulation (voltage sweep from

zero to -8V with a voltage step of 0.05 V and different step delay times in the range of $0.5\text{--}30\text{ sec}$. The N-shaped peak is observed after a threshold voltage of the order of -3.5V . Its intensity and peak position depend strongly on the step delay, time used, being larger for faster measurements. It disappears for very slow measurements, which shows that it is due to a transient current with large time constant. It is attributed to a displacement current from the substrate to the nanocrystals. For the MOS structure used (p-type substrate), it corresponds to hole charging of nanocrystal states of states at the $\text{SiO}_2/\text{silicon}$ nanocrystal interface.

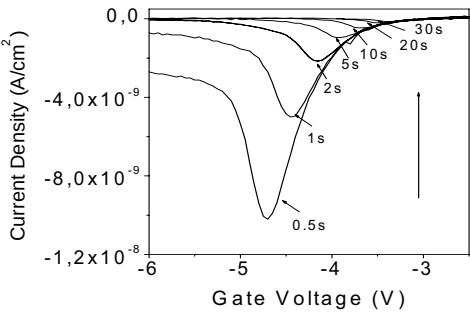


Figure 7.: Current density-voltage characteristics of the silicon nanocrystal MOS capacitor of fig.1, obtained using staircase voltage sweep with a step of 0.05V and a step delay time varying between 0.5 and 30sec . Voltage sweep started at zero Volts to a voltage of -8V . The maximum absolute voltage used was below the onset of Fowler-Nordheim tunneling. The observed peaks are much larger at small delay times than at large delay times. The measurements were consecutive, starting from a step delay time of 0.5sec up to the value of 30sec . No discharging of the structure was performed between each measurement by biasing the structure at inversion

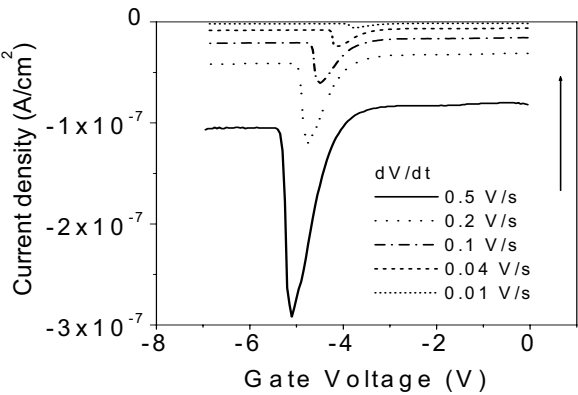


Figure 8.: Different current density-voltage measurements using constant ramp rate, between 0.01V/s and 0.5V/s . Measurements were consecutive, starting with a ramp rate of 0.5V/s to a value of 0.01V/s . Before each measurement the structure was biased at 3V for 10sec .

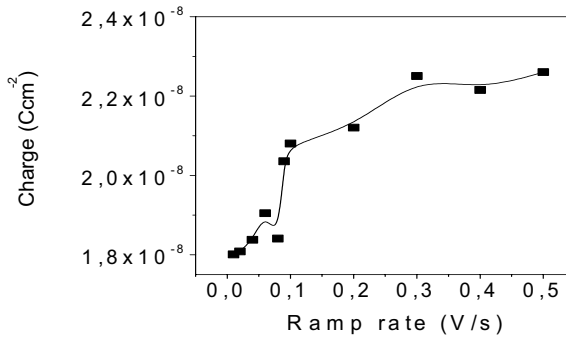


Figure 9.: Total charge under the transient peak as a function of the ramp rate used.

Similar behavior of the I-V curves is obtained by using ramp I-V measurements. In this case the N-shaped peak depends strongly on the ramp rate used (figs. 7, 8). From the ramp I-V curves the C-V curves are obtained by considering $C=I/(dV/dt)$.

By integrating the area under the peaks in a C-V curve we obtain the total charge involved in the displacement current during the voltage sweep. Fig. 9 shows the variation of the total charge as a function of the ramp rate used. When the ramp rate is small (slow measurement) the transient charge is also small and tends to zero, as expected. For larger ramp rates, the charge involved is larger and tends to saturation, as expected.

b) Capacitance - Voltage (C-V) measurements

C-V measurements were performed in the dark using a shielded probe station and an HP 4284A LCR meter.

a) Samples annealed at 900°C for 1 hour

Successive C-V curves obtained by using voltage sweeps which allowed to go progressively into deeper accumulation of the structure showed a shift of the C-V curves towards more negative gate voltages, which is attributed to hole trapping within the silicon nanocrystal layer. Similarly, by biasing the structure progressively into strong inversion, C-V shift towards more positive gate voltages is obtained, indicative of negative charge trapping. This behavior is illustrated in figs. 10, 11.

Full charging of the silicon nanocrystal layer is accomplished at average electric fields of 2.5 MV/cm for both polarities. By increasing the electric field above this value, no further shift in the C-V curves occurs. By considering the maximum shift of the flat band voltage, the charge density of trapping sites was calculated, which was equal to $2.1 \times 10^{12} \text{cm}^{-2}$ for hole charging and $2.5 \times 10^{12} \text{cm}^{-2}$ for electron charging respectively (fig. 12). After hydrogen annealing this density dropped down to $2 \times 10^{11} \text{cm}^{-2}$ other characteristic features deserved in C-V curves were: a) a dip at the accumulation region during forward sweep and a hump at the inversion region during reverse sweep. This is illustrated in fig. 13. The capacitance dip is strongly correlated with a peak in the accumulation region of the I-V curves and it is attributed to a transient current, due to charging of the silicon nanocrystal layer.

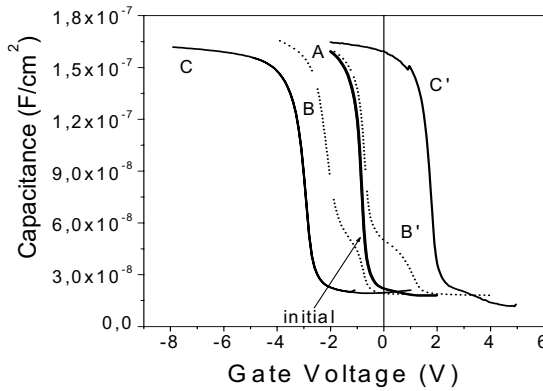


Figure 10.: High frequency C-V characteristics at 1 MHz showing charging of the structure, annealed at $900^\circ C$ and not subjected to hydrogen annealing. Curve A) is the initial curve prior to charging, while curves B) and C) result after biasing at $-4V$ and $-8V$ respectively. Curves B') and C') result after biasing at $4V$ and $5V$. The C-V curves were recorded from accumulation to inversion for negative gate biasing, while the reverse was followed for positive gate biasing.

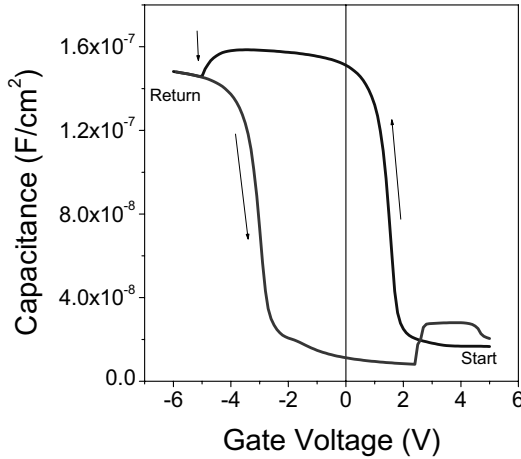


Figure 11.: Double sweep C-V showing hysteresis due to the combined effects of electron and hole charging. The measurement starts at inversion, it goes to accumulation and then back at inversion.

characteristics. Hysteresis in C-V curves is reduced. Also the peak in forward sweep and hump in reverse sweep are reduced. These results indicate that a great part of trapping sites is related to defect states at the silicon nanocrystal/ SiO_2 interface.

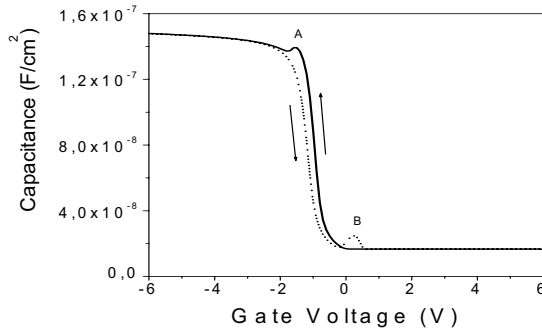


Figure 12.: High frequency characteristics of the sample annealed at 900°C and subjected to low temperature hydrogen annealing.

Annealing of the samples in forming gas induces considerable changes in the C-V

b) Samples annealed at 1100°C

Similar behavior as above was observed in samples annealed at 1100°C for 1 hour. Small parallel and symmetric shift in C-V curves was observed ($\approx 0.3V$). The threshold of the applied electric field for the transfer of holes to the nanocrystals was equal to 1MV/cm. The flat band voltage shift was saturated at 3MV/cm. The density of trapping sites was estimated to be, in that case, equal to $2.5 \times 10^{11} \text{ cm}^{-2}$, without hydrogen annealing, while no significant change was observed by hydrogen annealing. This result indicates that the 1100°C annealing of the structures had a clear effect on reducing defect states and promoting charging of nanocrystal states.

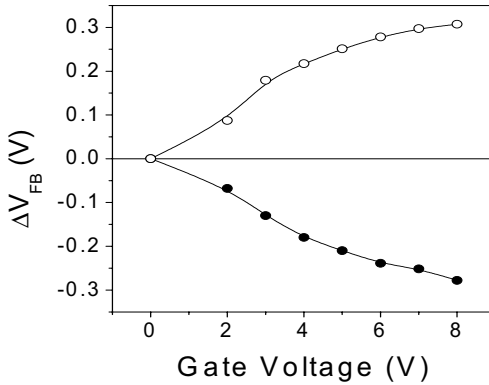


Figure 13.: Flat-band voltage shift of the sample annealed at 1100°C, obtained after progressive biasing of the structure at either positive or negative gate voltages. In contrast to the case of 900°C annealing, the charging of the structure is gradual. The resulting “memory window” shows a saturation tendency at high gate electric fields. The onset of high field conduction prohibits the use of higher gate voltages.

5. Conclusion

Charge trapping phenomena in silicon nanocrystals in-between SiO₂ layers were discussed for the case of silicon nanocrystals fabricated by LPCVD deposition of silicon on SiO₂, followed by high temperature oxidation and annealing. The influence of the annealing temperature and ambient was discussed. The above fabrication process seems promising for the fabrication of silicon nanocrystal memories.

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ON THE ROUTE TOWARDS A MONOLITHICALLY INTEGRATED SILICON PHOTONICS

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Abstract

Speed and complexity of integrated circuits are more and more increasing as integrated technology advances. The combination of ever-increasing chip size and decreasing feature size, however, has already raised its fundamental bottleneck in terms of speed, packaging, fanout, and power dissipation. Optical interconnects become more and more essential. Till now, the reliability and compatibility of many optical interconnect systems are quite far from a real integrated system and are based on hybrid approaches which make the fabrication difficult and costly. In the last years a big research effort was aimed to render Si an optical active materials so that it can be turned from an electronic material to a photonic material.

In this paper the state of the art of the research carried out at Trento on the main “building block” towards a monolithically integrated photonics based on silicon is presented: the studies on optical gain in silicon nanocrystals to realize a light source, the Si laser.

Keywords: Silicon nanocrystals; photonics; optical gain; x-ray absorption

1. Introduction

The large success of integration technology of nowadays microelectronic industry is essentially due to the presence of a single material, silicon, which is largely available, easy to handle and to manufacture, with very good thermal and mechanical properties, which render easy the processing of device based on it [1]. Moreover, the availability of a natural oxide to silicon, SiO_2 , which is an excellent insulator and an effective diffusion barrier; a single dominating processing technology, CMOS; the possibility to integrate more and more devices on larger and larger wafers; and an accepted common roadmap have rendered the microelectronics industry very successful. However, during these last years some concerns about the evolution of this industry have been raised [2]. In fact, the combination of ever-increasing chip size and decreasing feature size has already raised its fundamental bottleneck in terms of speed, packaging, fanout, and power dissipation. In spite of the possibility to release this bottleneck for several years by improving design and materials performance, the change towards optical interconnects becomes more and more essential [3]. Till now, the reliability and compatibility of many optical interconnect systems are quite far from a real integrated system and are based on hybrid approaches, which make the fabrication difficult and costly: i.e. optical interconnects through optical fibers and III-V laser sources are already used [4]. For some the future of Si-based photonic lies in hybrid solutions, for others in the utilization of more photonic functions by silicon itself. However, to achieve a monolithically integrated silicon microphotonics, the basic components have been already demonstrated [5, 6], but for any practical Si-based light sources: either efficient LED or a Si laser.

To have a Si laser, or in general, a laser, one needs three key ingredients: i) an active material, which should be luminescent in the region of interest and able to amplify light, ii) an optical cavity, iii) a suitable and efficient pumping scheme to achieve and sustain the laser action.

In this paper, we discuss about the first and main task: to make silicon an active material for optical amplification.

Silicon is an indirect band-gap material, light emission is a phonon-mediated process with low probability: spontaneous recombination lifetimes in the ms range and very low internal quantum efficiency ($\eta_i \approx 10^{-6}$) for bulk silicon luminescence [7]. In addition, fast non-radiative processes such as Auger or free carrier absorption severely prevent population inversion for silicon optical transitions at the high pumping rates needed to achieve optical amplification. Despite of all, during the nineties many different strategies have been employed to overcome these materials limitations [7] and are currently followed to build a silicon laser [8]. They differ both for spectral region of emission and for the physics behind. One approach consists in the enhancing of extraction efficiency of light from extremely pure bulk silicon by suitably texturizing the Si surface (power efficiency for Si-based LED approaching 1%) [9]. A somehow different approach was reported [10] on the idea of a reduction of the non-radiative channels by exploiting the strain produced by localized dislocation loops, which block the carriers and enhance radiative decay. External quantum efficiency of about 1 % are claimed for these LEDs. However, these approaches do not remove the two main problems of silicon which prevents population inversion, i. e. Auger recombination and free carrier absorption. Another problem is related to the wavelength of emission of these bulk Silicon LEDs, which is resonant with the silicon band gap.

2. Silicon nanocrystals

The most successful approach is based on nanostructured silicon, where the optoelectronic properties of silicon are modified by quantum confinement effects. This approach has been pioneered by the work on porous silicon (PS) [11, 12], which shows that when silicon is partially etched in an HF solution via an electrochemical attack, the surviving structure is formed by small nanocrystals or nanowires, which show bright red luminescence at room temperature. The PS approach has however a drawback in the high reactivity of the sponge-like texture which causes the rapid ageing of the LED and an uncontrollable variations of the LED performances with time. No optical gain was reported in bulk PS. From PS, silicon nanocrystals (Si-nc) can be obtained by scrapping or ultrasonically dispersing porous silicon. Then the surface chemistry can be adjusted and, in particular, oxide passivated. Evidences of amplification in these materials have been presented [13].

An alternative way is to produce silicon nanoparticles in a silica matrix to exploit the quality and stability of the SiO_2/Si interface and the improved emission properties of low dimensional silicon. Many different approaches have been proposed to form the silicon nanocrystals [7,8]. The most widely used are based on the deposition of sub-stoichiometric silica films, with a large excess of silicon, followed by a high temperature annealing [14]. The annealing causes a phase separation between the two constituent phases, i.e. silicon and SiO_2 with the formation of small silicon nanocrystals. The size and density of the Si-nc can be controlled by the deposition and the annealing parameters. Recently, thermal anneal of amorphous Si/SiO_2 superlattices has been proposed to better control the size distribution: almost monodispersed size distribution has been demonstrated [15].

Although the Si-nc system is very promising to achieve a laser and many breakthroughs have been recently demonstrated in this field [16,17,18,19], there are still some un-answered issues:

- i) what is the role played by the Si-nc and by the embedding medium,
- ii) what are the key parameters which determine the presence of gain in the Si-nc,
- iv) if low-losses active waveguides are possible to achieve,
- v) the nature of the four levels in the model.

Moreover, the light emission mechanism and the relation between the observation of positive gain values and structural information are still under debate. Hence, the knowledge of the chemical composition and structure of both amorphous matrix and Si-nc is important to address the un-answered issues related to optical gain. In the following we review and discuss experimental results carried out in Trento, which address some of these main important issues.

3. Structural characterization of PECVD-grown samples

Silicon nanocrystals have been produced by PECVD (plasma enhanced chemical vapor deposition) of substoichiometric silicon oxide (SiO_x) deposited on silicon or quartz substrate followed by high-temperature annealing that induces the formation of Si-nc dispersed in an amorphous matrix [14,20]. Stoichiometric samples ($x=2$) contain about 33% of Si atoms, while substoichiometric samples ($x<2$) have an excess of Si atoms available for the formation of Si-nc. Composition and thickness of the annealed samples were determined by RBS measurements, carried out by using a 1.6 MeV He^+ beam in random configuration. Samples were about 200 nm thick and homogeneous in depth. Different sets of samples have been produced and studied: changing the Si content (35, 37, 39, 42 and 46 at.%) with fixed annealing temperature (1250 °C in N_2 atmosphere for 1 h), and as a function of the annealing temperature (as deposited and 500, 650, 800, 900, 1000, 1100, 1200 and 1250 °C) with fixed Si content (39, 42, 44, 46 at.%). By varying the stoichiometry of the film and the annealing temperature, it is possible to change the mean size of Si-nc and hence the photoluminescence (PL) peak position, which red shifts for a given Si content with increasing the annealing temperature, and for a given temperature with increasing the Si content [14,20].

RBS measurements give the elemental composition of the samples, without distinguishing between Si atoms in the nanodots and in the amorphous matrix. Furthermore, RBS data indicate variable and significant content of N atoms (about 8-10%) due to the use of N_2O as gas precursor in the PECVD technique [14]. To have a quantitative compositional description, including information on the chemical bonds, RBS data have been coupled to XAS (X-ray Absorption Spectroscopy) data [21,22]. X-ray absorption measurements were carried out at Super-ACO (LURE - Orsay, F) on the SA32 x-ray beamline. The absorption spectra were recorded at the Si k -edge in the range 1830-1870 eV by detecting the total yield of electrons escaping from the sample. The sampling depth of TEY-XAS technique at Si k -edge energy is about 100 nm for both c-Si and SiO_2 [23], i.e. comparable to the thickness of samples (about 200 nm) but not too long to detect the contribution of the Si substrate.

TEY spectra show two main features (figure 1a, continuous lines): at about 1841 eV (due to Si-Si absorption) and at about 1847 eV (due to α - SiO_2). In a recent work [22], we have shown that the intensity of the x-ray absorption coefficient of Si in Si-nc increases with the Si content of the samples, confirming that excess Si atoms form Si-nc after the anneal at high temperature, although not all Si atoms. In fact, to quantita-

tively assess the amount of Si atoms in the nanodots, we have reproduced the experimental TEY spectra by a linear combination of *c*-Si and *a*-SiO₂ reference absorption spectra. As shown in figure 1a (dashed lines), the best-fit well reproduces the absorption coefficient; only the main absorption peak of silica at about 1847 eV is systematically underestimated. However, it is known that the silica peak is very sensitive to small changes in the local environment [24]. The amount of Si-Si bonds, as obtained by the fitting procedure of the TEY spectra, shows that the sum of this value and of the amount of Si atoms bonded to oxygen (evaluated from RBS data) is less than the Si total content obtained from RBS measurements (see Ref [22] for details). The fraction of excess Si not nucleated in the Si-nc remains in the amorphous matrix bonding with N atoms, which have been incorporated in the substoichiometric film during the PECVD procedure, due to the use of N₂O as gas precursor [14,22]. Hence, the amorphous matrix cannot be simply considered as amorphous SiO₂ but rather as Si oxynitride amorphous phase, characterized by low nitrogen content and weakly dependent on the total amount of silicon. In particular, we have shown [22] that at low Si content (35, 37 and 39 at.%) the nitrogen can be simply considered as substitutional of oxygen in the formation of tetrahedra participating to a silica-like network SiO_{2-x}N_x. At high Si content (42 and 46 at.%), the amorphous matrix assumes a more complex structure SiO_yN_x.

To study the nucleation and evolution of both Si-nc and embedding matrix, we investigated different sets of samples as a function of the annealing temperature. In figure 1b, it is shown an example (sample 42 at.% of Si) of the evolution of the x-ray absorption features. Besides the two features at about 1841 eV (due to Si-Si absorption) and at about 1847 eV (due to *a*-SiO₂), which are present for all the annealing temperatures, the as-deposited sample shows two broad absorption structures at about 1843.5 and 1844.6 eV, which decrease in intensity with increasing the annealing temperature [21]. On the basis of TEY measurements of reference samples, we can assign these structures to Si-nitride species: in fact, SiN_x samples show a broad absorption peak at about 1844-1845 eV, while reference samples of Si₃N₄ and Si₂N₂O present a peak at about 1844 and 1845 eV, respectively [22]. The evolution with the temperature of nitrogen-related features is also pointed out by the analysis of the derivative plots, which shows a negligible contribution of absorption related to Si oxynitrides for annealing temperatures higher than 1000 °C. By comparing the evolution of these abso-

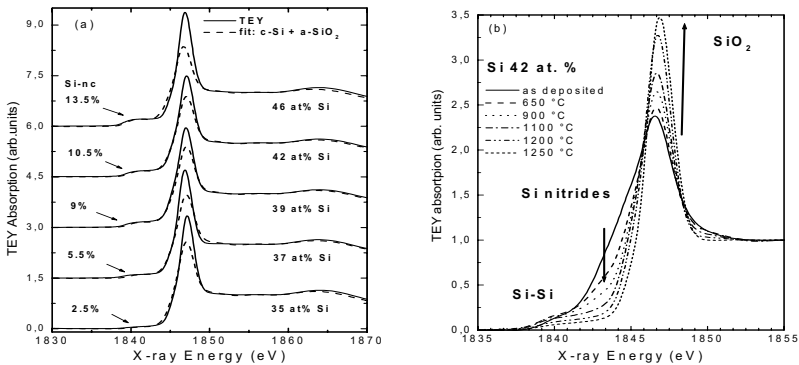


Figure 1. (a) TEY absorption spectra (continuous lines) at the Si *k*-edge of a set of PECVD samples obtained with increasing the Si content and annealed at 1250 °C. Simulated spectra (dashed lines) obtained by a combination of the *c*-Si and *a*-SiO₂ reference spectra. (b) TEY absorption spectra at the Si *k*-edge of SiO_x samples containing 42 at.% of Si as a function of the annealing temperature. Arrows indicate the trends with increasing annealing temperature.

ption features in samples characterized by different Si content (39, 44 and 46 at.%), it appears that for higher Si concentration the presence of these compounds is more relevant, but the trend is the same. It can also be noted that the intensity of the α -SiO₂ absorption peak increases with increasing the annealing temperature and small shifts of its maximum energy towards higher values are observed together with more symmetric absorption lineshape, suggesting a structural evolution of the amorphous matrix [21]. For high annealing temperatures these absorption features disappeared suggesting that the annealing induces the nucleation of Si-nc and allows migration of N atoms within the matrix forming a Si oxynitride amorphous phase [22]. This compositional picture pointed out by x-ray absorption measurements, is also suggested by PL measurements. PL measurements (fig. 2) were carried out by using an Ar⁺ laser (365 nm emission line, 20 mW) and a visible spectrometer with a CCD detector. The as-prepared and 650 °C annealed samples show a PL band at about 550-580 nm. With increasing annealing temperature this band weakens (fig. 2, right panel). For temperatures higher than 1100 °C, a PL band at about 800-900 nm rises. Red shift and change in intensity are observed with increasing annealing temperature from 1100 to 1250 °C (fig. 2, left panel). The comparison between TEY and PL spectra suggests that the PL band at about 550-580 nm is related to Si nitrides segregated in the amorphous substoichiometric film. As a matter of fact, light emission in this range can be related to defect-radiative states either in the Si oxide or Si nitride matrix [29]. As the annealing temperature increases, this PL band strongly reduces. At higher temperatures, Si nanocrystals form and PL emission occurs at 800-900 nm [14]. These results are also supported by Fourier Transform Infrared (FT-IR) measurements [25]. FT-IR spectra, recorded with a Jasco system operating in transmission mode, show the typical absorption bands of Si-rich α -SiO_x films containing H and N [26]. FT-IR spectra recorded on films annealed above 900 °C exhibit the typical absorptive bands of silica-based glasses at 1076 cm⁻¹ (Si-O stretching), but not the Si-H stretching band at $\approx$ 2250 cm⁻¹, which suggests that H has been completely removed during the annealing process above 800 °C. The disappearance of a peak related to Si-N bond (about 850 cm⁻¹) as the annealing temperature increases, together with the formation of a Si-N-O mixed phase (shoulder at about 970 cm⁻¹) and the shift of the Si-O-Si stretching mode confirm the structural evolution emerging from TEY, RBS and PL results. The formation of Si-nc within the thermally annealed films has been clearly evidenced by TEM measurements [14] and also by Raman scattering [25], which present typical features (spectral intensity, peak position and shape) of Si-nc formed in dielectric matrices.

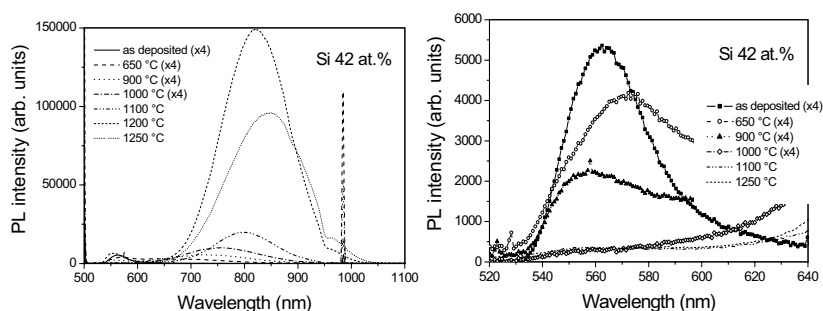


Figure 2. PL spectra of 42 at.% sample as a function of the annealing temperature; in the right panel a zoom is reported to better clarify the behavior of the band at about 550-600 nm.

In summary, the analysis of x-ray absorption and PL data, and also FTIR and Raman experiments has allowed us to assess that the nucleation of Si-nc is not a simple phase separation between Si-nc and a-SiO₂ but follows a more complicated scheme where nitrogen plays a role: the annealing induces the nucleation of Si-nc and allows migration of N forming a Si oxynitride network, whose stoichiometry depends on the Si content; moreover, the presence of nitrogen could influence the precipitation of Si-nc in SiO_yN_x thin films [27]. The presence of nitrogen atoms in the amorphous SiO₂ network plays a fundamental role both in lowering structural strains with respect to Si oxide [28, 29] and in modifying the optical properties as also confirmed by refractive index measurements on the same samples [30]. It introduces defect states localized at silicon-nitrogen bonds, which are active in hole trapping and transport, strongly influencing the balance between radiative and non-radiative decay processes [29,31]. PL measurements show high intensity signals, demonstrating that no large defect density is present [30], which would prevent radiative recombinations and would increase optical losses, as shown in the following where positive gain has been measured in some samples while optical losses dominate in other samples.

4. Optical gain in time-resolved measurements

In recent papers [32, 33, 34], we have shown amplified spontaneous emission (ASE) from Si-nc on PECVD-grown samples by means of VSL (variable stripe length) technique in the CW (continuous wavelength) and TR (time-resolved) regime and we have discussed in details experimental methods and critical issues to be addressed in order to avoid undesired experimental artifacts due to pump diffraction, light coupling and focal plane effects and irregularities of sample edges.

Here, we focus on time-resolved experiments on two different samples shown as examples of positive and negative optical gain. They are characterized by different total Si content: 42 at. % (named 3A, Si-nc mean radius 1.7 nm) and 39 at. % (named 5A, Si-nc mean radius 1.5 nm) both annealed at 1250 °C for one hour in nitrogen atmosphere. The oxide layer containing Si-nc was 250 nm thick and was embedded between two 100 nm thick stoichiometric SiO₂ layers to form a waveguide. Planar waveguides were formed on a transparent quartz substrate and had an optical confinement factor of 0.74 and 0.62 for samples 3A and 5A, respectively. Time-resolved experiments were performed in the one-dimensional amplifier configuration (pumping through the surface and collection of the guided light from one edge of the sample as a function of the pumping length) taking care to avoid experimental artifacts. High fluence (J_p) short optical pulses (6 ns, 10 Hz, 355 nm) produced by the third harmonic of Nd-YAG pulsed laser were used to excite the samples.

Figure 3a shows the time resolved ASE spectra of sample 3A at two observation time scales. For long integration times (500 μ s) the usual broad emission lineshape centered around 900 nm is measured [32]. This emission has similar spectral feature as the usual luminescence from Si-nc. On the contrary, when the first 100 ns are considered, a fast recombination component appears in the decay dynamics (figure 3b) and the spectral shape of the ASE signal appears strongly blue shifted, as shown in figure 3a (dotted line). The fast component disappears when either the excitation length ℓ is decreased at a fixed J_p or when J_p is decreased for a fixed ℓ . These observations rule out the non-radiative Auger processes as the origin of the observed fast component, since the J_p intensity does not depend on ℓ , whereas the fast recombination peaks are critically dependent on the pumping length, keeping fixed the excitation conditions. Moreover, the peak intensity of the fast component in sample 3A shows a super linear increase vs

ℓ for high J_p , which can be fitted with the usual one-dimensional amplifier equation yielding a net optical gain of $12 \pm 3 \text{ cm}^{-1}$ at 760 nm (figure 4a). Modal gain values ranging between 8 cm^{-1} and 20 cm^{-1} are measured depending on the detection wavelength. When the same fit is performed on the slow emission component, optical losses in the range $10\text{--}30 \text{ cm}^{-1}$ can be extracted.

The fast component peak intensity of sample 3A shows a threshold behavior vs J_p : at low J_p the emission is sub linear to a power 0.5, suggesting a strong Auger limited regime [35]; while for higher J_p , population inversion is achieved and a super linear increase to a power ≈ 3 is measured, suggesting the onset of the stimulated regime (figure 4b). Moreover, the lifetime of the fast component significantly shortens when the stimulated regime is entered. The emission threshold therefore separates two different regimes (Auger limited and stimulated emission) where more likely two distinct physical recombination mechanisms are present: either two different recombination centers in the same Si-nc (defect centers and quantum confined excitons) or two different emission centers in the system (distinct Si-nc populations, SiO_2 defects pumped efficiently through the smallest Si-nc). The presence of different recombination mechanisms in our samples is also evidenced by the clear difference in the spectral lineshape of the fast and slow emission components.

The fast recombination dynamic without threshold behavior vs J_p can be explained by Auger mechanisms [35, 36]: an example is sample 5A, which shows a fast recombination dynamics in the ns range, but unlike the amplifying sample 3A, no exponential VSL lineshape nor intensity threshold have been measured [32]. In fact, the fast dynamics of its own is not enough to claim for optical amplification. A strong competition between Auger fast processes and stimulated emission is present in Si-nc. For some samples Auger can prevail. On the contrary to sample 3A, negative gain of the order of -5 cm^{-1} has been found at the maximum pumping fluence. The loss behavior of sample 5A can be explained by the low refractive index of its light guiding layer ($n=1.66$ instead of $n=1.82$ of sample 3A), which suggests a low modal confinement, yielding too high optical losses that overcome the modal gain.

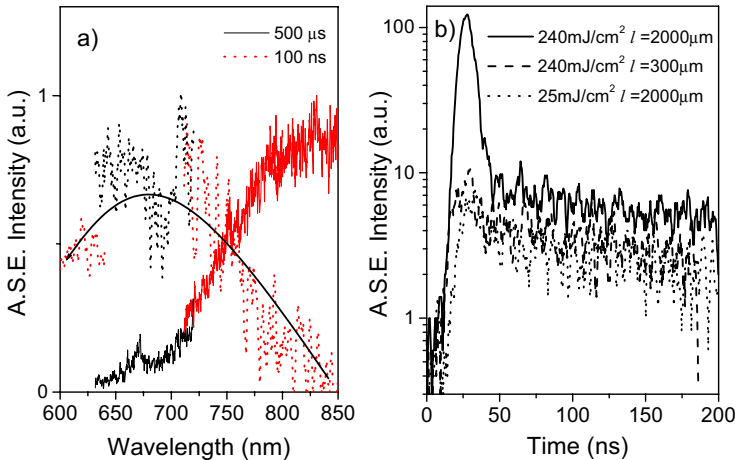


Figure 3. Sample 3A: (a) Amplified spontaneous emission (A.S.E.) lineshapes measured with the $500 \mu\text{s}$ time window (black continuous line) and with the 100 ns time window (dotted line) at the pump fluence of 200 mJ/cm^2 . The stripe length ℓ was $2000 \mu\text{m}$. (b) Time resolved A.S.E. decay measured as a function of pump fluence and pump length under variable stripe length configuration. Detection wavelength was 750 nm .

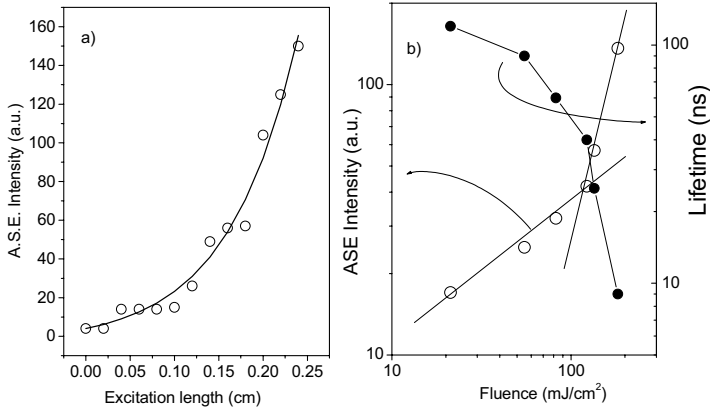


Figure 4. Sample 3A: a) ASE intensity versus excitation length at 760nm. Pump fluence of 200 mJ/cm²; b) ASE intensity (open circles) of the fast emission peak versus pump fluence, (black circles) fast luminescence lifetime versus pump fluence. The lifetime has been extracted from the experimental decays as the 1/e intensity time. Excitation length was 2 mm.

5. Optical gain in CW pump and probe measurements

Having demonstrated that probe amplification is possible in Si-nc [16] and that the dynamics of the amplification is extremely fast and, within the time resolution of our experimental set-up, coincident with the time dynamics of the stimulated emission [33, 34], and that TR transmission measurements as a function of the pumping intensity have shown a net amplification of the probe signal with respect to the incident probe signal [37], we present here the spectral dependence of the gain of sample 3 A in CW pump and probe experiments.

Careful alignment of the pump and probe beam on the sample surface is needed to avoid spurious effects such as those caused by sample heating. CW probe beam is provided by a monochromatized short-arc air-cooled 1000 W Xe lamp in presence of the chopped CW pump beam (457 nm or 365 nm lines of an UV-extended Ar laser). A large area photon counting detector is used in order to avoid possible artifacts caused by nonlinear effect such as lensing of the probe beam. At high pumping power density, a strong modulation of the transmitted signal is observed which follows the on-off modulation of the pump beam. No such effect is observed at low pumping power. After the initial transient (1 ms) the transmitted intensity signal is constant excluding major heating problems or damaging of the sample. On these bases we attributed the transmission enhancement to probe beam amplification.

As an example, figure 5 reports the spectral dependence of transmittance spectra (T_{OFF} and T_{ON}) measured on sample 3 Å. It should be noted that these are absolute transmittance measurements, normalized with respect to the intensity of the probe beam incident on the sample, which was measured by the same apparatus in absence of the sample. As shown in the left panel of figure 5, T_{OFF} does not depend on J_p . T_{OFF} shows clear interference fringes in the transparency region of the sample, which are caused by the multilayered structure of the sample. T_{ON} shows the same interference fringes (no dramatic heating effect on the real part of refractive indices). In addition, in a region centered at about 700 nm and 100 nm wide T_{ON} increases significantly with increasing J_p and reaches the transparency threshold ($T_{ON}=1$) at about 0.5 kW/cm². Note that the interference fringes structure is not affected by the pump power, i.e the maxima and

minima do not shift with J_p . For even greater J_p , T_{ON} is larger than 1. In this region the probe beam is amplified with respect to its value before the sample, i. e. the sample shows high values of the optical gain, which compensates even for the losses caused by probe beam propagation in the quartz substrate. No similar effect is observed in a reference quartz substrate without the Si-nc. Other samples show an increase in the transmitted intensity up to the transparency [37].

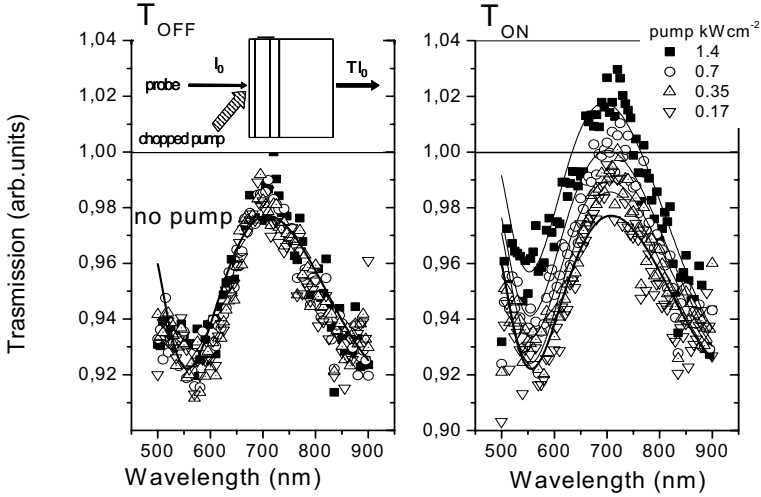


Figure 5. Transmission spectra (points) for increasing pumping power densities integrated during the time interval when the pump beam is off (left panel) or is on (right panel). The various pump powers and the relative symbols are given as legend in the graph. The lines are simulation of the experimental data for the various power densities. The thick line in the bottom panel is the no pump results of the simulation of right panel. (Inset) Sketch of the experiment scheme and of the sample structure.

In conclusion, net optical amplification of a probe beam through a sample where Si-nc have been formed has been measured. Other measurements and modeling of spectral dependence of gain are reported and discussed in Ref. [37].

6. Gain model: four levels system

Although a full theoretical model of the stimulated emission processes in Si-nc is still lacking and a clear understanding of the microscopic gain mechanism is still under debate, it has been suggested that interface radiative states associated with oxygen atoms can play a crucial role in determining the emission properties of Si-nc systems [38, 39, 40], in particular localized state recombinations either in the form of silicon dimers or in the form of Si=O bonds formed at the interface between the Si-nc and the oxide or within the oxide matrix. We have proposed an effective four-level model to treat qualitatively the strong competition among losses, Auger recombination and stimulated emission (figure 6 and 7). Two different kinds of Auger recombinations are considered to explain population inversion that can be studied on the basis of rate equations of the relaxation dynamics. This has explained the fast recombination component with the power threshold behavior observed in our time resolved VSL measurements [32,33]. In

fact, we have shown [32, 33] that the effect of pumping on the recombination dynamics results in a fast recombination component, as the pumping rate becomes high enough to create population inversion. The very same presence of the fast emission component together with the occurrence of a threshold intensity behavior and a superlinear ASE increase represent a strong indication that the fast emission is related to the stimulated emission of Si-nc. It is possible to observe optical gain whenever the stimulated emission rate is greater than the Auger recombination rate. It is possible to define a stimulated emission lifetime and an equivalent Auger recombination time as follows:

$$\tau_{se} = \frac{1}{B n_{ph}} = \frac{4}{3} \pi R_{nc}^3 \frac{1}{\xi \sigma c n_{ph}} \quad \tau_A = \frac{1}{2 C_A N_3}$$

where $B = \frac{\sigma c}{V}$, is the stimulated transition rate, σ the gain cross section at 750 nm, n_{ph} is the emitted photons numbers, R_{nc} is the mean radius of the nanocrystals and ξ the Si-nc volume fraction. It is worth noticing the inverse dependence of τ_{se} on ξ and on σ , as discussed in Ref [33]. It is clear that to observe optical gain $1/\tau_{se} \geq 1/\tau_A$. This poses a condition on the volume fraction, which could explain different results among different samples.

This is still a phenomenological model, which does not refer to a developed theory of the optical properties of Si-nc in SiO₂ and of their interfaces. However, we can suggest a possible nature for this four-level model.

X-ray measurements [41] showed the presence around the Si-nc of a modified SiO₂ region participating to the light emission process, but not extending to the whole silica matrix. Thus we proposed a structural model, where the Si-nc are capped by a modified SiO₂ region, which plays an active role in the luminescence. The model involves three regions: the core Si-nc, the capping modified SiO₂ shell and the embedding bulk SiO₂. The size of this intermediate region has been evaluated about 1 nm [41]. Ab-initio calculations [40,41] have been performed for the Si₁₀ nanocrystals in SiO₂ showing that the entire structure moves to a minimum-energy configuration, where a rearrangement of the starting crystalline surrounding SiO₂ both in bond lengths and angles is achieved.

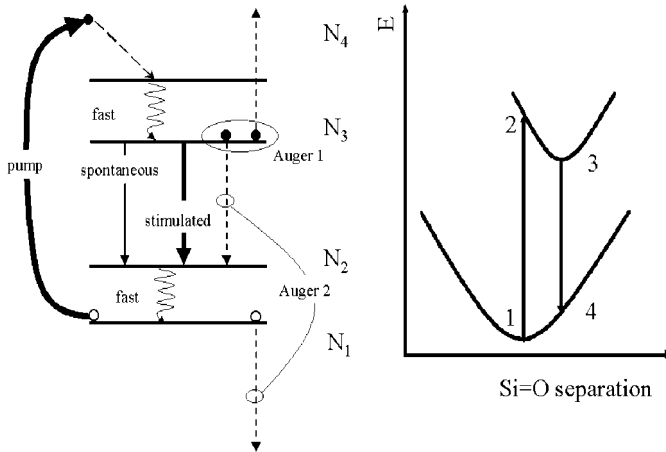


Figure 6. Effective four level system introduced to model qualitatively the recombination dynamics under gain conditions (see Ref [33,34]).

Figure 7. Energy configuration diagram of the silicon nanocrystals in an oxygen rich matrix. Level labelling refers to transitions in Fig. 6.

Thus the dots result to be surrounded by a cap-shell of about 0.8-0.9 nm thick modified SiO_2 which goes towards a pure crystalline matrix. The spatial distribution of the highest occupied (HOMO) and lowest unoccupied (LUMO) Kohn-Sham orbitals clearly show that the distribution is totally confined in the Si-nc region with some weight on the interface O atoms confirming the dot-nature of the near band-edge states but showing also the contribution of the surrounding SiO_2 cap-shell. The calculation of the absorption spectrum shows that these new states originate strong features in the optical region, which can be at the origin of the PL observed for Si-nc immersed in a SiO_2 cage.

These experimental and theoretical analyses [41] point out, for the first time, the important role played not only by the Si-nc but also by a modified silica host region in determining the optoelectronic properties of this system. Its relevance for the observed optical gain in Si-nc is to be associated with the four levels. In fact, one can speculate that this stressed SiO_2 shell enhances the formation of interface oxygen-related states (silanone?) on the surface of Si-nc or decreases the non-radiative Auger rate because of the resulting smoothing of the potential barriers.

6. Conclusion

Optical gain dynamics has been studied in different Si-nc PECVD samples. High power time-resolved VSL measurements show the onset of stimulated emission with fast inversion lifetime. Superlinear light emission and stimulated emission lifetime shortening have been shown together with an emission threshold behavior as a function of the fluence. Moreover, net optical amplification of a probe beam has been reported for CW UV excitation higher than 0.5 kW/cm^2 . A four-level model, which includes amplified spontaneous emission and Auger processes, has been proposed to explain gain dynamics. The comparison between different experimental techniques and theoretical calculations has allowed us to suggest a possible nature for this model and to assess that the nucleation of Si-nc produced by PECVD is not a simple phase separation between Si-nc and a- SiO_2 but follows a more complicated scheme where nitrogen plays a role that depends on the Si content, strongly influencing the balance between radiative and non-radiative decay processes.

The final vision is to move toward a Si microphotronics, thanks to the possible realization of a practical Si laser based on silicon nanocrystals embedded in an amorphous matrix.

Acknowledgments

This work has been supported by INFM through the Ramses project, and it is the results of the efforts of many people: we would like to acknowledge all co-workers in the Silicon Photonics group of Trento (<http://science.unitn.it/~semicon/>), F. Priolo and F. Iacona (Univ. Catania and IMM-CNR, Catania) and S. Ossicini and his coworkers (Univ. Modena) for their fundamental contribution.

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PHOTOLUMINESCENT NANOSILICON SYSTEMS

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Abstract

The porous silicon (por-Si) is one of the brightest example of nanosilicon systems. Non stability of the luminescent properties of porous silicon is the main reason that prevents por-Si applications for manufacturing efficient light emitting devices. For the solution of this problem the great deal of investigations was focused around different kinds of surface treatments.

It was observed that intensity of the visible photoluminescence (PL) of the samples rises after its exposure in the air at the room temperature because of oxygen impregnation to the deep layer of por-Si and formation of SiO_x clusters on the surface of Si-wires skeleton. The usage of second ion mass spectrometry (SIMS) allows to conclude that porous Si storage in the air ambient leads to the essentially non-uniformity distribution oxygen and hydroxyl groups after removing of surface layer thickness.

At the same time when the por-Si samples were subjected to pulse rapid thermal annealing (PTA) in an argon environment (the treatment temperature was 1100 K for a period 30 sec.) considerable transformation of spectral bands was observed: the integral spectra of por-Si shows two intensive bands at 720 and 540 nm.

As well silicon carbide films were deposited on the surface of por-Si samples by ion-plasma sputtering of a SiC target in argon-hydrogen vapor atmosphere. Deposition of thin (~80 nm) SiC films on the por-Si surface leads to decreasing of PL intensity in long-wave spectral range. Besides this, the new band of blue light emission appears. These changes in PL spectra of porous Si are explained by SiC clusters formation on the Si-wires skeleton of por-Si.

The spectral changes peculiarities of nanosilicon system depend from manufacturing methods and porosity of por-Si. Nevertheless, the system has the stable PL characteristics over the time.

1. Introduction

Nanocrystal materials are sufficiently new objects of research in the solid state physics and physical material science. These materials in their characteristics may be considered as approaching the so-called amorphous glass, since the latter along with the amorphous structure contains in its composition small order domains.

Microporous silicon, (por-Si), whose production methods and physical properties have been intensively investigated during the last fourteen years, may be classified as a specific type of nanocrystal semiconducting material with often unusual and sometimes even unique physical properties. Particularly, the por-Si layers containing nanocrystallites of only several nanometers give in the visible spectrum, as compared to single crystal silicon, a number of photo- and electroluminescence bands (PL and EL) [1-3] whose intensity and location depends on the method of the por-Si production and a treatment technique of samples.

The indicated properties of por-Si allow considering it a promising functional material for semiconducting microelectronics. This has conditioned a growing interest to this

material from many research teams and commercial firms.

The subsequent research of por-Si has revealed its biological compatibility as against single crystal and polycrystal silicon, which gives grounds to expect its possible wide application in biology and medicine.

Extremely developed inner surface of por-Si provides its high adsorption activity, thus making it possible to develop on its base different types of chemical and biological sensors. Capability of the por-Si surface to seize specific biological molecules (for example, DNA molecules) allows using it for development of miniature tool systems for fine biochemical analysis.

2. Experimental

All investigations were done on por-Si layers, produced by anodizing procedure of $10 \Omega \cdot \text{cm}$ p-type Si (100) substrates.

Two types of electrolytes have been used. The first type of electrolyte was composed of 48% HF and acetone mixture: it was mostly used for preparing the samples for investigation of the influence of the storage in the ambient air on its PL intensity. The second type of electrolyte was composed of 48% HF and ethanol mixture. This mixture was used mostly for formation of por-Si layers with further investigation of the influence of covering the sample surface by silicon carbide (SiC) or diamond-like carbon (DLC) films. The current density for both electrolytes was chosen 10-50 mA/cm².

The photoluminescence (PL) spectra were excited by using nitrogen laser ($\lambda_{\text{ex}} = 337.1$ nm, pulse duration $\tau = 10$ ns and pulse power $P = 5$ KW). The PL spectra were registered in the spectral region of 400 – 1200 nm and in temperature interval 77 – 420K.

In a number of cases the stroboscope registration system was used for detecting PL with nanosecond resolution. This gave us a possibility to study kinetics and PL spectra with time delay related to the maximum of the laser pulse.

In this study the ellipsometric characterization of por-Si layered structures was also done. The measurements of polarization parameters of a light wave reflected from a sample allow obtaining the optical constants and thickness of the layers of the reflecting system and therefore determining its structure.

In this study, the ellipsometric measurements were made for several wavelengths with the light beam reflected from different areas of the samples, which made it possible to study the complex structure of the sample surface region and to determine the por – Si optical constants, as well as its thickness, and also to determine such parameters for the outer layer on it.

The ellipsometric studies were carried out with a spectroellipsometer which operates according to the photoelectric compensatorless version of Beattie's method [4]. The ellipsometric parameters, such as the phase difference Δ between the p- and s-components of the E vector and the ratio of reflection coefficients $\text{tg } \rho$ in the p- and s-planes of the sample, were measured over a wide range of angles-of-incidence.

From the angular measurements, the principal angle Φ (the angle-of- incidence for which the phase difference $\Delta = 90^\circ$) and the relevant ellipticity $\text{tg } \rho$ at the principal angle were determined.

The samples of initial por-Si and por-Si + SiC were also subjected to pulse rapid thermal annealing (RTA) in an argon environment. The treatment temperature was 1073 K for a period of 30 sec.

The surface hydrogen plasma treatment (the treatment time was 5 min.) and covering the surface of por-Si samples with DLC or SiC films were also studied. Some

experiments were done after deposition of DNA molecules on the surface of initial por-Si samples.

Silicon carbide films were deposited by ion-plasma sputtering of a SiC target in argon-hydrogen vapor atmosphere. A triode system of sputtering was used when the plasma discharge was excited by thermoelectric emission and localized as a plane beam by the magnetic field of a permanent magnet. The regime used for the deposition of SiC films on the initial por - Si was: $t_{\text{sub}}=250^{\circ}\text{C}$, $\tau = 60$ s, $U_{\text{sput}} = 1000$ V, $I = 1$ A. Thickness of the SiC films was amounted to 80 nm (laser ellipsometer measurements).

DLC films were prepared by chemical vapor deposition (CVD) technology in RF (13.56 MHz) plasma discharge by the decomposition of a $\text{CH}_4\text{:H}_2$ gas mixture. The substrates for deposition were put directly on the cathode cooled by water and connected to the RF generator via a capacitor. The total pressure in the reaction chamber was 0.2 Torr. During the deposition experiments, RF discharge power was fixed and equaled to 175 W. The thickness of the DLC films varied in the region between 20 nm and 110 nm (profilometer "Dectac" and laser ellipsometry measurements), respectively.

The studies of the PS layer chemical composition and structure are carried out simultaneously with the experiments on improving determination of ellipsometric of and luminescent parameters. The impurity contamination of the samples surface layer was analyzed by Auger electronic spectroscopy (AES) and SIMS methods. The analysis of elements distribution in depth were done by layer - by layer Ar^+ ion etching of samples.

3. Results and discussion

3.1. RELATION BETWEEN THE COMPOSITION AND PHOTO-LUMINESCENCE PROPERTIES OF POROUS SILICON LAYERS

The provided luminescent and metallographic optical microscopy of the samples surface shows the following results. First of all, under the nitrogen-laser excitation, the initial por-Si layers, if cut under the 6° to the surface, show the strong PL intensity only after the ageing of samples in the ambient air. Those places at sample where the outer layers of polished specimen were broken under mechanical treatment are characterized only by weak PL.

The spectra of analyzed samples are shown in Fig. 1. One can see that the PL intensity of initial samples (the samples of type A) gives the minimal values. The weak PL

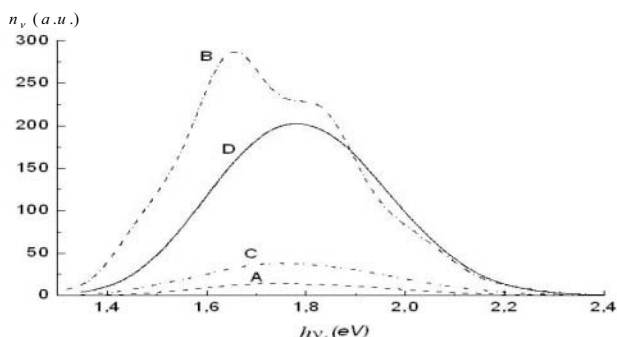


Fig. 1. PL spectra of PS samples: as-prepared (A); exposed to the air for a year (B); chemically etched for 20 s in HF after formation (C); a month after etching (D)

intensity also characterizes those samples which were subject of 48% HF treatment (type C), if the measurements were taken straight after. If after 48% HF treatment the samples were further exposed to the storage (air ageing) procedure, then their PL intensity grows considerably and monotonously with air ageing time and reaches its maximum after more than 20 days of storage. Under such a long storage term, PL characteristics of por-Si layers stabilize and practically do not change with ageing time increase.

For the samples of this last type (type D) the ageing time was fixed to 28 days.

One should also note that for the samples which were not subjected to HF treatment before the ageing procedure the PL intensity grows with ageing time, too; however, in this last case the velocity of PL-intensity growth is much slower than that of type D. For such samples the ageing time was fixed to one year (type B).

Fig. 2 shows the results obtained by SIMS depth distribution of ions Si^+ and impurity ions H^+ , SiH^+ , SiOH^+ , O^+ , SiO^+ for samples after the different treatments. As one can see from fig. 2 (a, b, c) for all samples the number of ion H^+ and groups SiH^+ , SiOH^+ decreases with the layer depth; while the number of ion Si^+ , O^+ and groups SiO^+ increases considerably (Fig. 2 d, e, f). Such increasing is especially noticeable for samples of type B and type D.

As one can see in fig. 2, the concentration of oxygen ion for B and D type of samples reaches its maximum values on the depth level of 60 and 130 nm respectively, while SiO^+ concentration reaches its maximum on a depth level of 30 nm for both sample types.

It is interesting to notice that when oxygen ion O^+ and SiO^+ concentration reaches its maximum, the further layer by layer etching shows the diminishing trend of these ion concentration to the por-Si layer depth. As for hydrogen ion H^+ and group SiH^+ concentration one can see that this characteristic monotonously decreases with por-Si layer depth.

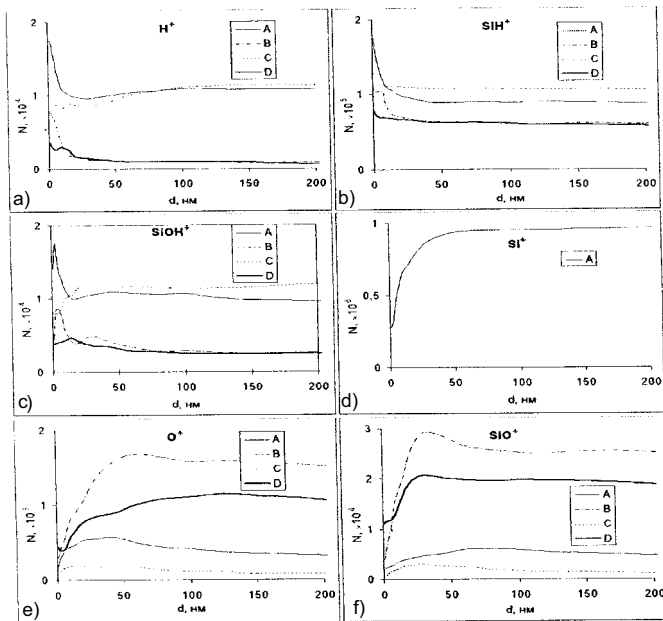


Fig. 2. Quantity Distribution of Certain Ions in the Depth of the Porous Layer

The data of further AES measurements of oxygen impurity atoms in por-Si layers depth confirm the results of the SIMS experiment. Moreover, while running AES experiment we note certain accumulation of electrical charge on the surface of samples at the initial stage of ion etching. The latter fact can be explained by the presence of thin dielectric films on por-Si surface.

Observing the aging process in por-Si in the first hours after production, a number of researchers registered not an increase but a decrease of the PL intensity [5]. This can be explained by a different velocity in release of the passivating hydrogen atoms from the nanosurface structure and saturation of the broken bonds with oxygen. The basic reason for short wave shift in PL of por-Si under aging is, probably, a decrease of a mean size of silicon nanoparticles resulted from oxidation, splitting of quantum wires into separate nanocrystallites (transformation of the two-dimensional quantum well into separate quantum dots) and formation of luminescence centers.

Earlier we have shown [6] that as a result of atmosphere oxidation of por-Si samples high values of the external quantum yield of the por-Si PL - up to 20% - are achieved. It might be well to point out that none of the known technological methods for increasing por-Si PL intensity including other oxidation techniques produce similar effect.

To our opinion, a relatively low quantum yield of PL in por-Si samples oxidized by other than natural ways is attributed to evident faults of the employed methods of oxidation. So, due to quantum-dimensional effects, the anode oxidation of por-Si proceeds most intensively near the pore bottom until the local disruption of silicon quantum wires takes place. As a result, the anode oxidation proceeds heterogeneously in the depth of the sample – the oxygen content is maximal in the por-Si layer adjacent to the substrate.

Thermal oxidation of samples also has its deficiencies since it is known that annealing facilitates structural transformation in the por-Si layers [7]. This transformation has a negative impact on the por-Si luminescence efficiency. Apparently, this is the reason of only two- three-fold increase of the PL intensity observed under fast thermal oxidation, as compared to fresh sample.

Natural oxidation of por-Si when the samples are held in the air does not have the faults inherent in the mentioned oxidation method, however even this oxidation method allows for heterogeneous oxygen saturation of por-Si in the layer thickness. Evidently, due to small size of the pores by which the atmosphere components penetrate inside por-Si, the oxygen concentration rapidly falls into the depth of the por-Si layer. As a consequence of this effect, a surface of the naturally oxidized por-Si sample is, in fact, covered with rather thick (about 300 nm) layer of dispersed oxide with possible patches of silicon nanocrystals, while the inner layers of por-Si contain silicon filaments which were covered with a thin layer of SiO_2 or separated particles of SiO_2 in por-Si matrix.

The results presented in this investigation suggest as conclusion that por-Si aging is a complex process, which largely depends not only on the parameters of the porous layer but also on the specific atmospheric conditions. Therefore, the use of por-Si layers as tool structures requires application of additional passivating coatings on their outer surface.

3.2. ELLIPSOMETRIC STUDIES OF POROUS SILICON

Geometrical and optical parameters of thin transparent oxide films on por-Si surface were defined as a result of ellipsometry analysis of these layered samples of principal angle Φ and ellipsicity $\text{tg } \rho$ in a frame of two-layers model, which permits determining both the thickness of transparent oxide films d_1 on por-Si surface and its optical constants (the index of refraction n_1 as well as indices of refraction n_2 of the substrate).

Additional ellipsometric measurements performed after chemical etching of transparent surface oxide layer as well as por-Si layer allow determining the same optical parameters also for single crystal substrate.

The data obtained [4] for optical constants of the surface oxide layer and for the layers of porous and single crystal silicon has been compared to the data from literature for single crystal silicon and silicon dioxide SiO₂ and are presented in table 1.

Table 1. Parameters of transparent oxide film (column1), SiO₂ (column 2), por-Si layer (column 3), single crystal silicon substrate (columns 4 and 5).

λ , nm	1		2 [18]	3		4		5 [8]	
	n_1	d_1	n_1	n_2	k_2	n_3	k_3	n_3	k_3
579	1.52	134	1.544	3.46	0.62	3.94	0.02	3.99	0.02
435	1.57	146	1.551	3.83	1.14	4.75	0.14	4.85	0.18
405	1.68	139	1.555	3.99	1.55	5.37	0.34	5.45	0.32

The analysis of the results, presented in table 1 permits to conclude that the values of optical constants n_3 and k_3 for single crystal Si substrate are almost the same as those commonly used in literature [8] for single crystal Si. At the same time, they much differ from those obtained for por-Si, mostly for the values of refraction index.

As for the nature of transparent outer layer, the comparison of the data from columns 1 and 2 in Tabl. 1 allows assuming that the outer layer is, in fact, a modification of silicon oxide whose composition is close to SiO₂, with possible impregnation of Si nanoparticles. The presence of those Si nanocrystals gives a natural explanation for the increase of index refraction n_1 for this film in comparison with amorphous SiO₂ films.

The obtained data permit us to propose the model of the investigated Si structure formed during electrochemical por-Si growth, presented in Fig. 3a. Such schematically presented Si – system is composed of three layers. The base layer 3 is the single crystalline Si substrate; the middle layer 2 is por-Si substance by itself. As for the transparent oxide outer layer 1, we propose to consider that it consists of SiO₂ film with impregnated Si nanocrystals (quantum dots).

This assumption permits estimating the fracture of Si single – crystal (in the form of nanoparticles) in the total volume of outer film using the obtained experimental data of refraction indices n_1 and n_3 , presented in Tabl. 1.

According to a simple calculation, the obtained value of impregnate Si particles fracture is found to be not more than 10%.

On the basis of the above structural scheme of por-Si, it is possible to attribute the established correlation between the PL intensity and a thickness of the transparent outer

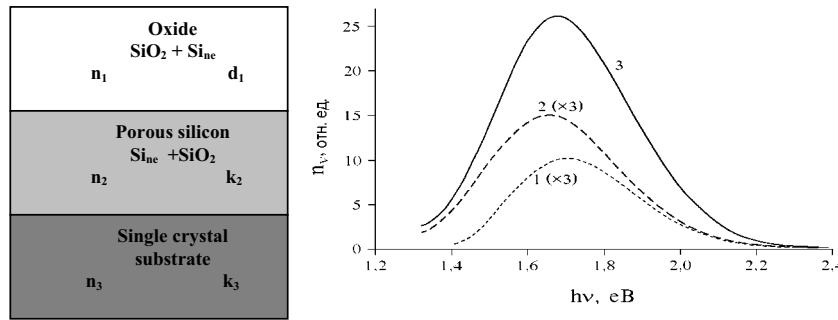


Fig. 3. Structural scheme of the studied systems with por-Si layer (a) and then PL spectra (b) on the sites with different oxide thickness d_1 , nm: (1) - 135; (2) -190; (3) - 324.

layer on the different sites of the sample (see the figure 3 b) to the increase of the total number of radiative luminescence centers.

In conclusion, it is worth noting that the performed ellipsometric measurements on the por-Si sample aged during one year has permitted establishing that the storage of the por-Si sample at room temperature during this time period practically does not change the thickness and optical parameters of the outer layer of silicon dioxide. The only noticeable effect of the sample aging as registered by the ellipsometric measurements was a decrease of the ellipticity value. Apparently, this circumstance has resulted from the change in the structure of the oxide layer (and possibly structure of the por-Si layer) in time.

At the same time it is noteworthy that PL on the fresh por-Si samples has occurred only in the periphery of the porous site of the sample where under electrochemical treatment there acted considerable mechanical stresses specified by the substrate fixing in the fluoroplastic glass. After holding the sample with por-Si during a year at the room temperature, a visible PL was observed in all sites of the sample. A role of mechanical stresses in the formation of the por-Si layers and their PL properties is in a detail considered in [10, 11] where it is shown that mechanical stresses in all cases stimulate PL in por-Si.

3.3. POROUS SILICON PHOTOLUMINESCENCE MODIFICATION BY IMPREGNATION OF CARBON BASED NANOCLUSTERS

Figure 4a shows the integral PL spectra of the por-Si and the por-Si + SiC structures. The initial por-Si has a band of PL characterized by a 680 nm peak position in the integral spectra (curve 1). The deposition of SiC films on the por-Si surface results in a decrease of the maximum PL intensity and a spectral up-shift of the PL maximum as well as an appearance of a new band of blue PL (curve 2), that probably is caused by Si-C covalent bonding. This assumption was confirmed by nanosecond (ns) spectra of the por-Si + SiC structure (Fig. 4b, curve 6), which has a strong PL band near the 450 nm range. It should be noted that in the ns-spectra of the initial por-Si, significant light emission in the region mentioned is not observed (Fig. 4b, curve 5).

The result of the RTA treatment is a substantial decrease of the PL intensity (~5 times) for PS in comparison with initial samples, and a considerable transformation of the spectral bands (Fig. 4a, curve 3). It is seen that the integral spectrum of initial por-Si, subjected to an RTA treatment, shows two intensive bands at 720 nm and 540 nm.

The PL band at 720 nm is explained by an emission from deep porous layers (quantum wires of large diameter) and caused by a long-lived component of PL [12, 13]. The short-wave band is interpreted with a short-lived component caused by modified near-surface quantum wires [14].

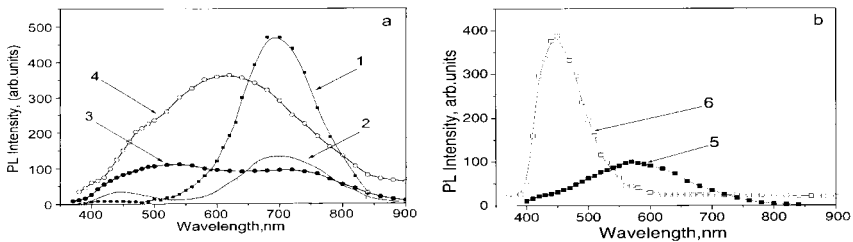


Fig. 4. a) Photoluminescence integral spectra of initial porous Si (curve 1), porous Si + SiC film structure (curve 2), porous Si subjected to rapid thermal annealing (curve 3) porous Si + SiC subjected to rapid thermal annealing; b) spectra of porous Si (curve 5) and porous Si + SiC (curve 6) observed with nanosecond resolution. The intensity of spectrum 4 is two times decreased for convenience.

The ns - PL spectrum (Fig. 4b, curve 5) of the initial por-Si has confirmed the origin of a short-wave band of the integral spectra.

The por-Si + SiC (Fig. 4a, curve 4) after an RTA treatment has shown the wide band of PL with a maximum intensity near the 600 nm region, and light emission in the 450 nm region. The PL intensity for the treated sample is six times larger as compared to initial porous Si subjected to RTA, and the strong up-shift (~ 100 nm) is observed relative to the non-treated por-Si + SiC sample. Probably, clustering processes with participation of SiC compounds onto Si quantum wires cause these spectral changes. The emission in the 450 nm band (Fig. 4b, curve 6) resulted from the presence of SiC compounds, which was confirmed earlier [15], when por-Si + SiC films of large thickness (200 nm) structures were also investigated. It has been established that after RTA treatment of such a structure the short-wave (~ 450 nm) PL band becomes more pronounced. Recently, the formation of p-SiC nanoparticles on Si nanowires was observed directly by transmission electron microscopy [16].

The other effective method for a por-Si properties modification is the por-Si + DLC film structure formation. As shown from Fig. 5, thin (20 nm) DLC film deposition on the por-Si surface leads to a partial low-energy shift of the PL peak (curve 3) as compared to the initial (curve 1). This fact is explained by a quantum confinement effect [14]. In this case the DLC film passivates deep porous layers and light emission from silicon nanowires of large diameter becomes more efficient. It should be noted, that the samples treated in hydrogen plasma prior to the DLC film deposition demonstrate a weaker shift as compared to the non-treated ones. This fact is considered to be provided by reducing the diameter of silicon nanowires after plasma treatment. It is especially important to emphasize that the spectra of por-Si + DLC thin film structure are well fitted by a single Gaussian and the PL peak position values and confirm the above presented explanations. The PL band peak position is shown in the top of the Fig. 5 by arrows.

In the case of a thick (110 nm) DLC film deposition, a substantial transformation of the spectral band is observed (Fig. 6). Along with, conventional for a por-Si long-wave PL band (curve 1 of Fig. 6), the emission in the 550-580 nm spectral range has appeared. The latter is concerned with a carbon based compound formation that is confirmed by the results of the spectra deconvolution. Indeed, the PL of por-Si + thick DLC film are well fitted by two Gaussians. The first of them is located near 680 nm and originated from a Si nanowire light emission similar to the por-Si + thin DLC film structure.

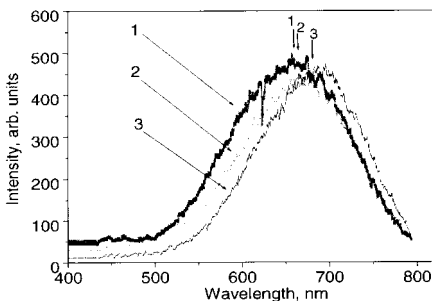


Fig. 5. Photoluminescence spectra of initial porous Si (curve 1), porous Si subjected to hydrogen plasma treatment and covered by a thin (20 nm) DLC film (curve 2), porous Si covered by a thin (20 nm) DLC film (curve 3). The top arrow labels correspond to the curve number.

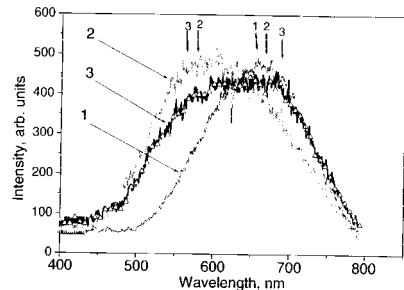


Fig. 6. Photoluminescence spectra of initial porous Si (curve1), porous Si subjected to hydrogen plasma treatment and covered by a thick (110 nm) DLC film (curve2), porous Si covered by a thick (110 nm) DLC film (curve3). The top arrow labels correspond to the curve numbers

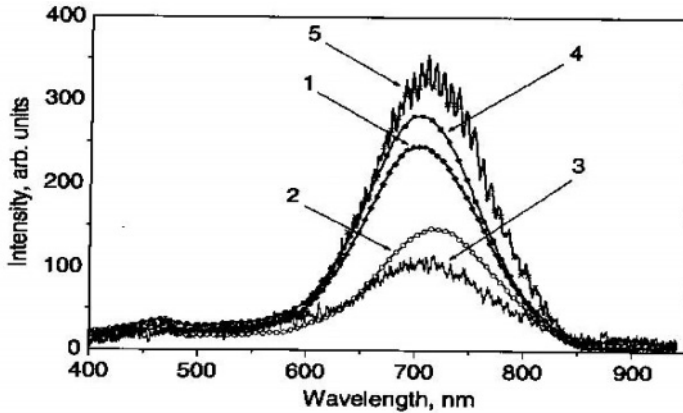


Fig. 7. Photoluminescence spectra of samples subjected to rapid thermal annealing: initial porous Si (curve 1), porous Si subjected to hydrogen plasma treatment and covered by a thin (20 nm) DLC film (curve 2), porous Si covered by a thin (20 nm) DLC film (curve 3), porous Si subjected to hydrogen plasma treatment and covered by a thick (110 nm) DLC film (curve 4), porous Si covered by a thick (110 nm) DLC film (curve 5).

Moreover, in both cases the PL band peak positions are very close (see arrows in Fig. 5 and Fig. 6). The second one is located near 560-580 nm. The PL band was stimulated by the partial absorption of laser excitation light in a rather thick DLC film and light emission from the film. It is evident that for a substantially thinner DLC film (20 nm Fig. 5) such an effect is not observed. The difference is observed between hydrogen plasma treated samples and non-treated ones (like in the previous case), which is caused by the same plasma etching effect. The conclusion is confirmed by practically the same PL band peak position (663 nm for the first case, see Fig. 5, and 666 nm for the second one, see Fig. 6).

The RTA treatment of such structures leads to light emission only in the long-wave spectral range (Fig.7). In principle, the por-Si structure depends on the etching conditions. However, as it was noted in [12, 13], the por-Si layered structure with Si nanowires depth distribution is a general feature of the material. It was confirmed by different methods, including transmittance electron microscopy [13] and photoluminescence [17]. Thus, por-Si has a layered structure, which is characterized by a nanowires size distribution from a small diameter (subsurface region) to a large one (in deep volume layers). The deep layers of the por-Si (nanowires of larger diameter) are more protected with the DLC film. As a result, the deeper layers properties are slightly modified after the RTA treatment. At the same time, thin silicon wires lose their PL properties during RTA. Therefore, the luminescence from a deep layer (with nanowires of larger diameter) is observed near 700-720 nm.

Another interesting result is the absence of any marked changes in the PL spectra (not shown here) of our por-Si + SiC and por-Si + DLC structures, neither just during PL measurements nor after the structure aging in atmospheric conditions for a few months. In conclusion, it has been shown that DLC or SiC film deposition allows us to modify the por-Si PL properties. In particular, the blue emission may be activated after SiC film deposition in combination with RTA treatment. Moreover, it was found that the por-Si + SiC and the por-Si + DLC film structures show stable photoluminescence properties.

4. Conclusions

Anode electrochemical etching of plates of single crystal silicon as a main material in modern electronics and microelectronics transforms their thin near-surface layer into nanocrystal state and forms a new functionally nanocrystal core in the form of filaments and branches surrounded by pores. Structure, composition and morphology of por-Si determine many of its physical and chemical properties, including adsorption, optical, electrophysical as well as photo- and electroluminescence properties.

Due to extremely developed inner surface, por-Si are characterized by a high adsorption activity, which, on the one hand, permits using this effect for development of different types of sensors, and on the other, creates difficulties for formation of light-emitting por-Si-based structures with stable operational properties.

Holding of fresh samples with por-Si layers at room temperature in the air, which leads to natural por-Si oxidation, is accompanied by an increase of external quantum yield of its PL up to 20%. Results presented in this research allow make a conclusion that natural oxidation of por-Si is a complex process, which largely depends on parameters of the porous layer and concrete conditions of oxidation.

It has been shown that DLC or SiC film deposition allows us to modify the por-Si PL properties. In particular, the blue emission may be activated after SiC film deposition in combination with RTA treatment. Moreover, it was found that the por-Si + SiC and the por-Si + DLC film structures show stable photoluminescence properties.

For better understanding physical nature of visible PL and EL of por-Si, prospects of por-Si practical application it is necessary to continue systematic research of both por-Si itself and tool structures formed on its basis.

Acknowledgments

The author would like to thank Prof. V. Litovchenko and Dr. N. Klyui, Dr. Yu. Piryatinskii, Dr. A. Rozhin for their help in time resolved photoluminescence measurements and helpful discussions.

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OPTICAL CHARACTERISATION OF OPAL PHOTONIC HETERO-CRYSTALS

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Abstract:

We introduce the 3-dimensional photonic crystal heterojunction on synthesised by successive growth of one opal film on another based on the self-assembly of monodisperse polystyrene beads of different sizes. These structures possess two minima in the transmission due to the Bragg photonic bandgaps in the individual films. Such heterostructure gives rise to an anisotropy of the reflectance spectrum and an interface photonic gap. Light sources were selectively embedded in the bottom film by alternate impregnation with oppositely charged polyelectrolyte layers and luminescent CdTe nanocrystals. The emission of CdTe nanocrystals was chosen to match the Bragg photonic bandgap of both opal films and experienced a strong spectral and spatial modification following the photonic bandgap anisotropy. An acceleration of the emission rate at frequencies within the interface gap has been observed and tentatively explained as the result of the emission being trapping in the near-interface volume.

1. Introduction

Incorporation of artificial defects for waveguiding, filtering and lasing is a current engineering aim for photonic crystals (PhC) [1]. Such target appears substantially more complicated for 3-dimensional PhCs compared to 2-dimensional ones. A dimensionality of defects themselves increases with increasing dimensionality of PhCs, i.e. 3-dimensional PhC can accommodate point, line and plane defects as well as arrays of these defects in arbitrarily combination. Being about a quarter- to a few-wavelengths in size, such defects pose a substantial technological challenge in the optical frequency range. Some of defects were realized so far in the case of successive assembly of lattices, for example, using a wafer bonding approach [2] or through combination of self-assembly and Langmuir-Blodgett deposition [3].

So far most experiments with 3-dimensional PhCs in the visible have been made with opals [4] and inverted opals [5] that makes them very attractive for further functionalisation. Artificial opals are self-assembled of monodisperse latex or silica beads, which tend to crystallise in the face centred cubic lattice (FCC) [6]. With respect to application of opals as photonic crystals [7], two major areas of interest can be identified. The first one is the impregnation of opals with efficient light sources without deterioration of the photonic bandgap (PBG), which targets PBG-controlled light emitters for the visible and near-IR spectral range [8]. This activity is associated with the fabrication of opals with intentionally introduced defects [9] aiming to achieve resonant conditions for the emission enhancement. It is especially desirable to accomplish the second aim within the self-assembly approach used for the opal preparation itself. Otherwise, the manufacture of opal-based functional materials

will be dependent upon increasingly complicated nanolithography technologies. The second one, which considers opals as optical elements for superrefraction [10], filtering [11], waveguiding and so on is represented relatively weak because of the insufficient quality of opals. Recently, we demonstrated some trends in the modification of opals, which combines different approaches towards synthesis of opals for optoelectronic circuits [12]. In particular, it is practically important to crystallise opals in pre-defined positions on the substrate. The method of synthesis in grooves and cavities prepared by nanolithography [13] was extended further to increase the thickness of opals in grooves and to eliminate cracks that damage the opal due course of drying the colloidal suspension [14]. On the other hand, post-synthesis modification of opals can be done by e-beam nanolithography resulting in artificial cavities and trenches in the body of opal [15].

Due to the statistical nature of self-assembly, approximately 1/100 of opal unit cells are damaged [16]. In this case, the distance between defects is comparable to the Bragg attenuation length. This factor makes *a priori* senseless any attempt of using artificial wavelength-size defects, because in currently available research grade opals it is technically impossible to control the location of a defect mode. Since the realization of thin film opals [17], the concentration of defects was reduced by at least an order of magnitude with respect to the best bulk opals. Another advantage is that thin opal films are always oriented along the [111] growth direction of their FCC lattice. Thus, this conventional approach can be used to create localised modes in the PBG by disturbing the lattice periodicity, when a sort of cavity is inserted in the body of thin opal film. However, this approach has to be accompanied by design of additional structure to couple the radiation in cavities to outside world that complicates further the realisation of the functional optical element.

An alternative solution can be the distortion of Bloch wave propagation across the PhC by, for example, a plane defect. Advantages of this strategy are the naturally formed channel of out-coupling of the radiation along the defect plane and the large volume of PhC, where modes are localised. The disadvantage is the 2D nature of a plane defect, i.e. the localisation applies to the transverse dimension only and the propagation is allowed along the defect plane. As the result, the achievable localisation is not a 3D one and the quality factor of such defect is intrinsically low.

As far as the propagation of PhC eigenmodes is concerned, a planar defect can be considered either as the distortion of the eigenmode ensemble of an otherwise homogeneous PhC or as a barrier in the PhC body. The former can be applied if the defect thickness remains comparable to the wavelength of interest and, consequently, the defect does not possess its own photonic bandgap structure. By carefully choosing the lattice parameter of the defect layer, it becomes possible to form a defect band inside the omnidirectional PBG of the host PhC [18]. Similar results were obtained for a defect layer in an opal with a directional PBG [19] (Fig.1), but the transmission spectrum in this case becomes a function of the direction of the light propagation. In the latter case, the PhC contains a thick alien PhC, which is characterised by its own PBG structure. Because the eigenmodes of two different PhCs follow different dispersion relations, it is necessary to couple the radiation flow from modes of one PhC to modes of the other at each interface, when this flow crosses the hetero-PhC. A simplification of a heterogeneous PhC would be an interface formed by two different PBGs.

So far, the theory of heterostructured PhCs has shown that the transmission properties can be tailored using photonic quantum well structures, heterostructures (HSs) and superlattices. Most studies are limited to heterostructures based on 1D PhCs with partly overlapping PBGs of the HS constituents [20, 21]. Efforts to simulate heterogeneous 3-dimensional PBGs are limited [22, 23] and have been devoted to either tunnelling of electromagnetic (EM) waves across PhC barriers and PhC superlattices composed of two different PBG structures

(perpendicular transport) or to EM wave propagation along PhC barriers (parallel transport). The formation of photonic minibands in PhC superlattice has been studied in more details [22]. So far, the driving idea for most theoretical constructions in the area of PhC HSs is the analogy with the electronic transport in heterostructured semiconductors, however, the limits of such analogy in the case of photonic hetero-crystals has not been explored yet.

From a general point of view, both perpendicular and parallel transport of EM waves take place if the radiation flow impinges at some angle on the interface between PhCs with different PBGs. The perpendicular transport here is the coupling of the radiation flow from eigenmodes of one PhC to modes of the other one. If the light frequency is far away from the PBGs of both films, scattering losses appear due to imperfect coupling. By contrast, when the light frequency matches the PBG on either side, the light propagation is blocked in this film. The eigenmodes of a PhC do not terminate exactly at the geometrical boundary, but decay exponentially to some depth in the adjacent PhC. Thus, two eigenmodes with the same frequency and wavevector but originating from different PhC reservoirs can co-exist in the interface volume. This is a pre-condition for interference and appearance of a common resonance. Such resonance at the PhC interface is a phenomenon, which, apparently, has no analogy in the electronic properties of semiconductor heterojunctions.

The simplest case of a hetero-opal is a bi-layer opal, where the opal film consisting of beads with diameter D_t , referred to as the top film in the text, is grown on top of another opal film being in contact with a substrate and consisting of beads with diameter D_b , referred to as the bottom film. If the interface between these films is sufficiently abrupt and the difference in the bead diameters is large enough, the photonic band structures of both opal films are similar, although scaled on both the energy and the wavevector axes in proportion to the lattice constant. The Bragg gaps along the same direction do not overlap in such a hetero-opal. Fig.1 shows the energy band model of a bi-layer PhC heterojunction along the QL direction in the Brillouin zone of the opal, which corresponds to the [3] growth direction of the opal lattice.

Early experimental studies of opals with step-like variation of the index of refraction (RI) demonstrated that two independent photonic bandgaps (PBG) co-exist in one piece of opal [24]. The preparation of a wide variety of heterogeneous opals becomes possible with thin opal films, which allow the successive crystallisation of opal layers with different PBG characteristics on top of each other [25]. Recently, we developed a technique to make a sharp heterojunction between two opal films of different lattice parameters, introduced light emitting bi-layer opals and demonstrated some structure-dependent aspects of their optical properties [26, 27]. Semiconductor nanocrystals (NCs) were used as a light source, the strong band-to-band emission of which is tuneable by changing the NC size as a result of the quantum size effect [28]. The most pronounced effect in these heterostructures is the strong anisotropy of optical reflectance and emission with respect to the interface plane of bi-layer opals.

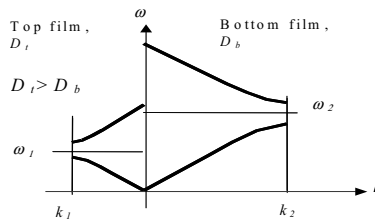


Figure 1. PBG diagram of a heterojunction in a bi-layer opal consisting of beads of different sizes ($D_b < D_t$) along the QL direction, which corresponds to the [111] axis in real space. Scaling is applied to both the frequency and the wavevector axis following the difference of the opal lattice constant of the top and bottom layers.

The range of possible bi-layer opals may include, for example, (1) the above-mentioned hetero-opals made from beads of the same material but different diameter the PBGs of which scale linearly with the lattice parameter, (2) hetero-opals and inverted opals made from materials with different dielectric constants leading to bandgaps of different width and dispersion in momentum space, or (3) hetero-opals combining direct and inverse opals with contrasting spatial distribution of the EM field.

In this paper a review of optical properties of light-emitting bi-layer opals is given, the opening of the interface photonic gap is discussed and the effect of this gap upon emission spectra is demonstrated.

2. Experimental techniques

Transmission/reflectance spectra were measured under white light illumination from a tungsten lamp. A well-collimated beam of 1 mm diameter impinged on the opal surface under certain angle of incidence θ . The reflected/transmitted light was collected in the configurations shown in Fig.3a within a solid angle $\Omega \approx 2^\circ$. Reflectance and transmission measurements were performed with either the top or the bottom opal film facing the detector. The photoluminescence (PL) was excited by the 351 and 457.9 nm lines of a continuous wave (cw) Ar-ion laser, with power up to 30 mW in a 0.1 mm diameter spot, and collected within a $\Omega \approx 5^\circ$ fraction of the solid angle from the film face opposite to that exposed to the laser beam, thus allowing the emission to traverse the PhC (Fig.3b). The excitation power was kept sufficiently low to avoid degradation of CdTe NCs. PL spectra were recorded after stabilization of the PL intensity with respect to the excitation power. In order to trace the emission anisotropy, PL spectra were measured at several angles θ with respect to the [111] axis of the FCC opal lattice.

In what follows, we define the film of the hetero-opal being impregnated with light emitting NCs as a source and the other film as a filter. The bottom film, which is in contact with the substrate, is always the source, and the top film is always the filter in our samples. PL spectra were taken from both sides by rotating the samples with respect to the laser beam and these are called "source PL" and "filter PL" in the text.

Self-assembly of monodisperse latex or silica beads is a widely used technique to produce 3D

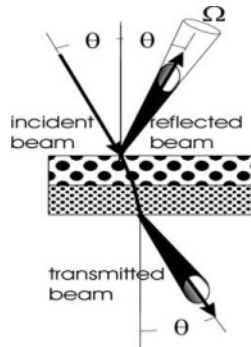


Figure 2. Layout of reflectance/transmission measurements in the Bragg configuration, in which the angle of incidence is equal to the angle of reflectance/transmission. θ denotes the angle with respect to the plane normal, which is the [111] axis of the FCC lattice in thin film opals. Ω is the solid angle of light collection.

artificial opals in the bulk and thin film forms [29]. This “bottom-up” approach is well documented and reproducible. When opals are used as PhCs, tuning of the PBG position from the visible to the near-IR spectral ranges can be achieved with different bead diameters.

Opal films used in this work were crystallised on glass or quartz slides using commercially available polystyrene (PS) beads with diameters $D = 240, 269, 300$ and 404 nm. 1-5 vol.% aqueous colloidal suspensions of PS beads were placed in a Teflon cylindrical cell of 7 mm inner diameter. The solvent was allowed to evaporate under a moderate flow of warm air. A gentle vibration of the colloid induced by air flow was found to improve the opal quality with respect to samples grown with undisturbed drying. The thickness of the films from 15 to 30 monolayers of beads, was controlled by the amount of colloid used. The formation of a stable opal film was accomplished by sintering at 90° for 1 h.

Bi-layer hetero-opals discussed in this paper were prepared in the University of Hamburg by growing one opal film on top of the other using PS beads of different diameters. Each film, in turn, contains 15-40 monolayers of PS beads. Fig.3 shows SEM images of non-epitaxially grown bi-layer colloidal hetero-crystals. In what follows, we denote this structure as, e.g., 300/240 nm opal, where a first (second) number representing the bead diameter in the bottom (top) film. A high degree of the lattice ordering is present in both opal films. The abrupt boundary between them indicates that the formation of the top film proceeds independently on the geometry of the bottom one. This can be due to the fact that the periodical profile supplied by the bottom film is not strong enough to distort the electrostatic interaction of the PS beads in the colloidal solution, especial in the case of incommensurate bead diameters in the

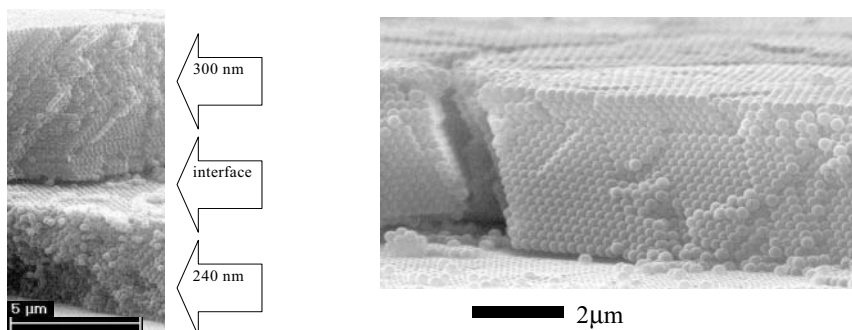


Figure 3. SEM images of a cleaved bi-layer hetero-opal. Courtesy of P. Ferrand.

The next step in the formation of luminescent opals is the selective incorporation of light emitters in hetero-opals. Infiltration of organic dyes [30] or luminescent semiconductor NCs [31] into the pores of colloidal crystals results in inhomogeneous impregnation over the opal volume or the non-uniform coating within the cages.

CdTe NCs were used to impregnate opal films in order to form a PhC-embedded light source. The choice of CdTe NCs obeys to the tuneability of the NC emission, the high emission efficiency and their small size. By changing the particle size from 2 to 6 nm the PL band of these NCs can be tuned through the visible spectral range. The PL quantum efficiency is about 25-30% at room temperature. The NCs are capped with thioglycolic acid carrying a negative charge [29]. In this work, the luminescent NCs were embedded by a layer-by-layer (LbL) deposition technique into the bottom film of the bi-layer hetero-opals. This technique is based on alternating adsorption of oppositely charged species. It was originally developed for positively and negatively charged polyelectrolyte pairs [32] and was later extended to the

assembly of polymer-linked nanocrystals [33, 34]. This method can be equally effectively used to coat both planar and highly curved surfaces [35]. Alternate layers of oppositely charged polyelectrolytes and NCs were deposited on the internal surface of the opal voids resulting in a uniform coating and providing a similar environment for the NCs. The impregnation of opals with NCs using this technique does not lead to deterioration of their structural quality as confirmed by SEM. Schematics showing the topology of the CdTe distribution in opal voids (Fig.4) overestimates the LbL-CdTe volume, which actually does not exceed 1-2 vol.% as deduced from the shift of the Bragg resonance after infiltration.

To impregnate bi-layer hetero-opals selectively, the opal film crystallised on the substrate was loaded with NCs as described above and, subsequently, the second opal film was grown above it. No migration of NCs from the LbL-modified bottom into the top film was observed.

Curve 1 in Fig. 5 is the PL spectrum of the 240 nm bead opal infiltrated with CdTe NCs recorded at $\theta = 70^\circ$. At this angle no PBG-related minimum has been detected in the transmission spectrum. This spectrum can be considered as the reference spectrum of CdTe NCs in the opal environment. Curve 2 is the spectrum of the same sample recorded at $\theta = 0^\circ$. The latter shows a well-defined dip due to the overlap of the PL band with the Bragg bandgap of the opal template along its [111] axis. The relative PL spectrum (curve 3) given by the ratio of spectra 1 and 2 estimates the magnitude of PBG-induced emission suppression in the modes propagating along the detection direction to be $\sim 40\%$. This value matches well the transmission reduction shown in Fig. 5. The discrepancy in the light attenuation obtained from the transmission and luminescence experiments is due to the distribution of the light emitting NCs along the optical path in the latter case.

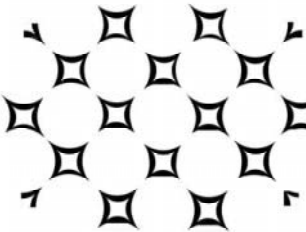


Figure 4. Schematics of the with LbL-CdTe NCs infilled opal cross-section by $(1/2, 0, 0)$ plane showing parts of coated octahedral voids. The volume occupied by CdTe NCs is inflated for sake of clarity.

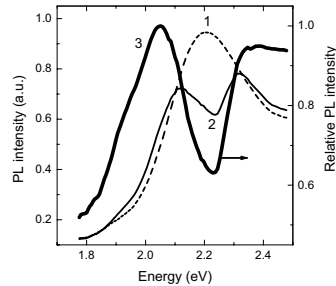


Figure 5. PL spectra of a single-layer CdTe-opal film (beads of $D=240$ nm). The minimum of the PL intensity at 2.23 eV (curve 2) is due to the overlap of the opal PBG with the emission band of CdTe NCs (curve 1). Curves 1 and 2 are normalised to have the same intensity at 1.8 eV, which is far below the PBG. Curve 3 shows the relative suppression of the PL emission of CdTe NCs to opal eigenmodes along the direction of the Bragg PBG.

3. Light diffraction in hetero-opals

3.1 OBSERVATION OF TWO BRAGG BANDGAPS

Transmission and reflectance spectra of the bi-layer opals clearly exhibit two minima and maxima (Fig.6). The most obvious evidence of the optical anisotropy of hetero-opals is their different colouration seen from the top and bottom sides of the hetero-opal, which results from the difference in mid-frequencies of the Bragg resonances in each film (Fig.6a). In general, the

reflectance spectrum of the bi-layer opal is a linear combination of diffraction resonances in individual layers, correspondingly, two Bragg maxima from both opal films can be observed. However, the reflectance from the film, which faces the detector, dominates the spectrum. In what follows, we will call for the sake of brevity this film as the “facade” film to distinguish it from the “distant” film, the optical signal of which should cross the “facade” film to reach the detector. Under these conditions, the diffraction resonance of the “distant” opal film can be observed if the “facade” film is relatively thin and the defect concentration in it allows quasi-ballistic propagation of photons. This consideration agrees well with the reflectance spectra shown in Fig.6a, where the dominating Bragg resonance corresponds to the “facade” film. Assembling two films in one sample does not change the midfrequency of the Bragg resonances with respect to that in the individual films (Fig.6), i.e. opal lattices retain their periods. The mid-frequencies of the transmission minima and reflectance maxima agree well for one and the same sample, thus confirming their diffraction origin (Fig.6a). Fabry-Perot oscillations, which are superimposed on the reflectance spectrum (Fig.6a), prevent the more detailed analysis of the weak features in reflectance.

The resonances in reflectance spectra of the 240/300 nm hetero-opal follow the Bragg law $\lambda^2 = (2 \times 0.816D)^2 (n^2 - \sin^2 \theta)$ for the diffraction at the set of [111] planes (Fig.13), where θ is the midwavelength of the reflectance band, n is the average index of refraction $n^2 = n_{\text{bead}}^2 f_{\text{bead}} + n_{\text{air}}^2 f_{\text{air}}$, which is the sum of RIs of beads ($n_{\text{bead}} \approx 1.5$) and interstitials ($n_{\text{air}} = 1$) weighted with their volume fractions in the opal lattice. Because the full width at the half height of these resonances is about 6% of their midwavelength, they do not overlap at any angle of observation. The fact, that we are able to trace the Bragg minimum in the transmission spectrum down to $\theta = 60^\circ$, is an argument in favour of a good crystallinity of these opal films, because it is comparable with structure quality of single-layer opals.

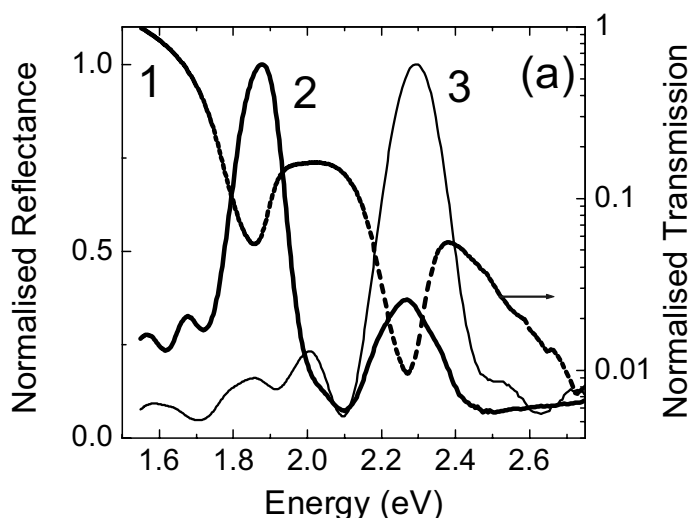


Figure 6. (a) The transmission spectrum of 240/300 nm bi-layer opal (1) at $\theta = 10^\circ$ and reflectance spectra at $\theta = 15^\circ$, if either the 240 nm bead film (2) or the 300 nm bead film (3) is the “facade” film. (b) and (c) Transmission spectra of a 240/269 nm bi-layer hetero-opal (thick lines) in comparison with the spectrum of a single-layer 240 nm opal (thin lines). Panels (b) and (c) compares the transmission in the case of the 300 and 240 nm bead film being the “facade” film, respectively.

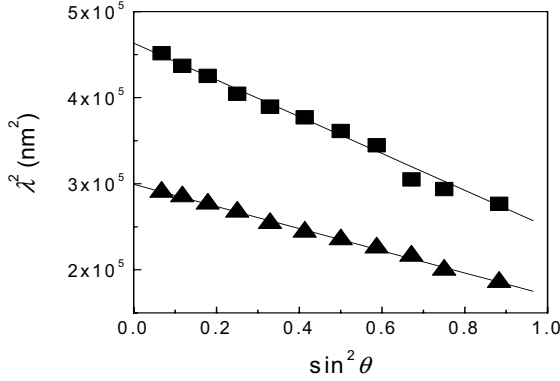


Figure 7. Experimental angular dispersions of the Bragg bandgap in 240 nm bead film (triangles) and 300 nm bead film (squares) of the 240/300 nm bi-layer opal. Lines represent the corresponding dispersions of the Bragg diffraction resonances. The non-monotonous behaviour at $\theta \approx 50^\circ$ is due to the dispersion branching between (111) and (200) opal planes.

3.2 THE INTERFACE GAP

Fig. 8 shows the transmission and reflectance spectra of two 240/300 nm bi-layer opals of different thickness. Two minima are observed in the transmission spectrum at 2.24 and 1.84 eV due to the Bragg diffraction resonances for each film of the 20 Om-thick bi-layer opal. The 7 Om-thick hetero-opal exhibits a less pronounced Bragg gap. Simultaneously, an additional transmission minimum at 1.97 eV becomes observable. This additional minimum, which we denote as the interface gap, appears between the two Bragg minima of films composing the hetero-opal.

The evolution of the transmission spectra of a thin 240/300 nm bi-layer opal with the angle of the light incidence is shown in Fig.9a. Similar spectra with the same angular dispersion were observed in the case of a 300/400 nm hetero-opal (Fig.10), which confirms the general

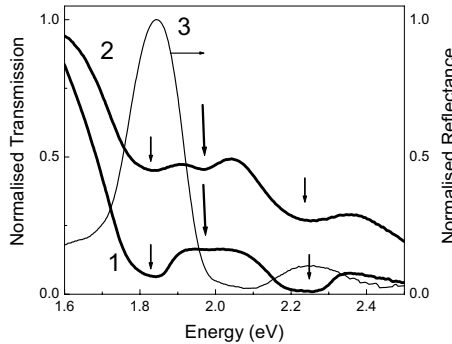


Figure 8. Transmission and reflectance spectra of 240/300 nm hetero-opals. Curve 1 is the transmission spectrum of the 20 Om thick hetero-opal along [111] axis ($\theta = 0^\circ$) of the opal lattice. Curve 2 is the spectrum of the ~7 Om thick sample. Curve 3 is the reflectance spectrum of the thin sample measured from the 240 nm bead film side at $\theta = 15^\circ$. Short arrows indicate the Bragg resonance-related minima, long arrows – the additional interface-related minimum.

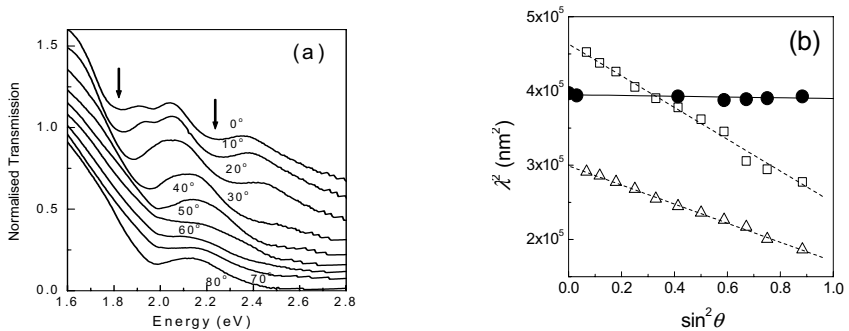


Figure 9. (a): Transmission spectra of 70 nm thick 240/300 nm hetero-opal at different angles of the light incidence. Numbers indicate the angle θ . Arrows show the Bragg bandgaps.

(b): Dispersions of the gaps in this hetero-opal. Open triangles and squares denote central wavelengths of the Bragg resonances in reflectance spectra as in Fig.7. Circles represent the angular dispersion of the interface gap extracted from transmission spectra of the panel (a).

character of the observed interface gap phenomenon. Bragg resonances of the constituent films of the hetero-opal shift to shorter wavelengths following the Bragg law, but the additional minimum does not (Fig.9b). The interface gap is observed, when it does not overlap with the Bragg gap of the top opal film. At larger angles, $\theta \geq 50^\circ$, it remains the only minimum because the directional bandgaps cannot be observed in transmission.

The dependence of the interface gap visibility upon the hetero-opal thickness suggests the limited volume of the crystal, which contributes to the corresponding minimum. There are two factors that pre-determine fading of the interface gap in thick film hetero-opals. The first one is the masking by diffraction on (111) planes of the opal lattice, the minima of which deepen monotonously along the film thickness increase. The second one is the gradual decrease of the contribution comprised by ballistically propagating photons in the total light flow crossing the hetero-opal, with the consequence of adding the diffuse background to the transmission spectrum.

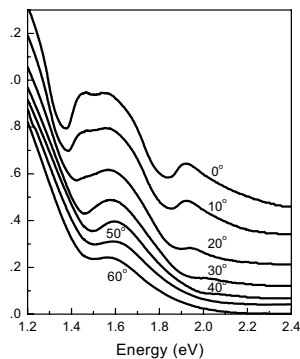


Figure 10. Transmission spectra of a 300/400 nm bi-layer opal. Numbers indicate the angle of incidence θ . Spectra are shifted along the vertical axis for clarity.

3.3 LIGHT SCATTERING AT THE INTERFACE GAP

An examination of transmission and reflectance spectra do not answer the question about the nature of the interface gap, because the interface gap was not resolved in reflectance. This

leaves open two possibilities. The first one relates the interface gap to the diffraction. In this case the minimum in transmission should be complemented by the maximum in reflectance. However, taking into account that the diffraction maximum is formed mostly within several few lattice layers at the air-opal interface, the weak reflectance by the interface can be overshadowed by strong diffraction peak. The second opportunity is the waveguiding effect, which extracts the part from the incoming light in the spectral range matching the guiding conditions along the interface. In this case there would be the minimum in the transmitted light, but no corresponding maximum in the reflected light. There is also a chance to meet the mixture of above effects because of the strong anisotropy of the interface, which allows the propagation of surface-like waves. Experimental studies of the scattering of the light in hetero-opals were undertaken to investigate possible deviations of the light flow.

Experiments with the forward scattered light in thin film opals revealed two minima, one of them appears due to the Bragg reflected light along the direction of the incident beam (“entrance” minimum) and the other (“exit” minimum) is the result of PBG-related anisotropy of the scattering directionality diagram along the direction of detection, which is separated by the aperture from the light scattered behind the opal film [36]. This experiment becomes feasible if photons from the incident beam propagate quasi-ballistically in the opal body, i.e. experience effectively one collision with the defect before leaving the opal. In the case of a fixed angle of incidence, the “entrance” minimum is bounded to the central frequency of the Bragg resonance, which is characteristic to this angle, whereas the “exit” minimum related to the variable angle of detection follows the angular dispersion of the Bragg gap.

Similar experiment with the hetero-opal demonstrates more complicated behaviour. The straightforward extension of the finding obtained with single film opals to the case of bi-layer opals suggests the presence of 3 minima in the scattering spectrum (Fig.11a). If the generalized defect, which cause scattering, belongs to the “facade” film (300 nm bead film in this experiment), the scattering spectrum should consists of the “entrance” θ -independent minimum of the 240 nm bead film at 2.24 eV, the “entrance” θ -independent minimum of 300 nm bead film at 1.97 eV and the “exit” minimum, which shifts along changing the angle θ . If this defect is in the “distant” film, there should be the “entrance” θ -independent minimum at 2.24 eV, θ -dependent “exit” minimum of the 240 nm bead film and θ -dependent “entrance/exit” minimum of the 300 nm bead film.

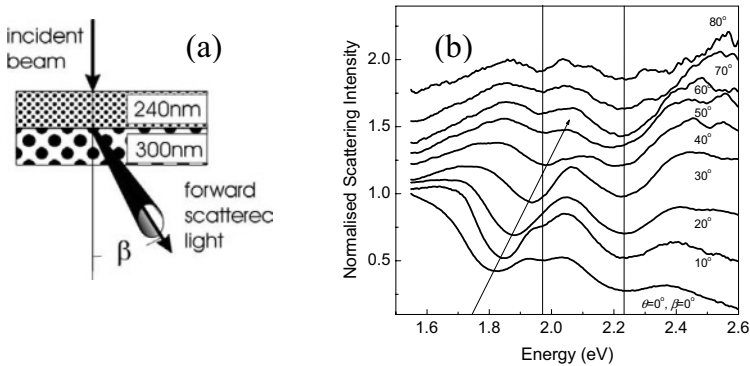


Figure 11. (a) Schematics of the experiment. (b) Spectra of forward scattered light in 240/300 nm hetero-opal. Spectra were recorded in configuration Fig.2b with an incident beam along the film normal $\theta = 0^\circ$ along different directions specified by angle θ , the value of θ labels the curves. Lines are given to guide the eye.

In fact, illumination of the 240 nm bead film along [111] axis produces the “entrance” minimum in the spectrum of scattered light at 2.24 eV, likewise the gap in the transmission spectrum along the film normal $\theta = 0^\circ$, $\beta = 0^\circ$. Another gap along the direction of detection demonstrates the β -dependent “blue” shift for 300 nm bead film. The interface gap appears at 1.97 eV for every angle, although it can be identified if the Bragg gap of 300 nm bead film does not overshadow it (Fig. 11b). The spectral behaviour of the “entrance” minimum agrees with our projections, because the intensity loss in 2.24 eV gap is irrecoverable, as well as that of the “exit” minimum of a “facade” film. Then, to satisfy the conditions for scattering, we have to assume that scattering takes place at the hetero-interface for all frequencies in the examined range. Thus, interface represents a continuous defect affecting the light propagation across the hetero-opal. It is instructive to note that the interface acts as a frequency selective scatterer, because it produces the transmission minimum by its own. Moreover, the central frequency of the interface gap remains the same, if the angle of incidence θ changes as well. Spectra of the back-scattered light show the remarkable difference compared to reflectance spectra obtained in the Bragg configuration. The reflectance spectrum is dominated by the diffraction maximum of the “facade” film (Figs.12 c,d). In contrast, in the spectrum of back-scattered light the observable features are the maximum, which corresponds to the interface gap and the remnants of the Bragg resonance of the “distant” film along the direction of the incident beam. Thus, the interface becomes visible in the back-scattered light together with the “distant” film, but, surprisingly, no scattering in a “facade” layer was observed. The latter is the direct consequence of the small thickness of the “facade” layer. In the case of thicker “façade” film the scattering maxima from both films can be seen, but the maximum from the interface gap fades away.

The feature from the “distant” layer is centred above the diffraction resonance position along the [111] axis (Figs.12 c,d) in accord with results obtained with single-layer films. For example, in 300 nm bead film the scattering maximum obtained in $\theta = 15^\circ$, $\alpha = 65^\circ$ configuration is centred at 1.91 eV, whereas the diffraction maximum along $\theta = 15^\circ$, $\alpha = 15^\circ$ peaks at 1.85 eV. The appearance of the interface gap as a peak of the scattered light conforms to the diffraction nature of the observed effect. A better visibility of the interface gap with the increase of the angle θ can be interpreted as a partial re-direction of the incoming light along the interface.

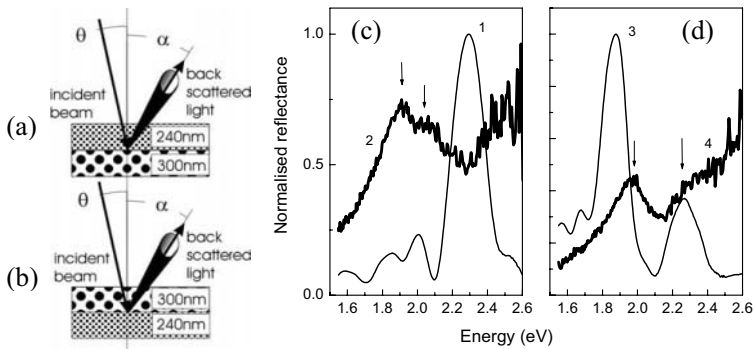


Figure 12. (a) and (b) Schematics of the back scattering experiments. (c) Reflectance spectrum in the Bragg configuration $\theta = 15^\circ$, $\alpha = 15^\circ$ (curve 1) and scattering spectrum measured in the configuration corresponding to the panel (a) at $\theta = 15^\circ$, $\alpha = 65^\circ$ (2). (d) Reflectance (3) and scattering (4) spectra in the configuration of the panel (b) at the same angles as in the panel (c). Arrows show the peak positions.

The last possibility was experimentally examined by measuring the light scattered at 90° geometry from the film cleave using micro-optical set-up (Fig.13). First of all, scattering spectra depend on the direction of the incident light. If the beam is incident on the along the normal to 300 nm bead film, the scattering spectrum shows a minimum respecting the diffraction resonance along this direction (compare Figs. 13 b and c), because the light penetrated in the opal interior has a deficit of intensity in the Bragg PBG range. Another sharp feature is seen at the position of the interface gap (compare to Fig.12). No feature related to the Bragg gap of the next along the light path film can be observed. Reversion of the light propagation direction is results in the inversion of the scattering spectrum, which shows for the light incident on the 240 nm bead film the minimum corresponding to the diffraction on this film and the minimum due to the interface gap. This observation allows to conclude that no light waveguiding along the interface takes place and the light diffraction is the most probable reason for the interface gap.

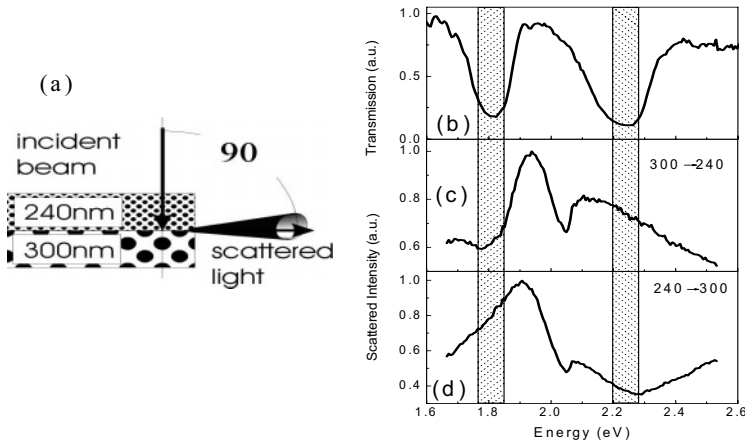


Figure 13. (a) Layout of 90° scattering experiment performed with microscope objectives for light illumination and collection from the cleave of the hetero-opal. (b) Transmission spectrum at $\theta = 0^\circ$. (c) Scattering spectrum for light incident on 300 nm bead film. (d) Scattering spectrum for light incident on 240 nm bead film. Courtesy of V.G. Solov'yev.

3.4 MODELLING OF THE INTERFACE GAP

Numerical modelling of the transmission of 3-dimensional PhCs is a time consuming process. In order to simplify this task, the finite difference time domain (FDTD) method was applied to simulate the transmission spectrum in the 2D PhC heterojunction of two triangular lattices with different lattice constants and rod diameters (Fig.14a). This model picks up some important features of the studied hetero-opal, like the RI contrast, the lattice constant ratio and the number of scatterer rows on either side of the junction, but does not reproduce the lattice symmetry of the hetero-opal cross-section. The latter depends on the orientation of the cross-section plane with respect to the opal lattice. The simulated transmission spectra of individual 2D PhCs are compared to spectra of the PhC heterojunction composed from these PhCs in Fig.14b. The interface gap emerges between two Bragg PBGs of individual PhCs with increasing number of rows and saturates after approaching 9x9 row-thick heterojunction. This numerical experiment reveals that evolving the interface gap requires the PhCs to be formed

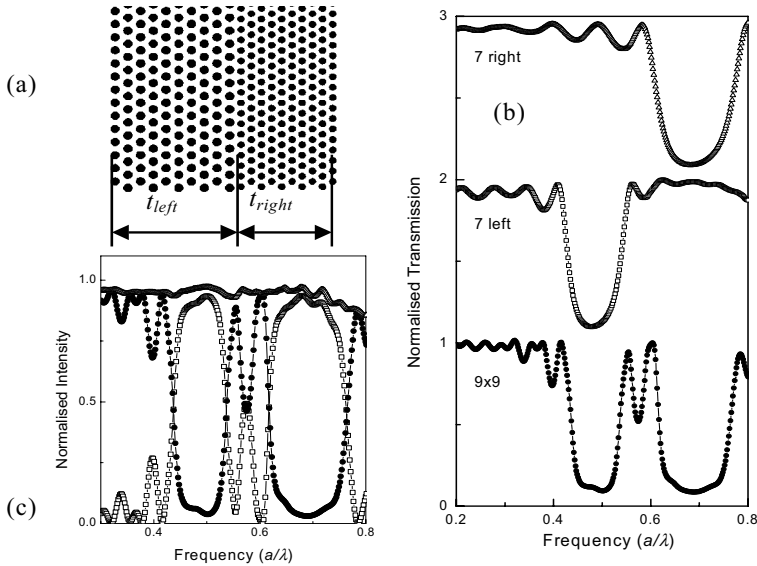


Figure 14. Modelling of the interface gap in 2D PhC heterojunction. (a) Model triangular lattice, t_{left} (t_{right}) are the number of the pillar rows on the left and the right sides of the junction. (b) FDTD simulations of transmission spectra of this hetero-PhC. The development of the interface gap indicated by arrow between two Bragg gaps with increasing thickness is shown. Numbers at curves denote the number of crystal planes. (c) Transmission (solid circles), reflectance (open squares) and sum of transmission and reflectance (triangles) of 9x9 PhC. Courtesy of D.N. Chigrin.

on both sides of the junction, but the transverse dimension of the hetero-PhC, where the interface gap is formed, is limited to 4-5 O_m for optical frequencies. Transmission and reflectance spectra of this model PhC show a complementary behaviour, moreover, and their sum does not differ on more than 5% from the unity (Fig.14c). This is evidence in favour of the diffraction nature of the calculated interface gap. Taking the arbitrary choice of the 2D PhC lattice into account, the correspondence between the numerically simulated and the observed interface gap demonstrates the general tendency towards the opening of the interface gap in the case of two PhCs being in a tight contact.

The obvious question is the physical origin of the interface gap. In this context, it is instructive to consider the PBG diagram of two opals in contact, because each part of the heterojunction is a periodic structure with a well-defined PBG at a distance far away from the interface. In the folded PBG diagram of the hetero-opal, which is constructed assuming the common wavevector axis, two bands intersect at about 1.98 eV (Fig.15) that fits well the experimentally observed interface band frequency. First of all, this consideration emphasizes the role of PhCs in the formation of the interface bandgap: the lattice determines the dispersion of EM modes and restricts the PhC mode reservoir as compared to the free space continuum. The decay length of eigenmodes of in the opal of another lattice constant gives an estimate of a transverse dimension of a volume, where the optical mode distortion takes place on both sides of the interface. Because this statement is applicable to optical modes of both opal films, they have to be considered on the common ground, which assumes assigning the common wavevector to them. However, these modes retain their frequencies and this fact is reflected by scaling the energy diagrams along the vertical axis. Thus the central assumption is the idea of the interface volume, where the mixed modes from both sides co-exist and do not respect the periodicity of the underlying lattice.

This construction allows the interference of modes of the same frequency in the interface region. This interference is the reason for opening the interface gap. The intrinsic drawback of applying the results of the plane wave expansion method for modelling the PBG diagram near the interface is the extension of the result obtained for the infinite lattice to the system with boundary. Correspondingly, the PBG diagram (Fig.15) is relevant only as the indicator of the energy range of the probable gap opening. It is instructive to note, that for the 2D PhC (Fig.14a) a folded PBG diagram suggests similarly the opening of the interface gap at exactly the same frequency range as obtained from FDTD calculations.

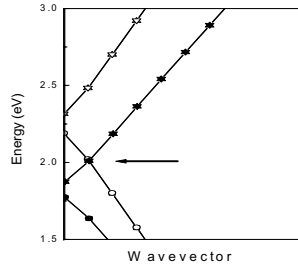


Figure 15. PBG structure of the opal heterojunction folded onto the θ -axis in the vicinity of the L point. Open (solid) symbols denote the PBG of the opal assembled from 240 (300) nm spheres. The energy axis is scaled to take into account the different lattice parameters. The arrow indicates the energy, at which the two band dispersions cross each other.

Numerical FDTD experiment does not give an insight in the physics of the phenomenon, but it allows to compare theoretically predicted and experimentally observed behaviour. For example, the saturation of the calculated interface gap minimum suggests the limitation of the transverse size of the near-interface volume to the decay length of alien eigenmodes on both sides of the interface. Being about 10 crystal planes wide for the RI contrast of 1.5:1, this size agrees remarkably well with the observation of the interface gap in thin film opals. The opposite example is that the modelling predicts the shift of the interface gap with the same rate as for the Bragg gaps contrary to the observed angle-independence of this gap. This discrepancy requires further analysis, because the gap dispersion is a symmetry-dependent property of PhC that was not taken into account in the first approximation. Here we can refer to the dimensionality of the interface gap. Our simulations show no interface gap in the 1D heteroPhC and a dispersive gap in 2D heteroPhC. It seems reasonable to link the apparent absence of the angular dispersion of the interface gap to the higher complexity of the Bloch waves in 3D PhC at frequencies above the Bragg gap compared to 2D one. It is known that the dispersion of the Bragg bandgap can be well described by the interaction of two spherical waves. In general, the development of the interface gap should follow another rule, because this is the interaction of the Bloch waves of different topology that requires to keep more plane waves in the expansion series to represent the interference.

4 Light emission in hetero-opals

4.1 ANISOTROPY OF PHOTOLUMINESCENCE IN HETERO-OPALS

The most straightforward consequence of the PBG anisotropy in hetero-opals, the source film of which is selectively impregnated with light emitters, is the corresponding spectral and

spatial anisotropy of the luminescence. Fig. 16 shows how the spectral separation of the PBGs in a bi-layer opal leads to an anisotropy of the luminescence from the filter and the source films. As expected, the power radiated in the source opal in modes propagating along the PBG direction is suppressed and shows no effect from the filter film (Fig.16c). Surprisingly, in the PL spectrum of the filter film only the intensity suppression along the filter PBG direction due to its band-pass filtering is observed (Fig.19d). The absence of the source PL minimum in the PL spectrum after the filter film suggests that photons are either emitted or scattered at the hetero-PhC interface. The difference between the transmission and emission experiments can be explained taking into account the number of boundaries, which are crossed by light. In the former, the incident beam experiences, firstly, intensity reduction due to the backward reflection at the air-hetero-opal boundary for PBG frequencies of the “distant” film and, secondly, at the internal interface for PBG frequencies of the “facade” film. By contrast, the intensity of the light radiated internally in the source film experiences only the Bragg reflection at the internal interface, moreover, the back-reflected part of the emission spectrum is scattered within the body of the “source” film. This observation agrees also with the spectra of forward scattered light (Fig.11).

An estimate of the emission anisotropy in the hetero-opal is given by the ratio of the source to the filter PL intensities, which compare the spectra of emission outgoing in opposite directions (Fig. 17). The PL ratio clearly displays a minimum and a maximum, which coincide with the transmission minima in agreement to the PBG origin on the emission anisotropy.

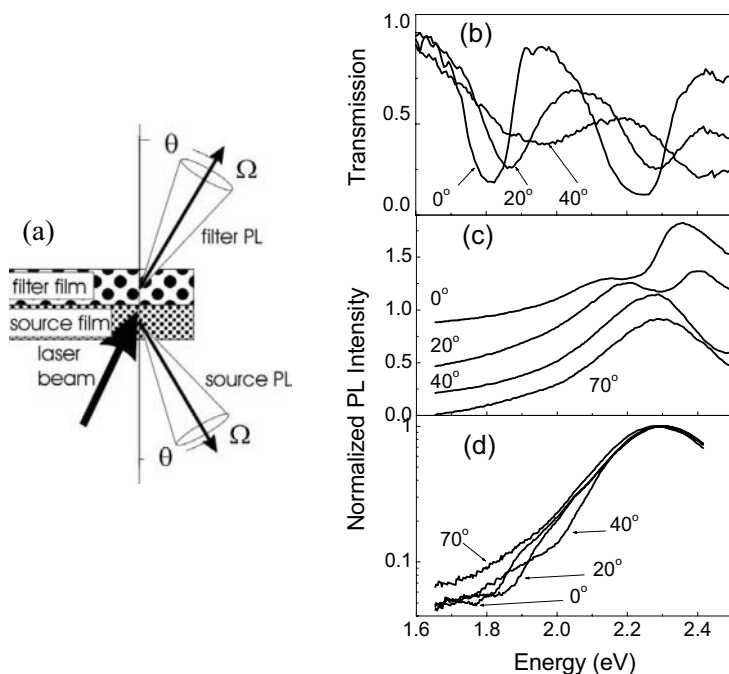


Figure 16. (a) Layout of PL experiment. Emitter power is detected within the solid angle θ along the direction identified by the angle θ . (b) Transmission spectra and PL spectra of source (c) and filter (d) films of a 240/300 nm CdTe-bi-layer opal. Panels show spectra obtained along different directions and labelled by the angle θ . Curves in the panel (c) are shifted vertically for clarity.

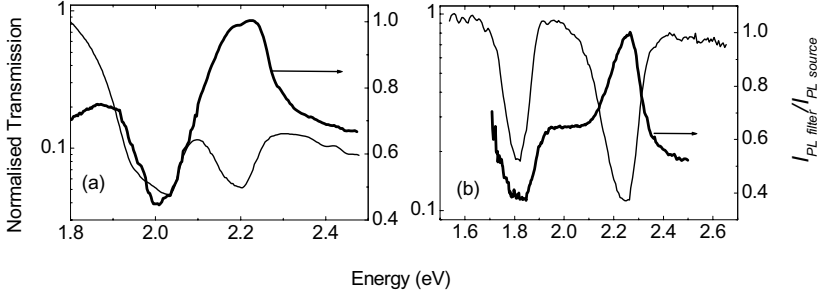


Figure 17. Transmission and PL intensity ratio spectra $I_{\text{filter}} / I_{\text{source}}$ of the 240/269 nm (a) and 240/300 nm (b) bi-layer opals. The angle of incidence and detection is 0° .

In addition to the spectral anisotropy, the co-existence of two PBGs in hetero-opals leads to different emission patterns observed at the same emission frequency from opposite sample surfaces (Fig.18). In order to understand this phenomenon, a realistic model of the light source is needed. We consider first the spatial location of light emitting NCs. The thin layer of CdTe NCs overlays the internal surface of opal voids. Due to the NC random orientation, there is no domination of any particular radiation direction that allows us to consider the average emission diagram as from a point source. Consequently, the radiation pattern of a point source embedded in opal should be superimposed with the spatial distribution of the opal optical eigenmodes at a given frequency. If the frequency falls in the PBG range, the corresponding wavefront acquires the spatial anisotropy due to forbidden propagation along directions of the diffraction resonance. An example of such wavefront in a single-layer opal is discussed in [37] and more details will be given elsewhere [38]. The intensity pattern of the source film evolves rapidly with emission frequency since the frequency crosses the PBG centred at 2.25 eV. In contrast, the angular diagram of the emission from the filter film remains nearly unchanged because all examined frequencies exceed the 1.85 eV midfrequency of the PBG in the filter film. Then, the emission flow after the filter film is concentrated towards the surface normal ($\theta = 0^\circ$).

In the first approximation, the filter film transforms the emission generated in the source film, as it would be with the emission from the distant external light source. As can be seen, the interface modifies the angular distribution of the emission intensity with respect to the radiation emitted in the source layer. This observation opens a possibility to control the directionality of the emission flux, as it was observed after passing the filter layer, by changing the mismatch of the PBG midfrequencies in bi-layer opals, the bandgap dispersion or the symmetry of the filter layer. More detailed investigation is necessary to extract the effect of the heterointerface upon the emission directionality.

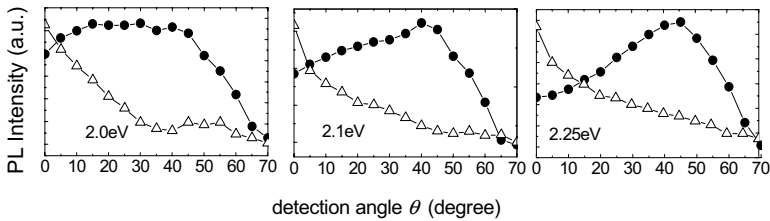


Figure 18. Directionality diagrams of the source (circles) and filter (triangles) emission at different frequencies (indicated in the panels) for a 240/300 nm bi-layer CdTe-opal.

4.2 EMISSION MODIFICATION AT THE INTERFACE

Emission studies in homogeneous opals have demonstrated the decrease of the spontaneous emission rate [37, 39] and the development of the emission stimulation [37, 40] at PBG frequencies. The non-linearity of the emission was visualised examining the PL spectra transformation with increasing excitation power. When the emitter possesses a multiple level electronic energy band structure and there is competition between radiative and non-radiative relaxation of the optically excited emitters, the emission intensity I saturates with increasing excitation power P . This functional dependence $I(P)$ can be fitted by the expression $I = I_0(1 - \exp(-P/P_0))$, where I_0 and P_0 are parameters describing the radiation power of the saturated emitter and the saturation threshold, respectively. Applying this fitting procedure to data obtained at different frequencies, the spectra of $I_0(\omega)$ and $P_0(\omega)$ were constructed. The $I_0(\omega)$ spectrum can be associated with the spectrum of the spontaneous emission rate in a given optical mode, because the saturated emission power is directly related to the emission rate in this case. Experimentally, the spatial selection of the mode can be achieved by decreasing the solid angle of emission collection. The $P_0(\omega)$ spectrum characterises the backreaction of the emitted radiation upon the emitter. In analogy with microresonators, the increase of the saturation threshold is an indication of the stimulation of the radiative recombination by the far EM field of a given mode accumulated in the resonator. Similar resonator conditions are fulfilled for the opal PBG optical modes as discussed in [37,41]. It is noteworthy, that such analysis of the saturation parameters is possible in the case of similarity of the emitter-mode coupling strength over the opal volume and essentially the ballistic propagation of photons across the opal film. The first requirement was fulfilled by using about 20-30 nm thick coating of the opal internal surface with emitting CdTe NCs, which topology correlates with the spatial distribution of the EM field strength in the opal interior. The second one was achieved by using thin opal films, where the mean free path of photons is comparable with the film thickness.

The $I_0(\omega)$ spectrum of the source film of CdTe-hetero-opal retains the spectral shape of the PL spectrum $I(\omega)$ including the PBG-induced minimum (Fig.19a). This correlation suggests the dominating role of the spontaneous emission in the emitted radiation. The $P_0(\omega)$ spectrum shows the global minimum in the frequency range of the emission band maximum and the peak at PBG frequencies. The rapid increase of the threshold towards the “red” edge of the

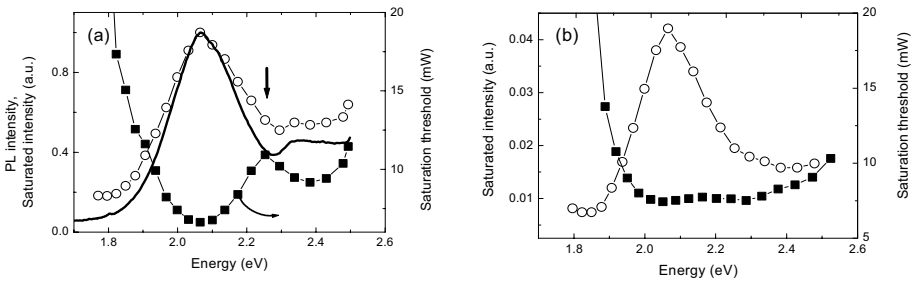


Figure 19. (a) PL spectrum $I(\omega)$ (line), saturated PL intensity $I_0(\omega)$ (circles) and saturation threshold $P_0(\omega)$ (squares) spectra of the emission of the source layer of CdTe impregnated 240/30 nm bi-layer opal along the [111] axis of the opal lattice. The arrow indicates the central frequency of the PBG in the source film. (b) Saturated PL intensity (circles) and the saturation threshold (squares) spectra along [111] axis of the filter opal.

emission band is the result of the ineffective energy transfer from the optical pumping to the states involved in the emission at these frequencies. The $I_0(\omega)$ spectrum of the filter film (Fig.19b) does not show a detectable minimum and the $P_0(\omega)$ spectrum shows only a weak modulation compared to that of the source film. This is an obvious consequence of the absence of emitters in the filter film and the probable scattering of the emission at the interface between the source and the filter films

The present level of understanding the emission modification in the opal-based PhC is not enough to model the saturation parameters. Therefore only the spectral variations of these parameters with the emission detection angle can be addressed.

A comparison of saturated emission spectra for different angles of detection (Fig. 20) shows that the direction-sensitive parts of these spectra overlap with the PBG frequency range. The saturated radiation power approaches its maximum at the PL band maximum independently on the angle of detection, whereas its minimum follows the angle dispersion of the Bragg resonance. Similarly, the angle dependence of the saturation threshold spectra (Fig.20) can be referred to the dispersion of the PBG. The saturation threshold approaches its minimum at the PL band maximum and peaks in the PBG. The threshold minimum shows no dependence on the detection angle, whereas its maximum appears the function of this angle. This behaviour is typical for the emission modification in the single layer opals, if the averaging over the emitter-mode coupling is practically eliminated and the sufficient portion of the emission flow approaches the detector with no scattering. Thus, no influence of the interface was detected in the emission of the source film.

A similar analysis of the filter film emission demonstrates opposite tendencies. The angular dependence of $I_0(\omega)$ spectra shows that a maximum develops at 1.94 eV with increasing angle, which does not shift its frequency but increases its magnitude. The central frequency of this maximum is not far from the position of the interface gap for this hetero-opal as detected in transmission spectra (Fig.9). In parallel to the peak in the linear component of the emission rate, the $P_0(\omega)$ spectra show the evolution of the threshold maximum at the same frequency, which becomes more pronounce along the angle increase. One possible explanation considers the resonance conditions for photons emitted in the source opal at the near-interface volume in

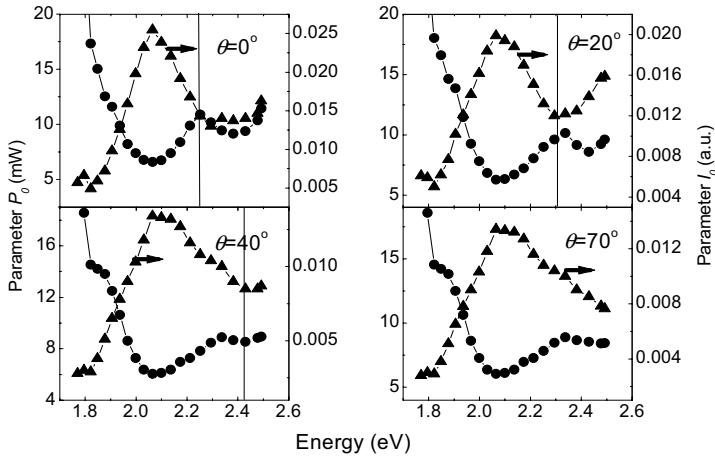


Figure 20. $I_0(\omega)$ and $P_0(\omega)$ spectra of the source film at different angles of detection. Panels are labelled with angles. Lines indicate the position of the PBG at corresponding angles.

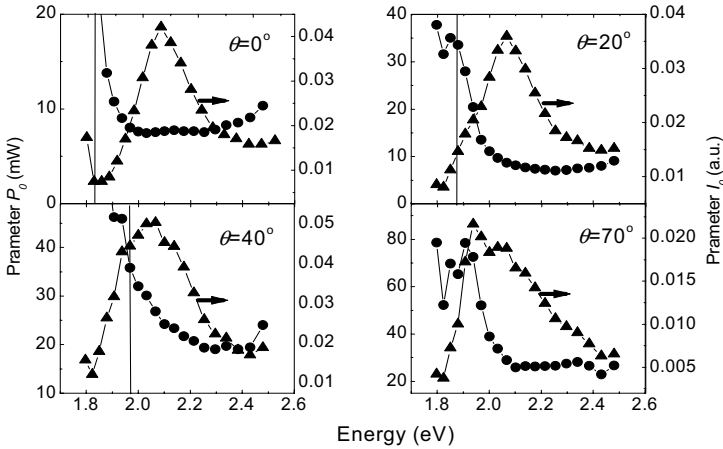


Figure 21. $I_0(\omega)$ and $P_0(\omega)$ spectra of the filter film at different angles of detection. Panels are labelled with angles. Lines indicate the position of the PBG at corresponding angles.

a frequency range of the interface gap. The properties of the optical modes in this limited volume, which is partly occupied by the light source, differ from those of eigenmodes of individual films. Apparently, the highly inhomogeneous interface modes with frequencies corresponding to the interface gap provide longer interaction time with optically excited CdTe NCs. In this case, the stimulation of the radiative recombination can be understood following the analogy with a resonator infilled with an externally pumped light source. Development of the interface-related feature in the parameter spectra at higher angles can be taken as a consequence of the longer lifetime in the resonator for modes propagating along the interface. Another way to show the anisotropy of the emission enhancement is to compare the spectra of the PL intensity ratio obtained as described in Fig.17. They show the development of the emission non-linearity at frequencies between two Bragg gaps of filter and source films

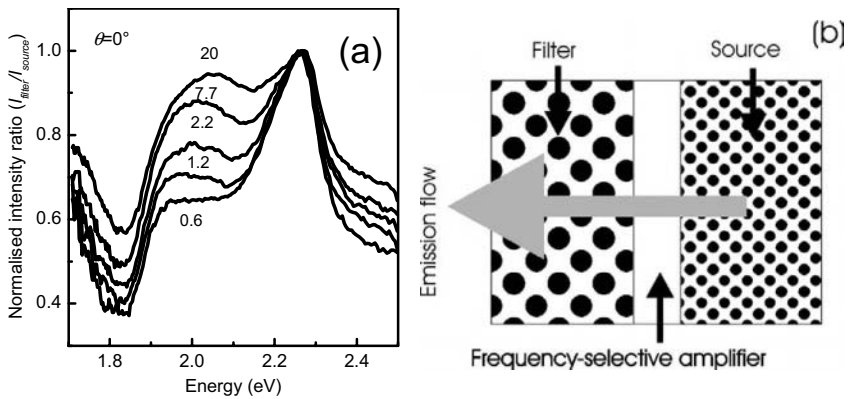


Figure 22. (a) The ratio of PL intensities of filter to source films of the 240/300 nm bi-layer opal at different pumping intensities. The emission was detected along the interface normal. The pumping power used is shown for each curve in milliwatts. (b) Spatial extent of the near-interface volume in a bi-layer opal.

(Fig.22a). In particular, the evolution of PL spectra of source and filter films proceeds in different ways with increasing excitation power: while keeping the spectral anisotropy associated with the mismatch of PBGs in these layers, the emission, generated in the interface volume acquires a relatively higher intensity at frequencies of the interface gap. In other words, the volume encompassing the interface acts as pass-band amplifier with respect to the emission of the source (Fig.25b).

A remarkable overlap of the frequency range, where the emission experiences an enhancement, with that of the interface gap suggests that the near-interface volume is a functionalised part of the hetero-opal with special properties. This finding opens a way to control the emission properties of opal-embedded light sources by tuning the interface gap in purpose.

5 Conclusions

Bi-layer hetero-opals were synthesised by successive growth of one opal film on top of another using self-assembly of monodisperse latex beads of different sizes. These heterostructures give rise to the anisotropy of the reflectance spectrum due to the presence of different PBGs in one and the same sample. The bottom film of the hetero-opals was selectively impregnated with luminescent CdTe NCs using a layer-by-layer deposition technique. The emission band of CdTe NCs matches the Bragg PBG of the opal films and, consequently, it experiences a strong spectral and spatial anisotropy due to the PBG anisotropy.

When the irreducible sets of optical eigenmodes are overlapping in the volume near the interface between opal layers of different PBGs an interface gap opens as a result of the interference of modes of the same frequency. Observations of the spectral features in transmission, forward- and back-scattered light in one and the same spectral range form a firm experimental background for further investigation of this effect. The interface photonic gap is tentatively explained as a result of the anti-crossing of opal photonic bands in the near-interface volume. The experimentally observed dispersion of this gap differs from that of the Bragg gaps in opal films but this yet to be examined by numerical simulations.

Studies of the emission non-linearity also indicate the presence of the special frequency range, where the modification of the emission rate takes place. Emission data are less consistent and do not demonstrate unequivocally the interface gap, because they treat the emitter-mode coupling rather than the mode structure itself. Anyway, with the account taken for the parameter scattering between different samples and a variety of experimental methods, the whole array of emission data indicates the presence of the specific frequency range, where the emission modification in hetero-opals differ from that of single-layer opals. Apparently, the emission conditions applied on light emitters in the near-interface volume give rise to a feedback between the intensity of the emitted radiation and the emission probability.

Concluding, interfacing PhCs of different PBG is a novel way to functionalise PhCs and control their emission properties.

Acknowledgments

The author gratefully acknowledge valuable contributions of his colleagues C.M. Sotomayor Torres, D.N. Chigrin, V.G. Solov'yev, P. Ferrand and collaborators A. Rogach, N. Gaponik, A. Eychmueller.

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MAGNETISM IN POLYMERIZED FULLERENES

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Abstract.

Polymerization of C₆₀ fullerenes at certain pressure and temperature conditions, as well as photopolymerization in the presence of oxygen leads to appearance of magnetically ordered phases. Ferromagnetic behavior is observed close to the conditions where the fullerene cages are about to be destroyed, and the effect is presumably associated with the defects in intramolecular or intermolecular bonding. The observation of magnetic domain structure in impurity-free regions provides strong evidence in favor of the intrinsic nature of fullerene ferromagnetism.

Keywords: Fullerenes, Carbon, High pressure, Polymers, Polymerization, Photopolymerization, Rhombohedral C₆₀, Organic magnetism, Curie point.

1. Introduction

An important milestone in the history of fullerenes [1] is the discovery of the polymerization phenomenon [2] which initiated a new research field: the preparation and studies of polymerized fullerene states. At atmospheric pressure, a polymeric phase is produced by irradiation with light, electron or ion beams, as well as by charge transfer. Polymeric phases are readily formed by high pressure – high temperature treatment of fullerenes [3], which leads to a great variety of polymeric forms [4].

C₆₀-based materials exhibit a number of important physical properties: superconductivity, ferromagnetism, nonlinear optical activity, and ultrahardness. In this series one can mention the experimental evidence of a room-temperature magnetically ordered state in fullerenes, polymerized by pressure [5 - 7], or by light [8], as well as in hydrofullerites [9].

Ferromagnetism in systems containing only p- and s- electrons is now a reality [10]. Pure organic substances have very low temperatures of ferromagnetic transition. There have been dozens of reports on room-temperature magnetism in carbon-based structures [11], but poorly reproducible results cast doubts on the intrinsic nature of magnetism. After the first observation of a finite spontaneous magnetization in polymerized fullerenes, similar results were obtained by several groups. Studies of the room-temperature fullerene-based magnets show that the fullerene cages are not damaged in structures exhibiting the ferromagnetic transition. A recent observation of a magnetic domain structure by means of magnetic force microscopy in impurity free parts of samples gives a strong argument in favor of the intrinsic character of ferromagnetism in polymerized fullerenes. [12].

The mechanism for the origin of magnetism in carbon-based materials is not well understood. This paper is arranged as follows: first we give a brief account of the magnetic properties of fullerenes in the pristine state, then touch upon the main properties of the ferromagnetic molecule TDAE-C₆₀ [13] and outline the mechanisms of fullerene polymerization. Then we describe the experimental results on room-temperature ferromagnetism in several fullerene phases and other structures, based on pure carbon. Finally, we bring together the existing evidence and concepts that can shed light on the origin of magnetic carbon phases, and indicate possibilities for applications of these new materials.

2. Magnetic properties of closed-shell carbon clusters

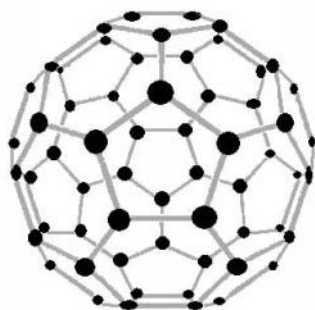


Figure 1. Fullerene C₆₀.

Fullerenes represent the third allotropic form of pure carbon, after diamond and graphite, and are stable closed-shell structures (Fig. 1). In carbon molecules, there is no spontaneous magnetic moment, and the response of these molecules is given by a sum of a diamagnetic contribution and a Van Vleck paramagnetic term. The diamagnetism of the C⁴⁺ ion is $-1.2 \cdot 10^{-8}$ emu/g [14]. The susceptibility of diamond is due to contributions from core and valence electrons, and a Van Vleck term, with a total value $-0.5 \cdot 10^{-6}$ emu/g [15]. The magnetic properties of graphite are dominated by the presence of ring currents circulating above and below the hexagonal lattice planes. The Pauli paramagnetic susceptibility in bulk graphite is negligible

because the density of states is suppressed at the Fermi level. Due to the in-plane delocalization of π -electrons, graphite has the highest diamagnetic susceptibility after superconductors, $\chi_{\perp} = -(22 - 50) \cdot 10^{-6}$ emu/g in the c -axis direction. It is usually accepted that in the basal plane direction the graphite susceptibility is also diamagnetic: $\chi_{\parallel} = -0.5 \cdot 10^{-6}$ emu/g. However, all measured values have a magnetic component coming from the intrinsically misaligned perpendicular planes, and the parallel susceptibility is probably several orders of magnitude smaller [16]. There is evidence for graphite paramagnetism at low fields [17] and for a complex behavior of the g -factor as a function of the applied magnetic field [18].

Fullerenes are classified as aromatic compounds [19], although not all connotations of "aromaticity" are applicable to fullerenes. Long before the experimental discovery of fullerenes, a term «superaromaticity» was used to describe diamagnetic currents around a hypothetical three-dimensional quasi-spherical carbon molecule having the shape of a truncated icosahedron [20]. Immediately after their discovery, fullerenes were expected to have unusual magnetic properties. However, the ring current susceptibility calculated using the London method was predicted to be vanishingly small [21]. Later the same group reported the existence of noticeable ring currents, despite of the vanishingly small ring-current magnetic susceptibility [22], and stated that the strong diamagnetic ring currents in 6-membered rings and paramagnetic currents in 5-membered rings mutually cancel their contribution to the magnetic susceptibility [23]. It was shown that the paramagnetic ring currents circulating below the pentagonal faces resulted from an intense electron flow about the double bonds abutting on the pentagons. The π -electron current density was represented schematically as a pair of counter-

rotating cogs, with the paramagnetic current density in the proximity of pentagonal faces arising from the combined action of five cogs rotating in phase [24]. Calculations of the nucleus-independent chemical shifts in a series of fullerenes $C_{32} - C_{180}$ helped to identify the regions of aromaticity and antiaromaticity, associated with hexagons and pentagons [25]. The term «ambiguous aromatic character», coined for the fullerenes, reflects the presence of both di- and paratropic ring currents.

Assuming additive contribution of pentagons and hexagons to the diamagnetic susceptibility, one can expect a steady increase in the diamagnetic ring current contribution, as the number of carbon atoms in the cage increases. However, this trend is found only for the giant fullerenes, C_n , $n > 100$, whilst the susceptibility of C_{540} exceeds the corresponding value for graphite [26]. Whereas electric polarizability increases linearly in the series $C_{60} - C_{70} - C_{84}$, magnetizability shows a maximum for C_{70} [27].

Experiment confirmed both a small magnetic susceptibility of C_{60} and an appreciable π -electron diamagnetism of C_{70} [28, 29], with the corresponding values of $\chi = -0.35 \cdot 10^{-6}$ emu/g and $\chi = -0.59 \cdot 10^{-6}$ emu/g. The data on the temperature dependence of fullerene magnetic susceptibility are represented as a sum of diamagnetic and paramagnetic contributions, the paramagnetic term being usually ascribed to the oxygen impurity. Some indications exist that the paramagnetism is also due to defects, such as a C_{60}^- ion. This contribution is absent for the high-quality single C_{60} crystal samples which are almost free from oxygen [30]. At the point of the orientational ordering phase transition a discontinuity in susceptibility is observed, explained by small intramolecular geometry changes due to lattice forces [30].

3. Ferromagnetic molecule TDAE- C_{60}

Despite the small magnetic response in the pristine state, C_{60} gave rise to a new class of magnetic materials [31], and formed a family of superconducting or antiferromagnetic compounds by intercalation of alkali metals, alkaline earth metals, rare earth metals or molecules [32]. Strong correlation exists between the relative orientation of near-neighbor C_{60} units and intermolecular magnetic exchange interactions; for example, the intercalation of neutral ammonia molecules into fcc K_3C_{60} transforms the crystal structure and changes its ground state from superconductivity to antiferromagnetism. This is the first molecular magnet controlled by molecular rotation.

The discovery of the ferromagnetic fullerene derivative TDAE- C_{60} demonstrated that π -electron ferromagnetism at comparatively high temperatures is a reality [13]. This substance, containing only light elements, has a ferromagnetic ordering temperature $T_c = 16$ K. Here we mention only the most important features of this organic ferromagnet: the role of TDAE (tetrakis-dimethylaminoethylene $C_2N_4(CH_3)_8$), the role of the structure, the type of ferromagnetism.

TDAE- C_{60} is a donor-acceptor type magnetic material, where the radical ions result from electron transfer from the π -orbitals of the donor molecule. There are indications that TDAE itself is not essential for the magnetic interactions since other charge-transfer C_{60} (never C_{70}) salts exhibit a low-temperature ferromagnetic ground state [33], but plays a certain role in the structural effects. TDAE- C_{60} crystal has a monoclinic structure with unusually short distances between the buckyballs. The material exists in two forms: ferromagnetic α -TDAE- C_{60} and paramagnetic α' -TDAE- C_{60} . The α' -form transforms into the α -form upon annealing. The mutual orientation of neighboring C_{60} molecules plays a key role in the ferromagnetic exchange. The ferromagnetic form shows a sigmoid magnetization behavior with a very small

residual magnetization, if any. The saturation magnetization in high-quality samples reaches 6 emu / g ($\sim 1 \mu_B / C_{60}$).

The insulating behavior of the crystal excludes band ferromagnetism. The magnetic resonance measurements exclude superparamagnetic and spin-glass behaviors and point towards an isotropic or nearly isotropic Heisenberg ferromagnet [31].

4. Polymerization of fullerenes

Undoped fullerenes can be polymerized by different methods: exposure to light with photon energy of at least 2 eV [2], irradiation by an electron or ion beam, or applying an electric discharge. High pressure and high temperature treatment of fullerenes has the advantage over other polymerization methods of being capable to produce different types of polymerization: one-, two- or three-dimensional polymers [4]. These phases occur due to the ability of the C_{60} molecules to form bonds by 2+2 cycloaddition, when double bonds on neighboring molecules break to form a sp^3 -bonded fullerene dimer. The polymerization type is governed by the pressure and temperature conditions, which can be estimated from the pressure – temperature phase diagram [34]. An orthorhombic phase (Fig. 2, a) forms at the pressures 1 – 9 GPa and low temperatures (below 650 K). Higher temperatures lead to an increase in the number of interfullerene bonds, and two types of two-dimensional polymers can be formed. The tetragonal phase with the interfullerene bonds along the $\langle 110 \rangle$ direction (Fig. 2, b) requires pressures about 2 GPa, whilst the optimal pressure for the rhombohedral phase (Fig. 2, c) is 6 GPa. This phase is more dense than the tetragonal, and polymerization occurs in the close-packed $\langle 111 \rangle$ plane. At temperatures above 1000 – 1100 K the fullerene cages break down, and a new phase appears described usually as a disordered cross-linked layered structure, disordered crystalline carbon or partially graphitized fullerene.

Although polymerization transforms sp^2 into sp^3 (diamond-like) bonds, the energy gap does not approach that of diamond; by contrast it becomes narrower. The dispersion of the conduction and valence bands is significantly stronger than in the *fcc* C_{60} case. The strong changes in electronic structure are mainly due to the fact that the features of the conduction and valence bands are determined by the topology of the π -electron system [35]. The interlayer interaction in 2D C_{60} polymer is considered to be of the van der Waals type, similar to graphite. In contrast to 2D polymerized fullerenes, the electronic structure of the 3D polymer is metal-like [36].

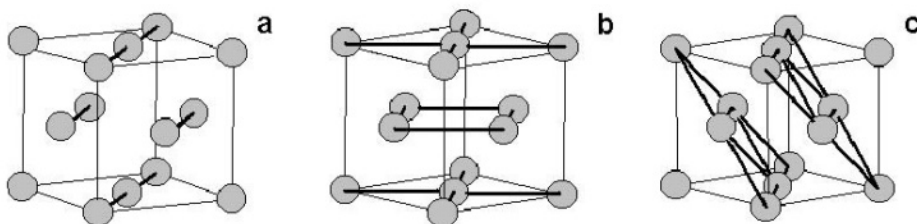


Figure 2. Transformations of fullerene C_{60} under pressure. (a): orthorhombic phase, (b): tetragonal phase, (c): rhombohedral phase.

5. Ferromagnetism in light -polymerized fullerenes

The first observation of room-temperature ferromagnetism of polymerized fullerenes dates back to 1996. Exposure of the C_{60} crystals to light in the presence of oxygen leads to the appearance of saturating behavior in the magnetic field with a hysteresis loop [8]. Oxygen-free C_{60} films and crystals are known to transform into a photopolymerized state under the action of UV and visible light [2]. When C_{60} is simultaneously exposed to oxygen and light, two processes occur: a photoassisted diffusion of molecular oxygen into solid C_{60} and an oxidation of C_{60} . The photopolymerization reaction occurs between the monomer C_{60} in the excited (triplet) state and another monomer in the ground state. It is commonly believed that the polymerization does not occur in the presence of oxygen, because oxygen quenches the C_{60} triplet state.

A non-linear magnetization curve is observed only for the fullerenes exposed to light in the presence of oxygen; without light only an enhancement of the paramagnetic Curie-term is registered. The magnitude of the susceptibility increases with increasing exposure time. When allowance is made for the superimposed Curie term, the susceptibility of light-and-air exposed fullerenes increases slightly with temperature. [37].

Pristine van der Waals C_{60} crystals are diamagnetic. As discussed above, the susceptibility value for the oxygen-free single crystals is negative and practically independent of temperature. Oxygen-exposed crystals remain diamagnetic at room temperature but show a paramagnetic upturn at low temperatures.

A different situation occurs if the sample is exposed to oxygen under the action of the strong visible light. The susceptibility changes its sign to positive in the whole temperature range. Exposure during 2.5 hours creates signatures of ferromagnetism: non-linear magnetization processes at low fields.

The physisorbed oxygen can be driven away from the C_{60} crystal by heating in vacuum. On the contrary, heating of the sample which was oxygen-exposed under the action of visible light, does not restore it to a pristine state. This sample still keeps the ferromagnetic behavior, but the paramagnetic background changes to diamagnetic one.

The magnetization increases with increasing exposure time. The saturation value at high fields is $1.4 \cdot 10^{-2}$ emu/g, corresponding to approximately $0.001 \mu B$ / carbon atom, remanent magnetization is about 10% of the saturated value, and the coercive force is 100 Oe.

Magnetization curves remain almost the same from 5 K to room temperature. Above 300 K magnetization starts to decrease, remaining finite to 800 K.

The small saturation value for the photopolymerized fullerenes was increased by separation of the material into a magnetic and a non-magnetic part [8]. Separation was made by dissolving in toluene, a solvent for pristine C_{60} . The undissolved part showed the same ferromagnetic behavior and can be considered as a concentrated ferromagnetic phase. This residue substance has a hundred times larger magnetization: $0.1 \mu B$ / carbon atom.

X-ray diffraction measurements and Raman spectra identify the orthorhombic phase of polymerized C_{60} . Insolubility of the ferromagnetic phase in toluene is an additional argument for its polymerized state. The suggested model takes into account both polymerization and oxidation of C_{60} . Oxidation of C_{60} molecules is regarded as a mechanism for unpaired spin formation. For the spins on neighboring polymerized molecules the exchange interaction is possibly stronger than for the spins on the same molecule [8].

6. Ferromagnetism in pressure -polymerized fullerenes

The presence of a magnetically ordered phase was revealed in rhombohedral C_{60} (Rh- C_{60}) prepared at a pressure of 6 GPa and in a narrow temperature range. Five of six samples prepared at 1025 K or 1050 K showed similar behaviour [5]. Magnetisation loops measured in the field range $-2 \text{ kOe} < H < 2 \text{ kOe}$, for temperatures 10 K and 300 K, show nearly identical hysteresis with $M_r = 0.015 \text{ emu/g}$ and $H_c = 300 \text{ Oe}$ (Fig. 3).

A saturation of the magnetisation is clearly seen above $\sim 2 \cdot 10^4 \text{ Oe}$. Using the spin concentration value obtained from the electron spin resonance data, $n = 5 \cdot 10^{18} \text{ cm}^{-3}$, the magnetic moment is estimated as $0.4 \mu_B$ per electron. From the temperature dependence of the magnetisation at a fixed field of 0.2 T, and also from the temperature dependence of the remanent magnetisation obtained at $H = 0$ after decreasing the applied field from 2000 Oe, the Curie temperature is found to be about 500 K (Fig. 4). 4 times higher magnetization and $T_c = 820 \text{ K}$ is achieved in another group [7]. The samples are prepared at the same pressure; and 5 of 8 samples prepared at $1020 \leq T \leq 1065 \text{ K}$ show ferromagnetic signal.

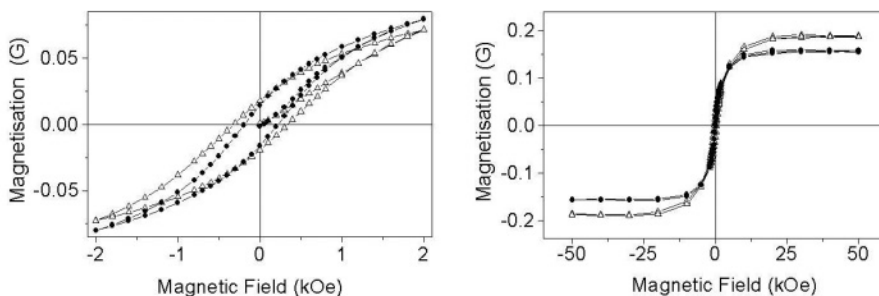


Figure 3. Hysteresis loops for the Rh- C_{60} obtained at $T = 10$ (triangles) and 300 K (circles). (a) Hysteresis is observed in the field range $-2 \text{ kOe} < H < 2 \text{ kOe}$; (b) saturation of the magnetisation is clearly seen in a broader field region. Reprinted from [5] with permission of Nature.

Figure 4. Magnetisation of the Rh- C_{60} in a fixed applied field of 0.2 T (upper curve, triangles) and the remanent magnetisation obtained at $H = 0$ (lower curve, circles) as a function of temperature. The Curie point is about 500 K. Reprinted from [5] with permission of Nature.

In order to elucidate the nature of the magnetic properties of pressure-polymerized fullerenes, different conditions of sample preparation have been tried [38]. Experiments were performed at the pressure of 2.5 GPa, which is favorable for the formation of the tetragonal phase. Similar results were obtained: the magnetic phase is formed in a very narrow temperature range with the maximum at 1025 K. The ferromagnetic behavior totally disappears for samples prepared at 1100 K and higher, and the susceptibility reverts to a diamagnetic behavior. The magnetic properties are very sensitive to preparation time, and the search for optimal preparation conditions is to be made in a 3-dimensional p-T-t space.

An increase in pressure to 9 GPa results in the following: for temperatures as low as 800 K the polymerized samples are paramagnetic (prepared from the pristine diamagnetic material). For the temperature of 900 K a distinct hysteresis is superimposed over the paramagnetic signal. Further increase in temperature leads to an abrupt transition to the diamagnetic behavior [6]. The magnetic phase of pressure-polymerized fullerenes invariably appears on the boundary

between polymerized fullerenes and postfullerene phases. The three points at which the magnetic properties were found to be most pronounced: (2.5 GPa, 1025 K; 6 GPa, 1075 K; 9 GPa, 900 K) are situated at the critical points of the pressure-temperature plane showing the various phases of C_{60} created under different conditions (Fig. 5).

Transmission electron microscopy shows that the radical centres are formed in the polymeric state before collapse, without damage to the buckyballs. The samples are polymeric and crystalline in nature. However, the amount of collapsed fullerenes can be negligibly small and undetectable in structural studies.

Several samples of Rh- C_{60} were investigated in order to understand the nature of ferromagnetism [39]. The studied samples do contain impurities, and their influence must be carefully studied, but the magnetization values do not show correlations with the impurity content. To check for a possible superparamagnetic behavior caused by small clusters of magnetic impurities, measurements of magnetization loops were performed at fixed various temperatures for all samples, and the small variation of remanence and coercivity gave no indications for magnetism of small particles. Temperature treatments of the samples revealed that they have different magnetic stability which is connected with different structural stability, determined by the preparation conditions [39].

The possible influence of impurities on the ferromagnetic properties of C_{60} polymer was investigated by laterally resolved particle induced X-ray emission (PIXE) and magnetic force microscopy (MFM). In pure regions (concentration of magnetic impurities $< 1 \mu\text{g/g}$), three different magnetic images were found: In region A, stripe domains are observed and the direction of domain magnetization is oblique to the sample surface. The stripes are almost

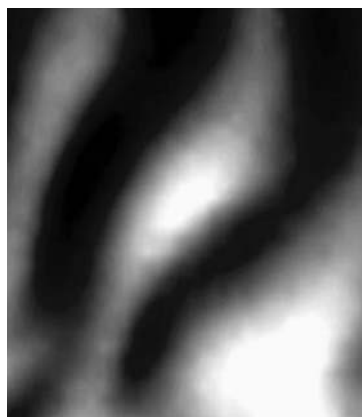
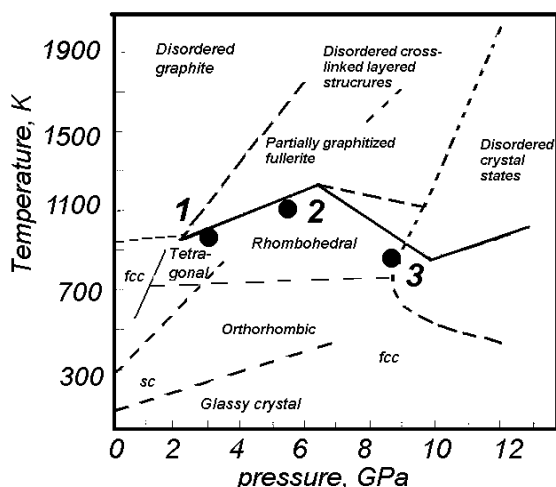


Figure 5. A map of the pressure and temperature conditions for creating different C_{60} phases. Points mark the conditions under which the ferromagnetic phase have been observed: 1 – [39]; 2 – [5]; 3 – [6]

Figure 6. Magnetic force gradient image taken in impurity free parts of samples. Here the scan area was $10 \mu\text{m} \times 10 \mu\text{m}$ and scan height 100 nm for MFM image. The authors thanks K.-H. Han and P. Esquinazi (Leipzig University) for providing this picture.

parallel to each other, the width is either 2 or 0.6 μm and the length in both cases is $\sim 20 \mu\text{m}$. In region B corrugated domain patterns are observed and the domain magnetization is oriented approximately normal to the surface. The region C does not contain any magnetic domains. The size of region A and B is $\sim 30\%$ of the pure region. The magnetic domains change with the external magnetic field, and the stripe domains almost disappear in a magnetic field of $\sim 0.01 \text{ T}$. Fig. 6 shows an example of magnetic domains, taken in a pure region. The results reveal that the polymerized C_{60} sample is a mixture of magnetic and non-magnetic parts and only a fraction of the sample contributes to the ferromagnetism [12].

7. Ferromagnetism in other fullerene derivatives

There have been observations of room-temperature ferromagnetism in fullerene compounds, other than polymerized phases. A small increase of electron paramagnetic absorption was observed in a dimethylformamide solution of polyvinylidene fluoride, in which C_{60} was ultrasonically dispersed [40]. Vacuum evaporation of the solution yields a C_{60} -containing polymer film free from metallic contamination. The observed magnetism is supposed to be due to the radical adducts represented as C_{60}R_n ($\text{R}=\text{H}, \text{F}, \text{CF}_3$ and polymer fragments), where n is odd.

Fullerene hydride $\text{C}_{60}\text{H}_{36}$ is a room-temperature ferromagnet with $M_s = 0.04 \text{ emu/g}$ [41]. The hydrogenated fullerenes were prepared by transfer hydrogenation procedures. Samples produced from several batches showed a similar dependence of magnetization versus external field, whereas other compositions preserved a diamagnetic character. Further investigations of hydrofullerites [9] confirmed the initial observations. The samples were prepared in a different way, under pressure in an excess of hydrogen, and twelve C_{60}H_x samples with x varying from 24 to 32 were obtained. Every sample shows a magnetic hysteresis with the coercivity about 100 Oe. Most hydrofullerites have low values of saturation magnetization, but three samples showed rather big values: 0.046, 0.054 and $0.16 \mu_B / \text{C}_{60}$. All three samples were synthesized under the same pressure-temperature conditions and had virtually the same composition $\text{C}_{60}\text{H}_{24}$ and the *fcc* crystal structure. A 1-year storage brings the samples to a diamagnetic state without noticeable changes in their composition and lattice parameter.

The $\sigma(H)$ curves are the same in the temperature range 80 – 300 K, showing that the Curie temperature lies well above room temperature for all samples including the ones stored in air. The combination of high Curie temperature and small values of magnetization shows that the sample is unlikely to be a bulk collinear ferromagnet. The explanation from the viewpoint of spin canting or defects in an antiferromagnetic structure is hardly adapted to aging of the samples with the transition to diamagnetic behavior: after the disappearance of spin alignment the sample would remain antiferromagnetic. Another possibility is that the samples comprise a mixture of diamagnetic and ferromagnetic phases: this is consistent with both the aging phenomenon and the scattered values of magnetization of as-prepared samples.

8. Ferromagnetism in all-carbon structures.

In the last twenty years there have been many reports on different metal-free organic compounds that exhibit ferromagnetic behavior up to room temperature. This evidence supports the theoretical predictions showing that electronic instabilities in pure carbon may give rise to

superconducting and ferromagnetic properties even at room temperature. Five types of room-temperature carbon-based magnets have been obtained experimentally: (i) chains of interacting radicals (ii) amorphous carbon structures containing three-valence elements like P, N, B; (iii) carbonaceous substances with a mixture of sp^2 and sp^3 coordinated atoms; (iv) nanosized and bulk graphite; (v) fullerenes [11]. The last three types consist solely of carbon.

“Of many candidates of the magnets, carbon compounds will be the most promising from the practical point of view, because the carbons exhibit a spontaneous magnetization at room temperature and are cheap to make, chemically and physically stable, and easy to process” [42]. The paper just cited reviews methods to prepare pyrolytic magnetic carbon preparation, and analyzes the relationship between the structure of the starting material and the value of saturation magnetization at room temperature. Pyrolytic carbons prepared at relatively low temperatures, 600 - 1300°C, have a highly oriented structure and contain a large number of unpaired electrons in the graphite skeleton. It is possible to expect spin exchange interactions between unpaired electrons in the graphitic network. The highest magnetization value achieved using this approach is 10.5 emu / g, corresponding to $0.022 \mu_B$ / carbon atom [43]. The origin of high magnetization values and the high stability of the material is due to the three-dimensional network structure consisting of both sp^2 and sp^3 carbons.

The electronic properties of finite graphene sheets (nanosized graphite) are different from those of bulk graphite: the presence of graphite edges drastically changes the π -electronic system. The “zigzag” edge states produce a peak at the Fermi level, and they contribute to the Pauli paramagnetic susceptibility which competes with the orbital diamagnetism [44]. In general, the origin of unpaired spins in carbon materials has been attributed to dangling σ bonds. A different origin for the spins in carbon materials has lead to the detection of novel molecular magnetism in combination with conduction electrons, and predictions of a possibility of ferromagnetism. Another source of unusual magnetic properties of graphite is the presence of topological defects which modify the band structure, producing flat bands [45].

There exist both theoretical predictions and experimental evidence that electronic instabilities in pure graphite can lead to ferromagnetic and superconducting properties even at room temperature [46]. Studies of the properties of bulk graphite by means of conduction electron spin-resonance give a cogent argument for the existence of an effective internal ferromagnetic-like field in graphite [18]. Measurements of weak ferromagnetism in various, well-characterized graphite samples [16] gave conclusive proof for the intrinsic nature of the ferromagnetic signal. This signal is caused either by topological defects (grain boundaries and edge states) locally changing the electronic structure or by itinerant ferromagnetism of a dilute 2D electron gas system due to a large electron-electron interaction [39].

9. Can polymerized fullerene be ferromagnetic?

Ferromagnetism is usually a feature of d and f electron systems, and purely organic ferromagnetism is a rarity. Under normal conditions the intermolecular exchange aligns spins of adjacent s - and p - unpaired electrons antiferromagnetically. The models of organic magnetism and the principles for the design of organic ferromagnets are described in Refs. [10]; a possible influence of magnetic proximity effects is addressed in Ref. [47] Here we mention only the fact, that a stable all-carbon structure with a ferromagnetic interaction has been predicted to exist. If some carbon atoms in a graphite two-dimensional network are substituted by sp^3 hybridized carbon atoms, the resulting magnetic moment can be extremely high: the theoretically

calculated magnetization value for such an intermediate graphite-diamond structure is 230 emu / g. This phase contains an equal number of sp^2 and sp^3 carbon atoms per unit volume which corresponds to the maximum possible concentration (50%) of unpaired-electron carriers, i.e. sp^2 carbon atoms [48].

The first attribute of polymerization is discussed in Sec. 4: it produces a structure containing both sp^2 and sp^3 hybridized carbon atoms. At the same time, the interfullerene bonds are directed at right angles and have considerably lower bond energy, i.e. are capable of providing an unpaired spin.

Polymerization creates the second prerequisite for spin ordering, namely, topological alignment of the molecules: molecules do not rotate freely and are oriented in the same way. As outlined in Sec. 3, there exists a strong correlation between the relative orientation of near-neighbor C_{60} units and intermolecular magnetic exchange interactions. Considering carbon structures, one should keep in mind possible oxygen or hydrogen contamination (Sec. 5, 7). This fact is not crucial for the existence of the high-temperature π -electron ferromagnetism, but may affect the model choice.

An analysis of the experimental data on pressure-polymerized fullerenes (Sec. 6) shows that the ferromagnetic behavior appears quite close to the boundary where the fullerene cages are destroyed. However, when sufficient amorphous-like carbon is mixed with fullerene molecules the ferromagnetic properties quickly decay. The defect nature of fullerene magnetism draws an analogy with the magnetism of nanographite (Sec. 8).

Two possibilities are considered: one is that the high pressure collapses some of the buckyballs, thereby generating unpaired electrons; another is that the buckyballs remain intact but unpaired electrons arise at the bonds between them. Fullerene polymers prepared under critical pressure-temperature conditions possess highly oriented structure and contain unpaired electrons. Magnetic phase appears as islands in a non-magnetic matrix forming stripe domains as well as corrugated domain patterns.

Understanding new magnetic materials requires fundamental knowledge of their structure, disorder and electronic properties. Detection and isolation of the pure magnetic phase is the primary task.

10. Conclusions

Ferromagnetism in polymerized fullerenes is an example of the more universal phenomenon: ferromagnetism in pure carbon structures. The discovery of unusual magnetic properties of fullerenes, activated carbon fibers, nanosized graphite, highly-oriented pyrolytic graphite have shown that the properties of carbon – the basic element of living substances – are far from being understood.

Two main reasons advance further studies of these phenomena. The first one is scientific curiosity: what cases magnetic behavior in a structure made of atoms that have no magnetic moment. Electronic instabilities in pure carbon are predicted to lead to various types of ordering, from ferromagnetic to superconducting, and carbon structures promise many surprises yet to come.

Second, new materials have always been a dominant factor in driving advances in material usage. An ideal structure containing alternating sp^2 and sp^3 hybridized carbon atoms theoretically exceeds the specific magnetization of α -Fe, making the system potentially attractive. Magnetic carbon materials are suitable as toner for copiers and other business

machines; they are welcome in medicine, for example, in drug delivery systems: it is a biocompatible magnet [11]. Possible high-tech applications include computer memory devices or spintronic devices, taking into account their semiconducting properties. Magnetic fullerenes together with carbon nanotubes can be used as building blocks in the all-carbon integrated circuits.

Since the industrial revolution, manufacturing has been creating wasteful by-products, usually harmful to life and expensive to disarm. Carbon is a material that meets the demands for environmental protection, public health and safety.

Acknowledgements.

This work is supported by the Swedish Research Council. The author takes this opportunity of thanking P. Esquinazi, R. Höhne, Y. Kopelevich, A. Shelankov and B. Sundqvist for fruitful collaboration.

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APPLICATION OF THE ELECTRONIC PROPERTIES OF CARBON NANOTUBES: COMPUTATION OF THE MAGNETIC PROPERTIES AND THE ^{13}C NMR SHIFTS

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Abstract:

This lecture is devoted to the study of the electronic properties of carbon nanotubes, within a numerical/theoretical framework. Although the tight-binding approach is retained in the most cases, comparisons with experimental results are presented. Our lecture is separated onto three sections. After a brief introduction, of the structure and the general properties of carbon nanotubes, the first section describes the tight-binding method and its applications to the study of the electronic properties of nanotubes: density of states, band structure, etc. The second section presents results on the magnetic properties of carbon nanotubes computed with the tight-binding method. Here, the eigenproblem is expanded on a gauge-included localised orbital basis set (London-Pople's non-perturbative treatment), which has been used successfully for carbon systems: linear response quantities such as magnetic susceptibility are predictable. Finally, in the third section, an application of this theory is addressed, namely the computation of the ^{13}C nuclear magnetic resonance chemical shift. Theory/experiment comparison is also reported.

1. Introduction

Since their discovery [1] in 1991, carbon nanotubes [2] have attracted much attention from the physicists because they are seen as good candidates for nanostructured multifunctional materials, to develop tomorrow's electronics. They are micrometer long hollow cylinders and can be defined as graphene sheets rolled-up like a cigarette, with a nanometer-scale radius. figure 1 is a schematic representation of a nanotube: carbon atoms are tricoordinated, covalently bonded to their neighbours. The first carbon nanotubes that have been synthesised were multi-wall carbon nanotubes (MWNTs), that are concentric sets of single layered structures, shaped like Russian dolls. These structures are individual rigid objects. Later, single-wall nanotubes were successfully produced using transition metals as catalysts. They are not individual structures, more often found in small 2D triangular arrangements called bundles or ropes. figure 2 shows transmission electron microscopy images of a MWNT and of a bundle of SWNTs.

As a generic model for carbon nanotubes, we will retain in this lecture, only single

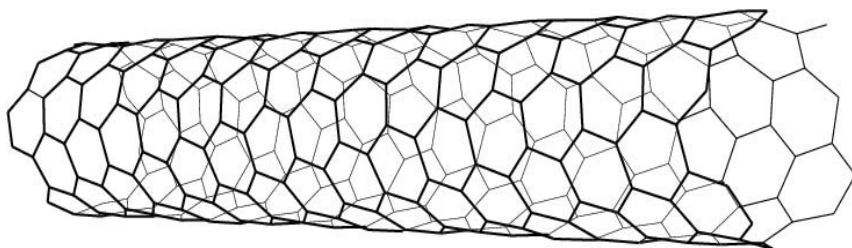


Figure 1: Schematic view of a carbon nanotube. This example is the (7,3) nanotube.

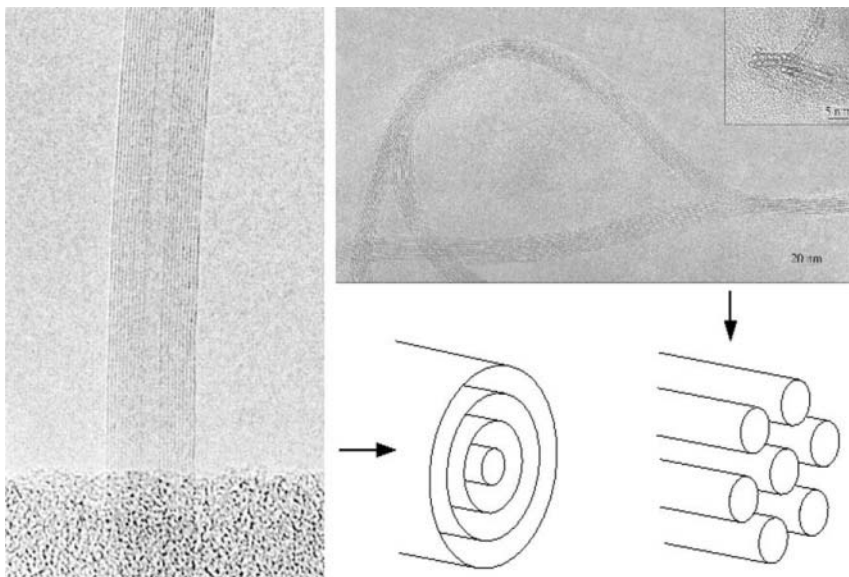


Figure 2: Transmission electron microscopy photographs of carbon nanotube. Left: A multiwall carbon nanotube (courtesy of Daniele Ugarte). Right: A bundle of single wall carbon nanotubes (courtesy of Julie Gavillet).

layered, individual and infinite carbon nanotubes. Of course, layer-layer interaction in a MWNT or tube tube interaction in a bundle will modify the electronic properties of each constituents, but the most relevant electronic properties are obtained with this simpler model.

This lecture is then devoted to the electronic properties of such individual and infinite carbon nanotube, studied by the tight-binding method. The first part describe the structural and general properties of the carbon nanotubes. The model of computation is quickly presented in this first section, and it is applied to the study of carbon nanotubes. Band structure and the corresponding density of state are finally computed. The second section addresses the orbital magnetic response of carbon nanotubes. Technical description and criticisms are developed. The computation of the susceptibility is described in order to understand the magnetic mechanisms in carbon nanotubes. Finally, in the last section, the nuclear magnetic resonance (NMR) chemical shift tensor is aborded, within this framework, and compared to experimental data.

2. Electronic properties of carbon nanotubes

2.1. STRUCTURE OF A CARBON NANOTUBES

The idea of viewing a nanotube as a rolled up 2D lattice allows to define a unique name for every single layer nanotube. This name is a couple of integer numbers like (n,m) . figure 3 shows this concept. We will use here the formalism developed by R. Saito, G. Dresselhaus and M.S. Dresselhaus [3], but other theoretical predictions were published, using similar approaches [4].

The chiral vector $\mathbf{C}_h$ represents the segment that is rolled up onto the circumference of the nanotube. It is expanded on the base of the primitive vectors of the hexagonal network $\mathbf{a}_1$ and $\mathbf{a}_2$ like

$$\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2$$

The translational vector $\mathbf{T}$ represents the length of the primitive cell of the rolled up structure

$$\mathbf{T} = t_1\mathbf{a}_1 + t_2\mathbf{a}_2$$

Where t_1 and t_2 are integer number determined by

$$t_1 = \frac{2m+n}{d_R} \quad \text{and} \quad t_2 = \frac{-2n-m}{d_R}, \quad \text{with} \quad d_R = \text{gcd}[2m+n, 2n+n]$$

The «primitive» cell of the unfolded tube, drawn on the hexagonal lattice is the rectangle defined by the vectors $\mathbf{T}$ and $\mathbf{C}_h$. The corresponding Brillouin zone of the unfolded tube is then defined by the two vectors $\mathbf{K}_1$ and $\mathbf{K}_2$.

$$\mathbf{K}_1 = \frac{2\pi}{|\mathbf{C}_h|} \quad \text{and} \quad \mathbf{K}_2 = \frac{2\pi}{|\mathbf{T}|}$$

All these geometric tools will be used for the calculation of the electronic properties.

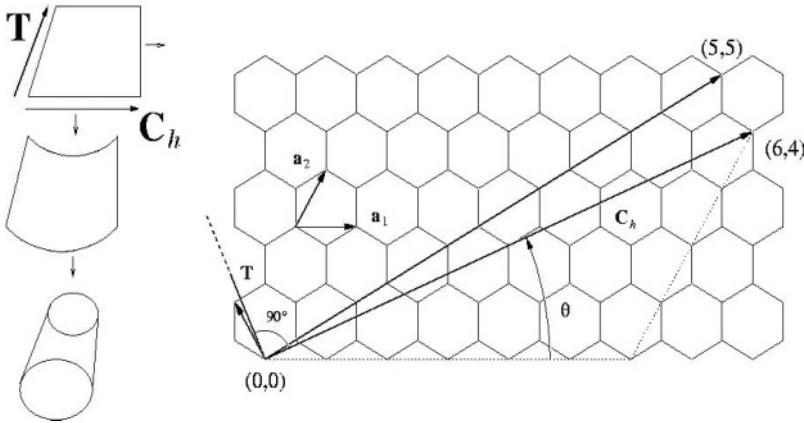


Figure 3: At left is drawn a scheme of curling a rectangular sheet onto a cylinder. The chiral vector defines the uncurled circumference and the translational vector represents the length of the nanotube primitive cell. The indices n and m , that define the chiral vector $\mathbf{C}_h$ are the projections of this vector on the basis set of the honeycomb lattice $\mathbf{a}_1$ and $\mathbf{a}_2$

2.2. THE TIGHT-BINDING MODEL

We start from the standard individual-electrons hamiltonian operator [5]

$$\hat{H} = \frac{1}{2} \hat{p}^2 + V[\hat{R}]$$

The tight-binding (TB) model is then an independent electron approach, that generalises the so-called Hückel model. It is based on the use of a localised basis set:

$$\{|\Phi_i\rangle\}_{i=1,N}$$

where N is the total number of orbitals in the whole system. Note that several orbitals can be located on the same atom. Every (eigen)state is then a linear combination of the localised orbitals like:

$$|\Psi_\alpha\rangle = \sum_{i=1,N} C_i^\alpha |\Phi_i\rangle$$

The matrix elements, concerning the basis states, of the Hamiltonian operator are the parameters of the model. They are tabulated like:

$$\langle \Phi_i | \hat{H}_0 | \Phi_i \rangle = \epsilon_i, \quad \langle \Phi_i | \hat{H}_0 | \Phi_j \rangle = \gamma_{ij}, \quad \langle \Phi_i | \Phi_j \rangle = S_{ij}$$

They are called respectively on-site energy, hopping integral and overlap integral. All other integrals are zero. In this lecture we will concentrate on a orthogonal TB model, that neglects the overlap integral. Hence:

$$S_{ij} = \delta_{ij}$$

Finally, the tight-binding Hamiltonian operator is written, using the translational symmetry : sum over orbitals runs on the primitive cell only. Application of the Bloch theorem leads to:

$$\hat{H}_0^{\text{TB}} = \sum_{i \in \text{Cell}} \epsilon_i |\phi_i\rangle \langle \phi_i| + \sum_{i \in \text{Cell}} \sum_{j \in \text{neigh}(i)} \gamma_{ij} |\phi_i\rangle \langle \phi_j| \exp(i \mathbf{k} \cdot \mathbf{t}_{ij})$$

where $\mathbf{t}_{ij}$ is the vector separating the positions of sites i and j . The set $\text{neigh}(i)$ contains the first neighbours of orbital i , in and out the cell containing i . The eigenvectors and

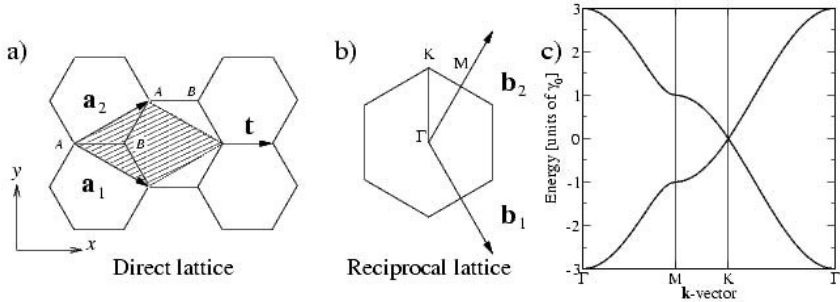


Figure 4: The band structure of the graphene plane. a) The hexagonal network, defined by the vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ the unit cell contains two atoms, labelled A and B. Primitive cell is dashed. b) The reciprocal lattice is triangular, hence the first Brillouin zone is an hexagon. High symmetry points are usually labelled Γ , K and M . c) Dispersion relation $E(\mathbf{k})$ of the p_z electrons. The π band is occupied whereas the π^* band is empty. Contact between the bands occurs only at the six K points.

eigenvalues are the solutions of the secular equation:

$$\hat{H}_0^{\text{TB}}(\mathbf{k})|\psi_{\alpha,\mathbf{k}}\rangle = E_{\alpha}(\mathbf{k})|\psi_{\alpha,\mathbf{k}}\rangle$$

The simplest Hückel model restricts the expansion over the p_z orbitals only (here, z is the axis orthogonal to the plane of conjugated molecules). Such a scheme is efficient for describing the electronic structure of aromatic molecules and their derivatives [6]. It can be used for extended systems such as graphite (we will use it below). The hopping integral is taken as a constant (its value is 2.66 eV in benzene, for example). Beyond this simplest approach, the Slater and Koster technique [7] takes all the valence atomic orbitals into account and gives a more realistic description. This technique needs a set of parametrized integrals that gives the hopping and overlap integrals via trigonometric relations.

2.3. ELECTRONIC PROPERTIES OF CARBON NANOTUBES: THE ZONE FOLDING METHOD

The zone folding (ZF) method is the simplest model to carry out the electronic properties of carbon nanotubes. It is detailed in reference [2]. The idea of this approach is to neglect the curvature of the graphene sheet: a nanotube can be seen as a rectangle with periodic boundaries conditions. In the reciprocal space, the first Brillouin zone (BZ) of the nanotube is a rectangle, smaller than the BZ of the graphene sheet.

We will first compute the band structure of the graphene 2D crystal. As shown by Wallace, we can restrict the model to the p_z orbitals (like in the benzene molecule), and extend the Hückel model to crystals. As shown in figure 4, the primitive cell of the graphene sheet contains two carbon atoms, hence the basis set contains two atomic orbitals: two bands only are taken into account in the band structure, they are labelled π (occupied) and π^* (empty). The first Brillouin zone of the graphene 2D crystal is also plotted : it is an hexagon. The band structure is given by

$$E_{\pm}(\mathbf{k})|\psi_{\alpha,\mathbf{k}}\rangle =_{2p} \pm \gamma_0(\mathbf{k}) \sqrt{|f(\mathbf{k})|}$$

where the sign plus (minus) labels the π band (the π^* band). The function f is given by

$$f(\mathbf{k}) = \exp(ik_x t) + 2 \exp\left(i \frac{k_x t}{2}\right) \cdot \cos\left(i \frac{k_y t}{2}\right)$$

where t is the distance between two neighbouring atoms and a is the norm of the primitive vectors. Also shown in FIGURE 4, the graphene sheet is a non standard metallic system: the Fermi surface is reduced to the six high-symmetry-points K and the density of states at Fermi level is zero[8].

The primitive cell of the unfolded carbon nanotube, drawn in the honeycomb network is then the rectangle defined by $\mathbf{C}_h$ and $\mathbf{T}$. Its reciprocal cell is also a rectangle, defined by $\mathbf{K}_1$ and $\mathbf{K}_2$. In this situation, a nanotube is topologically equivalent to a rectangular section of graphene with *periodic* boundary condition along $\mathbf{T}$ and *cyclic* boundary condition along $\mathbf{C}_h$. The k -points expansion occurs only for the $\mathbf{T}$ -translational symmetry (we assume that the nanotube is infinite, hence the k -points selection is dense along the nanotube). For this reason, and as shown in figure 5, the cyclic boundary conditions select a sampling of lines of k -points in the graphene Brillouin zone.

If the k -points sampling selects the K high-symmetry point of the graphene BZ, then

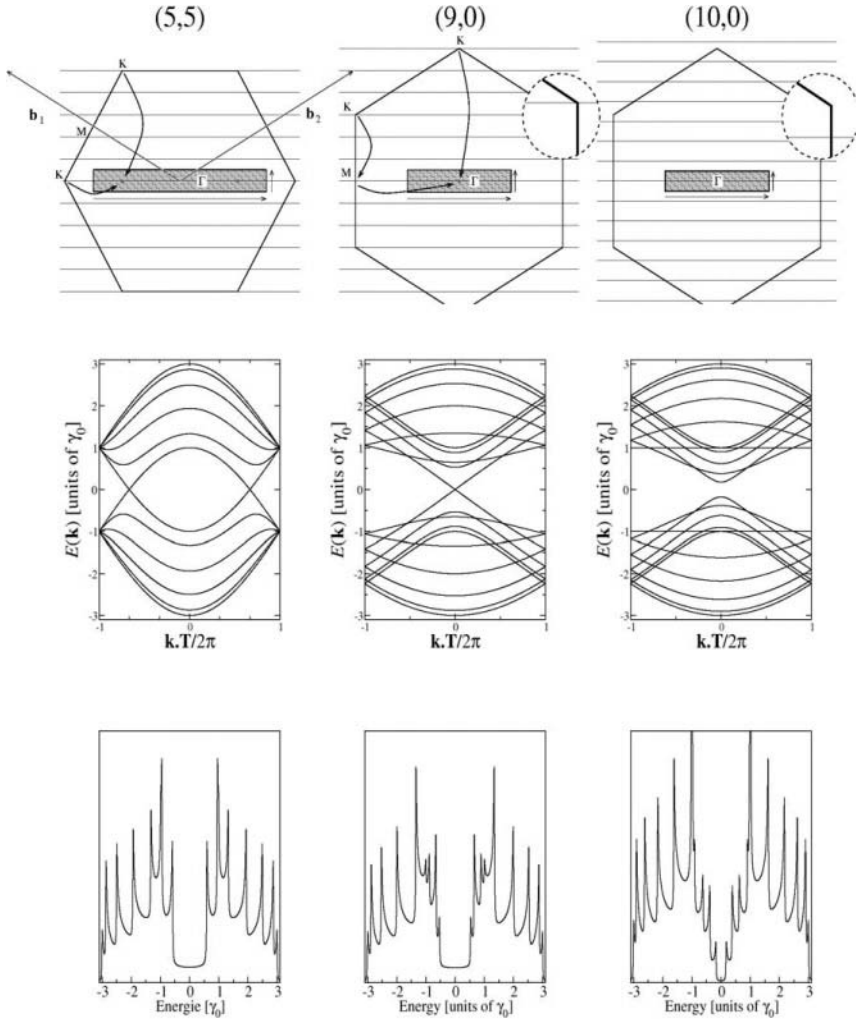


Figure 5: The zone folding model. We have chosen three examples of small radius nanotubes: the (5,5), the (9,0) and the (10,0) nanotubes.

Top: Schematic view of the folding of the graphene hexagonal BZ within the nanotube rectangular BZ. The selection of k -points (shown like solid thin lines) due to the cyclic boundary conditions is responsible for the band structure of the nanotube. If the k -points sampling reaches the K point of the graphene Brillouin zone, the nanotube will be metallic.

Center: The band structure of the nanotubes computed with zone folding technique. The (5,5) nanotube is metallic, with a Fermi moment different from zero. The (9,0) nanotube is metallic with a Fermi moment located at Γ point. The (10,0) has a band structure similar to the (9,0) but a gap is open: it is a semiconducting nanotube.

Bottom: The corresponding densities of states show typical 1D behaviour: at the bottom of every band, the DOS exhibits a Van Hove singularity (divergence of the DOS). The (5,5) and (9,0) metallic nanotubes have a uniform density of states around their Fermi energy.

the resulting nanotube band structure allows last occupied band and first empty band to touch, like in graphene. Hence, each time this K high-symmetry point is selected, the nanotube is metallic. It is semiconducting otherwise. A geometrical analysis shows that the criteria for determining the metallic/semiconducting behaviour of the nanotube is the following: if the difference ($n-m$) is a multiple of 3, then the sampling reach the point K. Within the ZF model, nanotubes follow this simple rule:

$$\forall q \in Z, \quad n - m \neq 3q \quad (\text{semiconducting nanotube})$$

$$\exists q \in Z, \quad n - m = 3q \quad (\text{metallic nanotube})$$

The zone folding model is then able to give a correspondence between the structural and electronic properties very easily. The figure 5 illustrates the electronic properties of three types of nanotubes, described with this ZF technique: (5,5) and (9,0) nanotubes are metallic whereas the (10,0) nanotube is semiconducting. In the case of metallic nanotubes, the 1D characteristic of the nanotube imply that its density of states goes not to the zero value for Fermi energy: the electronic DOS exhibit a plateau around the Fermi level. Moreover, a prediction on the metallic/semiconducting ratio can be obtained, if we assume that the growth mechanism does not favorise a given specie: a sample is containing 1/3 metallic and 2/3 semiconducting nanotubes.

Finally, in order to fit the experimental data from scanning tunnelling spectroscopy and resonant Raman scattering, the value of the overlap integral is [9]:

2.4. ELECTRONIC PROPERTIES OF CARBON NANOTUBES: MORE ACCURATE APPROACHES

In the precedent section, the curvature needed to roll up a graphene sheet onto a nanotube was neglected. What will be the effect of such a distortion on the electronic properties ? The principal outcome is the breaking of the planar symmetry of the graphene sheet. In this situation, we are not allowed to separate symmetric (σ) and antisymmetric (π) eigenstates, which will mix up together. In order to take this σ - π mixing into account, we expand now the eigenproblem over all the carbon atom valence orbitals, by using the Slater Koster (SK) approach. We have used two set of parameters, from S.G. Louie and D. Tomanek [10], and from J.C. Charlier, X. Gonze and J.P. Michenaud [11].

Few differences between ZF and SK band calculations are reported. Indeed, the position of Van Hove singularities in the DOS of carbon nanotubes is similar for both methods. More, they give the same value for the plateau around the Fermi level. In fact, only one, but spectacular consequence is a gap opening in the band structure of the «metallic» nanotubes, induced by the σ - π mixing, except the (n,n) nanotubes that remains truly metallic. This secondary gap follows a $1/R^2$ radius scaling, and has been measured by scanning tunnelling spectroscopy [12], after theoretical predictions based on *ab initio* calculations [13] and on symmetry analysis of the band character [14]. The comparison between experimental value of this gap and the results we obtained with the SK method are excellent, especially in the case of the Charlier *et al.* parameters set. Results are given in TABLE 1.

Table 1: Numerical versus experimental comparisons of secondary gaps in «metallic» carbon nanotubes ($n, 0$). If the Charlier *et al.* parameters, the theory/experiment comparison is excellent. See text for references.

Value of the secondary gap	Louie and Tomanek parameters	Charlier <i>et al.</i> Parameters	Ouyang <i>et al.</i> experimental value
(9,0)	108 meV	82 meV	80meV
(12,0)	60 meV	46 meV	42meV
(15,0)	38 meV	30 meV	29meV

3. Magnetic properties of carbon nanotubes

3.1. THE LONDON-POPLE THEORY OF THE ORBITAL MAGNETIC RESPONSE

In presence of a magnetic field $\mathbf{B}$, impulsion and linear moments are no longer equivalent. For solving the problem of an electron in a magnetic field within a quantum mechanics description, one has to replace the common Hamiltonian operator with this one:

$$\hat{H} = \frac{1}{2} \left[\hat{\mathbf{p}}^2 + \frac{1}{c} \mathbf{A}(\hat{\mathbf{R}}) \right] + V[\hat{\mathbf{R}}]$$

In this situation, the Hamiltonian operator is an explicit function of the magnetic vector potential $\mathbf{A}$ that is a multidefined object (choice of the gauge function), however eigenstates and eigenenergies are only function of the applied magnetic field, that is an external parameter. We will choose the following gauge [15]:

$$\mathbf{A}(\mathbf{r}) = \frac{1}{2} \mathbf{r} \times \mathbf{B}$$

In order to solve such a Schrödinger equation, one can use a perturbation expansion, however this lecture will report on another approach, that is non perturbative. The method used here has been developed very early by F. London, in order to estimate the magnetic susceptibility of aromatic molecules [16]. Later, J.A. Pople has generalised the approach for all the molecules [17]. Finally, J.E. Hebborn adapt it to crystals [18]. The method consists in expanding the problem on a Gauge-Included atomic orbitals (GIAO) basis set instead of a normal one. The GIAOs $|\chi_i\rangle$ are defined like this:

$$|\chi_i\rangle = \exp\left(-\frac{i}{c} \mathbf{A}_i \cdot \hat{\mathbf{R}}\right) |\phi_i\rangle$$

where $|\phi_i\rangle$ are the atomic orbitals, and $\mathbf{A}_i = \mathbf{A}|\mathbf{R}_i|$ is the vector potential at the position of the nucleus carrying the i^{th} orbital. Let write the matrix elements H_{ij} , projected on the GIAOs basis set

$$H_{ij} = \langle \chi_i | \hat{H} | \chi_j \rangle$$

This leads to

$$H_{ij} = \langle \phi_i | \exp\left(\frac{i}{c} \mathbf{A}_i \cdot \mathbf{R}\right) \cdot \hat{H} \exp\left(-\frac{i}{c} \mathbf{A}_j \cdot \mathbf{R}\right) \cdot | \phi_j \rangle$$

One can prove that

$$H_{ij} = \langle \phi_i | \exp\left(-\frac{i}{c} |\mathbf{A}_j - \mathbf{A}_i| \cdot \mathbf{R}\right) \cdot \left\{ \frac{1}{2} \left[\mathbf{p} + \frac{1}{c} (\mathbf{A}(\mathbf{R}) - \mathbf{A}_j) \right]^2 + V(\mathbf{R}) \right\} | \phi_j \rangle$$

The London's first approximation consists in neglecting the local vector potential $\mathbf{A}-\mathbf{A}_j$, in order to recover the zero field Hamiltonian, like

$$H_{ij} \cong \langle \phi_i | \exp\left(-\frac{i}{c} |\mathbf{A}_j - \mathbf{A}_i| \cdot \mathbf{R}\right) \cdot \hat{H}_0 | \phi_j \rangle$$

As mentioned by Pople, this approximation is a bit rough: an intra atomic part of the magnetic response is missed. We will discuss this problem later.

The London's seconds approximation consists in approaching the exponential function,

within the bracket, by a phase, like

$$H_{ij} \equiv \left\langle \Phi_i \left| \exp \left(-\frac{i}{c} (A_j - A_i) R \right) \cdot \hat{H}_0 \right| \Phi_j \right\rangle$$

where the phase is given by

$$L_{ij} = \frac{1}{c} \int_{r_i}^{r_j} \mathbf{A}(\mathbf{r}) \cdot d\mathbf{r}$$

Applying this theory on the former tight-binding Hamiltonian gives

$$H_{ij} = \epsilon_i, \quad H_{ij} = \gamma_{ij} \cdot \exp(iL_{ij}) \quad \text{and} \quad \langle \chi_i / \chi_j \rangle = S_{ij} \cdot \exp(iL_{ij})$$

In this situation, handling a magnetic field is simple: one only has to multiply every hopping element and overlap integral by a the London's phase. Resolving the secular equation leads to the band structure as function to the magnetic field. Indeed, the energy vs. field can be computed.

3.2. MAGNETIC SUSCEPTIBILITY OF CARBON NANOTUBES

The total magnetic susceptibility, at zero temperature is given by

$$\chi = - \left(\frac{\partial E(\mathbf{B})}{\partial B^2} \right)_{B \rightarrow 0}$$

where $\mathbf{B}$ is the applied field, and

$$E(\mathbf{B}) = 2 \sum_{n \in \text{occ}} \sum_{\mathbf{k}} \epsilon_n(\mathbf{k})$$

is the total energy of the system, where $\epsilon_n(\mathbf{k})$ are the field dependant eigenenergies. If a finite temperature calculation is required, one has to replace the total energy, by the grand canonical potential

$$\Omega(\mathbf{B}, T) = -k_B T \sum_n \sum_{\mathbf{k}} \ln \left[1 + \exp \left(\frac{\epsilon_F - \epsilon_n(\mathbf{k})}{k_B T} \right) \right]$$

where ϵ_F is the Fermi level. Using the London theory, within the ZF technique is successful for computing this orbital susceptibility [19]. The magnetic field parallel or perpendicular to the nanotube axis gives different results following the electronic properties of the nanotube.

In the first case of a parallel magnetic field, the dephasing due to the magnetic field acts as a global translation of the k -points sampling. The reason is that, for this geometry, the dephasing due to the field is added to the confinement due to cyclic boundary condition. The origin of the metallic behaviour is an occurrence of crossing of bands exactly at the Fermi level. Indeed, for a metallic nanotube with a weak parallel field, one have

$$E(B) = -\text{const.} \times B$$

since $E(B) = E(-B)$, the second derivative of the zero T total energy is divergent for the zero field limit. Finite temperature is needed to avoid this divergence, and metallic carbon nanotubes exhibit a Curie-like paramagnetic response, with the following scaling

$$\chi_{\parallel} \propto R/T \quad (\text{metallic nanotube})$$

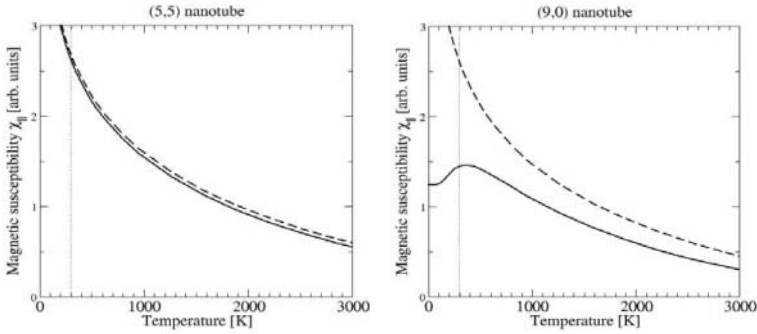


Figure 6: Temperature dependence of the axial magnetic susceptibility vs. the electronic temperature. The susceptibility computed with the Slater-Koster approach (4 electrons/carbon atom, Louie-Tomanek's parameters) is plotted with a dashed line, the susceptibility computed with the zone folding technique is plotted with a solid line. At left, few differences between methods of computations appears for the (5,5) nanotube. Both exhibit a $1/T$ dependence. At right, for the (9,0) nanotube, differences due to the secondary gap are clearly visible at low temperature: magnetic susceptibility is not divergent for zero temperature. The $1/T$ Curie behaviour is recovered above the room temperature.

In opposition to metallic nanotubes, semiconducting do not have a temperature dependant susceptibility, and are diamagnetic

$$\chi_{||} \propto -R \quad (\text{semiconducting nanotube})$$

In the case of an orthogonal applied field, the magnetic response is similar for metallic and semiconducting nanotubes. It is a temperature independent diamagnetic susceptibility

$$\chi_{\perp} \propto -R \quad (\text{all})$$

Since these results were obtained within a ZF approach, what will be the effect of the secondary gap, open in the band structure of the «metallic» nanotubes? As we can expect, this gap will only affect the axial susceptibility of metallic carbon nanotubes. On FIGURE 6 is plotted this axial susceptibility for (5,5) and (9,0) nanotubes. Since they have a similar radius, the magnetic response computed with the zone folding technique is identical. However, with the more accurate Slater-Koster model, differences of behaviour are clearly visible: the susceptibility of the (9,0) nanotube is still paramagnetic, but not divergent for $T=0$ and the Curie $1/T$ law is recovered above room temperature.

3.3. CRITICISM OF THIS MODEL: LOCAL CONTRIBUTIONS TO THE MAGNETIC RESPONSE

As we have mentioned previously, local contribution of the vector potential is removed when writing the hamiltonian operator matrix elements (first London approximation). If these local elements are kept before applying the second approximation, one obtains

$$H_{ij} = \exp(iL_{ij}) \langle \phi_i | \cdot \left\{ \frac{1}{2} \left[\hat{p} + \frac{1}{c} (A(\hat{R}) - A_j) \right]^2 + V(\hat{R}) \right\} | \phi_j \rangle$$

Before expanding this equation, we have to notice that the operator between the bracket is not hermitic ! The hermiticity of this hamiltonian must be forced like

$$\{O_{ij}\}_{\text{herm}} = \frac{1}{2}(O_{ij} + O_{ij}^*)$$

leading to

$$H_{ij} = \exp(iL_{ij}) \langle \phi_i | [\hat{H}_0 + \hat{H}_1 + \hat{H}_2] | \phi_j \rangle_{\text{herm}}$$

with the previous hamiltonian

$$\hat{H}_0 = \frac{1}{2} \hat{p}^2 + V(\hat{R})$$

and the new local contributions

$$\begin{aligned} \hat{H}_1 &= \frac{1}{2c} \left[(\hat{A} - A_j) \cdot \hat{p} + \hat{p} (\hat{A} - A_j) \right] \\ \hat{H}_2 &= \frac{1}{2c^2} (\hat{A} - A_j)^2 \end{aligned}$$

It has been proved by J.A. Pople, in reference [17], that only these local terms contribute to the magnetic response of non-cyclic molecules. Indeed, in this case, the contribution coming from $\exp(iL_{ij}) \langle \phi_i | \hat{H}_0 | \phi_j \rangle$ is strictly zero.

More, it has been shown in the same paper that the two local operator couple only orbitals that sit on the same atom. These effects are then internal to each atom, and not driven by the global electronic properties of the compound.

To be consistent, we must add a local intra-atomic contribution to the previous magnetic susceptibility

$$\chi_{\text{total}} = \chi_{\text{London}} + \chi_{\text{local}}$$

Unfortunately, computing the local part of the response $E_{\text{local}}(\mathbf{B})$ requires a measure of the electronic position. Hence the correct shape of the electronic wave function is needed. Tight-binding is not able to give such information.

Keeping in mind that the computed magnetic response misses this local part, we will apply it to estimate the shielding tensor, that is check by comparison with experimental data.

4. ¹³C Nuclear magnetic resonance shifts of nanotubes

4.1. SHIELDING TENSOR AND KNIGHT SHIFT

An important application of the theory described before is the computation of the screening tensor, and the NMR chemical shift, of carbon nanotubes. Indeed, the susceptibility given by the London theory is incomplete: as we have just established, the intra-atomic part is missing. More, a measure of the susceptibility will be a global average over all the nanotubes present in the sample. In order to separate the magnetic response between metallic and semiconducting nanotubes, the local response is needed. By measuring the shift of the Larmor frequency of the nuclear spin, NMR in solids gives informations about the chemical environment and the metal-like properties of a compound. The NMR shift which represent the perturbation of the applied magnetic field due to electrons consists of a sum of two tensorial contributions: the shielding tensor σ due to the electronic orbital magnetism, and the Knight shift K , which is a Fermi contact effect of electron spin which appears only in metals. The chemical shift

anisotropy is measured experimentally by comparing to a standard reference σ_{ref} as:

$$\delta = \sigma_{\text{ref}} - \sigma + K$$

The nature of the Knight shift imply a dependance on the contact probability between the conduction electrons and the ^{13}C nucleus, hence on the s character of the conducting bands. Whereas this Knight shift is the dominant contribution in (metallic) fullerenes, mainly due to a large density of states at Fermi level and a strong s character (≈ 0.08 in C_{60} for example), this is not the case for nanotubes. A simple geometrical analysis of the curvature of the graphene needed to form nanotubes with diameters close to experimental value [20] indicates that the s character is very low (≈ 0.005 in a (10,10) nanotube). For these two reasons, we will neglect the Knight shift in this work. But, in the same way than for the magnetic susceptibility, the shielding tensor is incomplete within the London theory:

$$\sigma_{\text{total}} = \sigma_{\text{London}} + \sigma_{\text{local}}$$

However, for the range of diameters experimentally measured, the total degree of σ - p mixing is rather constant. This means that the all carbon atoms in a sample will see an equivalent chemical environment. Hence, although the local contribution to the shielding tensor is not negligible, it will be the same for all the ^{13}C nuclei. Moreover, in high-resolution solid state NMR by rotating the sample to magic angle spinning (MAS), the orientation of the ^{13}C is averaged with respect to the magnetic field and the isotropic value of the chemical shift is measured:

$$\sigma_{\text{iso}} = [\text{Tr}(\sigma_{\text{total}})]/3$$

In our case, the local intra-atomic part, what is missed in the model, gives rise to a global shift of the whole magnetic response and will not allows to distinguish between different nanotubes. If we restrict the study to relative changes of the chemical shift, we can then safely remove the local contribution to the shielding tensor in the present calculation. For that reason, the origin of the shift measure is arbitrary, then we can assume $\sigma_{\text{ref}} = 0$.

4.2. THEORETICAL PREDICTIONS

From the previous discussion, we are left with the computation of the London shielding tensor. This is done by introducing a probe dipole $\mathbf{m}$ in our system, that simulates the ^{13}C nucleus. The moment interacts with the applied field $\mathbf{B}_0$ and with the electron-induced magnetic field. The shielding tensor can be defined through the corresponding Zeeman splitting due to the total internal field $\mathbf{B}$ as

$$2\mathbf{m} \cdot \mathbf{B} = 2\mathbf{m} \cdot (\mathbf{B}_0 + \mathbf{B}_{\text{ind}}) = 2\mathbf{m} \cdot (\mathbf{1} - \boldsymbol{\sigma}) \cdot \mathbf{B}_0$$

If now we remove the direct interaction between the applied field and the probe dipole, we get the following expression for the shielding tensor:

$$\sigma_{\alpha\beta} = \left(\frac{\Omega(B_0, \mathbf{m}, T) - \Omega(B_0, -\mathbf{m}, T)}{2mB_0} \right) B_0 \|\alpha, \mathbf{m}\| \beta$$

where α and β are the spatial direction x , y or z (the nanotube is assumed to be along the z direction), and Ω is the grand-canonical potential of the electronic system under the influence of both applied field $\mathbf{B}_0$ and dipole moment $\mathbf{m}$. The total vector potential

is then

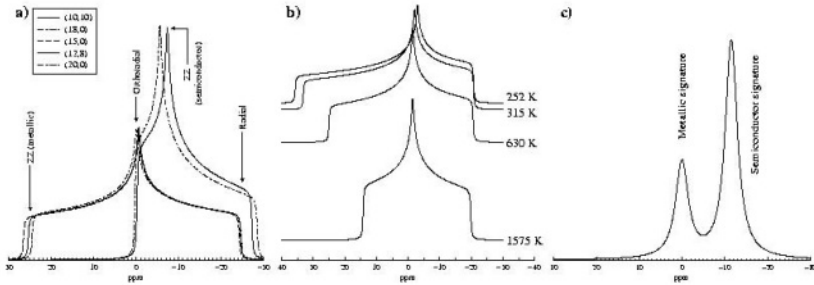


Figure 7: Calculated σ_{RC} tensor for infinite, isolated and perfect nanotubes. **a)** The line shape for different chiralities do not exhibit a strong difference and illustrates the distinct magnetic response depending on the specific electronic character of the nanotube: the axial principal value is paramagnetic ($\sigma_{zz} < 0$) for a metallic nanotube and diamagnetic ($\sigma_{zz} > 0$) for a semiconductor. **b)** The $1/T$ temperature dependence of the σ_{zz} element of a metallic nanotube. The given example is the (5,5). **c)** The simulated response of a bulk sample is shown as a distribution of isotropic lines, where the response of metallic and semiconducting tubes is clearly separated by 13 ppm.

$$\mathbf{A}(\mathbf{r}) = (\mathbf{r} \times \mathbf{B})/2 + (\mathbf{m} \times \mathbf{r})/r^3.$$

Since the general electronic properties of carbon nanotubes are correctly predicted with a simple Hückel approach, we have kept one orbital per carbon atom. However, the model we use is not exactly the zone folding technique, since the actual tubular geometry is taken into account. The reason is that the position of the probe dipole by respect to the electronic system is needed by the model. In order to keep working with periodic boundary conditions along the nanotube axis, and to avoid interaction from the moment with its image, we work with 9 nanometer-long supercell, containing one probe dipole.

The London shielding tensor is finally diagonalised and from the three principal values the static line shape of the NMR powder spectrum is obtained [21]. In our case, the σ_{zz} component is already a principal value of the tensor, as a consequence of the uniaxial symmetry of the nanotube. The two other components are the radial σ_{rad} and orthoradial σ_{ortho} principal values.

Figure 7.a) presents the computed powder spectra of London contribution to the shielding tensor for isolated and infinite nanotubes at room temperature. A very weak dependence on both tube radius and chirality are found. Only the σ_{zz} component is different according to the metallic or semiconducting character of the nanotube. The σ_{zz} principal value is T independent and diamagnetically shifted for semiconducting nanotubes. On the other hand, and as shown in figure.7.b), σ_{zz} is paramagnetically shifted, with a $1/T$ dependence. The principal values σ_{rad} and σ_{ortho} are always diamagnetic and σ_{ortho} is much greater than σ_{rad} . Therefore, NMR can resolve the electronic structure of the nanotube, but not the underlying structural properties.

As tube chirality can not be selected in the production process, we also provided a random distribution that simulates an actual sample. The ratio of the numbers of metallic and semiconductors is fixed to 1 to 2. The isotropic line is drawn in figure. 7.c) where a splitting of 13 ppm between metallic and semiconducting response is predicted. The metallic line is found to be paramagnetically shifted. This splitting and the relative intensities of the line could be measured by high resolution NMR experiments. This theoretical prediction has been published [22].

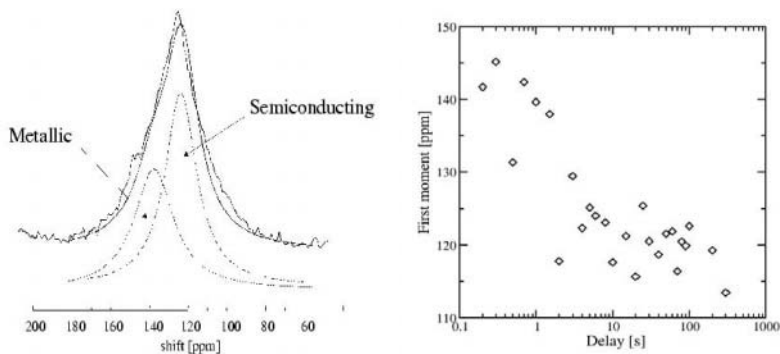


Figure 8: At left: measurement of the first moment of the static line during a saturation recovery experiment. At right: the 126 ppm isotropic line and its deconvolution with two Lorentzian lines attributed to metallic and semiconducting nanotubes in the sample. Taken from reference [25].

4.3. COMPARISON WITH EXPERIMENTAL DATA

Few papers on experimental ^{13}C NMR measures on single wall carbon nanotubes have been published since last years. In a pioneering paper [23], X.-P. Tang *et al.* have established that two populations of ^{13}C are present in a sample, by measuring their relaxation time T_1 . Indeed, two relaxation times have been estimated: one fast: $T_{1,f} = 5$ s, and one slow component : $T_{1,s} = 90$ s. The ratio is approximatively 40 % and 60 %, respectively. A similar behaviour have been confirmed later, by C. Goze Bac *et al.* who have also measured the isotropic line of the chemical shift tensor [24]. This MAS spectrum shows a unique line located at 126 ppm, which is common in sp^2 carbon materials. This spectrum is very broad since its width at half maximum is about 50 ppm., and was interpreted by authors as a distribution of isotropic lines, due to difference of nanotube diameters, presence of ferromagnetic catalysts in the sample, etc.

In order to evaluate the possible line splitting (between metallic and semiconducting nanotubes, as we predicted to be near 13 ppm), one can analyse the first moment (i.e. The mass center of the line) of the static spectrum, as the delay during a saturation recovery experiment. As plotted on figure 8, the large difference between the fast and the slow component of relaxation time implies a clear displacement of the first moment of the spectrum as function of the delay time: first moment is paramagnetically shifted for short delays. Since the ^{13}C nuclei located on metallic nanotubes are coupled with the conduction electrons reservoir, we can safely assume their relaxation time is the faster. In light of this analysis, a deconvolution of the isotropic line is done, using two Lorentzian lines with the relatives intensities found from T_1 relaxation measurements. This deconvolution leads to a splitting of 20 ppm, between metallic nanotubes (paramagnetically shifted) and semiconducting nanotubes (diamagnetically shifted) contributions, as shown in figure 8.

5. Conclusion

In spite of its simplifications (independent electrons, tabulated integrals between first neighbours only, etc.), we have shown that the tight-binding model is sufficiently accurate for studying the electronic properties of carbon nanotubes. With a Slater-Koster approach, the tight-binding band structure is in very good agreement with

experimental data, whereas in its simplest version, namely the Hückel model or zone folding technique, the TB model is not able to predict accurately the electronic structure near Fermi level. However, the position of the Van Hove singularities, probed by resonant Raman scattering measurements are correct. Above all, the ZF technique allows to understand easily the complex relations between electronic properties and the underlying structure.

In this lecture we have addressed the linear magnetic properties of carbon nanotubes, using a non-perturbative method of computation. Beyond calculating the field-dependant band structure only, we have tried to apply this approach to ^{13}C NMR chemical shift calculations. Assuming some approximations, this technique estimates successfully the relative positions of NMR spectra. However, in order to get the absolute chemical shift of carbon compound such as nanotubes, very efficient *ab initio* techniques of computations are now available [25], that is not possible (or difficult) in a TB scheme.

Finally, in this lecture, we have chosen to focus on the linear magnetic response in order to give an example of applications of the TB techniques. However, the tight-binding model is a very versatile technique, efficient to make predictions on many physical properties of carbon nanotubes: mechanical (elastic) properties and computation of the Young modulus [26], simulation of STM images and STS $I(V)$ characteristics [27], Landau levels [28] and (magneto)transport [29].

Acknowledgements

We would like to acknowledge Pr. Philippe Lambin, Pr Jacques Conard, Pr Patrick Bernier, Dr. Pierre Lauginie, Dr. Vincent Meunier and Dr. Stephan Roche for many stimulating discussions. This work benefits financial support from the European Community through its research training networks COMELCAN (HPRN-CT-2000-00128) and NANOPHASE (HPRN-CT-2000-00167), from the Spanish MCyT (MAT2001-0946) and from the Universidad del Pais Vasco (9/UPV 00206.215-13639/2001).

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NANOTUBE SPINTRONICS:MAGNETIC SYSTEMS BASED ON CARBON NANOTUBES

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Abstract.

The magnetic functionalization of carbon nanotubes or the incorporation of carbon nanotubes into magnetic systems opens up exciting research topics and technological applications. We describe recent results concerning the filling of carbon nanotubes with ferromagnetic materials. In addition, we discuss the aspects and experimental verification of spin-dependent transport phenomena through carbon nanotubes.

Keywords: Carbon nanotubes, nanomagnetism, spin-dependent transport

1. Introduction

Nanotubes represent a peculiar structural modification of Carbon and have been first observed as a residue in CVD processes [1]. A preparation of clean tubes by arc discharge techniques was first demonstrated by lijima *et al.* [2] in 1991. Their principal geometry can be imaged as a graphene sheet rolled up into a straight cylindrical tube which is closed on either end by a cap consisting of half a fullerene molecule. Such an object is called a *single-wall* carbon nanotube (SWNT). Several of these single-wall tubes may be grouped into bundles or ropes. Another geometrical form is the *multi-wall* carbon nanotube (MWNT) which can be regarded as a set of single-wall tubes with increasing diameter which have been coaxially stacked in a "russian-doll" manner. These multi-wall tubes may have inner and outer diameters of less than 10 nm and up to 100 nm, respectively. Their length may easily reach several micrometers. Just as the single-wall tubes, also the multi-wall tubes may form larger bundles or fibers. A recent review on the various aspects of carbon nanotube physics may be found, for example, in Ref. [3]. Carbon nanotubes exhibit a unique physical behavior in many respects. They have a high mechanical strength and belong to the most resilient materials known. Of particular interest are their electronic properties which are governed by the quasi 1-dimensional nature of the system and exhibit most pronounced quantum effects in single-wall tubes [4, 5]. Depending on the geometrical details of the rolling of the graphene sheet, the tube's transport behavior may be either semiconducting or metallic. As the electronic level

spacing is of the order of ~ 1 eV, single electron transport phenomena - for example, such as Coulomb blockade - may be clearly observed in SWNT [6]. Therefore, several applications in nanoelectronics have been suggested, ranging from carbon nanotubes as chip interconnects [7] to nanotube-based single-electron transistors (SET) [8].

A very important recent development in micro- and nanoelectronics is the explicit use of the electron charge *and* spin as control parameters in electrical transport processes. This led to the advent of a new research field called spintronics combining electronics and magnetism [9]. Spintronics has already brought about new electronic devices, such as versatile magnetoresistive sensors or magnetic random access memories (MRAMs) [10]. This situation raises the interesting question, whether and how molecular electronics can be augmented by an electron spin-based functionality. Carbon nanotubes may serve as a model system to explore the feasibility of future molecular spintronic device concepts. For this purpose, magnetic components and carbon nanotubes must be integrated in a system.

This integration can be achieved in two principal ways. First, the nanotubes themselves are magnetically functionalized by coating or filling them with a ferromagnetic material. In this way, one obtains magnetic quantum tubes or quantum wires which may have unique magnetic properties. The second approach concentrates on the electrical transport in carbon nanotubes, which may depend on the magnetic state of the contacting electrodes. In this contribution we will discuss both approaches and give some examples for the results.

2. Magnetic Functionalization of Carbon Nanotubes

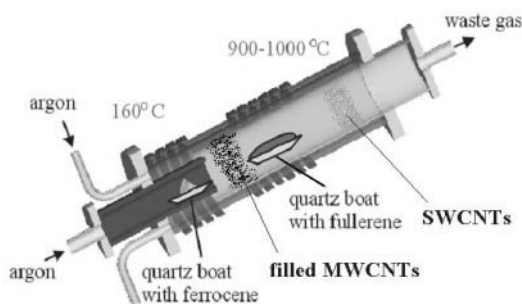
According to the present knowledge, carbon nanotubes do not have any intrinsic ferromagnetic properties at finite temperature. Therefore, a magnetic behavior of the tubular system can only be achieved by coating, intercalating, or filling the nanotube with a magnetic (mostly ferromagnetic) material. Among these different systems, the filled tubes represent the most interesting case when the high chemical reactivity of most ferromagnetic materials is considered. These tube systems may be seen as continuous or discontinuous magnetic quantum wires, encapsulated in a carbon shell, which prevents chemical reaction of the ferromagnetic core with the environment. Therefore, a long-term stability of the quantum wires can be expected which will facilitate the experiments and the handling of the samples. In the following, we will concentrate on the filling of MWCNT with the *3d* ferromagnets Fe, Co, and Ni.

2.1 FILLING CARBON NANOTUBES WITH Fe, Co, OR Ni

2.1.1 Fe-Filled Tubes. A preparation route to obtain MWCNT with a high yield employs chemical vapor deposition (CVD) techniques, in which a mixture of hydrocarbons (CH_4 , C_2H_2) transported by a carrier gas (usually Ar) reacts in the presence of a metal catalyst in the hot (~ 1000 °C) zone of the CVD reactor. The first successful filling of MWCNT with Fe has been reported by Rao *et al.* [11] and later confirmed by Grobert *et al.* [12]. In the latter approach, a mixture of ferrocene ($\text{Fe}(\text{C}_5\text{H}_5)_2$) and C_{60} was vaporized at high temperature and used as starting material in the CVD pyrolysis.

Preparation. In our experiments we modified the CVD process employed in Ref. [12]. Since the thermal decomposition of ferrocene (Fc) supplies both carbon and iron to the

reaction process, an additional carbon source such as C_{60} should not be necessary. In order to have a better control of the partial pressure of Fc, we utilized a two-stage furnace. In the first furnace stage, the Fc was sublimated at temperatures of about 160 °C and transported into the hot reaction zone by a controlled flow of Ar or an Ar/H₂ mixture (100 - 300 sccm) as carrier gas (see scheme in Fig. 2.1.1). At about 900 - 1100 °C the nanotubes are forming on the walls of the reaction chamber (quartz tube), or on substrates placed in the center of the reactor. The system is kept at these growth conditions for 30 - 60 minutes, after which the metallocene furnace is switched off and the high-temperature furnace is ramped down to room temperature within another 30 - 60 minutes while the flow of the carrier gas was maintained.



[Figure 1 Schematic configuration of the CVD setup used to grow metal-filled MWCNT.

Growth and structural results. The nanotubes grown onto the Si/SiO₂ substrate exhibit a distinct alignment perpendicular to the substrate surface (Fig. 2.1.1). Depending on the duration of the growth process, the tubes may reach an average length of 10 - 30 μm. Moreover, the nanotubes are found to grow preferentially on the SiO₂-covered areas of the substrate, rather than on the clean Si surface.

This finding may give some hints on the microscopic mechanisms affecting the nanotube growth process. It is commonly accepted now that the growth of both multi-walled and single-walled tubes is promoted by the presence of small metal particles, which act as a catalyst [13, 14, 15]. One of the growth mechanisms put forward for *individual* SWNT is the root growth model. This model assumes that carbon atoms are incorporated in the metal particle until a supersaturated state is reached. As a next step a fullerene-like cap is forming on the surface of the particle. If the particle is significantly larger than the diameter of this fullerene cap, the cap makes contact to the particle only at its edge. Additional carbon atoms are segregating to the particle surface and bonding to this edge, thereby effectively pushing the cap away from the particle and initiating the growth of a tubular structure. In the case of a multi-walled tube the process of cap formation must be repeated several times in order to achieve the coaxial stacking of the tubes. In general, the growth mechanism in multiwall tubes is still much less understood than in SWNT.

The root growth model also implies that the catalyst particles should have a certain critical size. On an inert surface, the particle formation is mainly governed by the surface diffusion of – in the present case – iron adatoms condensing on the SiO₂

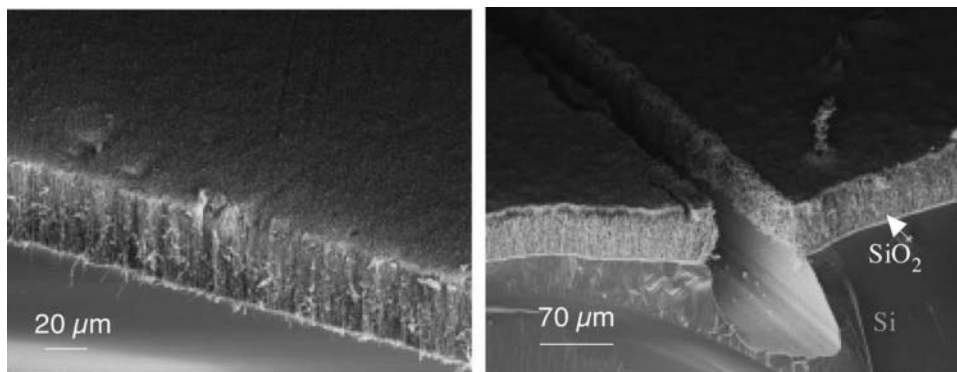


Figure 2. Left: Oriented growth of Fe-filled MWNT on Si/SiO₂ substrates. Right: Selectivity of the growth to oxide covered parts of the substrate. No visible growth of nanotubes takes place inside the groove in the center of the image where the oxide has been removed.

surface. On the Si areas, however, most of the Fe atoms migrate into the bulk material due to the high sample temperature and form a silicide. In this way the formation of catalyst particles of an appropriate size is suppressed, which may at least qualitatively interpret our observations. A similar argument may explain the growth of MWNT on particular regions of the reactor walls. Metallic catalyst particles of sufficient size – which depends on the temperature and surface condition – may form on certain areas of the quartz surface, thereby initiating the tube growth.

Although this root growth mechanism may describe the formation of empty single wall carbon nanotubes, one encounters conceptual difficulties when applying it to the case of filled and densely packed multi-wall tubes. As long as the tube is closed during growth not only the carbon shells, but also the material inside the tube must be delivered via the

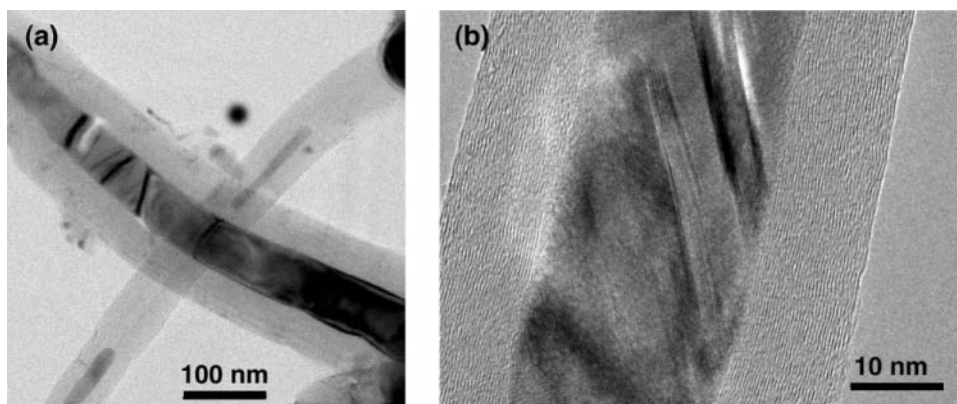


Figure 3. Transmission electron micrographs of Fe-filled MWNT. (a) A continuous filling is observed in thicker tubes, whereas in thin tubes a chain of discrete particles is forming. (b) High resolution studies show the well-ordered stacking of carbon shells bounding the magnetic nanowire.

catalyst particle. In other words, there should be a continuous flow of metallic material from the catalyst particle into the nanotube. In order to preserve the particle size the catalyst material must be replenished from the metal atoms condensing out of the gas phase on the substrate and migrating to the catalyst particle. This process requires an enormous mass transport through the catalyst particle. At the same time, the size of the catalyst particle must stay within certain limits to ensure a continuation of the nanotube growth. Particularly, if the tubes are gaining length and are densely packed as in our case of the oriented MWNT growth, atoms arriving from the gas phase at the surface are less and less likely to find their way down to the location of the catalyst particles. This should quickly lead to a self-limitation of the nanotube growth. Clearly, further studies are required to shed more light on the growth mechanism and the mass transport in the tubes.

In order to confirm the Fe filling of the tubes, individual tubes have been investigated by transmission electron microscopy (TEM). The high-resolution images reveal a cross-section of the coaxial stacking of the carbon shells and a darker area in the interior of the tubes (Fig. 2). As the metal filling has a higher electron density than the surrounding carbon material, it scatters the electron beam more efficiently, hence the lower intensity. In this area also stripe-like substructures can be discerned. These stripes are due to a crystallographic grain contrast, indicating that the metal core consists of an arrangement of monocrystalline grains. Subsequent TEM microdiffraction and global X-ray diffraction (XRD) studies indeed revealed a pronounced texture of the Fe filling. We also observe that the filling becomes more discontinuous and breaks up into a chain of individual particles, if the tube diameter is smaller. This may open up a way to study the magnetic behavior of both continuous and discontinuous nanowires.

Global and local EDX investigations of the oriented nanotube material confirm the filling with Fe (Fig. 3). The other features in the EDX spectrum arise from the nanotube (C)

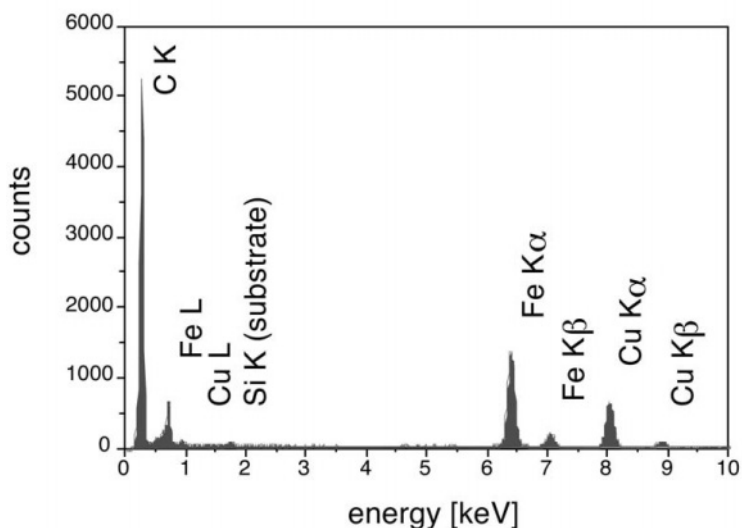


Figure 4 Local EDX spectrum of a cross section through an Fe-filled MWNT.

shells, the TEM grid supporting the sample (Cu), and spurious amounts of Si from the substrate. Still, the question remains whether the filling is predominantly iron or rather an iron-carbon compound. Some evidence for an at least locally pure iron filling comes from the microdiffraction results in TEM where selected grains exhibit a clear bcc structure with the iron lattice constant. Averaging XRD studies, however, find additional diffraction peaks related to the face-centered cubic (fcc) structural modification of iron, and a carbide Fe_3C . A careful analysis of the diffraction peak positions yields also more information about the texture. For the bcc crystallites it is the $[110]$ crystallographic axis, which preferentially points along the tube axis, whereas it is the $[111]$ axis for the fcc-type crystallites.

The content of these additional crystallographic and chemical phases varies strongly between individual samples and apparently depends critically on the preparation conditions, such as gas flow rate, temperatures, metallocene partial pressure, etc. It is also unclear where the individual phases are located in the tube. Recent Mössbauer studies on oriented nanotube samples also found indications of a coexistence of several phases at room temperature [16]. A comparison of transmission and conversion electron Mössbauer data suggests that the individual phases are not homogeneously distributed along the tube.

Magnetic Properties. The laterally averaged magnetic behavior of the samples has been measured by alternating gradient magnetometry (AGM). At room temperature we find pronounced hysteresis loops indicating a clear ferromagnetic response (Fig. 3). Considering the morphology of the oriented nanotubes shown in Fig. 2.1.1a, the metallic cores of neighboring tubes are separated by two carbon shells, i.e., the cores have a distance of 20 – 40 nm. Thus, a direct exchange coupling of neighboring nanowires should be weak and the magnetic coupling is probably dominated by long-ranged dipolar interactions. These are known, however, to stabilize a ferromagnetic behavior only at low temperatures. The presence of a ferromagnetic response at room temperature therefore indicates that the individual magnetic nanowires are ferromagnetically

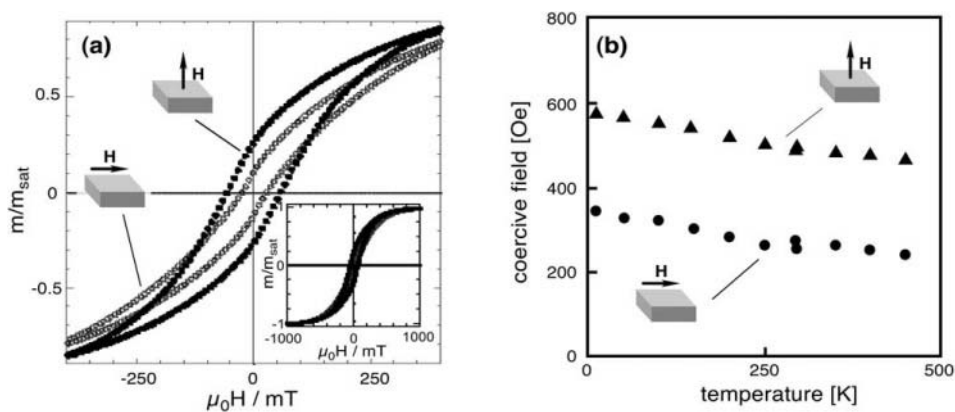


Figure 5. Magnetic properties of oriented Fe-filled MWNT. (a) Hysteresis loops measured parallel and perpendicular to the average nanotube axis, (b) temperature variation of the coercive fields in the easy and hard magnetization directions.

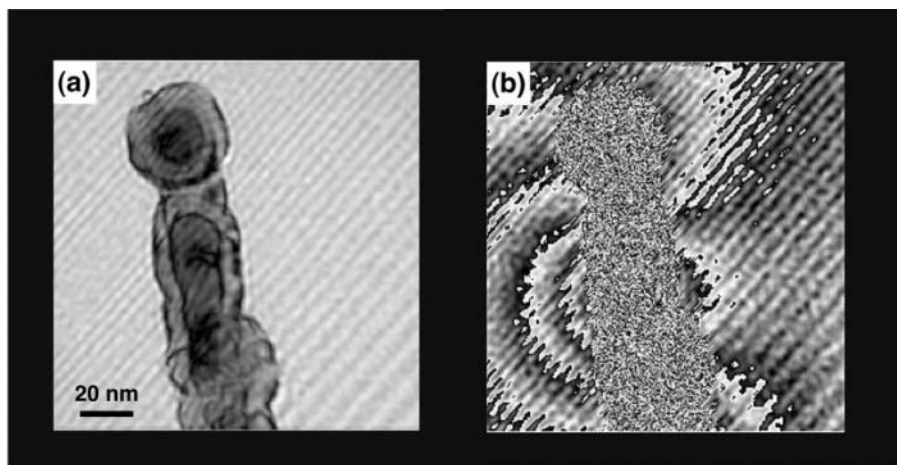


Figure 6. Electron holography on oriented Fe-filled MWNT. (a) Reconstructed intensity distribution showing the Fe particles as dark shades inside the tube, (b) reconstructed phase distribution outside the tube reflecting the distribution of the magnetic flux lines.

ordered. The experimentally measured signal must be interpreted as an average over nanowires of different diameter and length. It is interesting to note in this context that the superparamagnetic limit for bcc-iron particles is $d_{spm, 300\text{ K}} < 10\text{ nm}$ [17]. Magnetic nanowires with a few nanometers thickness and sufficient length can thus be expected to show ferromagnetism at room temperature.

Another important finding concerns the development of a magnetic anisotropy in oriented tube samples. The experiments reveal distinctly different magnetization loops, if the external field is applied parallel and perpendicular to the tube axis. The magnetic easy axis corresponds to the field direction along the tube axis. A more detailed analysis suggests that this easy axis is determined by the shape anisotropy of the wire geometry rather than magnetocrystalline contributions [18].

The temperature dependence of the coercive field H_C reveals a continuous increase towards low temperatures. A similar behavior is observed for the saturation magnetization M_S (not shown), with the increase of M_S between 300 K and 100 K being of the order of 10%. This increase is in part due to the size dependence of the magnetic ordering temperature. As a consequence, also smaller nanowires start to contribute to the ferromagnetic response at lower temperature and thus enhance the value of the saturation magnetization. It should also be pointed out that $H_C(T)$ does not exhibit any strong variations in the low temperature regime, in contrast to previous investigations [19]. These variations were attributed to an exchange coupling between the ferromagnetic bcc-Fe fractions and fcc-Fe fractions which are assuming an antiferromagnetic order at low temperatures. The coupling between ferro- and antiferromagnets leads to a unidirectional anisotropy – the exchange biasing – which affects the coercive field and shifts the magnetization loops on the magnetic field axis. The absence of this phenomenon in our samples suggests either a smaller abundance of fcc-Fe, a smaller particle size of the fcc-Fe fractions (with a smaller antiferromagnetic ordering temperature), or a spatial separation of the bcc- and fcc-Fe fractions.

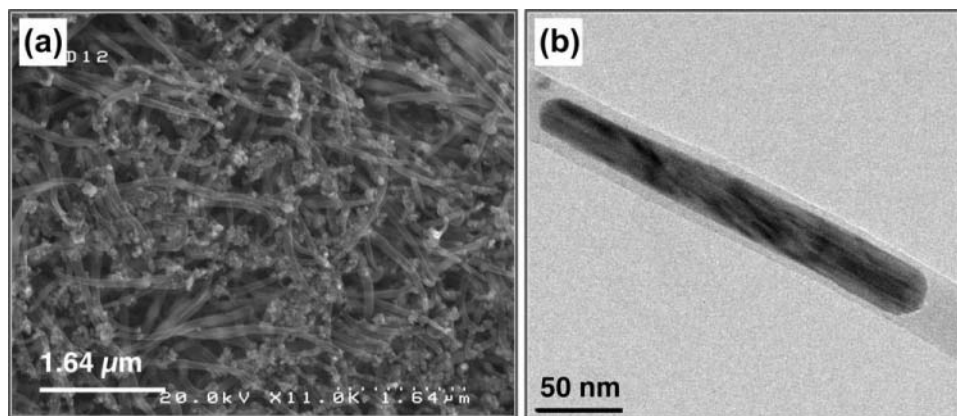


Figure 7. Co-filled MWNT. (a) Morphology of the material deposited on the wall of the reaction chamber, (b) TEM micrograph showing the Co nanowire inside the MWNT.

In order to obtain information about the magnetic behavior of individual quantum wires we have employed electron holography in a transmission electron microscope [20, 21]. In this interference-based approach the magnetic field distribution *outside* the nanowire can be imaged by analyzing the phase shift of the quantum mechanical wave function of electrons passing through different regions in the vicinity of the nanowire. This stray field information may be used to quantitatively reconstruct the magnetic domain pattern inside the nanowire. These experiments have been carried out at room temperature and one of the results is displayed in Fig. 5. It shows the magnetic flux line distribution in a system consisting of two Fe nanoparticles with a diameter of ~ 20 nm. The flux line pattern proves the ferromagnetic state of both particles, whereby the elongated particle in the center of the image behaves almost like a small dipole magnet. The second particle in the top part of the image is located in a section of the nanotube which points out of the image plane. Similar results have been obtained also on thinner nanowires with diameters of ~ 10 nm and less. If such a nanowire is discontinuous, i.e., consists of a chain of individual particles, we usually do not observe a magnetic flux pattern around all of them. This may be either due to some particles exceeding the superparamagnetic limit or a magnetic field orientation perpendicular to the imaging plane. These investigations demonstrate clearly that the magnetic state of individual nanowires can be accessed experimentally, at least on a qualitative level.

Currently, numerical simulations of the electron holography data are under way to arrive at a more quantitative interpretation of the phase distribution images.

A final important aspect with respect to technological applications is the long-term stability of the samples. We have therefore remeasured the magnetic properties of selected samples after several months and found no degradation within the experimental uncertainty. This proves that the carbon shells provide an effective protection against chemical reactions, for example, with oxygen.

2.1.2. Preparation. The preparation follows the same general procedure described in Sect. 2.1.1 by using Cobaltocene (Cc) as a starting material. The growth temperatures and gas flow were optimized. In an effort to promote the growth of oriented tubes, in some experiments also Fe-precovered oxidized Si wafers were employed as substrates.

Growth results. As in the growth of Fe-filled tubes we find MWNT growth on both the substrate and the reactor walls. These tubes and their fillings, however, are qualitatively quite different. The material deposited on the chamber walls forms a mat consisting of intertwined MWNT with outer diameters of 40 – 50 nm (Fig. 2.1.2a). The interior of these tubes is filled with Co nanowires of 10 – 30 nm thickness (Fig. 2.1.2b). Similar to the situation in the Fe filled tubes the Co nanowires are crystalline. However, the present structural data (XRD and local electron diffraction) seem to indicate that the crystal structure corresponds mainly to the *fcc* phase rather than the hexagonal phase which is the stable phase for Co at room temperature. Apparently, growing the Co nanowires in the tubes stabilizes the high temperature phase. The filling of the MWNT with Co is less regular as in the case of Fe and on average the Co nanowires are shorter. On the Fe-precovered substrate the growth proceeds again in an oriented manner perpendicular to the substrate surface. The tubes are found to be filled with magnetic material which, however, turns out to be an FeCo alloy rather than pure Co. The structural and magnetic results of these tubes are discussed in more detail below (Sect. 2.2).

2.1.3 Ni-Filled Tubes. The same preparation route as described above has also been employed with Nickelocene (Nc) as a precursor material. In this case, however, the quality of the MWNT grown on the reactor walls is rather poor. The tubes are rather short and quite irregular in diameter. The Ni filling factor is significantly smaller as in the Fe and Co filled tubes, and instead of elongated nanowires mostly chains of separated particles are formed inside the tubes. Variations of the growth temperature and/or partial pressures do not lead to a decisive improvement. These difficulties in obtaining well-defined Ni nanowires are consistent with the behavior observed in other laboratories [22].

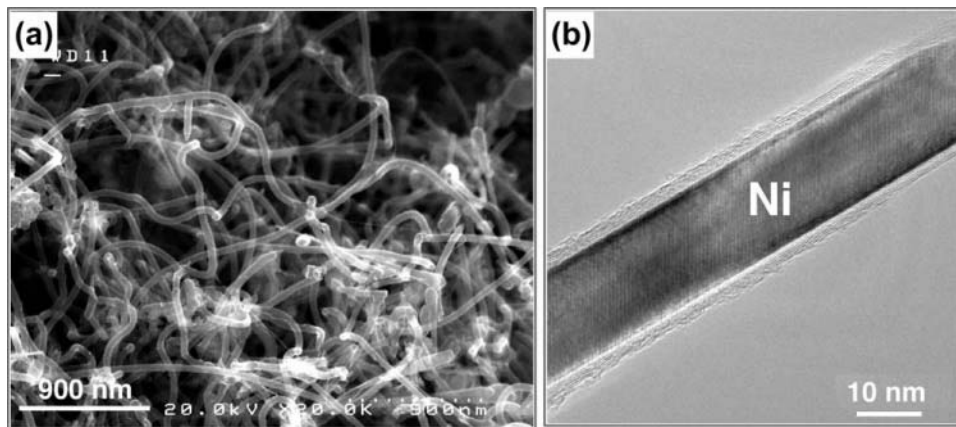


Figure 8. Ni-filled MWNT grown by catalytic decomposition of hydrocarbons over crystalline Ni particles, (a) Morphology of the material deposited on the particle surface, (b) TEM micrograph showing the Ni nanowire inside the MWNT.

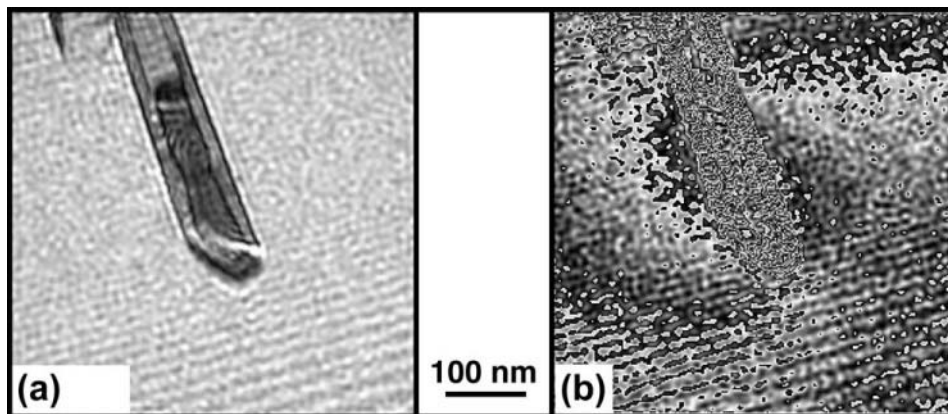


Figure 9. Electron holography from Ni-filled MWNT. (a) Intensity distribution showing the MWNT and metallic filling (darker contrast within the tube), (b) Reconstruction of the phase distribution mapping the magnetic flux line pattern.

For this reason we decided to pursue a different preparation route. It employs the catalytic decomposition of hydrocarbons at the surface of Ni catalyst particles. For this purpose, a boat with crystalline Ni particles was placed in the hot reaction zone and kept at a temperature between 700 and 1000 °C. The carbon for the reaction was provided by CH_4 or C_6H_6 passing over the Ni particles. The nanotubes grow directly on the Ni particles resulting in Ni filled MWNT with outer diameters of 20 – 40 nm. The diameter of the Ni nanowires is of the order of 10 – 20 nm. An example is shown in Fig. 2.1.3. The Ni nanowires are generally shorter than the Fe and Co nanowires described above. In contrast to the Fe and Co filled tubes the Ni filled MWNT exhibit a smaller number of carbon shells. Nevertheless, this is still sufficient to ensure a chemical stability. In passing we note that the findings in the Ni nanowire growth seem to be again in favor of the root growth model, because the Ni filling in the MWNT can only be supplied by the Ni particles.

The Ni filled tubes also show a ferromagnetic behavior which, however, is more difficult to prove. In global magnetometry measurements a contribution of the Ni seed particles cannot be excluded. Therefore, electron holography can give a more reliable information. In Fig. 8 we show the result of such an experiment for a relatively thick (~ 40 nm) and short nanowire. The phase reconstruction (Fig. 8b) reveals the presence of magnetic flux lines indicating a ferromagnetic order in the particle. In contrast to the results reported for the Fe filled tubes the density of fluxlines is smaller. This may be a consequence of the fact that the saturation magnetization of Ni is more than a factor 3 smaller than that of Fe. In addition, the Curie temperature of Ni is lower than that of Fe which increases the role of finite size effects on the long-range magnetic order.

2.2 FERROMAGNETIC ALLOY-FILLED CARBON NANOTUBES

In many applications in magnetism, binary and ternary compounds and alloys rather than elemental ferromagnets are employed. By means of the chemical composition the magnetic properties can be adjusted and optimized with respect to a specific application

field. For this reason, the filling of carbon nanotubes with – at least binary – magnetic compounds is of large interest. A first attempt was undertaken by N. Grobert *et al.* employing a specialized injection technique to mix ferro- and nickelocene in the CVD process [23]. As a result, they indeed obtained MWNT filled with an FeNi compound, the chemical composition of which was to be close to that of Invar. As the magnetic moment of Invar-like systems is very small, other magnetic compounds, for example, the FeCo alloy discussed below are more suitable for applications.

2.2.1 Growth and structural properties. As already mentioned above the pyrolysis of Cobaltocene on an Fe-precovered substrate results in the formation of oriented and filled MWNT. For these experiments, the thickness of the Fe precover layer was chosen somewhat larger, i.e., 10 nm. The TEM studies show the metal core to consist of crystalline grains just as in the cases described above. A close-up of the MWNT wall reveals the well-ordered stacking of the individual carbon shells (Fig. 2.2.1a). Compared to the Fe filled tubes, however, the number of carbon shells is lower.

The global EDX spectra indeed exhibit spectral signatures from *both* Fe and Co. Such an averaged signal may still stem from the remnants of the Fe catalyst layer and Co-filled nanotubes. Therefore, it is important to obtain an information on the local chemical composition of the tube filling which can be done by EDX in the transmission electron microscope. The local EDX spectrum corresponding to the tube section in the above image is displayed in Fig. 2.2.1. Also in this case we observe distinct signals from Fe and Co. This proves the filling to comprise an FeCo compound rather than pure Co. In the example depicted in Fig. 2.2.1 the composition can be estimated to about 50:50. The results of further systematic studies indicate, however, that the chemical composition of the tube filling may considerably vary along the substrate surface. For the following discussion we should point out that the above EDX results relate to a position close to the *tip* of a micrometer long tube. The finding of an FeCo compound inside the tubes raises interesting questions with respect to the growth mechanism. The Fe atoms in the tube can only originate from the Fe seed layer covering the substrate surface, whereas the Co is delivered from the gas phase. The growth temperature of 900 – 1000°C lies well below the melting points of either metals. If a similar root growth mechanism is held responsible for the formation of the alloy filled tubes, the Co atoms must be transported through the Fe catalyst particle during the growth. Alternatively, an FeCo catalyst particle is formed by incorporating Co from the gas phase, before the tube growth starts. However, both scenarios involve specific difficulties. In the first case, one should expect the tip of the tubes to contain an Fe-rich compound, as the Co atoms need to move into the catalyst or at least to the growth region where the tube makes contact to the catalyst particle. This may take place by diffusion along grain boundaries. This diffusion process is slow and sizable amounts of Co should not be expected to show up in the tube filling at the beginning of the growth, i.e., at the tube tip. If surface diffusion of Co atoms on the Fe catalyst particle is assumed, the situation may be improved. In the second case, the tube growth should exhibit a delayed onset until a FeCo catalyst particle of appropriate size and chemical composition is formed. As the growth of MWNT takes place on Fe catalyst particles also without Co, there is no reason for a delay in the presence of Co in the gas phase or on the surface. Thus, the second case is not very likely.

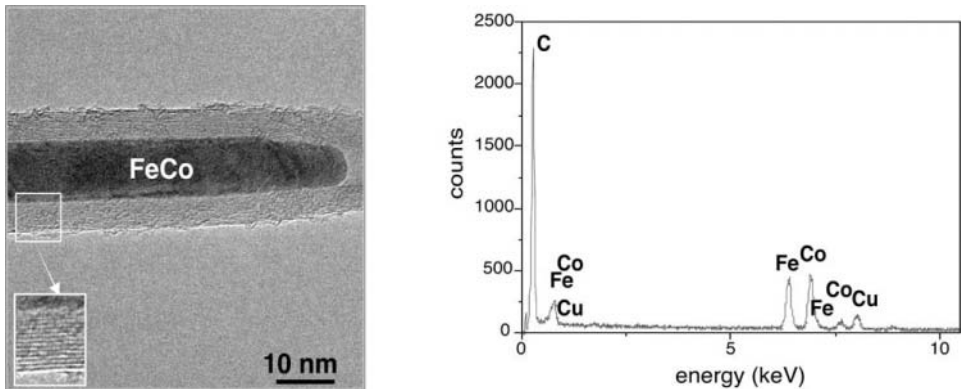


Figure 10. FeCo alloy filled MWNT. (a) TEM micrograph of the FeCo nanowire inside the MWNT. (b) EDX analysis of the nanotube filling showing clear Fe and Co signals.

In view of the conceptional difficulties encountered with the root growth model, it may be justified to consider other options. The presence of a high amount of Co in the tube tip and along the tube may indicate that Co atoms are implemented into the filling directly from the gas phase. In this case, however, the tube should be open and the mixing of the two elements

Fe and Co must take place via diffusion inside the tube. In particular, in long tubes this will lead to a sizable composition gradient along the tube axis. Clearly, further investigations of the chemical composition along the tube and the behavior of the catalyst particles will be needed to shed more light on the details of the growth mechanism of filled MWNT.

3. Spin Dependent Charge Transport Through Carbon Nanotubes

In the previous section we have dealt with the magnetic properties of functionalized (filled) carbon nanotubes. The magnetism of the metallic nanowires inside the MWNT relates to the interaction of magnetic moments which in turn are created by an imbalance of the spin-up and spin-down electron density of states at the Fermi level of the metal. The quantum mechanical origin for this behavior is the combination of a strong electronic correlation and the Pauli principle. The formation of a ferromagnetically ordered ground state has a further consequence. The charge carriers (electrons) in the vicinity of the Fermi level have a nonzero spin polarization. This property has an enormous impact on the electrical transport behavior in a magnetic material or in complex magnetic/nonmagnetic structures and is widely exploited in the field of spintronics [24, 25].

Also in carbon nanotubes the electrical transport is found to be a fascinating issue. This is due to the quasi one-dimensional nature of the electronic structure of the tubes which gives rise to peculiar quantum phenomena. From a theory point of view the electrons in a one-dimensional system are highly correlated, because the Coulomb interaction cannot be efficiently screened. Therefore, the electronic properties have to be treated in a Luttinger rather than a Fermi liquid picture. This has a considerable impact on the electrical transport properties and has led to the consideration of carbon nanotubes as prototype ballistic quantum wires. This situation holds strictly only for single-wall tubes. Pioneering experiments revealed, however, that the intershell coupling is weak and the current path through a multi-wall tube is largely confined to the outermost shell [26, 27]. Thus, Luttinger liquid-like features may be expected to show up in MWNT, too. In fact, large coherence lengths have already been observed in MWNT [28, 29].

3.1 SAMPLE PREPARATION AND CHARACTERIZATION

For the transport experiments we used MWNT prepared by the arc discharge method. These tubes can be grown without the help of metallic catalyst particles the presence of which may be detrimental for spin-dependent transport effects. The tubes were sonicated in ethanol and a drop of the resulting solution was left to dry on the oxidized surface (oxide thickness about 1 μm) of a Si wafer. Prior to the nanotube deposition, the wafer was provided with contact pads and positioning marks fabricated by optical lithography, thin film deposition, and lift-off procedures. The nanotube sample was then

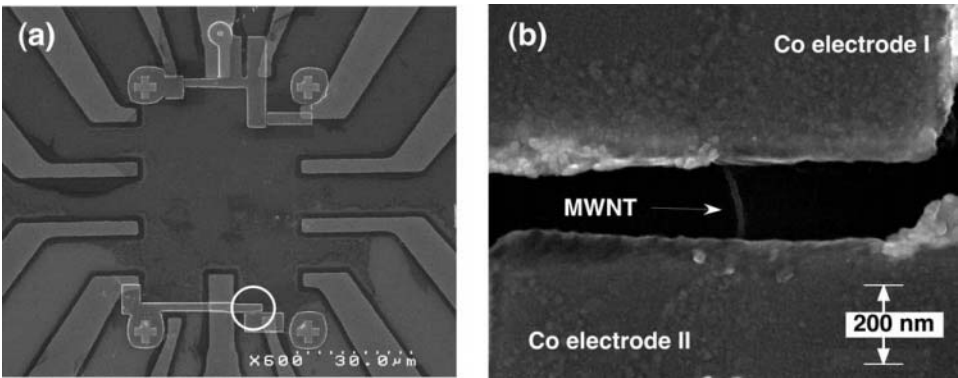


Figure 11. Multi-walled carbon nanotube between ferromagnetic (Co) contact pads. (a) SEM micrograph showing the contact layout and the position of the nanotube (ring), (b) High resolution SEM micrograph of the MWNT-electrode region.

inspected by scanning electron microscopy and the location of suitable tubes was recorded with respect to the positioning marks. The sample was then coated by resist and contact lines between the selected tubes and the contact pads were defined by electron beam lithography. In order not to damage the tubes during the localization and lithography procedure, the microscopy was operated with a rather low beam energy (5 keV). After development of the resist, we deposited a 50 nm thick Co film. After a subsequent lift-off

procedure the nanotube was finally contacted by magnetic electrodes in a 2-point measuring geometry. The sample was then placed in a chip carrier and mounted into a helium mixing cryostat for transport and magnetotransport measurements. After finishing the transport studies, some of the samples were also investigated by atomic force microscopy to determine their morphology.

The final configuration of the samples including the contact pads is shown in Fig. 3.1 [30]. The high-resolution SEM micrograph of the tube-contact region reveals only a weak contrast from the nanotube itself, but clearly shows that it is buried on both ends under the Co electrodes. The MWNT has a diameter of about 40 nm and the distance between the electrodes has been set to about 250 – 300 nm.

The morphology as addressed by AFM confirms this interpretation (Fig. 11). Because of the size of the AFM tip and the depth of the trench between the electrodes, however, the electrode separation appears smaller than in the SEM results. The AFM studies also give some information of the grain size of the electrode material which is found to be of the order of 10 nm, i.e., smaller than the nanotube diameter. As a consequence, the nanotube is probably not contacted by a "homogeneous" electrode, but rather by individual Co grains. This aspect will become important when discussing the magnetic behavior of the system.

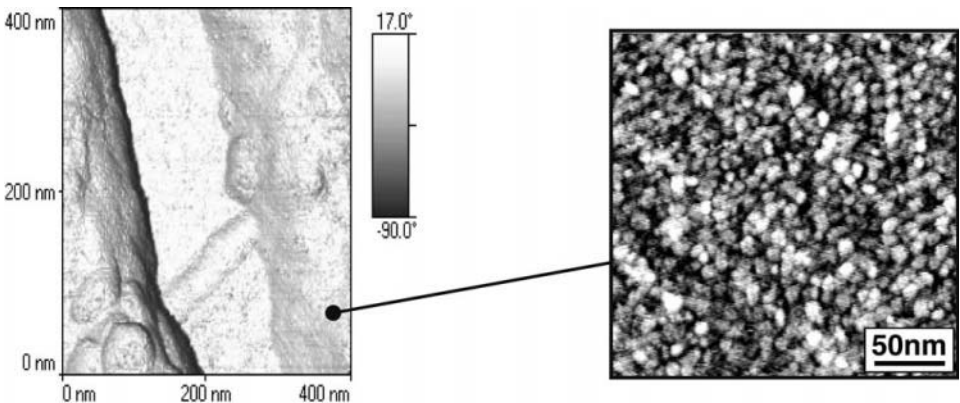


Figure 12. AFM analysis of the contacted MWNT. (Left) Height image of the contact area (compare Fig. 3.1a). (Right) Morphology and grain structure of the Co contact electrodes in the vicinity of the tube.

3.2. SPIN-DEPENDENT TRANSPORT IN MULTIWALLED NANOTUBES

3.2.1 Current-voltage characteristics. The first electrical characterization of the samples comprised a conductivity measurement (I/U curve) at room temperature. In all cases we found an Ohmic behavior (linear I/U variation) with total resistances ranging between 200 k Ω and several M Ω for different samples. Considering the fact that the quantum resistance of the nanotube itself should be around $R_0 = h/(4e^2)$ (about 9 k Ω), this result already indicates that our samples have low-transparency electrodes which will dominate the transport processes. The reason for the high contact resistances still needs to be clarified. From the results obtained at low temperature, however, we have strong indications for the presence of a tunneling barrier between the magnetic electrodes and

the nanotube. Our samples should thus be regarded as a serial circuit of two tunneling contacts connected by a nanotube conduction line. The tunneling barrier may be formed, for example, by oxidized fractions of the metal electrode (as the contacts have been microstructured and handled under ambient conditions) or a contamination layer on the outer nanotube surface. In any case, the result already points out the necessity to better characterize the MWNT-electrode interface in order to arrive at a refined understanding of the transport phenomena.

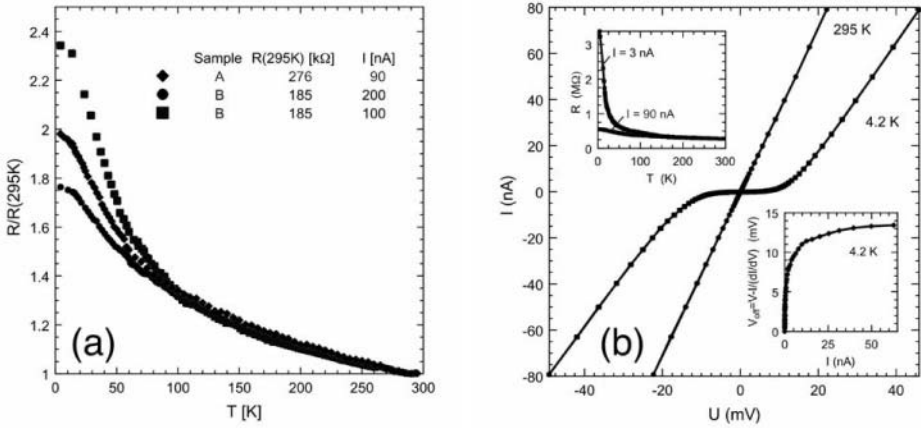


Figure 13. (a) Resistivity change of several Co-contacted MWNT samples with temperature, (b) I/U characteristics for a Co-contacted MWNT revealing an Ohmic behavior at 300 K and a zero-bias anomaly at 4.2 K.

3.2.2 Temperature behavior. Upon cooling the sample down to liquid helium temperature, the resistance increases continuously by about a factor of 2 – 2.5 depending on the actual sample (Fig. 3.2.2). More importantly, the I/U characteristics develops a pronounced non-linearity with an extended regime of suppressed conductivity at low bias voltages (zero bias anomaly).

This nonlinearity is similar to the one observed in the case of a Coulomb blockade behavior. In fact, a Coulomb blockade is often found in transport experiments with single wall tubes [6]. If we adopt this picture for the moment, the charging energy which can be determined for this case amounts to about $E_C \sim 14$ meV (inset Fig. 3.2.2). However, an unambiguous proof for a Coulomb blockade mechanism can only be derived from gate voltage variations, which should give rise to a characteristic oscillation pattern. These data are not yet available. We should point out that phenomena other than the single electron tunneling based Coulomb blockade, such as weak localization or environmental Coulomb blockade, can give rise to a suppressed conductivity at low temperature.

We already note that the electric transport properties of our Co-MWNT contacts exhibit several similarities to the results obtained from planar magnetic tunneling junctions.

3.2.3 Magnetically induced switching. According to the experiences with magnetic tunneling contacts, the regime of the zero bias anomaly should be a good candidate for observing spin dependent transport phenomena. By sweeping the magnetic field we indeed observe pronounced changes of the resistivity which have a hysteretic switching character (Fig. 3.2.3a). Moreover, we note that the switching fields for positive and negative magnetic field directions are distinctly different. In positive field direction the high resistivity state is only accessible in a very narrow field regime below 50 mT, whereas at negative field direction it can be observed almost up to -400 mT. The absolute magnitude of the resistivity change differs for the opposite magnetic field directions, but also varies strongly with the bias voltage (current). These findings clearly prove that the system exhibits a magnetoresistance, the origin of which, however, still needs to be clarified. They confirm the results of the pioneering experiments by Tsukagoshi *et al.* who found magnetic field induced resistivity changes of about 9% [31].

In a first approach, we may try to interpret the above results in analogy to spin dependent transport phenomena, such as giant (GMR) or tunneling magnetoresistance (TMR). The Co contacts may be regarded as spin-polarized electrodes, one of which acts as a *spin polarizer* and injects spin polarized charge carriers into the carbon nanotube. The other electrode takes the function of a *spin analyzer*. As long as the magnetization in both electrodes (M_1 and M_2) is pointing into the same direction, the quantization axis for the charge carriers is the same. Thus, the electrons can enter the second electrode almost without suffering spin dependent scattering, because there are sufficient empty states of the appropriate spin character available. This situation corresponds to the state of low resistivity found at sufficiently high magnetic fields, where the magnetization is forced along the same direction.

The scenario changes markedly if the magnetization of one of the electrodes is reversed, i.e., in the simplest case M_1 is aligned antiparallel to M_2 . With the magnetization direction also the spin quantization axis is reversed which has fundamental consequences for the charge transport. The electrons arriving at the spin analyzer now find only a few empty states of the right spin character. As a consequence, a strong spin dependent scattering of the charge carriers takes place, thereby increasing the resistivity. In order to be able to realize this high-resistivity state, the ferromagnetic electrodes must obviously be reversing their magnetization at different magnetic field strengths, i.e., their coercive fields must be distinctly different. This can be achieved by choosing either different magnetic materials or giving the electrode different shapes.

This behavior can be understood by taking into account the phenomenon of *exchange biasing*. Phenomenologically, exchange biasing acts as a unidirectional magnetic

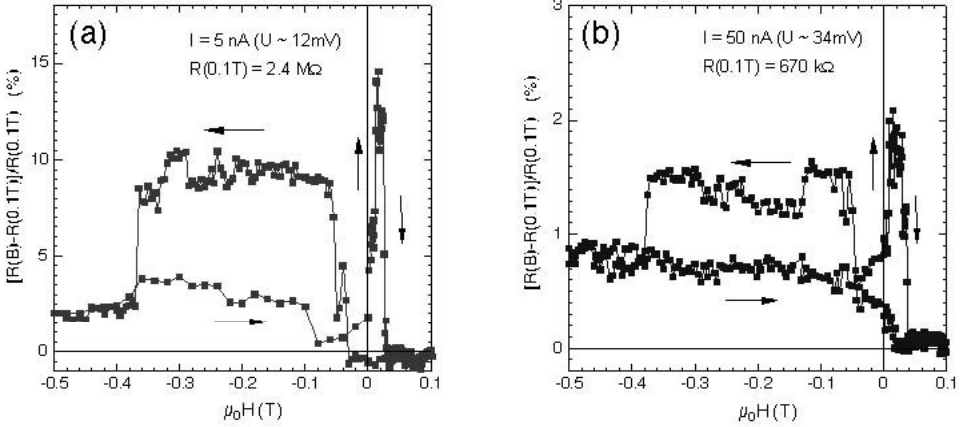


Figure 14 (a) Magnetic field induced resistivity change of a Co-contacted MWNT in the zero bias anomaly regime exhibiting a hysteretic behavior, (b) Same as (a), but at higher bias voltage.

Following the above arguments, one expects the $\Delta R(H)/R$ characteristics to exhibit a high-resistivity state which is symmetric with respect to the zero field condition, i.e., occurs at the same absolute values of the magnetic field for both field directions. The data in (Fig. 3.2.3a), however, exhibit an asymmetric magnetic field dependence. anisotropy and effectively causes a shift (exchange bias) of the magnetization loops with respect to the external magnetic field. As a consequence, the magnetization reversal takes place at different absolute values of the magnetic field for opposite field sweep directions. This is basically consistent with our observations above. The microscopic origin of exchange biasing is related to the exchange coupling between a ferro- and an antiferromagnet. The orientation of the magnetic moments in the antiferromagnet cannot be changed in moderate external fields. If the magnetic moments in the ferromagnet are coupled strongly enough ("pinned") to the moments of the antiferromagnet, the magnetization reversal of the ferromagnet is blocked.

3.2.4 Bias voltage dependence. Further insight into the microscopic mechanisms governing the spin dependent transport behavior can be obtained from the bias voltage dependence of the resistivity change. As was already shown in (Fig. 3.2.3) the magnetoresistance signal increases with decreasing bias voltage. In Fig. 3.2.4a the magnetoresistance data of this particular sample are plotted as a function of bias current (or bias voltage) for both directions of the magnetic field. At a low bias current of $I = 1$ nA a peak value of the magnetoresistance of $\Delta R/R \sim 30\%$ is obtained for the positive magnetic field direction.

The data in Fig. 3.2.4b were obtained from a similar nanotube system and display the magnetoresistance as a function of bias voltage. This sample showed peak values for the magnetoresistance of close to $\Delta R/R \sim 50\%$, when the bias voltage was reduced to $U = 5$ mV. The magnetoresistance of this sample essentially disappeared for bias voltages larger than 30 mV.

These results from Co-MWNT contacts exhibit a striking similarity to the observations of planar tunneling contacts (magnetic tunnel junctions, MTJ). The strong temperature

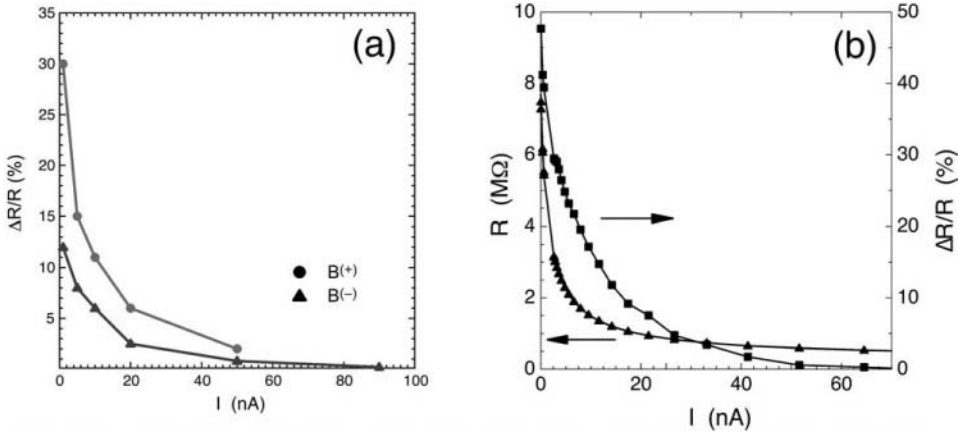


Figure 15. (a) Magnetoresistance $\Delta R/R$ of a Co-contacted MWNT system as a function of bias current. (b) Resistivity and magnetoresistance $\Delta R/R$ for a similar sample reaching maximum values of $\Delta R/R \sim 50\%$. All measurements have been performed at $T = 4.2$ K. Taken from ref. [30]

dependence is characteristic for MTJ with a tunneling barrier containing a large amount of defects. At elevated temperatures, the scattering at the defects becomes more prominent and destroys the spin coherence in the tunneling process. A similar mechanism is discussed in context with the bias voltage dependence. At higher bias voltages the energetic electrons are proposed to excite spin waves which in turn reduce the magnetic order and the spin coherence.

3.2.5 Role of the interfaces. In all of the examples discussed above, we have observe a "positive" magnetoresistance, i.e., the device resistivity is lower for a parallel magnetic alignment of the two Co electrodes. Some of the devices, however, exhibited the opposite behavior. In these cases, the resistance was high for a parallel alignment and dropped when the magnetization of one of the electrodes was switched in the opposite direction. In Fig. 3.2.5 we give an example of this "negative" magnetoresistance. First of all, we note that the geometrical parameters of the sample (tube diameter, gap width, etc.) were in the same range as those of the other sample studied. Nevertheless, the nonlinearity of the I/U -curve and the zero bias anomaly are much less pronounced, as can be seen by a direct comparison to the I/U -characteristics reproduced from Fig. 3.2.2 (broken line). Assuming a Coulomb blockade behavior the respective charging energy would take a value of $E_C \sim 4$ meV, i.e., significantly larger than the result extracted from Fig. 3.2.2.

A transition to negative magnetoresistance as a function of bias voltage is also already known from planar MTJs [33, 34]. It is tentatively related to the details of the electronic states participating in the tunneling process. These details are determined by the specific electronic configuration at the interface and the hybridization of spin-polarized electronic states of the various materials constituting the two electrode-barrier interfaces.

As a difference to the planar MTJs, however, we observe only a change in magnitude of the magnetoresistance signal, but not a change in sign as a function of bias voltage in our

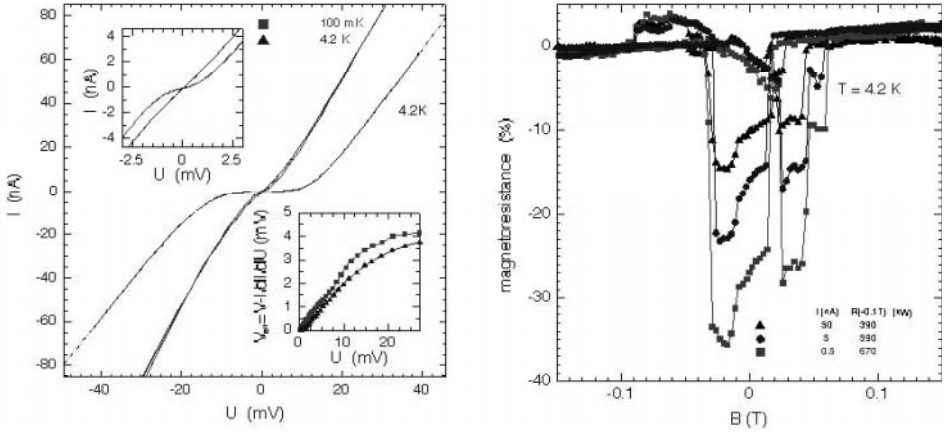


Figure 16. (a) Resistivity characteristics (I/U curve) of a device with negative magnetoresistance behavior for 4.2 K and 50 mK sample temperature. The insets give a blow-up of the zero bias anomaly region (top) and the determination of the charging energy in a Coulomb blockade model, (b) Magnetoresistance $\Delta R/R$ at 4.2 K for different sample bias voltages.

nanotube contacts. In addition, we note the presence of characteristic steps in the $\Delta R(H)/R$ dependence, the position of which does not significantly change with the bias voltage. These steps may be possibly caused by a sequential magnetic switching of different parts of the magnetic electrodes. These findings point out the necessity to characterize the electronic states and the magnetic switching behavior in these magnetic nanotube contacts on a very small lateral length scale.

4. Summary

The results discussed in this contribution show clearly that the combination of carbon nanotubes with magnetic systems gives rise to novel physical phenomena, such as the spin-dependent transport through carbon nanotubes. These nanotube-based devices are on the borderline of molecular electronics and may help to access a completely new field, namely molecular spintronics.

The filling of carbon nanotubes with ferromagnetic materials results first of all in magnetic quantum wires which are interesting entities in itself. The aspects of quasi 1D magnetism are just about to become a hot topic. On the other hand, these encapsulated nanowires may have immediate applications, such as tips for magnetic force microscopy or spin-dependent tunneling microscopy.

Acknowledgments

The authors wish to thank Mrs. B. Eichler, Mrs. D. Schüller, and Ms. Sieber for their expert technical support. Financial support by the Deutsche Forschungsgemeinschaft through grant Fi-439/10 is gratefully acknowledged.

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SPIN COHERENCE AND MANIPULATION IN SI/SiGe QUANTUM WELLS.

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Abstract

In this contribution we address two key problems in the realization of spintronics devices and spin-based quantum computers using low dimensional semiconductor structures: (i) the spin coherence time must be by orders of magnitude longer than the time required for spin manipulation, and (ii) individual q-bits (spins) should be selectable for manipulation, *e.g.* by application of a gate voltage. We demonstrate that Si-Ge structures are good candidates for that. Based on spin resonance experiments on two-dimensional (2D) conduction electrons in a single, modulation doped SiGe/Si/SiGe quantum well structure we show that the spin coherence is limited by the D'yakonov-Perel (DP) spin relaxation mechanism caused by the Bychkov-Rashba (BR)- spin orbit field. The latter is a consequence of the electric field that results from the one-sided doping. We find spin relaxation times of the order of microseconds and a 2D anisotropy of the line broadening (dephasing time), the longitudinal spin relaxation time and of the g-factor. Both the absolute values and their anisotropy depend also on the carrier density, as expected for the DP-BR mechanisms. For perpendicular orientation of the applied field, where the cyclotron frequency is high, both components of spin relaxation are strongly suppressed if the mobility is high. We also find a strong dependence of the g-factor on carrier density and on the Ge content. These effects allow direct selection of individual spins.

1. Introduction

So far, electronic devices for logic applications rely on the displacement of electrons in a semiconductor structure that provides two stable states. Switching between these states is accompanied by electric currents and thus it is dissipative. In addition, the displacement occurs at finite velocity and thus it takes time. In the past 50 years, transistor dimensions were reduced from millimeters to several 10 nanometers. Obviously this miniaturization improves the device performance both with respect to speed and heating. This, together with the integration of more and more devices, enabled the enormous progress in microelectronics. Naturally this progress will be limited by different basic physical phenomena: eventually, *e.g.*, when only a small number of electrons is confined to a volume with dimensions comparable to the de-Broglie wavelength of the electrons quantum effects will

occur that will change the device function drastically. In addition, statistical effects due to thermodynamics will cause noise and errors.

Therefore alternative approaches are discussed recently. In particular, some concepts invoke the spin of an electron and thus its magnetic moment instead of its charge [1, 2, 3]. In an $s=1/2$ state, the electron has two possible spin orientations which might serve as binary unit in some logic device. A number of advantages may be envisioned of such a device:

- the electron does not have to be moved macroscopic distances. Therefore the device could be small, simple, and switching could be almost free of dissipation;
- Spin-flip processes can be very fast;
- Some spin states can be long-living so that they might keep the stored information even without external supply of power;
- Combination with magnetic types of data storage can be envisioned;
- In the extreme case of only a few interacting spins with adjustable initial state “quantum computation” making use of spin interaction is discussed.² The inherent parallelism in quantum computing may allow unprecedented speed in solving particular mathematical tasks.²

Most concepts in this field, which became popular under the name *spintronics*, are still rather speculative, especially since it turns out that many of the relevant properties of spins in some host material are not (well enough) known. In particular, spin relaxation will be of crucial importance for any spintronic device. Obviously, spin lifetimes must be much longer than the time required to manipulate a spin.

In this paper, we review our work on spin manipulation and relaxation in low dimensional structures composed of silicon and Si-Ge alloys. It is well known for a long time that donor states in Si can have exceptionally long spin relaxation times of up to milliseconds [4]. Even free electrons are expected to have much longer relaxation times than *e.g.* in III-V compounds since the spin-orbit (S-O) interaction in Si is smaller by 3..4 orders of magnitude [5, 6]. Spin-orbit interaction appears in a variety of spin relaxation processes, involving coupling to lattice vibrations or zero field spin splitting which occurs in structures with lowered symmetry. Other processes, like relaxation via (i) paramagnetic centers or (ii) nuclear spins (hyperfine interaction) are small in Si because of (i) its purity, particularly when grown by state-of-the-art epitaxy, and (ii) the low abundance of ²⁹Si (4.7%), the only isotope with nuclear spin (1/2).

Nevertheless, the overwhelming number of papers published recently on spin properties concerns III-V compounds and the main experimental techniques applied involve optical spectroscopy [7]. Si, due to its indirect gap, the less favorable spectral range and longer time scales as compared to GaAs, has not been investigated by these techniques. In contrast, owing to the long spin lifetimes in Si and the resulting narrow line width, Si can be investigated by means of electron spin resonance (ESR) techniques [8, 9, 10, 11] which yield precise and direct information on spin properties.

We show that ESR can be used to investigate spin properties, like the longitudinal and the transverse spin relaxation rates, or the g-factor, and to manipulate spins. In addition, in the case of two-dimensional quantum wells, cyclotron resonance is also seen in ESR experiments, thus allowing to investigate also momentum scattering and to investigate the relation between the spin- and momentum relaxation. We find evidence (i) that the dominant decoherence process is ruled by a k-linear term in the spin Hamiltonian – most

likely the Bychkov-Rashba (BR) term [12] due to structure inversion asymmetry (SIA) - and (ii) that for high mobility the cyclotron motion causes an additional modulation of this type of spin orbit coupling which leads to an effective reduction of the spin relaxation. The fast modulation corresponds to a more effective motional narrowing, and, consequently, to an additional reduction of the linewidth by a factor $(1 + \omega_c^2 \tau_k^2)^{-1}$. Avoiding the BR field, we estimate a possible spin coherence time of up to 30 μ s, three orders of magnitude longer than the time required for inverting a spin by a microwave pulse.

The observed dependence of the g-factor on carrier density shows that it can be influenced by external fields [10, 13]. This variation is a consequence of both the BR field and of an isotropic term that appears also in bulk material.

2. Experimental

Quantum wells can be created in the conduction band of strained Si layers embedded between SiGe layers serving as barriers. Strained Si layers are obtained by pseudomorphic growth in molecular beam epitaxy on graded thick, relaxed SiGe buffer layers that reach a Ge content of typically 25% at the interface. A Si layer of 10-15 nm thickness grown on top of the (100) buffer is under tensile strain. The strain causes also a splitting of the six equivalent conduction band minima: the two ellipsoids oriented perpendicular to the sample surface are lower in energy than the four in-plane ellipsoids – only the former will be populated. Layers of that thickness exhibit already quantization in growth direction and therefore the constant energy contours are circles in the growth plane: the effective mass becomes isotropic and its value essentially corresponds to the value of the transverse mass of 3d Si. Owing to the lower effective mass and the accommodation of the donors in the subsequently grown top barrier at a distance of again 10-12 nm ionized impurity scattering is hardly effective and the mobility can be very high: at low temperatures values higher than 350.000 cm^2/Vs are achieved.

On such samples, conduction electron spin resonance (CESR) can be observed in conventional ESR spectrometers where the microwave absorption is obtained via the reflected signal of a critically tuned resonator that contains the sample. We used a standard rectangular TE102 cavity with a resonance frequency close to 9.4 GHz. The sample is placed in the center close to the nodal plane of the electric field where the magnetic field is maximum. The sample is placed in an

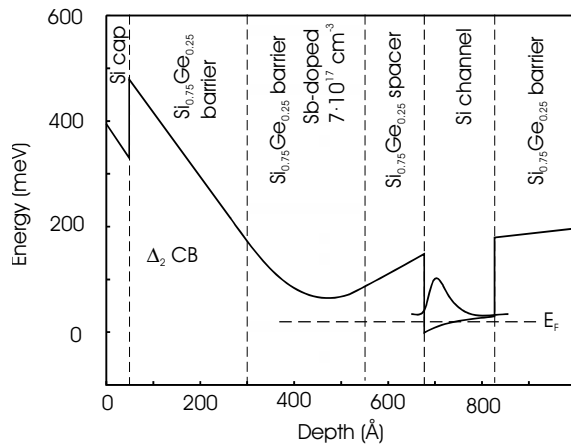


Figure.1: Sample structure and resulting conduction band edge.

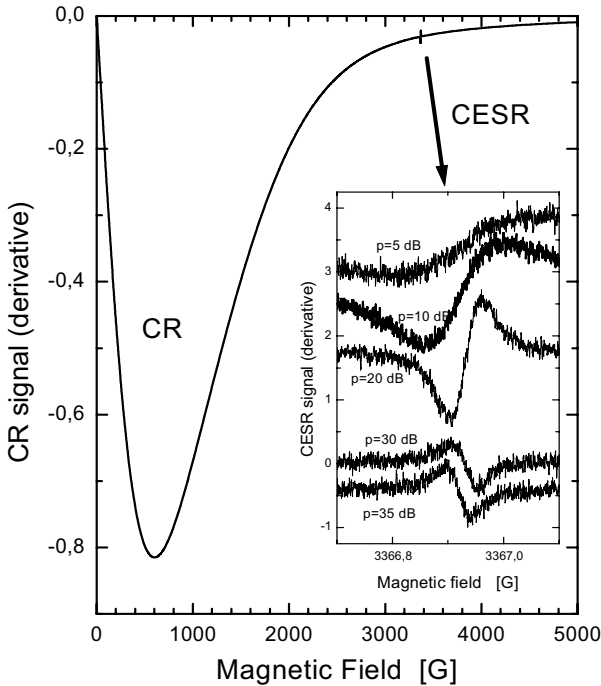


Figure 2: Cyclotron resonance (CR) and conduction electron spin resonance (CESR) of a Si quantum well. The inset shows the power dependence of the CESR signal which changes sign due to the admixture of the polarization signal.

ing to the characteristics of this signal we can attribute it to the cyclotron resonance (CR) of the sample. This signal can be used to evaluate two quantities: (i) the carrier density from the integral absorption and (ii) the momentum scattering time of the electrons in the quantum well from the line width – or actually by fitting the Drude model to the observed spectra.

The narrow signal is identified as CESR in terms of its Pauli type of susceptibility, its persistent character and its two-dimensional symmetry. Three types of CESR related signals are observed:

- the absorption signal that varies with the square root of the microwave power, $p^{1/2}$, at least well below the saturation regime;
- a signal related to a spin-polarization-induced change in the electrical conductivity, which is expected and observed to vary $\propto p^{3/2}$;
- an additional “dispersion” signal which is caused by the automatic frequency control of the standard ESR apparatus. This AFC is used to rule out contributions due to the real part of the magnetic susceptibility: as the magnetic field is swept across

intra-cavity glass-cryostat that allows cooling to 1.9 K.

In this type of measurement, the extremely narrow CESR signal (down to 3 μ T) is superimposed on a very broad background (linewidth of 0.1 T and more) whose width stretches as the static magnetic field is inclined from vertical to in-plane orientation: this signal depends only on the perpendicular field component and its strength increases with increasing carrier density. The latter can be adjusted making use of persistent photo-conductivity of moderately doped samples or by a Schottky gate contact (e.g. a Pd layer evaporated to the sample surface). Ow-

resonance, the microwave frequency is adjusted such that the signal remains in phase. Here this frequency change causes an extra signal due to the frequency dependent conductivity of the sample.

As an alternative method of detection, the conductivity of the sample can be used which is based on the same mechanism that causes the polarization signal [9]. This “electrically detected electron spin resonance” may eliminate the problem of deconvoluting the microwave signal into its three components which requires modeling. On the other hand, for a quantitative evaluation it would require a model for the influence of spin polarization on the conductivity which is not established yet.

The deconvolution of the 3 signals and their shapes and power dependences are indicated in Fig. 3a. The deconvolution is rather tedious as it requires a number of parameters that should be fitted consistently. Here we are interested only in the g-factor and the linewidth as a function of the microwave power. The latter dependence gives the saturation behavior which yields the spin lattice relaxation rate, and at low power the effective transverse spin-spin relaxation rate, $(T_2^*)^{-1}$. After some experience with modeling the three contributions, the line width can be evaluated quite accurately also directly from the asymmetrical line shape and the same holds for the g-factor. An example for the linewidth dependence on

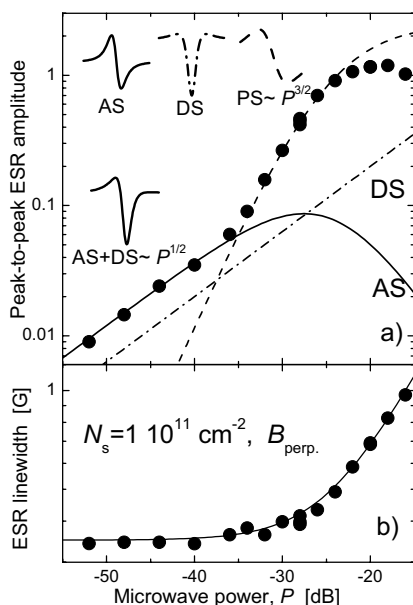


Figure. 3. a) ESR amplitude as a function of microwave power. Examples are given for line shapes with dominating absorption signal (AS), dispersion signal (DS) and polarization signal (PS) and their expected power dependences are given. 3b) ESR linewidth as a function of microwave power. (After Ref.12)

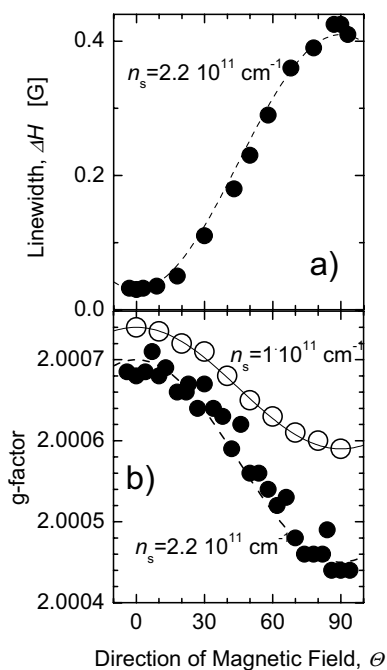


Figure. 4: Anisotropy of the linewidth and the g-factor as a function of the tilt angle of the static magnetic field (0° corresponds to perpendicular field). (After Ref. 13)

power is given in Fig. 3b. It shows a region at low power where the line width is constant – this corresponds to the unsaturated regime. Here the line width is characteristic for the effective transverse spin-spin relaxation rate which can be evaluated thus. At high power it increases according to a power law [14].

The extrapolated intersection of the two branches allows to evaluate the longitudinal spin-lattice relaxation time T_1 . Data for perpendicular field will be discussed below. It should be pointed out here that the evaluation of T_1 for tilted magnetic field is less reliable than for perpendicular field. The reason for that is that for tilted field there is a finite in-plane component of the electric microwave field which may be damped due to the high mobility carriers in the sample. The evaluation of T_1 , however, requires knowledge of the amplitude of the microwave magnetic field at the sample site in the microwave resonator. This would require complex modeling of the mode in the cavity including the actual sample structure which has not been done yet. The low field line width and g-factor are not affected by this effect and therefore we restrict the discussion of the anisotropy to these two quantities (s. Fig. 4) and that of the spin-lattice relaxation to the perpendicular field orientation.

3. g-factor anisotropy

Results for the g-factor as a function of the tilt angle of the static magnetic field are given in Fig. 4 for two different carrier densities, n_s , of the two-dimensional electron gas (2DEG). The anisotropy increases with increasing n_s , demonstrating clearly that we are dealing here with an effect of S-O coupling.

In Si, S-O interaction is exceptionally small due to the particular band structure [5] as can be seen already from the small deviation of the g-factor from the free electron value. In addition, in cubic symmetry, S-O interaction is also restricted by the inversion symmetry in contrast to III-V semiconductors. In lower symmetry situations there are additional effects connected with odd power products of spin and the k-vector of an electron in the spin Hamiltonian. Such terms have been treated by Rashba [15]. for bulk inversion asymmetry (BIA), as it appears in zinkblend structure, or in materials with inversion symmetry which is disturbed by some symmetry breaking field [12]. In our case, symmetry is lowered by the one-sided modulation doping of our samples which induces an electric field and thus an asymmetric wave function of the 2DEG. This class of effects is summarized under the name “structure induced inversion asymmetry”, SIA. The SIA in our case causes the loss of mirror symmetry thus permitting a finite k-linear term in the Hamiltonian. This term causes spin splitting for finite $\mathbf{k}$ -values that can be envisioned as an effective magnetic field seen by the electrons.

One term of first order, the Bychkov-Rashba (BR) term [12], originates from interaction of the type $H_{BR} = \alpha(\mathbf{k} \times \boldsymbol{\sigma}) \cdot \mathbf{e}_z$, where $\mathbf{k}$ is the k-vector of the electron and $\boldsymbol{\sigma}$ are Pauli spin matrices. The Rashba coefficient, α , depends on the S-O interaction in the material used and on the asymmetry of the quantum well. The BR term leads to k-dependent zero field spin splitting and it can thus be described by an additional magnetic field [12]:

$$H_{BR} = (2\alpha k_F / g_0 \mu_B) \mathbf{e}_k \times \mathbf{e}_z, \quad (1)$$

where k_F is the Fermi vector, g_0 the unperturbed g-factor, μ_B Bohr’s magneton and $\mathbf{e}_k$ and $\mathbf{e}_z$ are unit vectors in k- and z direction, respectively. This BR field is always in-plane for our quantum well and perpendicular to the k-vector of the electron.

For high external field the BR term leads to new eigenstates [16]. If magnetic quantization is still weak ($\omega_c \tau_k < 1$), however, H_{BR} can be added to the external field. Averaging for all directions of k_F , the dependence of the measured g-factor on the electron concentration n_s and on the tilt angle of the external field, θ , is obtained as:

$$g(n_s, \theta) = g_o \frac{\langle H_{eff} \rangle}{H_{ext}} \cong g_o \left(1 + \frac{H_{BR}^2}{4 H_{ext}^2} (1 + \cos^2 \theta) \right). \quad (2)$$

In this approximation, we obtain thus a g-shift due to the BR field by:

$$\Delta g(n_s, \theta) = \frac{\alpha^2 \pi \cdot n_s}{g_o \mu_B^2 H_{ext}^2} (1 + \cos^2 \theta). \quad (3)$$

Eqs. (2) and (3) show that there is a g-anisotropy that increases linearly with the carrier concentration and it allows to evaluate the BR coefficient directly. Results of such measurements as derived from Fig. 4 are given in Fig. 5a and the value obtained is: $\alpha = 0.55 \cdot 10^{-12}$ eV.cm. The mean value of the g-factor (Fig. 5b) shows an additional, isotropic dependence on n_s which has been observed also in bulk Si [4].

4. Line width anisotropy

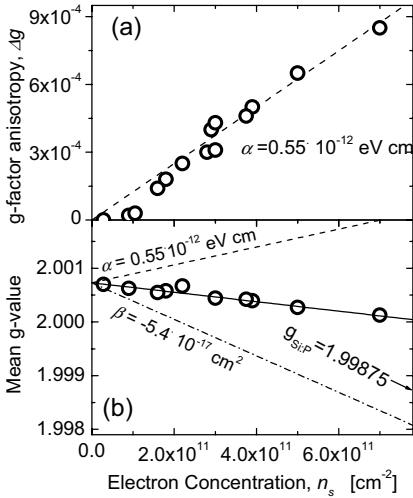


Figure 5: a) Anisotropy of the g-factor, $g = g(\theta=0^\circ) - g(\theta=90^\circ)$ and b) its mean value, as a function of the electron density. The anisotropy can be described in terms of a Rashba coefficient of $\alpha_{BR}=0.55 \cdot 10^{-12}$ eV.cm. For the description of $\langle g \rangle$, an additional isotropic term is needed, $g_o = g_{00}(1 + \beta k_F^2)$ with $\beta = -5.4 \cdot 10^{-17}$ cm² (after Ref.19).

Fig. 6 shows the linewidth anisotropy. It increases also with increasing carrier density, n_s as shown in Fig. 7a. The CESR line width is caused by field fluctuations. For perpendicular field,

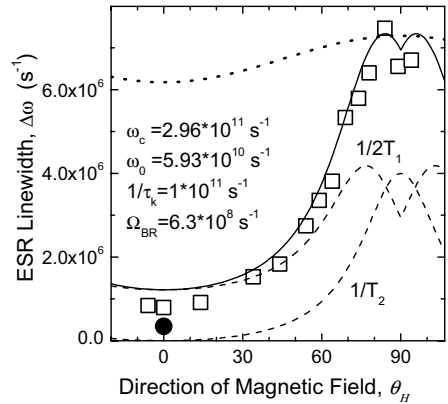


Figure 6: Angular dependence of the ESR linewidth. Dotted line: anisotropy predicted assuming motional narrowing by momentum scattering only. Solid and dashed lines: $1/2T_1$ and $1/T_2$ as described by Eqs. (4-6). (After Ref. [18])

H_z^0 , the line width originates from field fluctuations both in $\hat{z}$ -direction, $\delta H_z^2 \propto 1/T_2$, causing local variations in the Larmor frequency and thus dephasing, and in-plane fluctuations, $(\delta H_x^2 + \delta H_y^2) \propto 1/T_1$.

The latter are responsible for a finite lifetime of the transverse magnetization and for longitudinal equilibration. Together they cause a line width of:

$$\Delta\omega = \frac{1}{T_2^*} = \frac{1}{2T_1} + \frac{1}{T_2}. \quad (4)$$

Tilting the static magnetic field H_{ext} in-plane, *e.g.*, into the y-direction, interchanges the y- and z- components of the field fluctuations in the expressions for T_1 and T_2 . It is easily seen that even for $\delta H_z \ll \delta H_x, \delta H_y$, the linewidth should be the same for in-plane and perpendicular field. The only way to explain the observed anisotropy is thus in terms of highly anisotropic motional narrowing. The observed linewidth quenching for perpendicular field indicates that there is a fluctuating in-plane field at a characteristic frequency above the Larmor frequency, ω_L . Since the line width anisotropy depends on n_s , it is clear that this modulation must be connected with the motion of carriers in the 2DEG. Two origins, both connected with the Fermi motion of the 2DEG can be envisioned: (i) momentum scattering, and (ii) cyclotron motion. The missing link then is the connection between carrier dynamics and spin dynamics and that can be ascribed again to S-O coupling. In order to model spin relaxation, T_1 and T_2 must be calculated. The longitudinal relaxation is caused by fields fluctuating in time, in particular by the Fourier component at the Larmor frequency, $\omega = \omega_L$. The transverse relaxation, in contrast, is caused by dephasing which is ruled by field fluctuations in the low frequency limit, $\omega \ll \omega_L$. Assuming again the Bychkov-Rashba field as the driving mechanism in the spirit of the D'yakonov-Perel theory [17], we obtain [18]:

$$\frac{1}{T_1} = H_{BR}^2 (1 + \cos^2 \theta) \frac{\tau_k}{1 + (\omega_L - \omega_c)^2 \tau_k^2}, \quad (5)$$

and:

$$\frac{1}{T_2} = H_{BR}^2 \frac{\sin^2 \theta}{2} \frac{\tau_k}{1 + \omega_c^2 \tau_k^2}. \quad (6)$$

The frequency dependent terms originate from motional narrowing. In the case of low mobility, *i.e.*, when $\omega_c \tau_k$ and $\omega_L \tau_k \ll 1$ (ω_c : cyclotron frequency, see Eq. (7), τ_k : momentum relaxation time) motional narrowing is negligible and the linewidth becomes independent of θ according to eq. (4). In a previous paper [19] we considered only the effect of momentum scattering (i) which is sufficient if the mobility μ is not too high, *i.e.*, if $\omega_c \tau_k < 1$. More recently, samples with mobilities exceeding 300.000 cm²/Vs at 4.2 K at $n_s = 10^{11}$ cm⁻² became available that show clearly effects of the cyclotron motion (ii) as well. The CR frequency,

$$\omega_c = \frac{e}{m^*} H_0^z = \frac{e}{m^*} H_0 \cos \theta, \quad (7)$$

renders additional angular dependence in Eqs. 5 and 6. (for in-plane field, the cyclotron motion is quenched). This cos- term, arising from the CR, strongly quenches the motional narrowing effect of the momentum scattering for in-plane field and enhances the anisotropy strongly (s. Fig. 6).

5. Influence of carrier density and momentum scattering on spin relaxation

In order to gain more confidence in the interpretation of spin relaxation and dephasing in terms of the Bychkov Rashba field, we consider also the influence of the carrier density, n_s , and the momentum scattering time, τ_k . Both of these quantities can be evaluated *in situ* by modeling the CR which is seen also in the ESR experiments. Here we assume the Drude model for the dielectric function, taking into account both the CR-active and the CR-inactive mode since the microwaves in the TE₁₀₂ resonator are linearly polarized. The carrier density essentially is obtained from the (normalized) integral CR absorption and τ_k from the CR linewidth. The carrier density is varied making use of the persistent photoconductivity in some of the weakly doped samples, or by applying a voltage to a Schottky gate. In the latter case the CR shape is distorted and then n_s was obtained by C-V measurements. The data in Fig. 7 show that the ESR linewidth increases with n_s , as expected from Eqs. (4-6), and the CR linewidth decreases with n_s . The latter shows that τ_k also increases with increasing carrier density which has been explained in terms of screening breakdown in the limit of low carrier density [20].

According to Eq. 4, the ESR linewidth contains contributions of both T_1 and T_2 . Therefore it is easier to consider the effect of scattering on T_1 first. In Fig. 8 experimental data for $1/T_1$ (as obtained from measurements shown in Fig. 3b and normalized to the carrier density, n_s) are given. Fig. 8 shows that for high scattering rate (*i.e.* lower mobility) the normalized longitudinal scattering rate increases.

The increase of $1/T_1$ with increasing scattering rate is a characteristic feature of the Elliott-

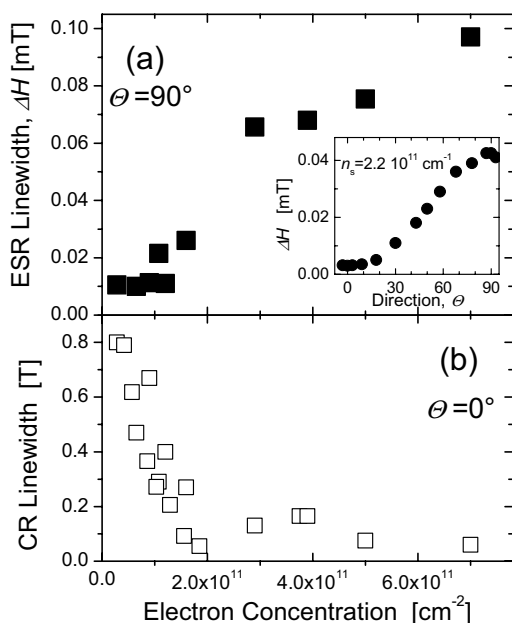


Figure. 7: a) ESR and b) CR linewidth as a function of carrier concentration. (after Ref. 18)

Yafet (EY) spin relaxation process [21]. The EY mechanism originates from the fact that the band states in a semiconductor are no pure spin states in the presence of S-O interaction. For finite k-vector there is a k-dependent admixture of other spin states. Therefore momentum scattering, which changes k, changes also the spin admixture and thus scattering is accompanied by a finite probability for a spin flip. The resulting spin relaxation rate is thus proportional to the momentum relaxation rate: $1/T_1 \propto \alpha_{EY} \cdot 1/\tau_k$, where α_{EY} is a constant depending on the strength of S-O interaction. The dashed-dotted line in Fig. 8 gives this proportionality which represents an upper limit for the EY process since the EY process is an unavoidable, intrinsic mechanism. Thus we obtain an upper

limit for the EY constant of: $2.4 \cdot 10^{-6}$.

For high scattering rate the longitudinal relaxation will be limited by the EY mechanism. For lower rates, the longitudinal relaxation rate is bigger than predicted by EY. Obviously, in this high mobility regime another relaxation mechanism takes over and it is tempting, of course, to assume the D'yakonov-Perel-Bychkov-Rashba mechanism there. In their original work, DP consider motional narrowing [17] and thus the relaxation rate is proportional to the momentum relaxation *time* (dashed line in Fig. 8), contrary to the EY mechanism which has the inverse dependence [21]. In Eq. 5, we have included also the CR which causes additional modulation of the BR field and this mechanism renders the appearance of τ_k also in the denominator. Therefore the originally anticipated proportionality of the relaxation rates to τ_k could, in principle, be observed only in the limit of low mobility ($\omega_L \tau_k, \omega_c \tau_k \ll 1$), but then the EY mechanism prevails. For high mobility, however, the D'yakonov-Perel mechanism dominates and thus both the anisotropy of the line width and the mobility dependent longitudinal spin relaxation can be explained in terms of it.

6. Conclusions

We have shown that the spin resonance of the two-dimensional electron gas in a strained and modulation-doped SiGe-Si-SiGe quantum well exhibits characteristic anisotropy of the g-factor and the ESR linewidth. The longitudinal relaxation rate for perpendicular field has been investigated also as a function of the momentum scattering rate. All three quantities can be explained consistently by a k-linear term in the spin-Hamiltonian and in the absence of a rigorous theoretical treatment we ascribe this term to the Bychkov-Rashba interaction which is a consequence of the symmetry breaking modulation doping and the electric field resulting from it.

The BR field is an extrinsic effect. Therefore it should be avoidable. First attempts to get rid of it by symmetrical doping failed, most likely because of the proliferation of

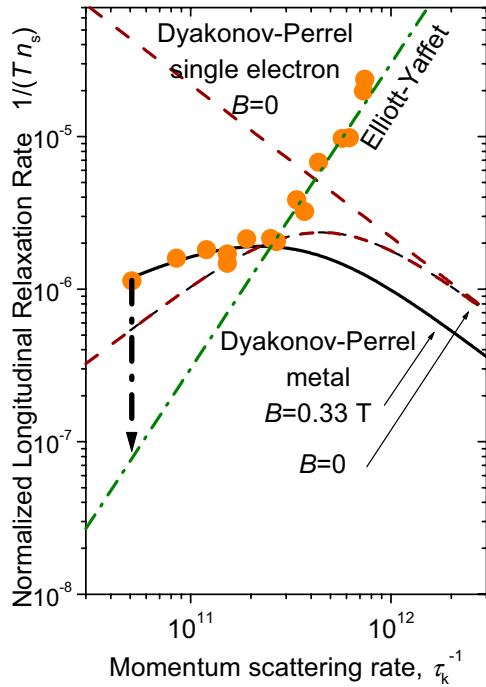


Figure 8: Longitudinal relaxation rate (dots) for perpendicular field as a function of momentum relaxation rate. Dash-dotted line: EY rate. The full curve was obtained taking into account degeneracy ($k=k_F$) and cyclotron resonance (s. eq. 5)

doping atoms in growth direction and thus towards the 2D channel. As a consequence the mobility was much lower for such channels and the line width typically was wider by an order of magnitude. Experiments on one-sided doped samples having a front- and a back-gate are under way. In Fig. 8 the possible gain in T_1 is indicated by the dash-dotted arrow: apparently for the highest mobilities obtained so far, T_1 could be increased by a factor of 15. In the present case, the longest values obtained were about $2\ \mu\text{s}$ so that we can expect an intrinsic EY spin relaxation time of about $30\ \mu\text{s}$. For perpendicular magnetic field H_0 , the effect of the BR field on T_2 vanishes and T_2 becomes very long [13]. The linewidth (eq. 4) and the coherence time are thus limited by T_1 . If symmetrization of the quantum well will not reveal another process then we may hope to obtain also for T_2^* a value close to $30\ \mu\text{s}$.

This value should be compared to the spin manipulation time. Spin manipulation by ESR pulses has been successfully demonstrated already in spin-echo experiments. In these experiments the microwave pulses required for a π -pulse had a duration of about 30 ns, indicating that within the spin coherence time about 1000 operations could be performed. In order to obtain the postulated factor of 104 one can optimize microwave power and quality factor of the microwave resonator in order to reduce the manipulation time further. In addition, also optical methods for spin manipulation with substantially shorter manipulation times can be envisioned.

A substantial increase in spin coherence time is also expected from the reduction of dimensionality: for a quantum computer, individual electrons will be accommodated and manipulated in quantum dots. It has been demonstrated already that the spin lifetime in a dot is substantially longer than in a 2D gas as the continuous density of states breaks up into discrete states – leaving less possibilities to accommodate the relaxation energies. Altogether, the achievement of the postulated factor of 10^4 does not appear as a hopeless task.

A last question to be answered in this paper concerns the addressability of individual quantum dots. Here a possible mechanism is g-factor tuning. The concept of g-tuning involves some electric field applied to a quantum dot by which the g-factor is changed. If the change is sufficiently big, an electron in the dot can be brought to resonance in an external magnetic field and suitable microwave frequency whereas the other electrons are off-resonance. One requirement is thus that the g-factor and thus the ESR must be tunable to an extent that exceeds the linewidth. According to our ESR results two solutions are conceivable. The first one involves the use of SiGe alloys in the channel [3]. If there is a gradient in z-direction, an electric field in z-direction will displace the wavefunction and the g-factor will change accordingly. We found that adding 5% Ge to a 2D Si channel changes the resonance field H_0 already by more than the ESR line width. At the same time, however, the linewidth increases by an order of magnitude. The mechanism for this broadening are not completely clear yet but it is obvious that the alloy will add to the inhomogeneity of the system [22]. In addition, the vertical electric field will change also the Rashba field and thus the spin lifetime.

The second option can be derived from the results of Fig. 5b: the observed g-factor depends also on the Fermi energy. Therefore a change in confinement will change also the g-factor. If a split-gate arrangement is used to define the quantum dots as proposed by Divicenzo *et al.*² then the adjustment of the confining potential can be used also to adjust the g-factor without the additional complication of alloy broadening. In addition, the center of the dot can be kept at low electric field and thus additional effects due to the BR field will be smaller.

In summary, we found exceedingly long spin lifetimes in the μs regime in Si quantum wells. Analyzing the spin relaxation mechanisms responsible we find that the D'yakonov-Perel mechanism - extrinsic in Si - appears to be the dominant one. This result indicates that spin lifetimes of the order of 30 μs are conceivable if the SIA can be removed. We propose lateral confinement as a means for g-factor tuning and thus to select individual spins in arrays of quantum dots.

Acknowledgments

We thank F. Schäffler (JKU) for generously providing samples and helpful discussions. Work supported within the Grant PBZ-KBN-044/P03/2001 in Poland and in Austria by the *Fonds zur Förderung der Wissenschaftlichen Forschung*, and ÖAD, both Vienna

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FUNDAMENTAL PROPERTIES OF FERROMAGNETIC MICRO- AND NANOSTRUCTURED FILMS FOR APPLICATION IN OPTOELECTRONICS

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Abstract

Magneto-optical Kerr effect magnetometer, optical spectroscopy and conductivity methods were applied to study the effects of electron transport and irradiation on remagnetization of nanostructured films of layered and granulated types, just as metallic spin-valves, based on Co/Cu/Co trilayers on Si substrate, lanthanum manganites, doped with Sr in two phase state, ferrite-garnets with artificially created periodic inhomogeneities. Some common peculiarities of the field and light induced effects in this structures are described in connection with their transport properties.

1. Introduction

Thin film ferromagnetic structures changing their properties under applied magnetic field or irradiation are promising for spintronic and optoelectronic applications [1] in spite of a lot of the fundamental problems have to be solved on their way to devices. Systems with magnetically ordered free carriers open the possibilities for engineering electronic properties since the transport changes of any origin can cause correspondent changes of their magnetic, optical, mechanical characteristics. Magnetic field can strongly modify the energy levels of electrons and holes, so its application with the spectral and magneto-optical (MO) methods is effective for studying the energy levels, electron transport, etc. At the same time optical irradiation can influence the substance and change its characteristics. That is create a lot of fundamental problems of light interaction with electronic and magnetic subsystems as microscopic mechanism of carrier-lattice interaction of optically generated carriers. The light induced effects were observed in materials with all types of conductivity - almost insulating ferrite-garnets [2], alternating manganites [3], some Co-contained inorganic solids [4] and even pure metallic Cu [5] etc. This effects give rise to study magnetoelectronic and magnetophotonic properties of the crystals, promising for development of the tunable optoelectronic components. Therefore this work deals light irradiation as measuring as influencing tool in order to compare the response on irradiation and influence of magnetic field of the materials with different conductivities as well as to determine the mechanism of the above mentioned interaction.

A few systems from all ranges of conductivity were taken for consideration: i) sandwiched spin-valves, based on Co/Cu/Co nanosized trilayers, deposited on Si substrates; ii) lanthanum manganites, doped with Sr in two phase state; iii) ferrite-garnets with both layered and volume inhomogeneities. This materials are either directly sensitive to irradiation (as garnets and manganites) either contain the components displaying the light sensitivity in another compositions.

The first part of this work concern magneto-optical and spectroscopic studying of the spin-valve structures. The second part deals with lanthanum manganites, doped with Sr (as $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$), that is an example of the so-called spin crossover system, where the electron transport changes occurring under applied magnetic field result in changes of magnetic ordering. Moreover the transport changes can serve as a push for a number of another effects as giant volume magnetostriction, field-dependent reflection etc. Near the phase instability point this effects are increasing drastically. The third part describes the yttrium ferrite-garnets (FG) doped with Si or Lu. Magneto-optical transparent FG films are promising for integrated optics as e.g. light transducers, non-linear integrated optics elements, tunable switches, etc. The common feature of the above materials is formation of the phase instability state near the room temperature. So a weak influence of light can be better exhibited as macroscopic effect just in the vicinity of the phase instability point. However the reasons of such instability are different. It is usually applied magnetic field for spin-valves, mechanical stress for manganites and temperature effect for ferrite-garnets.

2. Experimental

In order to study the properties of metallic trilayers the Co/Cu/Co structures were thermally deposited in vacuum (10^{-5} Pa) on monocrystalline silicon Si(100) substrates. The thicknesses of Co and Cu layers from monolayer to a few nanometers were formed varying the time of deposition of calibrated sources and determined in-situ by the low energy electron diffraction (LEED) spectroscopy. In another series of the samples only individual Co layers of various thicknesses were deposited on Si substrates for comparison.

Magneto-optical Kerr effect magnetometer was used for investigation of the dynamic and quasistatic remagnetization while the applied magnetic field, light intensity, mechanical strain were being changed. Proceed from the hysteresis curve view, that is adequately display the interaction between the "soft" and "hard" (more coercive) magnetic layers, the films with the most suitable layers thicknesses were selected for further experiments. The hysteresis loops were recorded both in a total and local (up to a few microns) film areas. In the latter the He-Ne laser beam ($0.63 \mu\text{m}$) was focused in a spot of 0.01 - 10 mm in diameter, so the light density on the surface was from 0.1 till 10 W/cm^2 . In the former case a filament lamp with the filters and polarizers was used for spectral investigations. Measurements of magneto-optical Kerr effect and IR spectra (2-25 microns wavelength) in various geometries simultaneously with conductivity measurements were carried out under the influence of irradiation of polarized light in order to clear a correlation of transport, magnetic and optical properties. Remagnetization of some other Co-contained films with more complicated composition produced by r.f. sputtering as well as the single Co layers of various thicknesses on Si substrate, spin-valves CoFe/Cu/NiFe and Co nanoparticles embedded in Si matrix were also observed for comparison of their behaviour under applied bias.

Magneto-optical studying of the transparent FG films is distinguished by some peculiarities. A few methods were applied as combined Faraday and Kerr effects measurements, application of spatially periodic magnetic fields with the submicron sized inhomogeneities. The effective method of analysing of magnetic inhomogeneities is to measure the distribution of light intensity in the diffraction patterns.

A thin waveguided layer in epitaxial FG film of composition $(\text{Tm,Lu,Bi})_x(\text{Fe,Ga})_y\text{O}_{12}$ with 5 microns thickness and "easy plane" anisotropy was formed by annealing in the air at temperature exceeded 950°C . This additional uniaxially anisotropic layer adjacent to

substrate was formed in the initially strained film (due to lattice mismatch) because of Ga or O^{2-} ions diffusion into the film [6], that caused the strain drop. Thus varying the lattice mismatch one can change the film anisotropy, magnetization, optical dichroism and form nearest to phase instability state of magnetic subsystem.

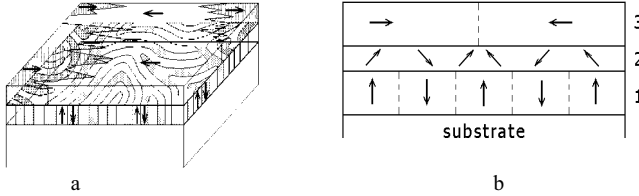


Figure. 1. Scheme of the domain structure and distribution of magnetization in the additional (1) and separating (2) layers.

The thickness of the additionally formed layer h_1 is proportional to time of annealing as well as to temperature. The domain structure, formed in this layer 1 (Fig.1) became labyrinth with the period $d \sim \sqrt{h_1}$ and maximum value $d_{\max} \approx 4$ microns at $h_1 = h$ (h - total film thickness) when all the film became uniaxially anisotropic. Hysteresis loops of such two-layered structure look like superposition of two curves every produced by each layer, similar as then it will be observed in spin-valves (Fig.2). The properties of intermediate sublayer 2 can be determined magneto-optically using the inclined laser beam. It is obvious that contribution of the local magnetization in Faraday effect in various areas of the film will be different, depending on the value of correspondent magnetization component on the direction of light propagation. The equation for Faraday rotation φ_F can be written as follows:

$$\varphi_{Fi} = V \{ \pm M h_1 \cos \alpha \pm 2 M h_2 [\sin \beta \sin(\alpha - \pi/2 \sin \alpha)] / \pi \pm M h_3 \sin \alpha \}$$

where: M - magnetization per length unit; α - angle between the direction of light propagation and perpendicular to film plane; V - Verde constant; h_n - thicknesses of the correspondent sublayers; index "i" correspond to propagation of the light through different domains; sign $\pm$ depends on the relative directions of magnetization and light wave vector. Solving this equations and the same one for perpendicular incident beam it is possible to determine h_2 - the thickness of the intermediate layer. In the films of the above-mentioned composition its value was about 0.05-0.3 microns depending on thickness of layer 1.

From thermal influence of light on the film that decrease polarization-dependent light induced effects it is possible to determine a threshold light intensity

$$I = \frac{4\pi^2 K t \Delta T [1 - \exp(-\sigma I)]}{D^2} \text{ when thermal influence yet less then photoinduced one } (K -$$

heat conductivity coefficient; D - beam diameter; σ - absorption coefficient). For transparent FG films $I < 2 \text{ W/cm}^2$.

Magneto-optical method allows to determine a period of domain structure less than wavelength. For such purposes the beam scan across the domain borders and periodic change of the light intensity exactly follows the domain periodicity. From Gauss distri-

bution of the light intensity $I(x) \sim e^{-\frac{x^2}{2}} \cdot \sqrt{(R^2 - x^2)} / 2\pi$, where R - radius of light beam it is possible to determine the relative intensities of light, passing through the "dark" and "light" domain stripes. Taking into consideration the light absorption, proportional to $\exp(-\sigma)$ and $\cos^2 \varphi_F$, the light intensity changes vs number of the domains going in the light spot area can be depicted as presented on the next graph (Fig.2).

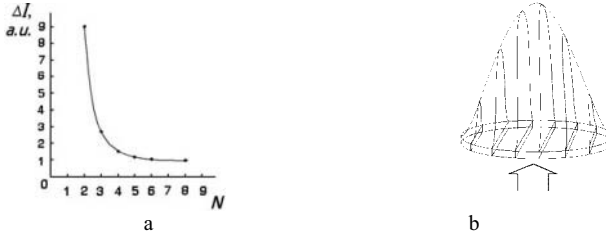


Figure 2. Dependence of light intensity changes while periodic DS is scanned vs number of the domains (a) going in the light spot area (b).

3. Spin-valves

The observed hysteresis loops had a specific shape (Fig.1a,b) that looked like superposition of two different contributions from the "hard" (high coercive) and "soft" magnetic layers. A loop of the soft layer was opened first (1, 2) and then was added a component of the hard one (3). The loop of the soft layer could be shifted (4) due to the hard layer influence in case of applied magnetic field smaller than the field of hard layer remagnetization.

The in-plane anisotropy can be evaluated measuring the field of opening the hard layer hysteresis loop (Fig.1c). In presented experiment the angle between the axes of easy magnetization in two Co layers separated by Cu spacer was about 14° . In antiferromagnetically coupled hard layer spin-valve the difference between the layers coercivity is essentially higher then in case of the same Co layers with various thicknesses (Fig.3).

The difference in conductivities in the opposite directions perpendicular to the film plane exceeded two orders. Switching of the spin-valve results in changes of the electric current: GMR $\Delta R/R$ (at $T=20^\circ\text{C}$) was 1% in up to 200 Oe field and $\approx 10\text{-}15\%$ (dispersion for samples even more) in up to 3000 Oe field. Magnetoresistance in the forward direction in the fields up to 16 kOe did not exceed 15% at room temperature. Contrary the current can influence the domain wall displacement that is not seen on the loops but can be registered by spectrum analyser as increasing of the second harmonic of the hysteresis loop electric signal.

Transport measurements were carried out in the fields up to 16 kOe. Magnetoresistance $\Delta R/R$ (at $T=20^\circ\text{C}$) of Co/Cu/Co spin-valves did not exceed 4% in the fields up to 200 Oe. Due to Co/Si Schottky barrier the difference in conductivity in the opposite

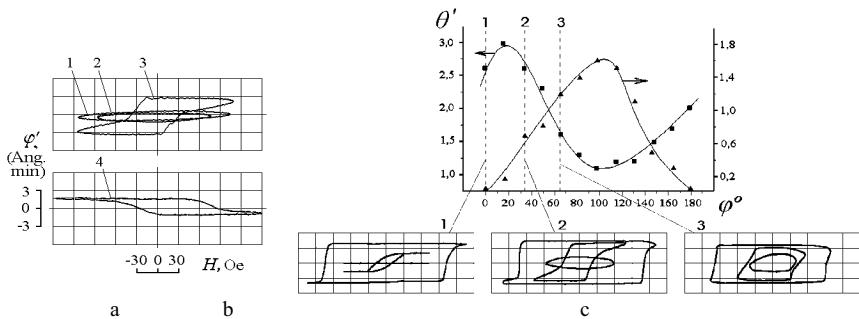


Figure 3. Changes of the hysteresis loops of Co/Cu/Co structures vs magnetic field (a); shift of the soft layer loop (b) influenced by hard (coercive) layer; c - anisotropic in-plane magnetization; inserts (c 1-3) show corresponding hysteresis loops with increasing magnetic fields under the pointed azimuthal angles.

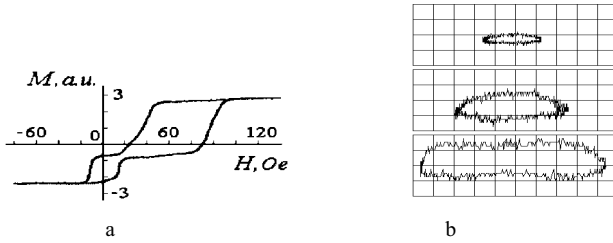


Figure 4. Hysteresis loop of CoFe/Cu/NiFe spin valve (a) with obvious contributions of the soft and hard layers in remagnetization cause the trapezium-like distortion of the loop in low fields (b).

directions perpendicular to plane exceeded two orders. This conductivity could be changed by means of irradiation by polarised light.

IR spectra for Co/Cu/Co/Si and pure Si were recorded on SPECORD spectrometer mainly for confirmation of the amount of Co presence on Si, in particular by the absence in reflectance spectrum of 600 cm^{-1} (16.7 microns) excitation peak.

The different mechanisms of light interaction with charge carriers are responsible for light induced effects: photoelectrons in semiconductors, optical electron transfers in insulators, photoinduced defects and excitons of short lifetime and photoexcited states of long lifetime. The similar effects, observed in metals are connected with photogalvanic current due to anisotropic dependence of the electron transition probability on the direction of light polarization, in combination with the diffuse reflection of electrons on metal surface [5]. Another mechanism is connected with light quasimomentum transfer to conduction electrons. Manifestation of the light induced effects depends on existence of the metastable states. The problem of creation of such states is connected with composition, quantity of the dopants and character of their effect on the energy levels. It is of course a problem to realize such states in metals. Nevertheless some progress on this way are on development as evidenced paper [7]. It's supposed that proposed method of multilayers selection will open the possibilities to design the perfect light control nanostructures, contrary to today's materials in which light influence mainly limited by the so-called "magnetic aftereffects". Such effects consist in a slow variation of the magnetization after the system has been subjected to rapid change of magnetic field or temperature and can be observed in a lot of materials, including the above mentioned.

As for the above spin-valves, so in attempts to reveal the influence of light on ferromagnetic metal films we have measured magneto-optically hysteresis loops

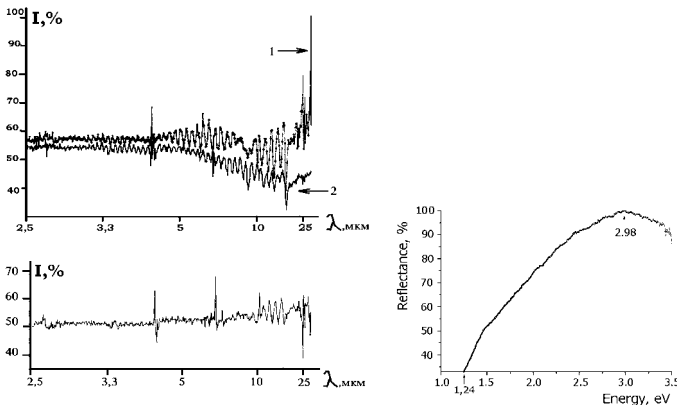


Figure 5. Optical transmittance and reflection spectra of Co/Cu/Co/Si.

simultaneously irradiating the sample with more powerful polarised beam. Estimations of thermal effect of light limited by not more than 0.01-0.1 K possible increase of the sample temperature. The preliminary results of coercivity changes were not in severe correlation with orientation of light polarization, first of all because of the Barkhausen jumps, that cause coercivity deviation. Nevertheless it is seems obvious that polarised light as well as an electric current influence on the domain walls displacement, that manifests as dynamic changes of coercivity while the film is remagnetized.

4. Manganites

Substituted with Sr lanthanum manganites, possessing colossal magnetoresistance at room temperature is especially interesting for application and fundamentals due to a lot of the observed phenomena that still need a a detailed description. The manganites are perovskite oxides with a composition $R_{1-x}A_xMnO_3$, where R is a rare earth and A is a divalent alkali element. In the doping range $x \sim 0.2-0.5$ this material is ferromagnetic with a large drop of resistance near the transition temperature when magnetic field is applied. The properties of manganites are very sensitive to lattice distortion due to substitution, lattice mismatch or external pressure. The effects of light on domain structure or ferro-antiferromagnetic phase transition were earlier observed for only a few types of materials as e.g. manganites, doped with Pr [8]. In order to clear the surface magnetic state of the $La_{0.7}Sr_{0.3}MnO_3$ films MOKE and gradient field magnetometers were applied for studying the local and total hysteresis curves at temperatures below a Curie point (340 K). The angle of rotation of polarization in the longitudinal geometry was about 0.2 min/Oe for 0.63 microns wavelength and about 0.3 min/Oe for 0.48 microns. A typical shapes of the loops at room temperature were similar to rectangle with 12-30 Oe coercivity, about 240 Oe saturation field and the average field of the domain wall displacement of about 3 Oe. Rising up the temperature lowered the remanence and step-by-step transformed the integral loop into longer rectangle with the invariable coercivity (Fig.6).

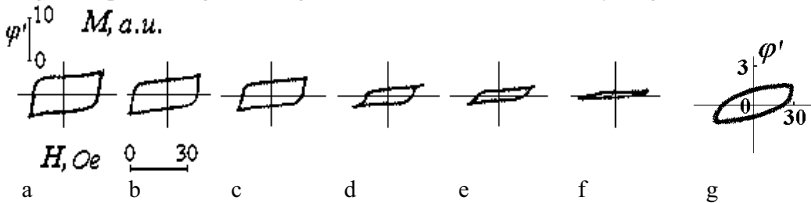


Figure. 6. Magneto-optical Kerr (a-f) and Faraday (g) hysteresis loops in $La_{0.7}Sr_{0.3}MnO_3$ at changing temperature.

Comparison of the loops obtained with Kerr and Faraday effects and on the surfaces modified by etching have shown the difference in the surface and volume magnetization and its dependence on the surface roughness. Measurements of the loops in the vicinity of the phase transition point with 10^{-2} W/mm² beam power revealed both thermal and photoinduced influence of light on a local magnetization. It was manifested as a slight break on the temperature dependence of magnetization. To separate polarization-dependent contribution we registered the differences in changes of magnetization while orientation of the light polarization changed from parallel to perpendicular, relatively to magnetization vector.

It is well established [9] that phase separation in manganites occur because of competition of double exchange and kinetic contribution into the energy function:

$$E = -znt \cos \frac{\theta}{2} + zJS^2 \cos \theta$$

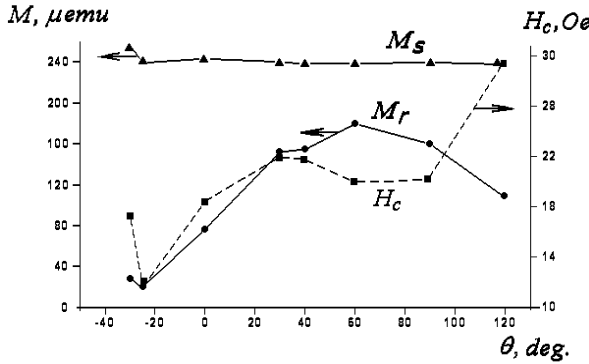


Figure. 7. Saturation magnetization M_s , remanence M_r , and coercivity H_c vs azimuthal angle for $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ film.

where t - transition integral, J - exchange integral, n - electron density, z - number of the nearest neighbours. That results in a profitable state with inhomogeneous spin arrangement and formation of the nuclears (drops) of new conductive phase with radius

$$\text{(taking into consideration only free electrons in the drop)} \quad R = a \cdot \sqrt[5]{\frac{\pi |t|}{4zJS^2}}$$

(a - lattice constant) of approximately 1 nm.

Optical spectroscopy (from UV till IR) was used to characterize content and electronic states of the films. Special interest of the reflectance spectra interpretation is connected with the changes occurring in the vicinity of the phase transitions. In manganites of the above composition, irradiation influence the phase distribution by means of conductivity changes and thus assisted spin-reorientational transitions.

5. Ferrite-garnets

Contrary to relatively small influence of light on manganites and metallic films, irradiation of yttrium FG can remagnetize the film up to saturation [2]. Accomplished calculations [10] assumed the possibilities of their application as tunable magnetophotonic crystals with a transmittance waveband changing under applied magnetic field. The goal of current experiments was to clear the possibilities of light control with two component 2D/3D superlattice nanostructures that due to predictions [7] can drastically enhance interaction of light with periodic magnetic structure, changing optical transmission in a tunable waveband.

We measured transmission of polarised light through the waveguided pure and Bi-contained FG films (along the film plane) while the domain structure (DS) was being reconstructed under applied magnetic field. The efficiency of TE-TM mode conversion depends on film composition, thickness, average period of the domain structure and the angle of specific Faraday rotation. A striped initial domain structure was formed due to cubic anisotropy with 3 easy directions in the film plane and uniaxial anisotropy, perpendicular to plane. Polarised light with 1,15 microns wavelength could pass through 6 mm waveguide formed between the entrance and exit points (prisms).

The typical obtained changes of TM mode (light polarization perpendicular to the film plane) intensity were up to 25% in the magnetic field of the DS saturation (50 Oe). Somewhat smaller changes of TE mode (polarization parallel to the film plane) - up to

12% are partially connected with the theoretical predictions [11] as well as with the experimental setup contribution. The Bi-doped FG films with equilibrium labyrinth DS had a large dispersion of IR light transmission coefficient that can be explained in terms of Maxwell's equations taking into consideration variation of the film parameters. For simulation of the light interaction with a real magnetophotonic crystal a period of the DS must be compulsory changed to the values of about 1/4 or 1/2 of the light wavelength. The obtained efficiency of TE-TM mode conversion vs magnetic field also showed drastic dependence on anisotropy, exchange coupling (measured magneto-optically from the angular dependence of hysteresis loop and light scattering on the domain walls), type of the domain structure, relative orientation of polarization (mode), etc. Analysing the data obtained from remagnetization as well as from conductivity and spectroscopic measurements it is possible to determine contribution of polarization-dependent electron transitions in magnetization and to estimate the optima film parameters.

6. Conclusions

Magneto-optical methods can be effectively applied to study the nanostructures. Their advantage consist in possibilities to change magnetic characteristics of the substances simultaneously with measurements. In insulating films with the small dopants for creation of minimum conductivity irradiation by polarized light can change magnetic, optical, mechanical properties. In the transition structures (from insulating to conductive state in the vicinity of ferro-antiferromagnetic phase transition) the influence of light displayed mainly on mesoscopic level, as e.g. in colossal magnetoresistive manganites, where the light inspired growth of the drops of new phase. In ordinary metallic multilayers manifestation of light influence reduce to magnetic aftereffects but the possibility of its increasing is still an open question.

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POROUS SILICON FOR CHEMICAL SENSORS

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Abstract.

In this work we highlight the advantages of using Porous Silicon (PS) as a material for chemical sensors. Two different applications of PS are investigated: (a) as a matrix for the inclusion of catalytic materials, such as Pd or Pt, and (b) as a material for the fabrication of suspended micro hotplates, for improved thermal isolation. For the first application, the catalytic behavior of Pd-doped PS samples is estimated and the parameters that influence the kinetics of the chemical reaction are evaluated. It is found that the catalytic activity of Pd-doped porous silicon is significantly higher than that of a planar surface covered with Pd. On the other hand, the effectiveness of PS for local thermal isolation on a silicon substrate is examined and the thermal properties of suspended porous silicon (PS) micro-hotplates are investigated. The micro-hotplates are fabricated by a novel technique, based on the isotropic etching of silicon under a PS layer, in a high density plasma reactor. Very high local temperatures on the micro-hotplates (higher than 600°C) with very low power consumption (only a few tens of mW) have been obtained, due to the very low thermal conductivity of PS, which is comparable to that of thermal oxide and it is much lower than that of silicon nitride, typically used for thermal sensor applications.

1. Introduction

During the past decade, Porous Silicon (PS) has attracted the research interest of many groups and has provided a very interesting ground for interdisciplinary research, not only due to its interesting light emitting properties [1] but also to its applications for electrical and thermal isolation on bulk silicon [2-6] and for bulk silicon micromachining [7].

One of the characteristics that make PS very promising material for application in chemical and biochemical sensors is its extremely large internal surface. Depending on the porosity, the internal surface of PS may be as high as 700-800 m²/cm³. For that reason PS films constitute an ideal matrix for the inclusion of catalytic materials. Chemical sensors using PS layers have been reported, which operate at room or at higher temperatures [8-12]. Their operation is based either on the change of PS resistance when the material is exposed to a gas atmosphere, or on the detection of heat produced from combustion of a combustible gas on the surface of PS. Moreover, doped porous polycrystalline silicon films may be fabricated by electroless techniques [13] and used in different applications instead of mono-crystalline porous films. This enhances the flexibility in device design and processing, since in this case the doped porous material can be implemented at various stages of the fabrication process.

On the other hand, one of the main advantages of using PS for the fabrication of chemical sensors, operating at high temperatures, is the minimization of thermal losses. As the dimensions of the thermal transducers are decreasing, the conductive heat flux to the substrate, through the contact of the micro hotplate with the substrate is becoming the dominant factor for heat losses. In order to reduce the thermal losses, alternative device designs, as well as new materials have to be used. PS offers an attractive alternative towards this direction, since the thermal conductivity of PS is significantly lower than that of bulk silicon (two or three orders of magnitude depending on the preparation of the PS layers)

Porous silicon (PS) layers on bulk silicon have been used for local thermal isolation in silicon thermal sensor devices [6, 14]. Moreover, closed-type PS membranes have been fabricated by Maccagnani et al. [15]. 20 μm thick PS membranes were fabricated which, after stabilization, based on partial nitridation of the PS layer, were released by backside etching of the silicon substrate in KOH solution. The thermo-insulating properties of these PS structures were found to be similar to those of standard 0.2 μm thin nitride membranes, despite the increased thickness of the PS membranes. Improved thermal characteristics are expected in the case of suspended PS membranes that are in contact with the substrate only through supporting beams. A front-side micromachining process for the fabrication of such type of PS membranes in the form of bridges or cantilevers, has been recently presented, by the authors [16,17].

In this work we highlight the advantages of using Porous Silicon (PS) as a material for chemical sensors, both as a matrix for the inclusion of catalytic materials, such as Pd, and as a material for the fabrication of suspended micro hotplates, for improved thermal isolation.

2. Porous silicon as matrix for catalytic materials

Porous silicon layers have been obtained on p-type (100) silicon wafers with resistivity 1-10 Ωcm . An ohmic contact was formed on the backside of the wafers by boron ion implantation at a dose of $8 \times 10^{15} \text{cm}^{-2}$ and energy 60 KeV. The samples were annealed at 1050°C for 30 min in O_2 and the thermal oxide was removed after annealing. The anodization process was carried out in a 6:4 v/v HF-Ethanol solution in an electrolytic cell as it has been reported previously [7]. The anodization current was 20 mA/cm^2 and the anodization time ranged between 1 and 10 min. For the current conditions used, the thickness of the PS layers ranged from 1 to 10 μm and the porosity was $\sim 60\%$. The metal solution was obtained by diluting PdCl_2 in water in the presence of HCl. The concentrations of PdCl_2 and HCl in the solution were 10^{-3}M and $4 \times 10^{-2}\text{M}$ respectively. Different samples were immersed in the solution for different times at room temperature. After immersion, PS samples were rinsed in distilled water and dried by blowing with N_2 gas. Finally the samples were annealed at various temperatures (300-500°C) and ambients.

The presence of Pd inside the pores was analysed by using Energy Dispersive X-ray (EDX) Analysis within a Scanning Electron Microscope (SEM), Rutherford Backscattering (RBS), and Transmission Electron Microscopy (TEM) with EDX analysis. EDX analysis within an SEM gives an estimate of the Pd concentration within the whole volume of the porous layer (the electron beam has been chosen accordingly), while information for the in-depth profile is obtained from RBS and TEM. It is important to note that the accuracy of EDX and RBS techniques is limited by the fact that the material is porous, and the obtained results give only a rough idea

about Pd deposition inside the layer. In contrast, TEM analysis is a more appropriate technique for the characterization of PS layers, since it provides direct evidence of the distribution of Pd within the porous layer, as well as the extent of porous layer in silicon.

Quantitative EDX analysis was performed on porous silicon samples of different thicknesses, ranging between 1 and 10 μm , immersed in the Pd-containing solution for different times. Pd was detected in all samples. The percentage of Pd concentration in porous silicon was obtained using EDAX software. Fig. 1 shows the Pd/Si signal as a function of PS thickness for different immersion times into the Pd solution. We see that the ratio of Pd/Si signal increases by increasing the immersion time, which suggests that the quantity of Pd in PS increases with time. The other interesting result is that the ratio of Pd/Si signal for a given time is independent of film thickness when the thickness is more than 3 μm . These observations suggest that Pd enters the pores only up to a certain depth from the surface. Further in-depth diffusion of the material is then blocked by pore filling at the surface layer. Pd nanoclusters, of a lateral size of several tens of nm, are uniformly distributed on the surface, as it is also seen in SEM images (see for example fig. 2).

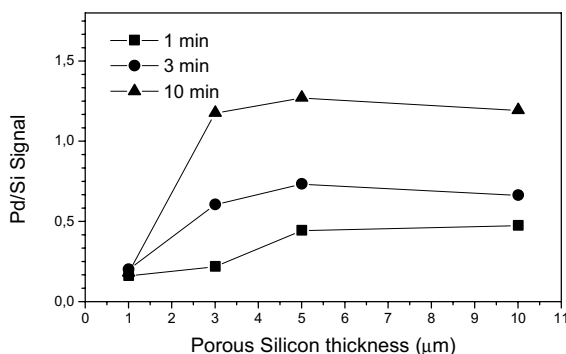


Figure 1. Pd/Si signal as a function of PS thickness for different immersion times.

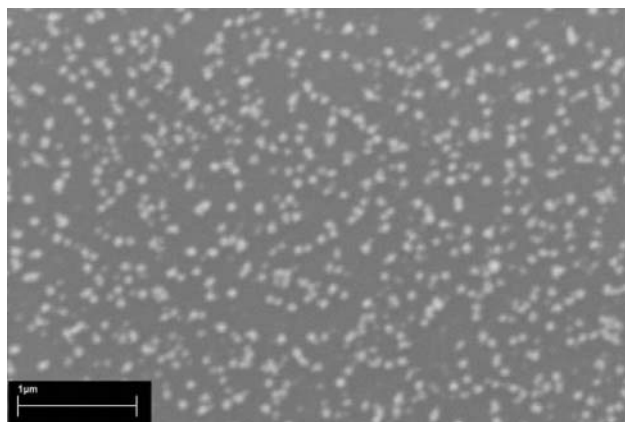


Figure 2. SEM image of PS surface after immersion to the solution for 1 min. Pd nanoclusters, of a lateral size of several tens of nm, are uniformly distributed on the surface.

When the PS layer is thin ($\sim 1\mu\text{m}$) the ratio of Pd/Si signal does not appear to increase significantly with time. This suggests that the quantity of Pd deposited within the pores and on the surface of PS layer is limited. This might be due to bubbles of hydrogen, produced during the reduction of Pd. Some bubbles may adhere to the surface and prevent further deposition of metal on the surface. Similar phenomena were reported by Coulthard and Sham [18], where the non-uniformities observed during the deposition of Cu on thicker PS layers were attributed to bubble formation. A more rigorous analysis of the distribution of Pd in PS was made by Transmission Electron Microscopy (TEM) combined with EDX microanalysis. TEM characterization provides a more accurate technique for the determination of the in-depth distribution of Pd-doped PS layers. Fig. 3 is a cross section micrograph of a $3\mu\text{m}$ PS layer immersed in the solution for 3 min. From this figure we can see that Pd is deposited both on the surface and within the PS layer. Partially crystallized Pd nanoclusters can be identified on the surface of the PS layer, in agreement with the SEM observations. Moreover, the diffusion of Pd within the PS can be clearly seen as a contrast difference between doped and undoped regions. This diffused layer extends a few nanometers ($\sim 50\text{nm}$) below the surface. The same figure illustrates the existence of Pd nanoclusters within the PS layer.

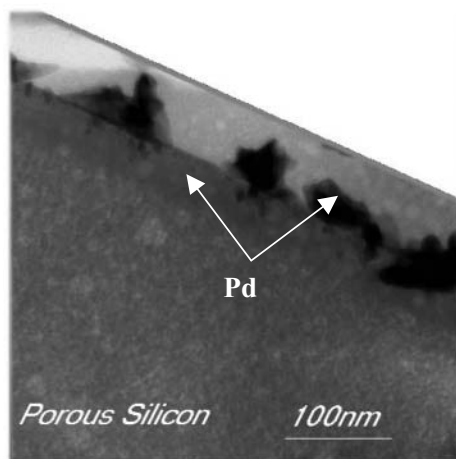


Figure 3. Cross sectional TEM micrograph of a Pd-doped PS layer after immersion for 3 min into the Pd solution. We can see the Pd nanoclusters on the surface and in the PS layer. Pd diffusion within the PS layer is less than 100nm , as it is seen from the contrast difference.

The catalytic activity of the films was investigated by using a closed batch reactor [19]. A direct measurement of the hydrogen consumption on the surface of the catalytic material was possible. Experiments were performed at operating temperatures ranging from 160 to 490°C . Hydrogen conversion data due to the reaction of hydrogen with oxygen were expressed by the parameter X , defined as

$$X = \frac{C_o - C}{C_o},$$

where C_o is the initial H_2 concentration of the gas mixture and C is the H_2 concentration at different instances from time zero. All the experiments were carried out several times and conversion data corresponding to the average values between

the successive runs were obtained. The variation observed was less than 10%.

At first, the reactivity of the catalyst support (undoped PS layer) was investigated. Isothermal runs were carried out for temperatures ranging from 160 to 490°C for a reactants composition of 1% (v/v) H₂/air. During these experiments no hydrogen conversion was observed for temperatures below 300 °C, whereas at higher temperatures i.e. 400, 490 °C a low reactivity was evidenced, which was found to depend on the reaction temperature, as it can be seen in fig. 4. The latter phenomenon is commonly observed in cases where the catalytic system is directly formed by the catalyst support matrix at high temperatures [20-21]. In that case the pore structure of the catalyst matrix allows the chemisorption of the reactants on active sites of its surface, which operate as Lewis type acids or bases. The chemisorbed molecules or atoms can easily create chemical bonds between them and so to start the respective chemical reaction.

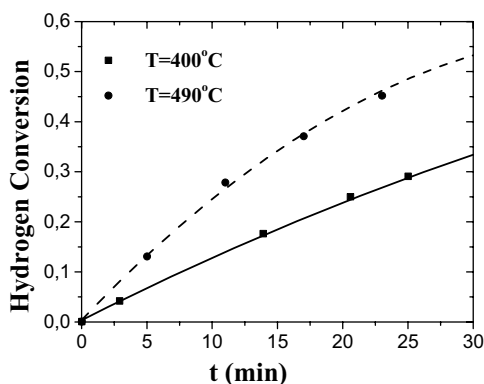


Figure 4. : Catalytic activity of undoped PS samples as a function of temperature.

Following the characterization of the homogeneous reaction and the catalyst support, a series of experiments was carried out, where the catalytic activity of Pd-doped porous silicon was investigated and the influence of processing parameters, such as impregnation time in the Pd solution, annealing temperature and ambient on the catalytic activity was examined [19].

Fig 5 shows the hydrogen conversion rate of Pd-doped PS samples, for various impregnation times into the Pd-solution (30 s, 1 min and 5min) and for reaction temperatures ranging from 160 to 450°C. The thickness of PS layer was 5 µm for all the samples. Prior to the measurements the samples were annealed in N₂ at 500°C for 30 min. These experimental runs showed a reactivity of H₂ oxidation higher than that of the pure catalyst support at all temperatures. There are two observations that we can make from this figure. At first we notice that the catalytic conversion of hydrogen is only slightly dependent on the reaction temperature. The activation energy of the process that determines the catalytic activity was found to be in the range of 0-5 kcal /mole. This low activation energy value is indicating that the overall hydrogen reaction is controlled by the transport phenomena and it is in good agreement with relevant literature data [22-23].

Moreover, in the same figure we see that, within the accuracy of the performed experiments, the catalytic activity is independent of the impregnation time in the Pd solution. This indicates that after the deposition of a critical amount of active component i.e. Pd during the first 30 s of the impregnation treatment, further

immersion into the solution does not have significant influence on the catalytic activity of the material. Similar conclusions were obtained when the samples were annealed in an oxygen containing atmosphere, as it can be also seen in the same figure.

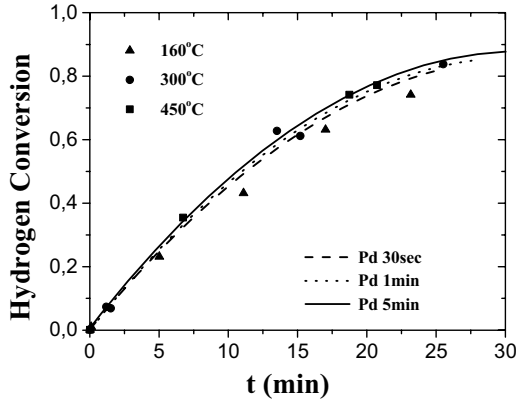


Figure 5. Catalytic activity of various Pd-doped PS samples, as a function of the reaction temperature. The symbols correspond to measurements of the 30sec immersed PS sample, for various temperatures (160-450°C). The lines correspond to data fitting for samples immersed for various times in the Pd solution (30sec, 1min, and 5 min). All samples were annealed in N_2 ambient for 30 min at 500°C.

Similar experiments were performed in order to evaluate the influence of the annealing temperature and the annealing ambient on the catalytic activity of the samples. These experiments showed that the catalytic activity (a) decreases as the oxygen concentration in the annealing atmosphere increases and (b) increases as the annealing temperature increases. This effect may be due to a slight modification of the catalyst chemical and physical structure, as a function of annealing temperature and ambient.

All the results presented so far have been expressed in terms of hydrogen conversion rate X . From this parameter we can estimate the hydrogen concentration $C_H(t)$ as a function of time and the hydrogen loss rate $R_H(=dC/dt)$ due to the catalytic reaction of hydrogen with oxygen. By dividing the hydrogen loss rate with the area of PS samples, we can estimate the flux J_H (moles $s^{-1} cm^{-2}$) of hydrogen atoms that react on the Porous Silicon surface. In order to get an estimate of the efficiency of Pd-doped samples, a comparison was performed with a theoretical model predicting the water production rate of uniform Pd films. The model was proposed by Fogelberg [24], to explain the operation of Pd-Metal Insulator Semiconductor (MIS) structures, when exposed to hydrogen and oxygen under ultrahigh vacuum conditions. Later, Johansson et al. [25] showed that the model can also be applied to explain the operation of Pd-MIS structures under normal operating conditions, ie. at atmospheric pressure and temperatures up to 250°C. It was found that water production at 160°C and for 1% hydrogen concentration is enhanced by two orders of magnitude for Pd-doped PS layers compared to uniform Pd films, deposited on silicon dioxide layer as is the case of the MIS structures. Moreover, experiments that have been performed by the authors showed that the catalytic activity of Pd doped porous silicon is enhanced

by about one order of magnitude at 160°C, compared to uniform Pd layers deposited directly on a silicon surface. This means that the rate of heat production, due to the catalytic reaction of hydrogen with oxygen to produce water, is enhanced in the case of Pd-doped PS layers, compared to non-porous metallic Pd films of the same thickness. The increased reactivity is due to the porous structure and the increased internal surface of the Pd-doped PS film. Such a behavior has been observed experimentally [12].

3. Porous Silicon on bulk silicon for efficient local thermal isolation

For the fabrication of the suspended PS micro hotplates, p type <100> silicon wafers with resistivity 1-10 Ωcm were used. The PS membrane was formed as described previously. After the formation of the PS layer, a 100nm TEOS insulating layer was deposited on top of the wafer, in order to provide electrical isolation between the heater and the substrate. Subsequently, a patterned resistance was formed consisting of either boron-doped polysilicon or Ti/Pt layer, in order to form a heater on top of the membrane. Release of the PS membrane is achieved by means of lateral isotropic etching of the bulk silicon substrate in a High Density Plasma reactor. The etching process is highly selective both to PS and to the photoresist used to protect the active elements of the device. High lateral etch rates can be achieved (of the order of 6-7 $\mu\text{m}/\text{min}$) in a high-density plasma reactor, which permit a reasonable etching time for the release of the membranes and the simultaneous formation of a cavity underneath, used for thermal isolation of the final device. The details of the fabrication process of the micro-hotplates are reported elsewhere [16-17].

Fig. 6 is an SEM image of a PS micro-hotplate with four supporting beams. The dimensions of the membrane are $100 \times 100 \mu\text{m}^2$, the width of the supporting beams is 25 μm , and their length 100 μm . The thickness of the PS layer is 4 μm . It is important to note that the supporting beams as well as the rim surrounding the membrane are composed also of PS. The depth of the cavity under the membrane is more than 60 μm .

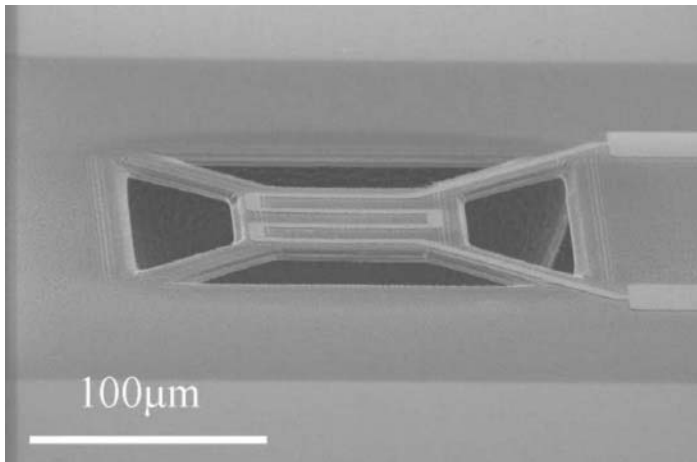


Figure 6. : Suspended PS micro-hotplate with a Pt heater. The thickness of the membrane is 4 μm .

The thermal characteristics of the micro-hotplates were modeled using Coventorware software from Coventor. This is a powerful finite element analysis program, which can be used in Microsystems analysis. Simulations were performed for various membrane geometries (suspended-type, bridge-type and closed-type) and taking into account, the conductive and convective heat losses, as well as radiation. Fig. 7 shows the maximum heater temperature as a function of the thermal conductivity of the membrane material, for two cases: the suspended type (with two supporting beams) and the bridge type membranes, taking into consideration in the simulation only conductive losses. From this plot we can see that for a given geometry the thermal conductivity of the material is important, so if PS is used (thermal conductivity $1.2 \text{ W m}^{-1} \text{ K}^{-1}$) the maximum temperature reached is much higher than if the material is silicon nitride with a thermal conductivity value of $20\text{--}30 \text{ W m}^{-1} \text{ K}^{-1}$. Moreover, we can also notice that the thermal isolation obtained from suspended membranes is superior to that of bridge-type or closed-type membranes (not shown in fig. 3), even if they are made of a low thermal conductivity material, as PS [15].

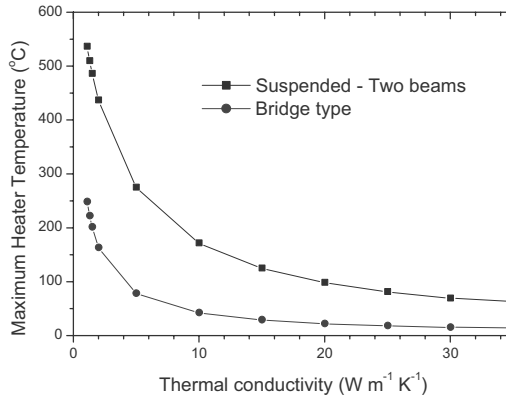


Figure 7. Maximum heater temperature as a function of the thermal conductivity of the membrane material for suspended- and bridge- type micro-hotplates.

Characterization of the micro-hotplates was performed under static conditions. A constant current was supplied to the heater and the voltage drop was measured. From these values, both the supplied power and the resistance of the heater were estimated. Fig. 8 shows the change of a polysilicon heater resistance as a function of the supplied power, for the micro-hotplate of fig.6. We see that the heater resistance increases very rapidly with increasing the power, due to the very high temperature reached on the heater. The position of the arrow indicates the power at which the heater starts to emit light, visible in an optical microscope. This is indicative of the very high temperatures achieved with power as low as few tens of mW.

In order to estimate the temperature that develops on the micro hotplates as a function of the supplied power, an analytical model was used [27] which can predict the change of the total heater resistance on the various parts of the micro hotplates (central region, supporting beams, contact with substrate) as a function of the maximum temperature that develops on the membrane. Comparison of this model with experimental data shows a temperature increase of 20°C/mW on the micro hotplate of fig. 6 may be achieved. This rate is quite high and is due to reduced thermal losses through PS. We have to note that the good mechanical stability of

porous silicon compared to other used materials gives the flexibility of alternative designs, which minimize further the thermal losses and thus achieve higher temperature increase for the same supplied power.

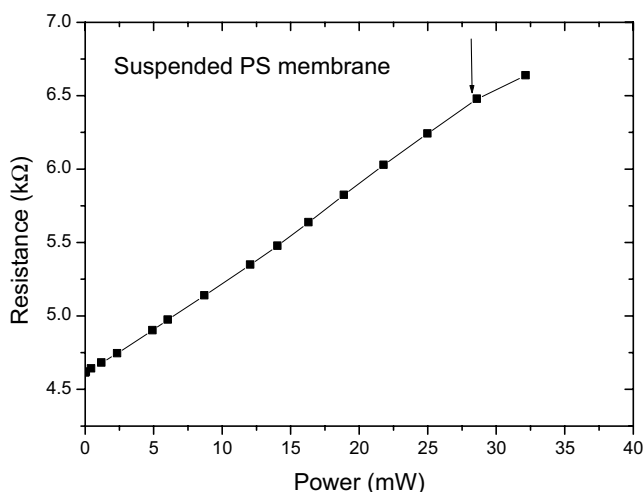


Figure 8. : Polysilicon heater resistance as a function of the supplied power for a 4 μ m thick PS micro-hotplate. The arrow indicates the power at which the heater starts to emit light detectable by an optical microscope.

4. Conclusion

In this work we presented two different applications of porous silicon as an active material for chemical sensors: (a) as a matrix for the inclusion of catalytic materials, such as Pd or Pt, and (b) as a material for the fabrication of suspended micro hotplates, for improved local thermal isolation on bulk crystalline silicon. It was shown that in both cases the use of porous silicon can provide significant improvement to device performance and is a very promising material for this field of applications.

Acknowledgements

The authors would like to acknowledge C. E. Salmas, K. S. Hatzilyberis and Prof. G. P. Androutsopoulos, members of Dept. of Chemical Engineering, NTUA (Athens), for performing the catalytic activity experiments, Dr. A. Travlos (IMS/NCSR “Demokritos”) for TEM analysis and Dr. A. Tserepi (IMEL/NCSR “Demokritos”) for plasma etching experiments.

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SILICON MICROMACHINED SENSORS FOR GAS DETECTION

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Abstract

The paper presents the main principles of detection for the gas sensors silicon based. The silicon sensors present the advantages of miniaturization, integration of the processing signal circuits on the same chip with the sensor, reproducibility, low power consumption and high sensitivity. The realisation of gas microsensors on silicon using the micromachining techniques will be presented. The usual gas sensors silicon based can be divided in: Chemoresistive, Field effect transistor and resonant sensors. The layout and the micromachining technological steps for an interdigitated integrated capacitor used for gases detection, covered with phthalocyanine (Pc) as sensitive layer, the resonant gas sensors realized by silicon micromachining (design, simulation, technology, experiments) and the CHEMFET sensors will be shortly presented.

1. Introduction

The gas sensors are commonly used for pollution control measuring low concentrations of pollutant gases in air, generated by motor vehicle or industrial emissions, for volatile organic compounds detection or for biological and medical applications.

All chemical sensors comprise an appropriate, chemically sensitive material interfaced to a transducer. Interaction of the analyte molecules with the chemically sensitive material generates physical changes which is sensed by the transducer and converted into an output signal /1/.

The range of gas sensitive materials is potentially very broad and can be divided up in a number of ways either by material type or by the nature of the interaction with the analyte. The interaction between the analyte and the sensor material can be reversible or irreversible. In the first case the analyte molecules dissociate from the sensor material when the external concentration is removed, and overall they undergo no net change.

In the irreversible case, the analyte undergoes a chemical reaction at the sensor surface catalyzed by the sensor material. Here the analyte is consumed in the sensing process, although the number of molecules reacting is often a very small proportion of the total number within the samples. The sensitivity and selectivity of the sensors are determined by the choice of the catalytic surfaces. Since the chemical reactions occur between adsorbed

species at the surface of the sensor the intermolecular forces between the sensor and the analyte still play some part in the overall process.

Chemical sensor materials can be divided in three categories according to the type of material used: a) Inorganic crystalline or polycrystalline materials; b) organic materials and polymers; c) biologically derived materials.

There are many ways to produce sensors. The only one way that will be presented in the following is the realisation of microsensors on silicon using the micromachining techniques.

2. Chemoresistive gas sensor phthalocyanine based

The operating principle of the sensors is based on the change in conductivity due to the chemisorption of gas molecules at the sensitive layer surface. The integration of standard CMOS technology with conducting sensitive layer as phthalocyanine (Pc) deposited by EDL technique was one of the goal of our research. We deposited three types of layers phthalocyanine based: copper phthalocyanine (CuPc), nickel phthalocyanine (NiPc) or iron phthalocyanine (FePc) films to be used as gas sensitive layers for the detection of NO_x and NO₂ in ambient air.

The layout and the technological steps of a gas sensor based on an interdigitated capacitor integrated with a polysilicon heater, micromachined on a silicon membrane, CMOS compatible, and the test measurements for NO_x and NO₂ are presented.

The microsensors deposited with phthalocyanines were investigated by impedance measurements in a vacuum box controlled by a gas analyzer. Small quantities of these gases can be detected by measuring the resistance of a Pc film. The gas sensors were tested in a box at a constant temperature and their resistance was determined function of NO_x and NO₂ concentration and in presence of an inert gas N₂. The integrated heating element consists of a polysilicon layer underneath the active area. A temperature sensitive resistor will enable precisely temperature control. The sensor is integrated in CMOS technology adding special micromachining processes.

It comes out that these sensors prove stability and sensitivity in polluted air.

2.1. SENSOR DESIGN AND FABRICATION

The schematic drawing of the sensor chip is presented in Fig.1. The scheme present the layout and the cross – section of the sensor chip presenting information about technological steps and sensor design. The layout is a simplified version, the interdigitated electrodes having a higher number of fingers/2/. The real structure of the sensor will be presented by SEM pictures. The fabrication process starts with thermal oxidation of the silicon wafers and patterned before the selective ion implantation. High dose boron ($9 \cdot 10^{15} \text{ cm}^{-2}$, 100 KeV) is implanted and diffused followed by a boron doping from solid source + diffusion (1050°C, 4 hours). In this way it was realized the p-n junction, 12 μm depth, for anisotropical stop etch, in two steps, for obtaining the requested depth. After boron diffusion the thickness of the oxide grown on the silicon surface is $X_{\text{ox}} = 8000 \text{ \AA}$. The masking layer for the anisotropic etching on the backside of the wafer and for isolation is obtained by the deposition and configuration of a 2000 $\text{\AA}$ Si₃N₄ layer. The next step is the deposition and the configuration of a 4000 $\text{\AA}$ boron doped polysilicon layer. After

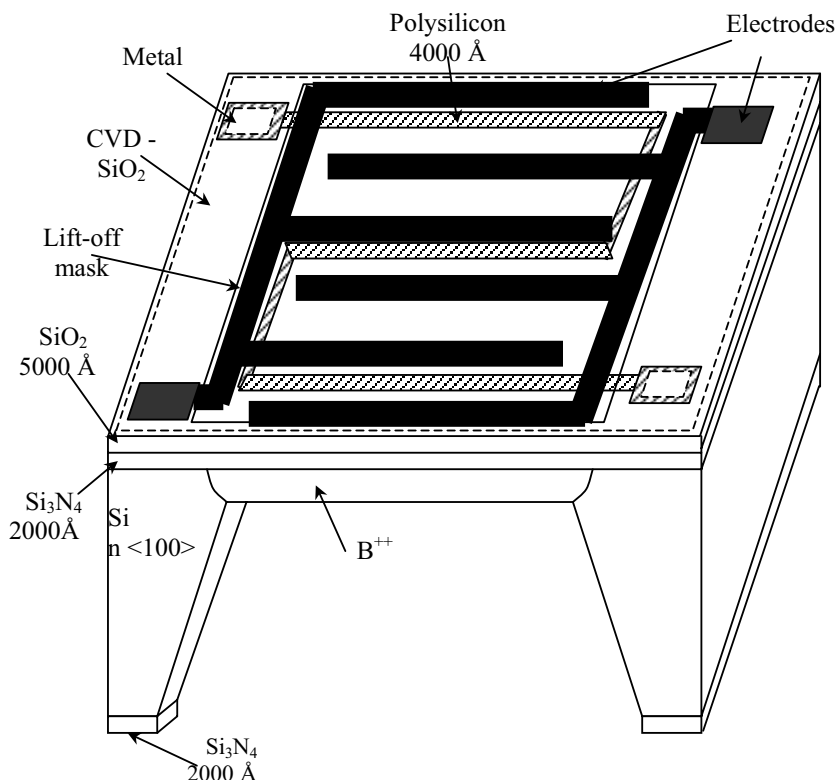


Figure.1. Scheme of the sensor chip

polysilicon configuration, the resistor serving as heating element is obtained. A simplified version could be to use the silicon membrane high doped with boron as heater, without polysilicon resistor. A CVD oxide is deposited such as dielectric layer and the contacts at polysilicon layer are open. Cr-Au deposition and configuration follow. Then the interdigitated electrodes, the resistor for monitoring the chip temperature and the necessary bond pads are defined by photolithography above the insulated heater element. The gold (Cr-Au) was used as electrode material to achieve a good contact with the Pc film. The utilisation of Al as electrode material give us, also, very good results.

The following step was the deposition and the configuration by double side alignment of 2 μm borophosphosilicate glass (BPSG), as mask material for the anisotropic etching, which has a low temperature deposition ($<400^\circ\text{C}$) and can be used after metal deposition.

BPSG layer can be easily removed and the contact and the pad windows are opened. The etching is stopped at B^{++} doped regions where the etching rate is very slow and the thickness of the membrane is also, defined. In the case of silicon anisotropic etching in EDP type F (ethylenediamine: pyrocatechol: water:1000ml:160ml:160ml), BPSG can be replaced by densified CVD/3/. The utilisation of BPSG, densified CVD as mask materials and EDP as etching solution allow us to obtain the compatibility of the anisotropic etching with the I.C. technology.

Phthalocyanines films of various thickness (40nm for CuPc and NiPc; 20 nm for FePc) were vacuum evaporated onto the substrates of the interdigitated electrodes in order to analyse their sheet resistivities. The phthalocyanine film temperature could be very accurately controlled by the integrated heating element and thermoresistor. For an accurately deposition of Pcs in the active area of the device, the lift off technique will be used. The SEM picture of the encapsulated sensor, covered with phthalocyanine is presented in Fig.2. The active area of the sensor contains the metal electrodes. The thickness of the metal layer (Cr-Au) is 400 nm. It is important to study the uniformity of the covering with Pc in order to prevent degradation by clustering of the contact metal.

On a substrate with electrodes on top, Pc film forms not a continuous film over the edge of the electrode strips because during the evaporation of the film the incident angle of the Pc molecules is not exactly normal to the substrate and on one side the strip edge forms a kind of shadow /4/. The film thickness at his point is probably smaller than the average thickness. The electrode strips are much higher that the Pc film deposited on top. We expect a relative bad covering of the strips and a relative high number of cracks caused by the edges of capacitor strips. Pcs films deposited on electrodes had high resistance measurement values: 10 M Ω for CuPc, 15 M Ω for NiPc, 30 M Ω for FePc. The cracks can be observed in Fig.3. For a better integrity of Pcs layer we will act for design and technology changes in order to obtain the planarization of the substrate.

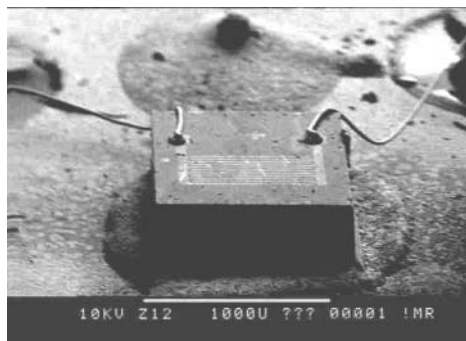


Figure. 2. SEM picture of the sensor chip

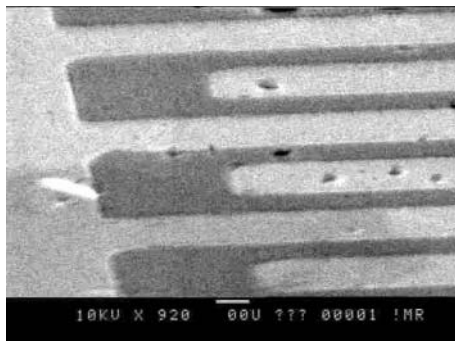


Fig.3. SEM picture of the electrodes covered with 20 nm FePc area

2.2. EXPERIMENTS

Thin sensitive phthalocyanines films were deposited by evaporation /5/ to obtain gas sensors. The sensors have been tested in a plexiglass box at a constant temperature and the resistance was determined function of NO₂ and NO_x.

For the NO₂ analyse, 2ml of concentrated HNO₃ allowed to evaporate in a Petri dish inside the Plexiglas box and the responses were measured after every 20 seconds. The entire experiment was done in an automatic manner and the electronic circuit was entirely enclosed in a Plexiglass box to avoid electrical interferences.

Sensitivity of NO_x and NO₂ has been tested with a gas analyser; calibrations of each gas have been repeated at least 5 times, typical reproducibility of the sensor response were at 1-3mV.

The method used for Pc deposition was EDL, as evaporated Pcs at $200 \div 400$ °C under high vacuum ($\sim 10^{-5}$ Torr) forms a film of 40-50 nm for CuPc or NiPc and 20 nm for FePc onto the chip with interdigitated electrodes for conductance measurements. The thickness and the speed ($10^{-4} \div 1$ nm/s) of deposition of the metal phthalocyanine film was controlled with a quartz balance.

It comes out that these metal phthalocyanines films are very stable and sensitive in very aggressive environments. The measurements were made at room temperature but a medium temperature is applied ($< 200^\circ\text{C}$) after measurement, for cleaning the material in order to reuse the sensor; in our case the temperature applied was 150°C for one hour.

The figure 4, 5 show the sensor characteristics for 40 nm CuPc film in NO_2 and NO_x .

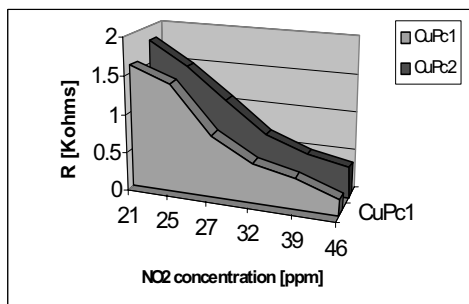


Figure.4. Resistance versus NO_2 concentration for CuPc

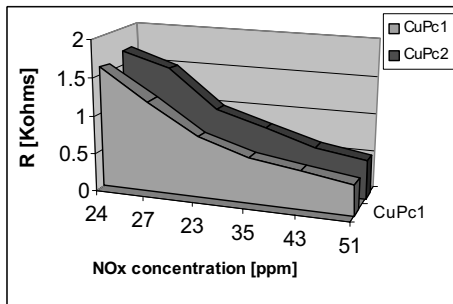


Figure .5. Resistance versus NO_x concentration for CuPc

Metal phthalocyanines exhibit changes of conductance in presence of very small (ppb) concentration of oxidizing/reducing gases; their bulk conductance ranges from 10^{-6} to $10^2 \text{ ohm}^{-1} \text{ cm}^{-1}$.

2.3. RESULTS AND DISCUSSIONS

The measurements indicate us the decreasing of the resistance with the increasing of the concentration for NO_2 and NO_x gases and for all types of phtalocyanines and sensors (Fig.4-9). Two different area are used for sensors in order to study the sensitivity function of layout. Different read out values has been obtained, showing the influence of the sensors dimensions in response. The reproducibility of the silicon technology will allow us to obtain identical and reproducible sensors.

Phthalocyanine structure is a large planar molecule with a delocalized electron system, which can easily be ionized. A phthalocyanine molecule is a good electron donor. The ring of N atoms around the central metal forms a potential well, which is responsible for the semiconducting properties.

Metal phthalocyanines are very stable from chemical and thermal point of view, as a result of their intrinsic structural characteristics. The operating principle of the sensors is based on the change in conductivity due to the chemisorption of gas molecules at the semiconductor surface. Depending on whether the reaction is oxidizing or reducing, acceptors or donors will be produced at the film surface leading to the formation of a space-charge layer and modification of the free carrier density

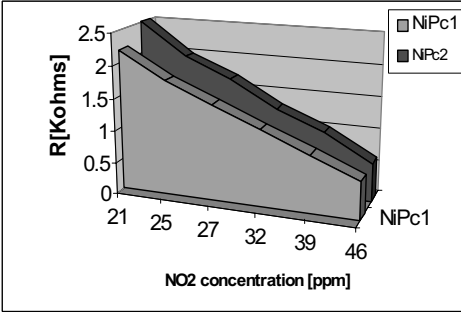


Figure.6. Resistance versus NO_2 concentration for NiPc

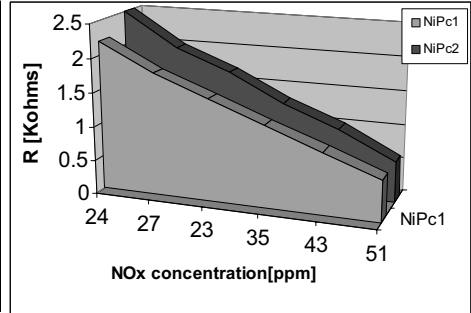


Figure .7. Resistance versus NO_x concentration for NiPc

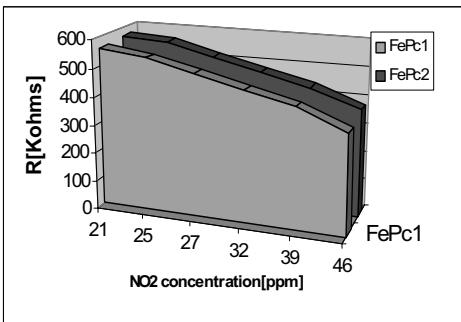


Figure. 8. Resistance versus NO_2 concentration for FePc

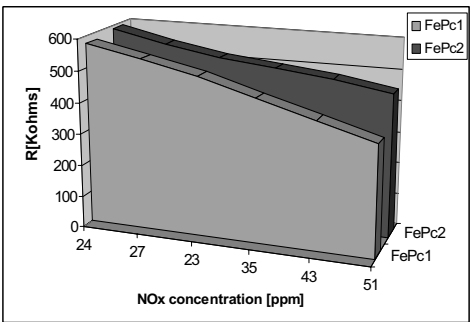


Fig.9. Resistance versus NO_2 concentration for FePc

The differences in sensitivity for Cu, Ni, FePcs can be explained by the electronic configuration of metals coming in Pcs composition. The simple Pcs conductivity is usually low (approximately $10^{-14} \Omega^{-1} \text{cm}^{-1}$). The transitional metals help the conduction due to electron transport through redox system. The metal is much more efficient if it forms plan complexes with conjugate ligands (Pc). An excellent example is CuPc which has the highest mobility between of all organic compounds ($75 \text{ cm}^2/\text{v.s}$). Here “ dz^2 ” orbitals of copper superpose with “ 3d ” orbitals of azomethane of adjacent molecules with 0.388 nm interplanare distance.

When air alone was exposed to the Pc film, the signal change was insignificant compared with that on exposure of the air and nitrous oxide mixture. When the exposure time of gas was longer than 5 minutes, there was no further current increase recorded showing that the Pc film has been saturated.

3. Resonant gas sensors

The resonant gas sensor consists of a resonant polysilicon microbridge and the measurement circuitry to pick up the resonance frequency of the bridge. By coating the bridge with sensor active material it is possible to use these devices as mass sensitive gas sensors

3.1. RESONANT GAS SENSORS REALIZED BY SURFACE MICROMACHINING TECHNIQUE

The microdevice was realised in surface micromachining technique, including the deposition of thin films and the use of a sacrificial layer. For the combinations: construction material/ sacrificial layer we choose polysilicon/silicon oxide (PSG) pair. The microbridge oscillation is activated electrostatically and detected capacitively. The resonant structure is achieved by a sacrificial layer technique. The sense and drive electrodes were patterned by phosphorus implantation and together with the polysilicon microbridge they form variable capacitors; capacity changes due to gap variations can be used to detect the bridge oscillations. The capacity detection is performed by a highly accurate CMOS detection circuit on these devices.

The electronic circuits for excitation - detection are integrated on the same chip with the microbridge, having the main aim to amplify the small current (nA) offered by the variable capacitors from detection way. Fig.10 shows an optical microphotograph of the resonant sensor chip with electronics integrated on the same chip, having an area of $1.5 \times 1.4 \text{ mm}^2$.

Both, the microresonator and the excitation-detection circuits are processed on n-type single-crystal silicon. The technological steps for processing a double-ended clamped polysilicon bridge with electronics on the same chip are based on CMOS aluminum gate technology.

The polysilicon microbridge is $1 \mu\text{m}$ thickness. The polysilicon deposition for the bridge was realised by LPCVD, followed by lithographic configuration and planar plasma ($\text{CF}_4 + \text{O}_2$) etching. The sacrificial oxide was then removed in BHF 10:1, 170min to release a $50 \mu\text{m}$ width bridge. For better stability the hard bake process for the resist mask was repeated after every 20 min of etching of the sacrificial layer.

The released microbridges can be destroyed by a usual procedure of rinser/dryer. The rinse is recommended in a batch DI water, and the dry is realised on a hot plate or an oven. No sticking of the microbridge with the substrate was observed.

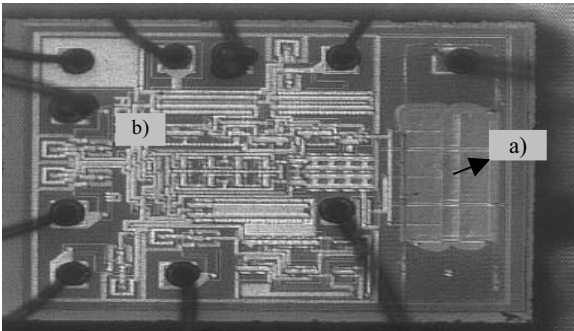


Figure.10. Sensor chip top view:
a) bridge; b) electronics

4. Experiment and Results

The bridge oscillation was observed under the electronic microscope SEM (Fig.11) or optical microscope by applying an AC voltage to the drive electrode (pads 1,2 on the Fig.10). A supplementary supply leads to the microbridge break. Therefore, we can

conclude that the microbridge was released. This method can be used on the wafer or on the encapsulated structures (fig.12) to discriminate between released and unreleased microbridges

The sensor was put in a metal package without cap. The package remains open (Fig.12) for easily test and observed the oscillation of the structure, for apply a sensitive layer and characterize the sensor in harsh environment. The electronic circuit area is covered by phosphosilicate glass (4%wt P₂O₅).

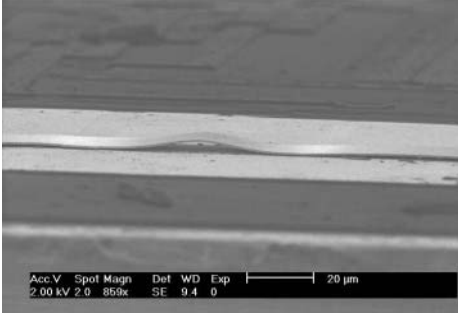


Figure.11. SEM picture of a released microbridge in oscillation

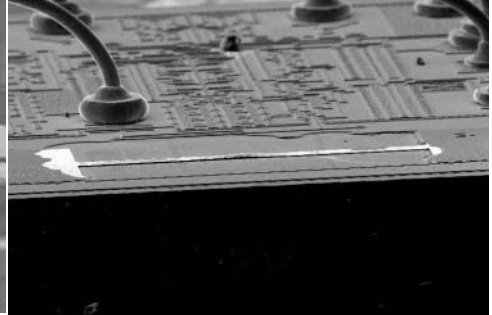


Figure. 12. SEM picture of the encapsulated sensor chip with the microbridge in oscillation

The bridge was covered by a 30-nm thick copper phthalocyanine ($M_p=80000$) film. This polymer adsorbs molecules of SO₃ from the environment and, together with O₂, forms the complex molecule at a temperature between 37⁰C and 40⁰C. The process is reversible at a temperature over 40⁰C. Inside the polymer film there are two regions, namely the bulk region with thickness d_p and the surface region with thickness $\Delta=\Delta_{in}+\Delta_{out}$. Δ_{in} is the thickness on which the volatile compound enters the polymer forming the complex molecule and Δ_{out} is the increase in total thickness due to this complex. There are introduced the following ratios by which the mass of the two will be expressed:

$$f_{out\_in} = \frac{\Delta_{out}}{\Delta_{in}}, \quad f_s = \frac{\Delta_{in}}{d_p}$$

Finally, the mass of the surface region and respectively the mass of the bulk region are:

$$m_s = r_c \cdot M \cdot n_{tot} \cdot A \cdot \Delta$$

$$M_B = A \cdot \rho_B \cdot (d_p - \Delta_{in}) = m_p \cdot (1 - f_s)$$

where A is the area of the polymer film, M is the mass of the resulting complex molecule and m_p is the initial mass of the polymer.

For a polysilicon microbridge with the following dimensions: thickness 1,5-μm, length 100-μm, width 10-μm; Young modulus $E=150$ -GPa, density $\rho_b=2,3$ -g/cm³; the thickness of the gap beneath the bridge 3-μm, we obtained the resonance frequency for the unloaded bridge and for the loaded bridge (by introducing in the reaction chamber). There were obtained the values for the eigen frequencies of the bridge and the corresponding specific elongations (fig.13). In reality only the first resonant frequency is used, the maximum elongation obtained for it being $Y_{max}=0.5$ -μm.

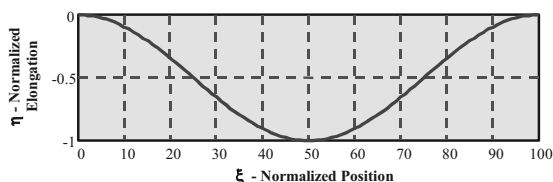


Figure.13. The first resonance shape for the bridge

In the *fig. 14* there are presented the eigen resonance frequencies for the bridge in a normalized form, where $\zeta = \omega/\omega_0$, $\omega_0 = 1/\tau$. In the positions in which the determinant of the system intersects the normalized frequency axis one can find the values for the eigen resonant frequencies. Because the number of points associated to the representation is not enough the graph in fact does not intersect the horizontal axis (due to the computation capabilities) and these values can be read in a qualitative manner.

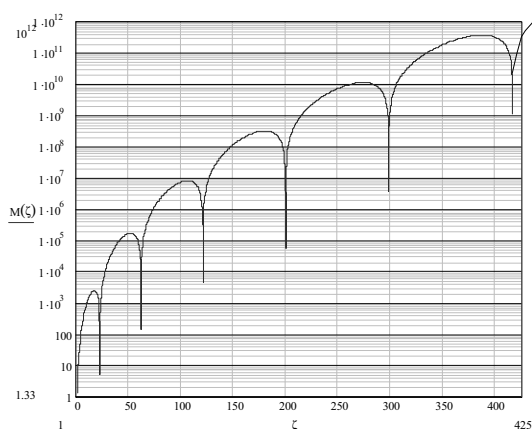


Figure.14. The eigen frequencies (normalized form) in logarithmic scale on Oy axis

A good remark is that, due to the proper normalization proposed, the graph obtained is invariant to changes of the mass of the polymer film. In order to see any effect we must undo the normalization.

In the *fig.15* it is presented the fractional coverage of the surface polymeric region in normalized time.

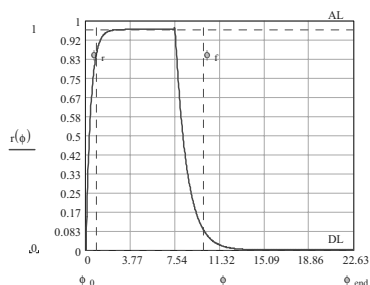


Figure. 15. Fractional coverage of the adsorbant surfaces

The frequency shift is presented in the fig. 16

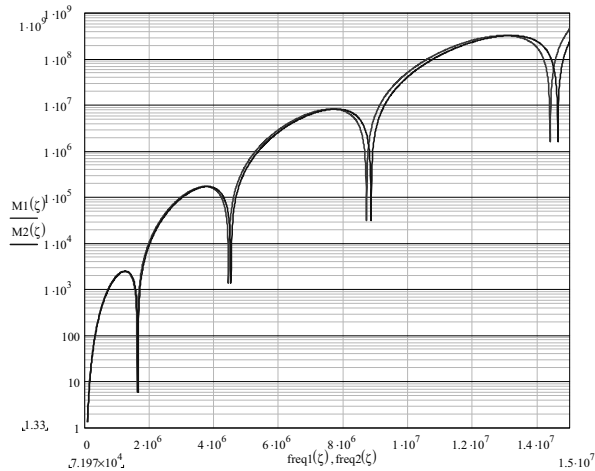


Figure. 16. Frequency shift due to adsorption

The resonant sensors can be used for building complex devices like an electronic nose for volatile organic compound detection.

4.1. RESONANT CANTILEVER ARRAY FOR VOLATILE ORGANIC COMPOUND DETECTION

The sensor is based on a micromachined array of ten silicon cantilevers (Fig.17). Each of the cantilevers is functionalized by coating it with a specific sensor layer to transduce a physical process or a chemical reaction into a nano or micromechanical vibration. The motion is detected by a beam deflection technique or by the variation of the resistivity due to the piezoresistive property of the silicon cantilevers.

By determining the resonance frequency of the cantilever before and after mounting a small sample at the cantilever apex the mass of the sample can be measured with sub picogram resolution [12]. By coating the cantilever with a sensor layer, the resonating cantilever can detect a wide range of analyte concentrations in the environment.

A cantilever is characterised by its geometrical dimensions, its spring constant and the resonance frequency. The resonance frequency of a long and thin cantilever is calculated as follows (after Y):



Figure.17. Cantilever array

$$f_o = (2\pi)^{-1} \left(\frac{E}{\rho} \right)^{-1/2} t_{cant} l_{cant}^2, \quad \text{where } \rho = \text{the density of the cantilever;}$$

t_{cant} , l_{cant} are the thickness, length of the cantilever, respectively, and E the Young's modulus of the material used.

Adsorption of analyte vapor in the sensor layer produces stress at the interface between the cantilever and the sensor layer, leading to a bending of the cantilever. Stoney's law gives the dependence of the surface stress change on the bending radius of the cantilever:

$\sigma = Et_{cant}^2 (6R(1-\nu))^{-1}$, where ν is the Poisson's ratio of the cantilever material and R is the bending radius of the cantilever. For the silicon cantilevers the following constants have been used: $E = 1.7 \times 10^{11} \text{ N/m}^2$, $\rho = 2.33 \times 10^3 \text{ Kg/m}^3$, and $\nu = 0.25$.

Considering the oscillation and the resonance frequency of one cantilever, very small changes in cantilever mass (nano and even picograms) can be detected. The mass change depends on the resonance frequency of the cantilever after the relation:

$\Delta m = k (4 n \pi)^{-1} (f_1^{-2} - f_0^{-2})$, where k = the spring constant of the cantilever, n = the geometry dependent correction factor, f_0 = the resonance frequency of the unloaded cantilever, f_1 = the resonance frequency during the experiment.

The dimensions of one cantilever are: length = 500 μm , width = 100 μm , thickness = 10 μm . The ten cantilevers are identical due to micromachining technique which allows a very high degree of reproducibility.

The cantilevers can be covered with different sensitive layers, in this way the detection of different gases or volatile organic compound being possible. A such device is appropriate for utilisation in the construction of an electronic nose.

The deposition of a droplet of polymer solution having a thickness of 2-3 μm on top of each cantilever allows the determination of the resonant frequency and deflection of cantilevers when they are introduced in a reaction chamber, in the presence of an analyte.

We have been used PMMA (polymethylmethacrylate) [12/ for the first determinations and validation of the theoretical principle. The figure 18 and 19 show the variation of the frequency shift and the maximum deflection respectively [13/ with the concentration of ethanol vapors.

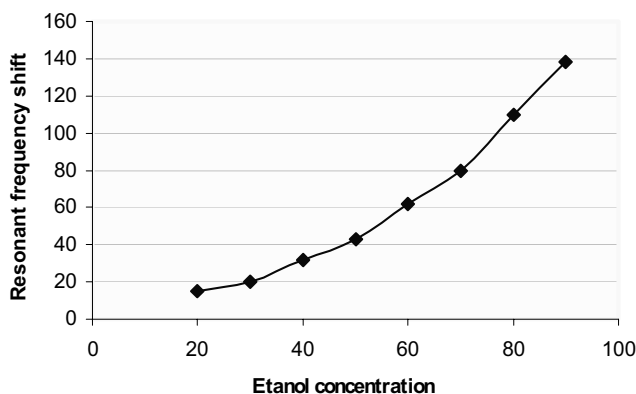


Figure 18. Resonant frequency shift function of the analyte concentration

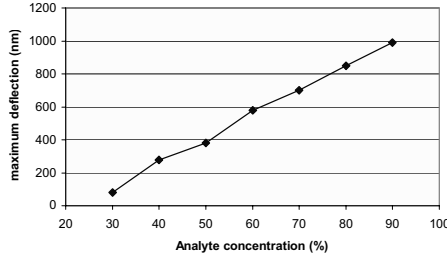


Figure 19. Cantilever deflection function of the ethanol concentration

5. Field effect gas sensors

Field effect gas sensors are based on metal-insulator-semiconductor structures in which the metal gate is a catalyst for gas sensing. Typical catalytic metals used in this application are palladium, platinum, and iridium.

CHEMFET Sensors use the field effect transistors to detect chemical quantities. Examples are biological and medical applications. The surface field effect is a desirable mechanism for a generating potential that provides high chemical selectivity and sensitivity. The CHEMFET is essentially an extended gate field effect transistor with the surface of the transistor and the reference electrode/5/. Conventional ion selective membranes can be deposited on top of the gate insulator to provide the selection of different chemical sensors, electrochemical potential inserted between the non-metal. The major goal is to obtain a single-used CMOS compatible ISFET based on bio or chemical sensitive layer for biological and medical applications. The basic research target of the project is to integrate the CHEMFET sensors on an microprobe that

can be used for measurements of different chemical gaseous species of interest (NO , NO_2) and the development of the suitable sensing materials. For a particular layout and technology, the simulation with SUPREM gives the ISFET characteristic (Fig.21) and the cross section of the device (Fig.22).

The basic research target was to integrate the chemosensors on an implantable microprobe that can be used for in vitro and in vivo measurements of different chemical species of interest (NO , Ca^{+2} , Mg^{+2} , Na^+ , K^+) and for pH monitoring.

The major results are:

- ◆ Development of new sensing materials as superlattices of $\text{SiO}_2/\text{Si}_3\text{N}_4$ or silicon oxynitride with variable compositions (for Na^+ and K^+ ions) and photosensible modified polymers with ionophore phases (for Ca^{+2} , Mg^{+2} ions)

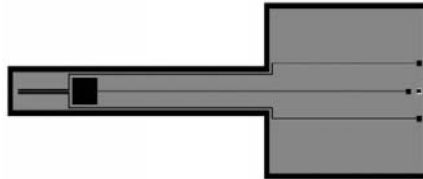


Figure 20. Layout of a microprobe with FET sensor on the tip

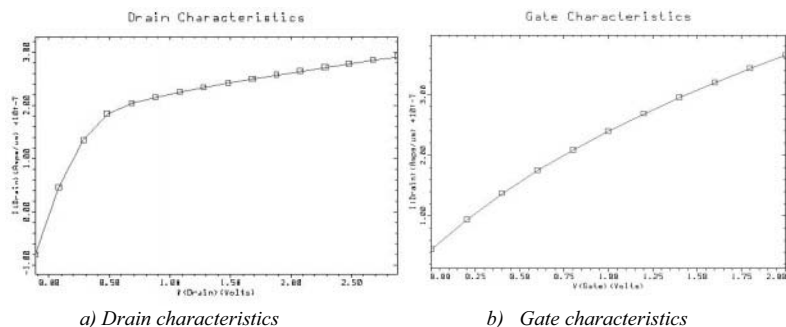


Figure 21. Characteristic Voltage–Current for an ISFET sensor

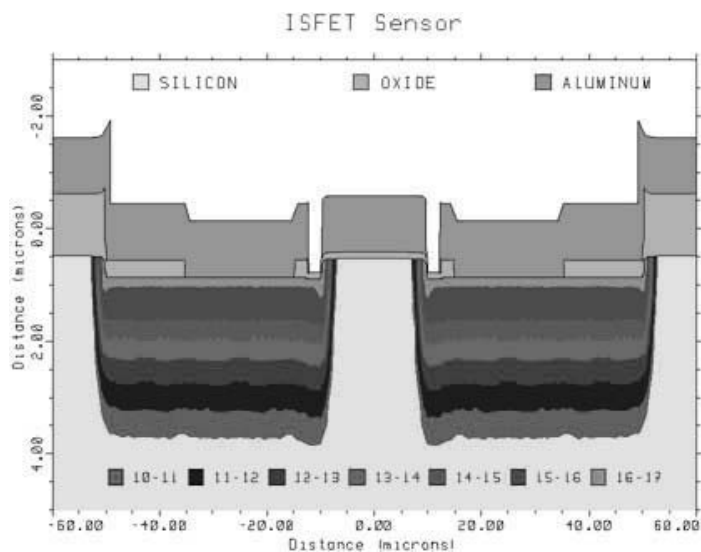


Figure 22. Simulation of the ISFET sensor

Compatibilization of all technological process with CMOS technologies and development of new packaging methods

The ISFET based sensors will be made on an implantable microprobe (Fig.20) and will be integrated on the same chip with the electronics /14/.

6. Conclusions

1. A chemoresistive sensor is analysed and three main types of thin phthalocyanines films have been studied from point of view of NO_x , NO_2 , SO_3 sensitivity: CuPc, NiPc, FePc. They exhibit changes of conductance in presence of small concentration of nitrogen oxides gases. Resistance measurements have been done without contact problems for Pcs films

deposited on interdigitated electrodes.

The sensitivity and stability of the chemoresistive sensor are sufficient for applications during the measurements made at room temperature of polluted air and even aggressive environments such as the NO₂ steams from HNO₃ 100%. The temperature of 150 °C was applied for one hour, for cleaning the material (metal phthalocyanines films) in order to reuse the sensor. The sensor is entirely integrated, MOS compatible, cheap, easy to be used and has a low power consumption.

2. A microbridge structure together with electronic circuits on the same chip is presented. The surface micromachining processes are used and optimized. Small and reproducible microstructures can be obtained due to the planar technology. A silicon-based sensor was obtained which can be tested in various applications.

A resonant cantilever array is studied in order to be used for an electronic nose device. We demonstrated the application of micromechanical cantilever array as chemical sensors having the simultaneous detection of the resonant frequency and bending. Information on cantilever bending and resonant frequency shifts during the exposure to analyte vapor are used for characterization and recognition of chemical substance such as etanol.

A CHEMFET sensor is studied in order to be used for biomedical applications. The micromachining technique allows us to realize a FET on a thin tip of an implantable microprobe.

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MICROPOROUS ZEOLITE MEMBRANES – A USEFUL TOOL FOR GAS SENSING SYSTEMS

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Abstract

MFI-type zeolite membranes containing aluminum have been prepared on the surfaces of aluminum coated porous alumina asymmetric substrates. The metallic layer functioned as a source of aluminum during hydrothermal synthesis of a zeolite polycrystalline layer on the substrates. XRD, EDS and SEM showed that the metallic layer resolved and a continuous zeolitic layer was formed.

The zeolite membranes were modified with ion-exchange procedures to obtained a high catalytically activity. The gas separation properties were investigated by gas permeation measurements. The catalytic properties were characterized by the dehydration of ethanol. The successful incorporation of a zeolite membrane in a commercially methane gas sensor showed an improvement of the methane selectivity in the presence of alcohols.

1. Introduction

The quality of a sensor is determined by its sensitivity, reproducibility and stability. Most of sensing materials, e.g. SnO_2 showed a high sensibility and unfortunately the sensitivity is insufficient. For example, a methane SnO_2 -based gas sensor also detect ethanol or other related organic compounds. A suitable filter before or on the sensitive material should be able to reduce this disturbances.

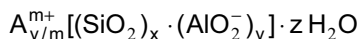
The separation of gases with the help of the membrane technique already achieved the state of the art for different industrial applications. The use of inorganic membranes offers advantages in the view of stability and regenerative power. Inorganic membranes are operated at higher temperatures where most heterogeneously catalysed gas phase reactions are taking place. Operating gas sensors at ambient temperatures requires ceramic membranes [1, 2].

In the development of ceramic membranes for gas separations selectivities are expected to be improved by decreasing the pore diameter of separating layer. Because of their unique thermal, structural and chemical stabilities and reactivities, zeolites have found widespread applications in gas separation and catalytic reactions [3, 4].

Zeolites occur in nature and have been known about 250 years as aluminosilicate minerals (e.g. faujasite, mordenite, offretite, ferrierite, erlonite and chabazite. Today about 40 naturally occurring zeolites and more than 200 synthetic zeolites are known [5].

Zeolites are highly porous crystalline materials. They exhibit a number of unusual chemical and physical properties determined by their special crystal structure, which contains uniform pores and channels having dimensions of the order of smaller molecules.

The elementary building units of zeolite are SiO_4 and AlO_4^- tetrahedra. Adjacent tetrahedra are linked at their corners via a common oxygen atom. So an inorganic macromolecule is built with a structurally distinct three-dimensional framework. The framework of a zeolite contains channels, channel intersections and cages with dimensions from 0.2 to 1 nm. Inside the voids there are water molecules and small cations which compensate the negative framework charge. The chemical composition can be represented by a formula of type:



A is a cation with the charge m, (x+y) is the number of tetrahedral per crystallographic unit cell and x/y is the framework silicon/aluminium ratio (Si/Al). *Figure 1* shows the structure of four selected zeolites.

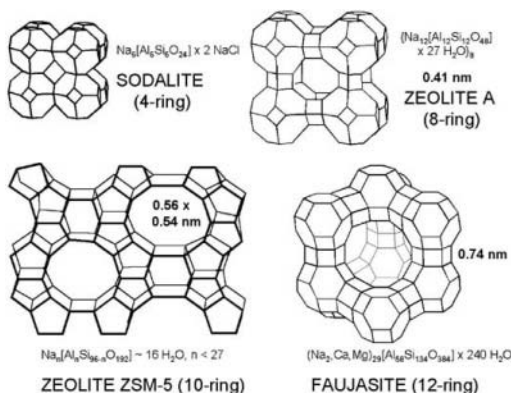


Figure 1: Structure of four selected zeolites

In their dehydrated state the zeolite crystals have a very large internal surface area ranging from 400 to 1000 m^2/g , which results from their systems of channels and cavities. The strong electrostatic fields within the crystals and the close contact of the sorbate molecules with the zeolite framework, combined with the large internal surface, give rise to a high adsorption capacity. Zeolites are able to convert molecules catalytically in a structurally selective manner.

The main areas of applications of zeolites are their use as catalysts in a number of important reactions, as adsorbents and as ion exchangers. Among the most important properties of zeolites with respect to their use as catalysts is their surface acidity. Both, Brönsted and Lewis acid sites occur in zeolites and can be generated via ion exchange [6, 7].

Much zeolite research and development is still aimed at the traditional uses mentioned above. However, within the last few years considerable effort has been directed to new uses of zeolites as advanced materials, e.g. in the field of chemical sensors [8, 9].

A sensor can be defined as a small device that converts any microchange of temperature, pressure, concentration or other properties into a detectable signal. The success of a chemical sensor is determined by its sensitivity and reproducible performance. The sensing element is expected to incorporate at least the following attributes: selectivity and site reversibility with respect to guest binding, fast response, small size, ruggedness, low cost, and the potential for facile integration into an automated system.

The majority of semiconducting gas sensors now in service use tin dioxide as the reactive element [10]. Tin oxide is extremely sensitive to trace concentrations of reactive gases in air. The sensing material is normally held at temperatures between 300 and 500 °C. A simple sensor (SnO_2 -based gas sensor) for the detection of specific molecules from a molecular mixture is schematically represented in *Figure 2*.

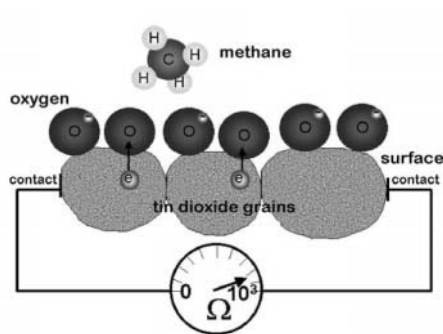


Figure 2a: Oxygen preadsorbed on the semiconductor surface

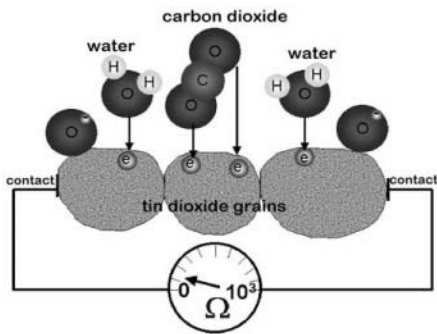


Figure 2b: Methane combustion into carbon-dioxide and water

At first oxygen is preadsorbed on the SnO_2 -surface and will then trap electrons from the conduction band. The oxygen species ionosorbed on the semiconductor surface are expected to be O_2^- and O^- . The amount of oxygen chemisorbed is controlled by the oxygen concentration and the amount of reducing or combustible gases in the atmosphere. In *Figure 2a* a low methane concentration promotes a nearly completely oxygen-covered negatively charged SnO_2 -surface. The number of electrons between the grain boundaries decreases and the resistance increases. If the concentration of methane rises, then a large amount of the chemisorbed oxygen reacts with the combustible gas methane. *Figure 2b* illustrates the reaction between methane and oxygen to give carbon dioxide and water. Each desorbed oxygen species reinjects an electron into the conduction band of the semiconductor. Also, the decrease of resistance depends on the methane concentration [11].

Unfortunately, this process is not very selective. Each reducing or combustible gas is able to react with the chemisorbed oxygen species. For the enhancement of the selectivity of gas sensors, it is possible to modify the semiconductor material (metal oxide) with several catalytically active metals, known from heterogeneous catalysis [12]. Another way is the use of active filter materials, e.g. zeolites, in front of the sensitive layer. The great experience in the commercial use of zeolites in various organic reactions was very helpful for the design and development of a sensor system containing a commercial methane sensor and a catalytic zeolite membrane.

2. Experimental

Among different zeolites, we focused on the synthesis of ZSM-5-(MFI)-membranes, because this zeolite has an average pore size of 0.55 nm, and it is possible to modify this zeolite with catalytically active ions [13].

The conventional route of producing ZSM-5 membranes is the synthesis on the basis of silicon dioxide, an aluminum source, sodium hydroxide, template and water. The preparation is generally carried out by growing a continuous layer on a porous support under hydrothermal reaction conditions. Such continuous zeolite layers must develop from surface nuclei growing into interlocking crystallites. Growing a closed layer on the support is still difficult.

The separation performance of zeolite membranes is strongly related to the degree of zeolite crystallites integration into the pores of the substrate. Frequently defects occur during the synthesis and the thermal subsequent treatment.

The range of conditions for successful membrane growth may be expanded by using an aluminum layer on the surface as a source for aluminium, which can be inserted into the zeolite framework. The zeolite crystallites begin to grow on the interface.

Zeolite ZSM-5 membranes were synthesized using the hydro-thermal method described by Argauer and Landolt [14], without an aluminium source. The surfaces of asymmetric alumina substrates (average pore size between 3 μm and 5 nm, about 50 % porosity) were cleaned with water and acetone in an ultrasonic bath. Then they were dried carefully, and the aluminum film (approx. 300 nm thickness) was sputtered with a Sputterup LBA 500 (15min, 100 W).

The gel used for synthesis consisted of tetrapropylammonium-bromide (TPA-Br, 99 %, Merck), NaOH (99,99 %, Merck); the silica source was SiO_2 (Cab-0-Sil, 99 %, Fluka). All components were dissolved in water and stirred 12 h at room temperature.

The pretreated substrates (5 and 18 mm diameter) were placed vertically in a 150 ml Teflon-lined stainless-steel autoclave using a Teflon holder. The synthesis gel (120 ml) was filled in, and the autoclave was placed in a convection oven at 180 °C. After five days the autoclave was removed, cooled down to room temperature, opened and the membranes were thoroughly washed and dried in air for 12 h at 110 °C. The membranes were calcined carefully at 560 °C under Argon with a heating rate of 0,5 K/ min and kept at the final temperature under synthetic air for 12 h. Afterwards the organic template was completely removed.

The obtained zeolite film, consisting of Na-ZSM-5-crystallites, was converted into H-ZSM-5 by aqueous ion-exchange with highly concentrated NH_4NO_3 -solution. In some cases, the as-synthesized zeolite membranes were impregnated with transition metals. After ion-exchange, the membranes were dried and calcined carefully.

The structure of the as-synthesized membrane was determined by X-ray-diffraction (XRD) patterns. XRD was carried out on a Siemens powder diffractometer using $\text{Cu K}\alpha$ radiation. The morphology and thickness of the as-synthesized membrane were examined using a scanning electron microscope (SEM), Camscan 44.

The catalytic properties were checked using the conversion of ethanol (fuel component) into ethene and other hydrocarbons [15]. The permeation was measured in a Wicke-Kallenbach cell for synthetic air. The measurement of direct coupling of commercially SnO_2 -sensor (UST, GGS 3000) and zeolite membrane (5 mm diameter) were realized in a modular sensor device coupled to a gas chromatograph and an automated gas mixture facility.

The sensor device was tested with mixtures of ethanol and methane between 10 and 600 ppm, because the improvement of a methane sensor was targeted. The catalytic filter material combusts interfering gases, but allows the target gas to pass through and react with the sensor surface. The change of the SnO_2 -sensor resistance was measured in dependence of the concentration of hydrocarbons.

3. Results

Figure 3 shows characteristic XRD-Pattern of ZSM-5 zeolite on the former aluminium coated surface. For comparison XRD-Pattern of the uncoated alumina layer and Na-ZSM-5 powder are represented.

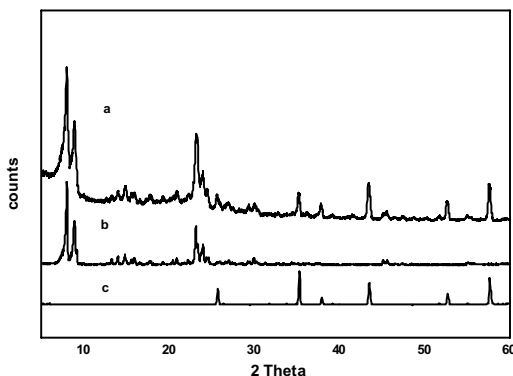


Figure 3: XRD of a zeolite membrane (a) synthesized on porous alumina- support (c); crystalline H-ZSM-5 (b)

No Signal for metallic aluminum was found. The aluminum was completely converted and inserted into zeolitic framework. Pure and highly crystalline ZSM-5 was formed. EDS analysis (EDAX) of synthesized membranes did not show an enhanced aluminum content in the interface between ceramic support and zeolitic layer. The element distribution shows, that the zeolite grew also in the inner surface of ceramic layer. The zeolite crystals, averaged up to 3 μm , form a dense layer covering the whole support. Figure 4 shows that the zeolite crystals grew from the former aluminum surface and a dense zeolitic layer was obtained, whose chemical composition proved to be $\text{M}_n[\text{Al}_n\text{Si}_{96-n}\text{O}_{192}]\cdot 16\text{H}_2\text{O}$ with n in a range between 2 – 15.

The successful preparation of ZSM-5 membranes using porous Al_2O_3 -discs with 5 mm in diameter was a major challenge with respect to create membranes for commercial gas sensing systems, e.g. methane warning detectors.

Via catalytical tests a good suitability of the synthesized zeolite could be found for the conversion of ethanol at temperatures above 200 $^\circ\text{C}$. This temperature was also determined as optimal operating temperature for the ethanol conversion. Later measurements showed, that in the sensor housing above the SnO_2 -layer (operating temperature approx. 325 $^\circ\text{C}$) a temperature of 250 $^\circ\text{C}$ existed.

As products of these conversions of ethanol, we found traces of CO_2 , H_2O and ethene. If the zeolites were modified additionally with transition metals, we detected only CO_2 and water. Therefore, the fault component ethanol was successfully eliminated.

The permeation measurements on the synthesized membranes showed good gas separation properties without any leakage loss. Methane could pass the zeolite channels and ethanol was adsorbed and converted at temperature above 200 $^\circ\text{C}$.

The use of the synthesized membranes in front of the sensor showed a substantial improvement regarding the detection of methane in the presence of ethanol in air.

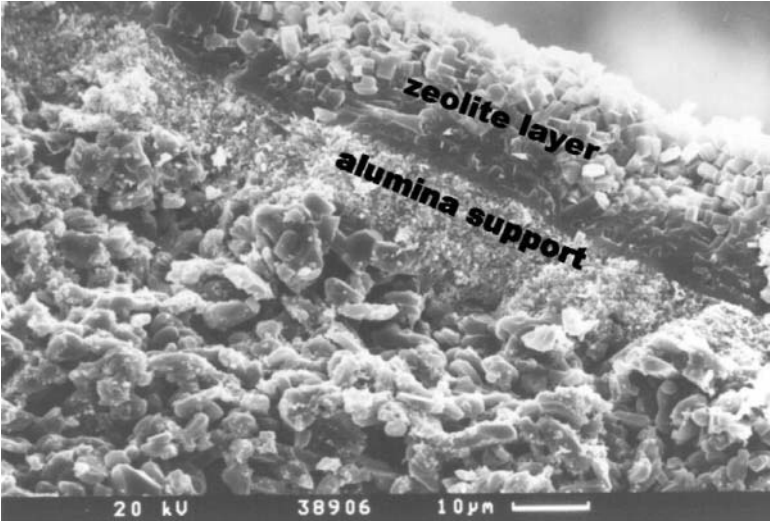


Figure 4: SEM: cross section of a zeolite membrane synthesized on porous alumina- support

Figure 5 illustrates a typically sensor test diagram. The newly synthesized membranes (Al-SilH+a and Al-SilH+b), covering the sensitive SnO₂-layer of a commercial methane sensor (GGS 3300, Fa. UST), showed the same characteristics in resistance change as an unmodified sensor. The other zeolite membranes are gas-tight for methane, thus no signal change was found.

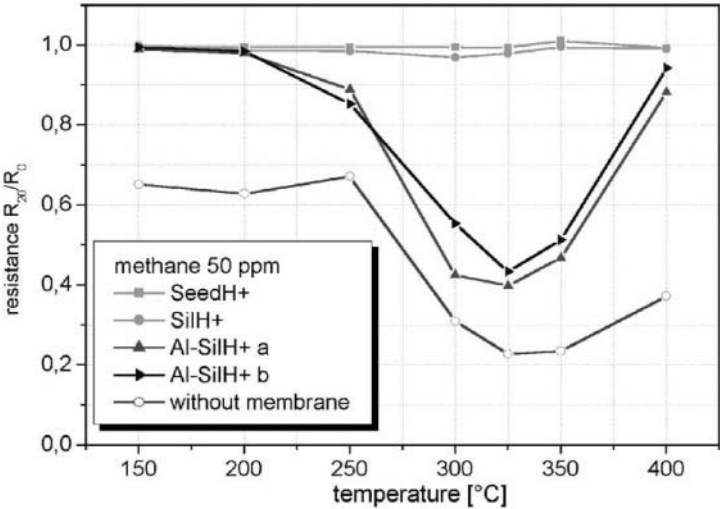


Figure 5: Sensor test of GGS 3300-sensors with various zeolite membranes, SeedH+- and SilH+- membranes were synthesized with conventional hydrothermal synthesis, Al-SilH+a and Al-SilH+b were synthesized with the new synthesis path, using aluminum coated supports, diagram shows single gas methane measurement (50 ppm in air)

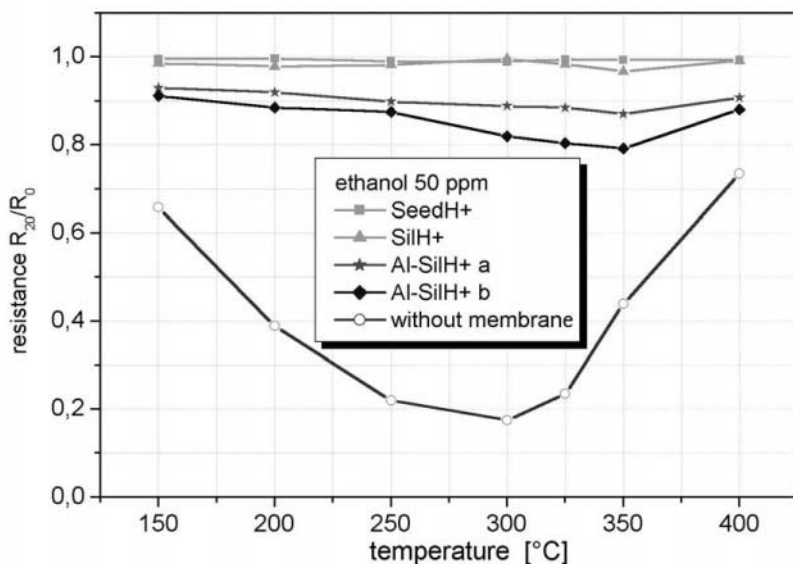


Figure 6 Sensor test of GGS 3300-sensors with various zeolite membranes, SeedH+- and SilH+- membranes were synthesized with conventional hydrothermal synthesis, Al-SilH+a and Al-SilH+b were synthesized with the new synthesis path, using aluminium coated supports, diagram shows single gas ethanol measurement (50 ppm in air)

Figure 6 shows the successful elimination of ethanol by the help of zeolitic membranes in front of the sensitive layer SnO_2 . No change in resistance could be measured in presence of ethanol, using zeolite membranes as filter material.

Conclusions

The successful synthesis and characterization of zeolites and microporous zeolite membranes, as well as the application of ion-exchanged zeolites as a filter layer on a semiconductor sensor device, is reported here. A concept for the use of zeolite membranes in gas sensing systems was developed and tested in a variety of experiments.

In table 1, a short characteristic of a selection of examined zeolite filters can be found. The suitability for the use as filters for sensors is marked by “+”. Particularly advantageous are the zeolites modified with copper, cobalt and nickel. These zeolites brought about a total conversion of ethanol into CO_2 and water in a wide range of temperatures (200 – 500 °C). Based upon the presented experiments, and with the novel synthesis path using Al-coated supports, it is now possible to combine the outstanding catalytic and molecular sieve properties of zeolites with a simple low cost commercial gas sensor device for use in various gas detection systems.

The suitability of zeolites as catalytic filter materials for SnO_2 -based gas methane sensors, used for reducing the cross-sensitivity towards ethanol, has been demonstrated by the present work. In future, tailored zeolite membranes should be used as catalytic layers, which are able to remove a variety of disturbing volatile substances before they reach the gas sensing layer sensor.

Table 1: Zeolites as filter material for methane gas sensors

Sample	suitable as filter material for methane gas sensor
Na-ZSM-5	-
silicalit	-
H-ZSM-5	++
H-ZSM-5/Co	+++
Na-ZSM-5/Co	++
Na-ZSM-5/Ni	++
H-ZSM-5/Cu	++
Na-ZSM-5/Cu	+++
Na-ZSM-5/La	-
Na-ZSM-5/Nd	-
Na-ZSM-5/Er	+

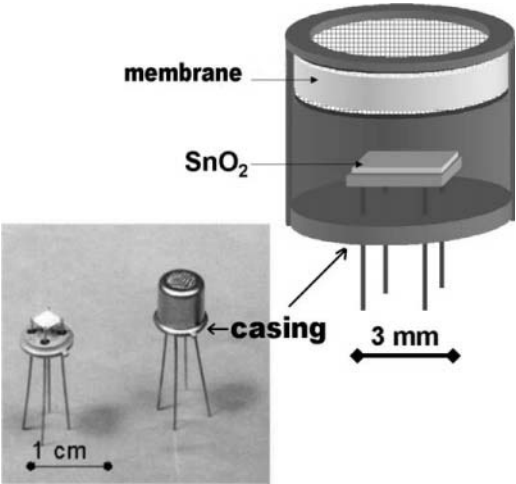


Figure 7: Commercial methane sensor GS 3300, based on SnO₂, with zeolite filter in front of the sensitive layer

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GENOMAGNETIC ELECTROCHEMICAL BIOSENSORS

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Abstract

The use of nucleic acid technologies has significantly improved preparation and diagnostic procedures in life sciences. Nucleic acid layers combined with electrochemical or optical transducers produce a new kind of affinity biosensors as DNA Biosensor for small molecular weight molecules. Electrochemical DNA biosensors are attractive devices for converting the hybridization event into an analytical signal for obtaining sequence-specific information in connection with clinical, environmental or forensic investigations. DNA hybridization biosensors, based on electrochemical transduction of hybridization, couple the high specificity of hybridization reactions with the excellent sensitivity and portability of electrochemical transducers. The main goal in all researches is to design DNA biosensors for preparing a basis for the future DNA microarray system. DNA chip has now become a powerful tool in biological research, however the real clinic assay is still under development. Recently, there has been a great interest to the magnetic beads and/or nanoparticles labelled with metals such as gold, cadmium, silver, etc. for designing of novel electrochemical DNA biosensor approaches resulting in efficient separation. The attractive features of this technology include simple approach, rapid results, multi-analyte detection, low-cost per measurement, stable, and non-hazardous reagents, and reduced waste handling. Some of these new approaches and applications of the electrochemical DNA biosensors based on magnetic beads and its combining with nanoparticles labelled with metals are described and discussed.

Keywords: Magnetic beads, Nanoparticles, DNA hybridization, Electrochemical DNA biosensors, Genosensors.

1. Introduction

Since the electroactivity in nucleic acids was discovered at the beginning of the sixties [1], different electrochemical tools for DNA based diagnostics and other areas of biotechnology have been performed for detecting DNA, RNA, and various genetic substructures to analyze or quantificate of nucleic acids [2-7]. Immediate applications will include directly quantifying DNA samples for use in sequencing or polymerase chain reactions (PCR), or pharmaceutical testing and quality control. Eventually, they could be applied to producing credit card-sized sensor arrays for clinical applications such as detection of pathogenic bacteria, tumors, and genetic disease, or for forensics [6]. Recent advances in automated DNA synthesis and the convenient site-specific labeling of synthetic oligonucleotides with advances in microelectronics, have generated a number of attempts at the development of novel biosensor devices for the analysis of specific gene sequences and for the study of nucleic acid-ligand interactions.

Various combinations of biological material associated with different types of transducers are an attractive subject of research. A biosensor is a device that incorporates a biologically active layer at the surface as recognition element and converts the physical parameters of a specific biological interaction into a measurable analytical signal. It associates a bioactive sensing layer with any suitable transducer and gives an output signal. Biomolecular sensing can be defined as the possibility of detecting analytes of biological interest, like metabolites, drugs and toxins, by using an affinity layer like enzymes, receptors, antibody or nucleic acids. The affinity layer can be a natural system or an artificial one, able to recognize a target molecule in a complex medium among thousands of others. The major processes involved in a biosensor system are analyte recognition, signal transduction and readout. Owing to their desirable characters, e.g, accuracy, speed, and easy automation, such analytical devices hold great promise for clinical and industrial food applications.

DNA biosensor, normally employs immobilized DNA probes as the recognition element and measures specific binding processes such as the formation of DNA-DNA and DNA-RNA hybrids, and the interactions between proteins or ligand molecules with DNA at the sensor surface [5]. Typically, the design of a genosensor involves the following steps [8]: 1) modification of the sensor surface to create an activated layer for the attachment of the DNA probe; 2) immobilization of the probe molecules onto the surface, preferably with controlled packing density and orientation; and 3) detection of target gene sequence by DNA hybridization at the sensor-liquid interface.

The detection of specific DNA sequences provides the basis for detecting a wide variety of microbial and viral pathogens. Traditional methods for DNA sequencing, based on the coupling of electrophoretic separations and radioisotopic (^{32}P) detection, are labor intensive and time consuming, and are thus not well suited for routine and rapid medical analysis, particularly for point-of-care tasks.

Electrochemical hybridization biosensors may greatly reduce the assay time and simplify its protocol. Such fast on-site monitoring schemes are required for quick preventive action and early diagnosis. The development of DNA hybridization biosensors holds great promise for obtaining sequence-specific information in connection with clinical, environmental or forensic investigations. Nucleic acid hybridization is a process in which inconsonant nucleic acid strands with specific organization of nucleotide bases exhibiting complementary pairing with each other under specific given reaction conditions, thus forms a stable duplex molecule. This phenomenon is possible because of the biochemical property

of base-pairing, which allows fragments of known sequences to find complementary matching sequences in an unknown DNA sample [9]. DNA hybridization biosensors can be employed for determining early and precise diagnoses of infectious agents in various environments [10,11] and these devices can be exploited for monitoring sequence-specific hybridization events directly [12, 13] based on the oxidation signal of guanine or by DNA intercalators (some antibiotics, metal coordination complexes, etc.) which form complexes with the nitrogenous bases of DNA [14-23]. DNA hybridization was detected by redox-active metal complexes that associated selectively and reversibly with double stranded immobilized DNA [18, 20].

Wang et al. [12] reported direct monitoring of DNA hybridization without the use of an external redox indicator. This reported method have relied primarily on monitoring changes in the guanine oxidation process accrued from the hybridization event. The detection of Factor V Leiden mutation and the discrimination of the mutation type using the oxidation signal of guanine was performed by using differential pulse voltammetry at the detection limit level as 51.14 fmol/mL [13]. A bis-intercalator anticancer drug, ECH was introduced as an good candidate for a redox indicator for electrochemical DNA hybridization sensors by Jelen et al. [21]. Marrazza et al. [22] developed a new procedure for detecting genetic polymorphisms of Apolipoprotein E (apoE) in human blood samples by using daunomycin (DM) as an electrochemical DNA hybridization indicator. Erdem et al. [20, 23] reported that methylene blue could be used as a promising indicator for the electrochemical detection of mismatched bases in oligonucleotides. Electrochemical transducers offer a very attractive route for converting the hybridization event into a useful analytical signal [23-26].

2. Genomagnetic electrochemical detection assay

Different kinds of beads can be used in flow or batch electrochemical biosensing systems used range from non-conducting or conducting, to magnetic materials. The magnetic particles are strongly affected when exposed to external magnetic fields. These microparticles are available with a wide variety of surface functional groups, material properties, and sizes. The size of the commercial magnetic beads changes typically from 1 μm through 10 μm . These materials normally contain metals such as iron, nickel or cobalt [27].

The use of monosized magnetic beads gives the convenience of magnetic separation. These particles are superparamagnetic, meaning that these microparticles can be easily separated from the liquid phase with a small magnet, but can be redispersed immediately after the magnet is removed [28]. The use of magnetic particles can bring novel capabilities to bioaffinity assays and sensors. Bioanalysis has benefited from the use of magnetic beads in electrochemical immunosensors [29] or for fluorescence DNA hybridization approaches [30]. The basic concept in magnetic bioseparations is to selectively bind the biomaterial of interest (e.g, spesific cell, protein, or DNA sequence) to a magnetic particle and then separate it from its surrounding matix using a magnetic field. The new biomagnetic process combines efficient magnetic mixing and separation into a single mechanism [31]. The usefulness of the magnetic beads in the development of microfluidic systems enables miniaturization and automation, resulting in less reagent and sample consumption, more efficient and faster hybridization [32].

Table: *A summary of the recent electrochemical investigations based on magnetic beads.*

Technique	Electrode	Response	DL	HT	Ref
PSA	PGE, CPE	Guanine	60 pM	10 min	33
DPV, SWV, LV	SPEs	α -naphthol	500 pg in 50 μ L sample	20 min	34
CSV	HMDE	Adenine	Below 2 nM for adenine	30 min	35
PSA	CPE, MCPE	Guanine	--	--	36
AdTS-SWV	PrGE	Guanine/Adenine	Higher than ppb level	30 min	37
LSV		1-naphthol	3 fmol		
PSA	SPEs	Silver	1.2 fmol	30 min	38
PSA	MFE	Cadmium	100 fmol in 50 μ L sample	10 min	39
CSV	HMDE	Iron	10 ng in 50 μ L sample	15 min	40

TRANSDUCERS: Carbon paste electrode (CPE), magneto carbon paste electrode (MCPE), hanging mercury drop electrode (HMDE), Screen printed electrode (SPE), pencil graphite electrode (PGE), pyrolytic graphite electrode (PrGE), mercury film electrode (MFE)

VOLTAMMETRIC TECHNIQUES: differential puls voltammetry (DPV), potentiometric stripping analysis (PSA), square wave voltammetry (SWV), cathodic stripping voltammetry (CSV), adsorptive transfer stripping voltammetry (AdSTV), linear voltammetry (LV) and linear square voltammetry (LSV).

DL: Detection limit

HT: Hybridization time

Ref: Related reference

The new electrochemical approaches based on magnetic beads [33-40, represented also in table] for detection of DNA hybridization by using these techniques; such as, differential puls voltammetry (DPV), or potentiometric stripping analysis (PSA), square wave voltammetry (SWV) etc. brings the spesific detection of DNA hybridization observed in exceedingly low detection limits as resulting in efficient magnetic separation.

Novel genomagnetic electrochemical assay related to BRCA1 breast-cancer gene based on the coupling of the label-free guanine detection route was reported by Wang et al. [33]. The results has showed that the magnetic separation has been extremely useful for discriminating against unwanted constituents, including a large excess of co-existing mismatched and non-complementary oligomers, chromosomal DNA, RNA and proteins. The new protocol involves the attachment of biotinylated oligonucleotide probes onto streptavidin-coated magnetic beads, followed by the hybridization event, dissociation of the

DNA hybrid from the beads, and PSA measurements at a renewable pencil graphite pencil electrode (PGE).

The coupling a magnetic isolation with electrochemical detection of DNA segments related to the breast-cancer BRCA1 gene showed an enzyme-linked sandwich solution hybridization isolation, with a magnetic-particle labeled probe hybridizing to a biotinylated DNA target that captures a streptavidin-alkaline phosphatase (AP) [34].

Paramagnetic Dynabeads oligo (dT)25 (DBT) was used in another genomagnetic reported assay [35] by using a hanging mercury drop electrode (HMDE) for detection label free detection of DNA and RNA based on the determination in ppb levels of adenines released from nucleic acids by acid treatment. In this proposed technology, the specific determination of hybridization of polyribonucleotides, mRNA, oligodeoxynucleotides, and a DNA PCR product length in 226 base pairs was also demonstrated.

The reversible magnetic-field stimulated DNA oxidation by using dual carbon paste electrode was reported by Wang et al. [36] based on guanine oxidation signal. This proposed technology with site-specific activation of DNA oxidation shows a promise for new DNA arrays.

Enzyme linked immunoassay for the detection of the DNA hybridization was developed by using PrGE [37]. Alkaline phosphatase as enzyme was used and consequently by using LSV technique, 1-naphthol was measured as product of enzymatic reaction due to DNA hybridization. Also the authors reported the comparison between determinations of the long oligomers as 67 mers using guanine oxidation signal, the direct determination of DNA-Os, bpy adduct and the product signal of enzymatic immunoassay; as a result of this comparison, the most sensitive method was reported as enzymatic immunoassay.

There are some reported genomagnetic assays connected by using nanoparticles labeled with metals. In one of them [38], a new nanoparticle-based protocol for detecting DNA hybridization based on a magnetically induced solid-state electrochemical stripping detection of silver with the peak potential as + 0.28 V by using SPEs. The selectivity of this assay was checked co-existing of the larger excess of three-base and single-base mismatched oligonucleotides and noncomplementary oligonucleotides beside target oligonucleotide.

In another study of Wang et al. [39], the detection of DNA hybridization following the genomagnetic assay as magnetic-bead/ DNA hybrid/ cadmium sulfide nanoparticle by using mercury-film electrode.

Two different particle-based assays for monitoring DNA hybridization based on PSA detection of an iron tracer were reported [40]. The probes labeled with gold-coated iron core-shell nanoparticles were used and thus the captured iron-containing particles are dissolved following hybridization step, the released iron is quantified by cathodic-stripping voltammetry by using HMDE, in the presence of the 1-nitroso-2 naphthol ligand and a bromate catalyst. The results showed that this protocol offers high sensitivity and minimal contributions from non-complementary nucleic acids.

The reported genomagnetic assays show a very attractive bioanalytical performance. The advantages of this technology include simple approach, rapid results, multi-analyte detection, low-cost per measurement, stable, and non-hazardous reagents, and reduced waste handling. One of the future prospects is that the detection of point mutations will be detected after combining genomagnetic assay with novel challenging protocol based on peptide nucleic acid (PNA) probes. Such coupling of magnetic hybridization surfaces with renewable transducers and label-free electrical detection eliminates the needs for external

indicators and advanced surface modification or regeneration schemes, and hence results in a greatly simplified protocol. The magnetic beads can also be well suited for incorporation in a microfluidic device. The application of microfluidic systems in this field enables miniaturization and automation, resulting in less reagent and sample consumption, more efficient and faster hybridization, etc.

3. Conclusions

Nanomaterials have unique chemical and physical properties that offer important possibilities for analytical chemistry. It is hoped that continued development in nanoscience through combined efforts in microelectronics, surface/ interface chemistry, molecular biology, and analytical chemistry will lead to the establishment of genosensor technology as a major component of analytical biochemistry [8].

Immediate applications will include directly quantifying DNA samples for use in sequencing or polymerase chain reactions (PCR), or pharmaceutical testing and quality control. Eventually, they could be applied to producing credit card-sized sensor arrays for clinical applications such as detection of pathogenic bacteria, tumors, and genetic disease, or for forensics.

A quantitative understanding of such factors that determine recognition of DNA sites would be valuable in the rational design of new DNA targeted molecules for application in chemotherapy and in the development of new tools for the point-of-care tests and diagnosis based on DNA.

On-going works on electrochemical genomagnetic assay will further explore its potential a development in flow detection systems combined with the advantages of solid state chemistry, for detecting nucleic acid variations in a variety of applications.

Acknowledgements

This work has been supported by the Turkish Academy of Sciences, in the framework of the Young Scientist Award Program (KAE/TUBA-GEBIP/2001-2-8). A.E wishes to express her gratitude for scientific and technical contributions from the members of DNA biosensor teams at Senso-chip lab in New Mexico State University (NM, USA) during the course of the related studies.

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NANOCAPSULES – A NOVEL TOOL FOR MEDICINE AND SCIENCE

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Abstract.

The most promising tool for future applications in the field of science as well as in medicine is the use of nanotechnologies. Especially self-assembly systems with tailored properties on a nanometer level fulfil the requirements to nano-organized systems in a satisfactorily manner. Hence the development of so-called nanocapsules prepared by means of Layer-by-Layer technique was a great progress on the way to individual drug delivery systems or nano-sized bioreactors. The preparation of hollow shells for drug delivery use requires polyelectrolytes as well as a charged core that are not cytotoxic. According to this purpose CaCO₃ crystals with different shapes were introduced as removable template for capsules with changeable permeability as a result of pH variations. Due to the low toxic potential of the core it could be valuable for applications in human body.

Furthermore the nano-organized shells are suitable as coating of living cells or artificial tissue. With this “second cell wall” it is possible to target the encapsulated material to predefined organs, and to prevent immune response. Moreover one can choose between the breakage of the covering using the capsule only as targeted carrier or the production of proteins inside the remaining shell. The requirements for this application are a polyelectrolyte pair that is not toxic to the human body as well as to the coated cells.

In the present paper a system was utilized to investigate the processes leading to capsule breakage. For this purpose a mutant yeast strain (*Sacharomyces cerevisiae*), which express GFP-tubulin under a galactose regime, was observed by means of a confocal laser scanning microscope. The measurements reveal an increased surface charge in the region of developed buds prior encapsulation. Moreover coated buds were no longer developed and a new budding was initiated. The polyelectrolyte capsule did not hinder the duplication but delay it.

In order to test the used polyelectrolyte couple to other biological organisms the germinating conidia of the fungi *Neurospora crassa* was coated. The received results with fluorescence microscopy support the observation of increased negative surface charge in the growing region of cells. Furthermore a stronger staining of the conidia poles was observed.

Summarizing the capsules exhibit interesting properties as valuable tool in science and a promising candidate for application in the field of medicine.

1. Introduction

A new generation of capsules with a dimension depending only on the used charged template was achieved by a method called Layer-by-Layer technique (Decher 1997). With this technique capsule walls are constructed by alternating deposition of oppositely charged polyions inducing shells, which are stable even after the core removal (Caruso et al. 1998). The polyelectrolyte capsules are nearly inert against acid or base in a wide pH range and also against solvents (Sukhorukov et al. 2000; Antipov et al. 2002). Furthermore wall properties like permeability or thickness may be tailored by changing pH, ionic strength, counter ions and the choice of polyelectrolytes during the adhesion of the layers to the template. These parameters alter the conformation of weak polyelectrolyte like PAH (poly-(allylamine hydrochloride)) by varying the charge density inducing a change from a completely charged elongated structure to a random coil (Fery et al. 2001). The closed structure is likely characterized by the presence of cavities or pores whose sizes depend on pH or ionic strength during layer deposition. The occurrence of such cavities may explain the dependence of the wall permeability on pH or ionic strength. The use of polyions like quaternary ammonium e.g. PDADMAC (poly-(diallyldimethylammonium chloride) or PEI (poly-(ethylenimine)) that are sterically hindered and prevent the coiling of the molecules in dependence of pH or salt concentration also varies the wall properties (Baba et al. 2000; Estel et al. 2000). Further the counter ions e.g. using potassium instead of sodium (Büscher et al. 2002) induce denser layers and change the permeability of the shell. Especially for the polyelectrolyte pair poly-(allylamine hydrochloride) (PAH) and poly-(styrenesulfate sodium) (PSS) the influence of the above mentioned parameters are well-studied on flat surfaces by Decher (1997) or onto melamine formaldehyde cores (Sukhorukov 2000).

Another crucial factor in hollow capsule properties is the core removal. The template annihilation condition and the resulting size of core fragments must be taken in consideration. In particular for the destruction of fixed blood cells with sodium hypochloride (Moya et al. 2001) or for melamine formaldehyde (MF) latex particles with acid changes of the chemical polyelectrolyte structure or the wall permeability were stated. A withdrawal of the widely used MF particles is the increasing size of the oligomers with time due to cross-linking and presence of residual material inside the capsule in the range of 20% in weight (Gao et al. 2001). However MF particles are well investigated and are characterized by a small size distribution, a smooth surface and good encapsulation properties.

Hollow polyelectrolyte capsules are a promising tool as drug delivery system because they can be loaded after core removal with charged proteins, enzymes or molecules at low pH when wall cavities are "open" and trap these molecules at higher pH when the pores are "closed". Hollow capsules were successfully loaded with FITC-dextran and FITC-BSA by Sukhorukov et al. (2001).

Since the only limitation in the choice of cores is the necessity of a charge, a large variety of templates is used like fixed blood cells (Möhwald 2000), ionic crystals (Silvano et al. 2002, Antipov et al. 2001), crystallized fluorescent dyes (Shi et al. 2001) or proteins (Balabushevitch et al. 2001). Furthermore the capsule can serve as protective shell for

living cells (Soon-Shiong 1999, Diaspro et al. 2002), transplants (Haisch et al. 2000) or artificial tissue against immune response.

2. Experiments

2.1. HOLLOW CAPSULES

One aim of our study was the development of ionic cores, which are non-toxic and easy to prepare. We used CaCO_3 due to the possibility of changing the crystal shape via polymorphism. We mainly followed the procedure of Kitamura (2001) to achieve CaCO_3 with different shapes. So we obtained a large variety of shapes like completely round crystals (fig. 1A), peanut-shaped ones (fig. 1B), and rhombohedral ones (fig. 1C) by changing the amount of Mg^{2+} ions. The images were taken by means of scanning electron microscopy (SEM).

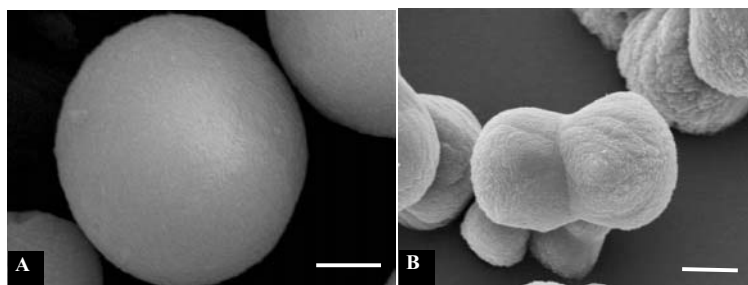


Figure 1.: SEM images of CaCO_3 crystals in dependence of magnesium concentration (A) With 12 mM Mg^{2+} ; bar: 2 μm , (B) with 49 mM Mg^{2+} ; bar: 5 μm , and (C) without Mg^{2+} ; bar: 10 μm .

Kitamura (2001) found that Mg^{2+} ions stabilize the metastable spherical form and hinder the change to the thermodynamically stable cubic calcite morphology. We confirmed these data for high amounts of magnesium but we observed in this case only peanut-like crystals. These crystals were assemblies of nano-crystals as clearly visible in fig. 1B. Reducing the Mg^{2+} concentration leads to round crystals (fig. 1A) but storage in water for 1 day shows that the spherical shape is not stable, even of a delayed structural change to rectangular particles was monitored (a detailed paper is in preparation). A preparation of thermodynamically stable rhombohedral crystals usually consists of 90% cubes and 10% round-shaped crystal (fig. 1C).

To overcome the problem with structural changes in the crystals they were dried immediately after preparation at 50°C in the oven and by storing them as a powder until we encapsulate them. The size distribution of the crystallites ($5 \pm 1 \mu\text{m}$) is wider then for commercial available melamine formaldehyde or CdCO_3 (Silvano et al. 2002). Due to the fact that we are only interested in the shape of the crystals we did not determine the exact crystal morphology with x-ray.

Here we focus on the capsule properties templated onto round-shaped crystals. For these experiments we coated the crystals with 8 polyelectrolyte layers with the Layer-by-Layer technique developed by Decher (1997) for flat surfaces and well studied by Möhwald and

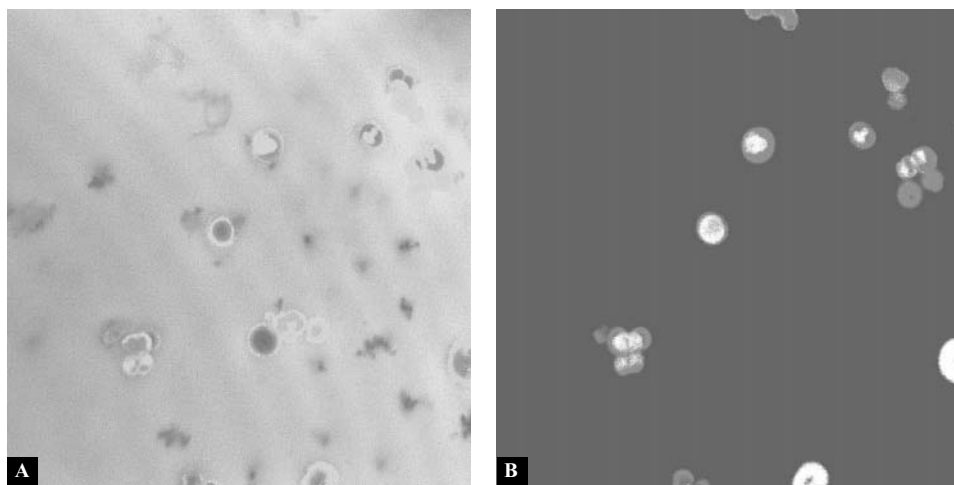


Figure 2.: CLSM images of hollow 8 layer polyelectrolyte capsules templated onto round CaCO_3 crystals. (A) FITC dyes (green) are excluded at pH 9, capsule labelled with Alexa (red). (B) Addition of HCl induces entrance of FITC inside the capsule and disappearance of the signal outside.

his workgroup (Sukhorukov et al. 2000) for colloids. Both polyelectrolytes PAH (15 kDa) and PSS (70 kDa) were deposited onto CaCO_3 from a 0.5 m NaCl solution. Once completed the alternate PAH/PSS adsorption, the core was removed with HCl. Because of the negative charge of the crystals in the salt solution we start the coating with PAH.

In the present paper the influence of pH on the permeability of the empty capsules was investigated (fig. 2) by means of CLSM. We visualized the capsule wall by means of the red-fluorescent Alexa dye (Alexa Fluor® 555 carboxylic acid, succinimidyl ester) which was covalently bound to the cationic PE following a protein labelling procedure described elsewhere (e.g. Donath 1998). Adding the small green fluorescent FITC (MW: 389.38 g/mol) to the 8 layer hollow shells at pH 9 we observed an exclusion of the green fluorescence from the shell interior for at least 1 h (fig. 2A).

We detected two populations of capsules mainly: one is completely round with black inside and bright red fluorescence of the capsule. The other population consisting of capsules that are peanut-like shaped have the same fluorescence inside and outside and a brighter green signal of the capsule wall (data not shown). By lowering the pH below 9 with HCl we could monitor the entrance of FITC into the interior of round capsules (fig. 2B). As a result the pH sensitivity of the dye we loose the fluorescence signal outside at low pH. Furthermore we can conclude from our observation of bright green fluorescence in the capsules that the pH inside and outside is different.

2.2. CAPSULES ONTO LIVING ORGANISMS

Previous experiments (Diaspro et al. 2002) with commonly used bakery yeast (*Saccharomyces cerevisiae*) showed that the cells are in good vital condition after encapsulation, e.g. none of the polymers is cytotoxic for them and nutrients can permeate through the capsule wall thus allowing the coated organisms to duplicate. While budding

they break the capsule and develop a daughter cell outside, so fluorescent marked mother cells with unstained daughters can be observed.

In the first set of the presently reported experiments we encapsulated the yeast strain PSY T3 with 4 polyelectrolyte layers. For this yeast the GFP-tubulin fusion under GAL-promoter was achieved growing the strain for one night in galactose (15 %) at 28°C. To enhance the viability of the coated cells they were incubated for 30 min at 28°C in YPD (yeast extract 10 %, Peptone 20 %, glucose 20% in water) medium prior visualization. Longer storage in this medium leads to loose of the GFP fluorescence. The imaged cells remained in medium under the microscope to follow the budding and the capsule breakage. Figure 3 shows a CLSM image of a coated yeast cell after 1.5 h under the microscope.

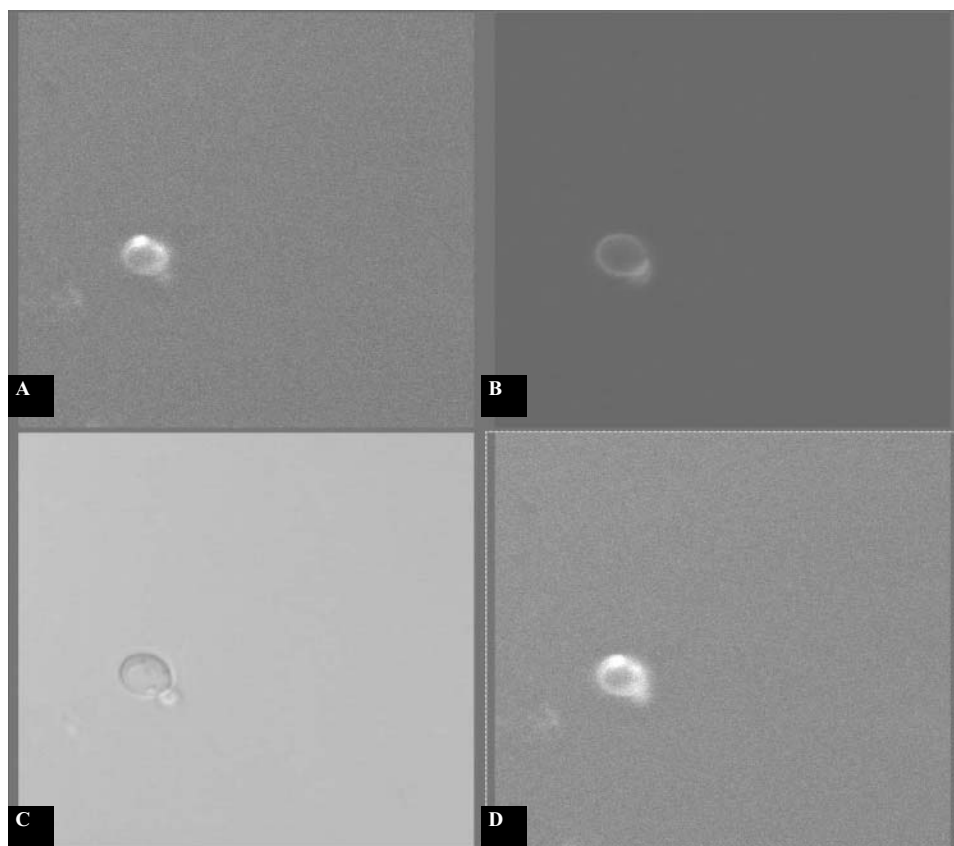


Figure 3. CLSM and phase contrast images of GFP-tubulin expressing yeast cell inside the polyelectrolyte capsule (red). (A) GFP fluorescence of the spindle. (B) Red fluorescence of the Alexa-labelled PAH indicating the shape of the polyelectrolyte capsule. Brighter red signal indicate higher charge. (C) Phase contrast image of the cell with bud. (D) Merging of (A)-(C) show the origin of the spindles is opposite the bud and the region between bud and mother cell is brightly stained by the capsule.

A bud in an early stage of development was marked (bright red) with an enlarged polyelectrolyte layer during encapsulation. Usually an intense green GFP signal oppositely to the bud could be observed. In this specific case we followed the cell process for about 2 h under the microscope.

The image shows that a spindle incorporating GFP-tagged tubulin fusion protein is clearly distinguishable inside the encapsulated yeast cell. The dynamic of spindle elongation was followed during cell division. We found that, since the bud growing point presented a higher concentration of polyelectrolytes and was visible as a red bright point, it will be an interesting tool for studying the orientation of the spindle respect to the cell budding polarity axis. Furthermore the encapsulation terminated the development of the first daughter cell and new spindles start to appear in a different region. Due to the enlargement of the capsule in the region of the first bud we conclude that budding induces a higher surface charge or different concentration of charges on the cell wall. This fact is aim of future studies to determine how charged compounds in the cell wall of growing cells bind preferentially to positive PE. This observation will also represent a valuable feature for specific delivery on bud emergence site and possibly for localization of compounds even before the newly formed bud is visible. Summarizing our observations are encouraging and useful in the field of cell wall studies and determination of cell division axis.

We also found that the capability to follow the duplication and division process under the microscope demonstrated that encapsulation procedures were not cytotoxic and did not interfere with cytokinesis or suppress the budding process.

The second investigated cell system was the orange-coloured bread mould *Neurospora crassa* a filamentous fungus. During *Neurospora* germination, conidia (the asexual spore) form a hypha that contains numerous nuclei and partial cross walls. Hypha emerges, like a tube germ, from a region of the conidia. It is not known if the choice of the region is random or under genetic control or influenced by environmental factors. We encapsulated conidia at different states of germination with 4 polyelectrolyte layers.

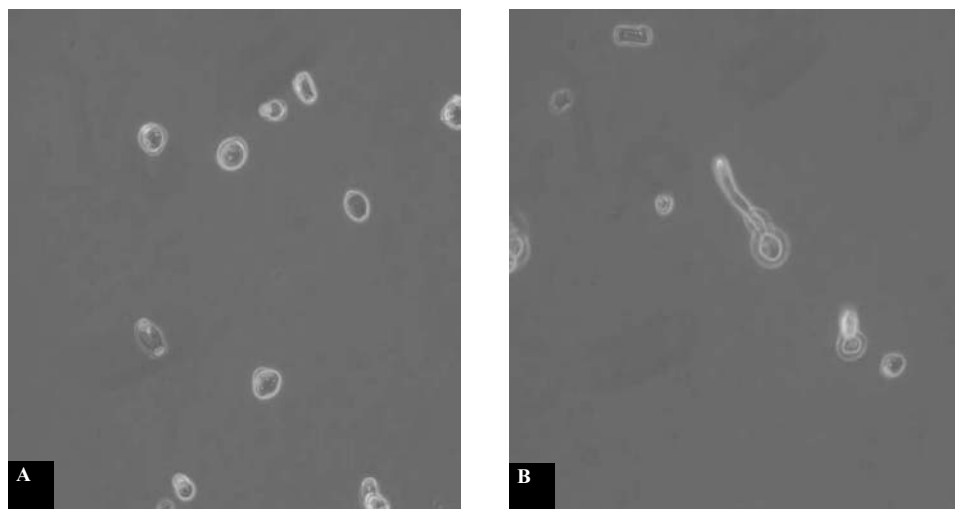


Figure 4. Merged conventional fluorescence and phase contrast images of the polyelectrolyte capsule (red) onto growing *Neurospora crassa* conidia (A) at time 0 and (B) stored for around 4 h in medium.

In figure 4A conidia at time 0 were imaged. In this conventional fluorescence image two brightly red stained poles are observable. Other conidia were grown for several hours in liquid minimal medium at 28°C in agitation, and samples were taken and encapsulated after 2, 3 4, and 6 hours. One of the brightly marked poles usually disappears after 2 h. Fig 4B shows a germinating conidia after 4 hours of growth. The high fluorescence intensity, localized mainly in the apical part of the hypha, indicates that now a very highly charged surface is concentrated in this region.

We do not know the factors that influence the choice of the growing direction of the hypha. Preliminary evidences obtained using *Neurospora* mutants indicate light as one of the factor influencing this process (Linden et al. 1999; unpublished data). We are interested in determine the nature of the fungal walls molecules that influence the concentration of fluorescent coating at the level of two poles initially and then in the growing tip. For the moment we know, from experiment of coating with single PE layers, that the germ tube presents a concentration of negatively charged molecular compounds. Additional studies using antibodies against specific wall fractions or alternative staining procedure and strains of *Neurospora* mutants will be carried out to determine the surface proteins or molecules bind to PAH. Further experiments with encapsulated conidia at time 0 suggest an inhibitory effect on the initial step of germination in fact we observed a delayed growth of the hypha (compared to uncoated samples), accompanied by a complete destruction of the polyelectrolyte capsule (data not shown). What causes the delay is another matter of investigation.

Summarizing the results we have shown that polyelectrolyte nanocapsules can be templated onto different cores like ionic crystals or living organisms. It was shown that capsules on CaCO₃ crystals exhibit comparable properties to that produced on melamine formaldehyde. From the results of living cell encapsulation experiments we infer the presence of a significantly higher surface charge density in growth region for budding yeast cells as well as for germinating conidia of *Neurospora crassa*.

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22. Acknowledgement

The authors acknowledge gratefully Prof. Möhwald and his group for the introduction to the Layer-by-Layer technique. Moreover they thank Emilio Bellingeri performing the SEM measurements. This work is supported by the EU as a research fellowship grant (EU Project HPRN-CT-2000-00159). P. B. and P. F. thank Instituto Pasteur Fondazione Cenci Bolognetti for partial support.

BIOLOGICAL MOLECULE CONFORMATIONS PROBED AND ENHANCED BY METAL AND CARBON NANOSTRUCTURES: SEIRA, AFM AND SPR DATA

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Abstract

The use of the method of enhancement of infrared absorption by rough metallic surface (surface enhanced infrared absorption – SEIRA) allows one to increase the probability of infrared transitions and to reveal a series of spectral manifestations of structural features of biological molecules. We analyse various experimental techniques that give the possibility to achieve enhancement in the infrared (IR) spectra. We studied the applicability of the SEIRA techniques for conformational analysis of nucleic acids and proteins (bovine serum albumin – BSA) on gold substrate of 200-500 Å thickness. Under the conditions of our experiment and according to literature data, there was observed enhancement factor equalled to 3...20 for vibrations of various molecular groups. Concentration of BSA solution and thickness of the protein film on gold substrate influence the conformational composition. Conformational state of protein in solution plays a key role after its precipitation on gold substrate. Different roughness of gold surface leads to changes in enhancement factor. Peculiarity of another optical amplifier, namely, colloidal gold that effectively used for enhancement of signal in IR absorption and Raman scattering, have been studied. The structural features of DNA – colloidal gold and BSA – colloidal gold system that obtained in SEIRA and SPR (surface plasmon resonance) experiment are discussed. Atom forth microscopy (AFM) technique was applied to test the roughness of the metal surface. The IR experimental evidence for enhancement of the vibrations of residual graphite on the surface of carbon nanotubes is presented. We made an attempt to model the factor of enhancement of electrical field and their frequency dependence for different metal surfaces and obtained that silver, gold and copper are the best.

Key words: DNA, bovine serum albumin (BSA), Fourier transformed infrared spectroscopy (FTIR), surface enhanced infrared absorption (SEIRA), gold substrate, gold-colloidal particles, surface plasmon resonance (SPR), atom forth microscopy (AFM).

1. Introduction.

The work with biological objects, such as nucleic acids, proteins, lipids, imposes some restrictions on the use of traditional techniques and makes necessary specific approaches and methods. Notwithstanding the use of modern equipment, one does not always succeed in obtaining good results. One from the moments here is the restricted amount of the substance under study that the searchers should work with. For this reason, for registering the IR spectra and analysis of the samples of extremely small amount, we proposed a modified technique on the basis of the effect of enhancement of infrared absorption by rough metallic surface (SEIRA). The enhancement of optical process by a factor $10^2 \dots 10^{12}$ near rough surface of metal (Au, Ag, Fe, etc.) is known already for twenty years, for both optical transitions in adsorbed molecules (Raman scattering of light, luminescence, IR absorption) (Chang et al., 1982; Harstain et al., 1980; Masatoshi Osawa et al., 1991) and the processes which do not depend on the presence of molecules on the metal surface (for example, second harmonics generation) (Kosobukin, 1983). The effect lies in an essential increase of the intensity of transition (for example, effective cross-section increases by factor $10^5 \dots 10^{12}$ for Raman scattering and $10 \cdot 10^4$ for IR absorption) or efficiency of the process near metal surface. The explanation of the effect is not simple and includes several mechanisms, such as: 1 – the increase of the electromagnetic field near rough metal surface or island metal films, 2 – the increase of the dipole transition moment of the adsorbed molecules, etc. According to (Kosobukin, 1983), the coefficient of enhancement of the electric field is a function of dielectric permeability of the metal. One should note, however, that the influence of the metal under some conditions and characteristics of the surface or adsorbed substances can lead not only to enhancement but also to weakening of the optical transitions of the molecules near the metal surface (Bondar et al., 1980).

A theoretical interpretation of the effect of enhancement is presented in (Kosobukin, 1983) in general form. It includes two possible ways: enhancement of the electromagnetic field due to interaction with local (surface) plasmon oscillations which emerge on the imperfections of the metal surface, and specific increase of the dipole transition moments of the molecules adsorbed on the metal surface.

In modern biological experiments it is very important a conformation analysis of biological molecules under external stimuli: pH, interaction with small and big molecules, temperature, etc. The FTIR method, namely SEIRA is a good tool for the experiments on conformational analysis of biological molecules in real time and *in situ* (Masatoshi Osawa, 2002).

2. Experimental methods of the use of SEIRA effect.

The energy scheme of the mechanism of the enhancement effect is presented in *Figure 1*. Under the conditions of different SEIRA experiment we worked at the wing of the plasmon resonance for golden substrate, as it is shown in the insertion in *Figure 1*.

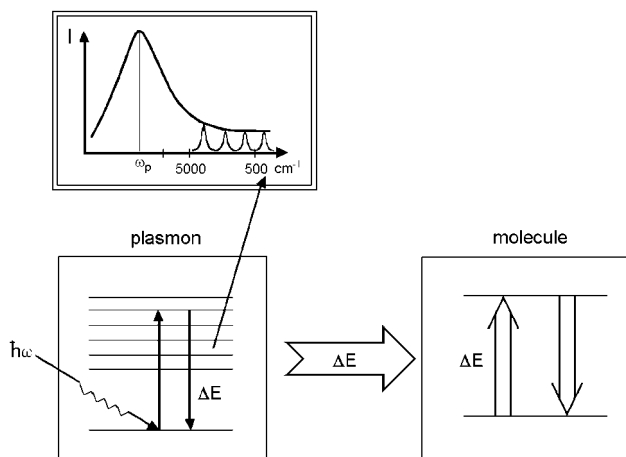


Figure 1. The energy scheme of the mechanism of the enhancement effect.

The energy is transferred from photon to local (or surface) plasmons oscillations. The plasmons oscillations have resonant character and the form of the boundary determined their frequency. The surface charge that emerges on the surface roughness causes the Coulomb returning force. The energy from plasmon vibrations is transferred to the adsorbed molecules, which causes increased molecular absorbance.

In literature, there are presented three experimental realizations of the SEIRA method:

1. First - the SEIRA method in reflectance geometry (Figure 2). The enhancement occurs due to increase of the intensity of electric field at excitation of local plasmons in roughness of metal film. Earlier (Dovbeshko, Chegel et al., 2002) we studied the validity of the use of the effect of enhancement of infrared absorption by metal surface for nucleic acids and lipids deposited onto golden substrate as compared with the reflectance experiments.

The results show that when using the SEIRA method for the study of IR absorption of nucleic acids (and similarly for lipids (Dovbeshko et al., 2001)), no deformation of contour of the absorption bands is observed as compared with the spectrum on neutral CaF_2 substrate.

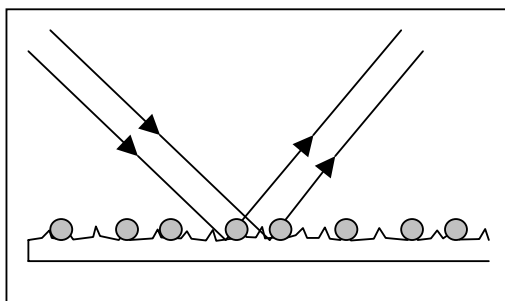


Figure 2. Scheme of SEIRA experiment in reflectance geometry.

Some frequency shifts are present, but for the most part of the bands they are small (1-2 cm^{-1}). This allows us to make conclusion about possibility of the use of this method for the problems of this type (Dovbeshko et al., 2001). The experimentally observed coefficients of enhancement of integral intensity of the absorption bands which correspond to vibrations of various molecular groups of DNA were found to be equal to 3...5 as dependent on the thickness of the layer of sputtered gold (*Table 1*).

2. The second method realizes enhancement in the geometry of attenuated total reflectance (ATR). There exists possibility of resonant enhancement of electric field near ideally flat metal surface due to nonradiational surface electromagnetic wave that is excited in the ATR method (*Figure 3*).

Table1. *The enhancement factor for integral intensity of the DNA absorption bands.*

DNA on CaF_2 band position, cm^{-1}	DNA on Au, Band position, cm^{-1}	Factor of enhancement		Assignment
		Experiment	Calculation	
3350	3345	5	48	Str. O-H, N-H, C-H
1655	1653	3	14	C=O, C=N, N-H Adenine, Thymine, Guanine, Cytosine
1238	1230	3	9	str. PO_2^- asym.

One can show that for the prism - metal - dielectric medium configuration, where the media have dielectric permeability ϵ_2 , $\epsilon(\omega)$, and ϵ_1 , respectively, and their boundaries are located at $z=0$ and $z=d$ (Kosobukin, 1983).

If flat light wave with amplitude $E_0(\omega)$ falls from inside the prism onto its surface $z=0$ at angle $\theta_i > \arcsin(\epsilon_2 / \epsilon_1)$, then for x -component of the field on the surface of metal $z=d=0$

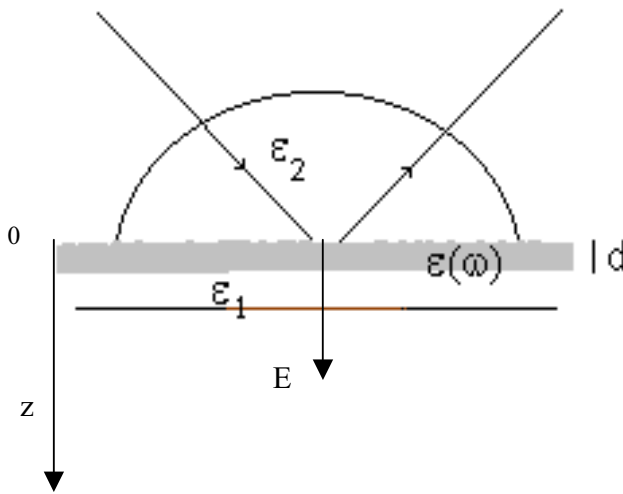


Figure 3. Scheme of the ATR method in Kretschmann geometry.

within the framework of macroscopic electrodynamics for $\omega = \omega_s(k_{\parallel})$ we obtain:

$$\left| \frac{E_x(d)}{E_{0,x}} \right|^2 = \frac{16}{1 + \left(\alpha_1 / \beta_2 \right)^2} e^{-2h_1 d} \left| \frac{\varepsilon'}{\varepsilon''} \right|^2 \quad (1)$$

where $k_1 = \left(k_{\parallel}^2 - \varepsilon_1 \omega^2 / c^2 \right)^{1/2}$, $\alpha_1 = \varepsilon_1 / k_1$, $\beta_2 = c \sqrt{\varepsilon_2} (\omega \cos \theta_i)^{-1}$.

This equation is obtained in the suppositions $e^{-2k_1 d} \ll 1$ and $|\varepsilon'| / |\varepsilon''| \gg 1$, $|\varepsilon'| \gg 1$ for $\omega = \omega_s(k_{\parallel})$. Under the first condition, the law of dispersion of surface electromagnetic waves determines the spectrum of surface electromagnetic waves $\omega_s(k_{\parallel})$. The first condition secures small radiation damping of surface electromagnetic waves, and under the experimental conditions (where we have $k_1 d \ll 1$) it is not too strong or strict. Equation (1) reflects the fact that at excitation of surface electromagnetic waves on smooth surface there exists resonant enhancement of electric field, and its magnitude is characterised by the factor $|\varepsilon'| / |\varepsilon''|$, similarly to the situation for local plasmon vibrations. The possibility of enhancement of electric field by polaritons at flat surface and its manifestations in optical surface were considered theoretically for such processes as absorption of light by molecules near resonance with surface plasmons and Raman scattering by molecules in ATR geometry. The consideration of the mechanism of enhancement of electric field by surface polaritons predicts essentially smaller enhancement than the enhancement of electric field due to local plasmon oscillations. For this reason, there exists an interest in attempts to separate the contributions from local plasmon oscillations and surface electromagnetic waves into enhancement of Raman scattering on adsorbed molecules by rough surface (Kosobukin, 1983).

The theoretical study of the effect of enhancement revealed that the magnitude of enhancement of electric field $g(\omega_r)$ (which is $g(\omega_r) \sim \omega_p / \gamma \sim |\varepsilon'| / |\varepsilon''|$ at resonance) is characterised by concurrence of the processes of excitation and decay of surface electromagnetic waves or modes (SEM). SEM are Bose excitation which for great numbers of occupation transform to classical modes. For this reason, the level of pumping of SEM (in the specified external field E_0) is limited only by the processes of their decay. As this is shown in (Kosobukin, 1985), when describing SEM on the basis of dielectric function, the parameter $1/\tau$ describes the full rate of decay of SEM:

$$1/\tau = 1/\tau_d + 1/\tau_s + 1/\tau_r \quad (2)$$

Here we single out the following channels of decay of SEM:

- 1) dissipative (relaxation time τ_d), connected with passage of the energy of SEM to heat;
- 2) radiative (decay to photons for time τ_r);

3) surface (scattering of SEM to other SEM for time τ_s).

In this connection one should note that the observed efficiency of the enhancement of electric field by local plasmon oscillations and surface electromagnetic waves could be connected with different influence of the roughness toward local and delocalised plasmon oscillations. Indeed, when creating the roughness of surface with scale smaller than the wavelength of light, there increases the possibility of formation of local plasmon vibrations. However, this is accompanied by rapid decrease of the lifetime of surface electromagnetic waves and enhancement of electric field due to them, which is determined by the processes of their radiation decay and scattering on the roughness (Kosobukin, 1983).

3. The third method realise the effect of enhancement on colloid particles of gold or silver (Figure 4).

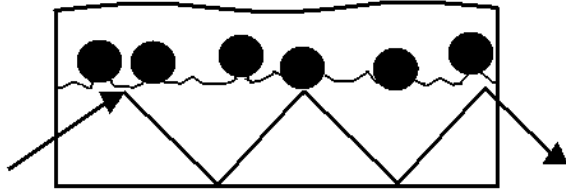
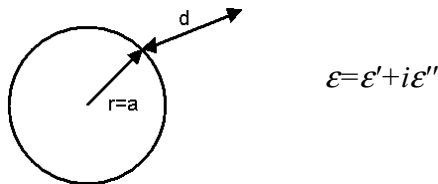


Figure 4. Scheme of the RATR (repeated attenuated total reflection) method.

For our purpose, one can use the geometry of transmission or one can increase the sensitivity and use the repeated attenuated total reflection (Figure 4). Or one can create a colloidal solution where the substance under study is being adsorbed on the colloidal particles. We observed the effect of enhancement of the absorbance intensity of different molecular groups near the metal surface. In (Kamnev et al., 2002), the authors studied the proteins, which were adsorbed at colloidal particles (golden ones, with average diameter 15 - 30 nm). The authors obtained the dependence of the coefficient of enhancement on the size and the type of the particles. The results showed that the SEIRA method is sensitive to interaction of protein molecules adsorbed on colloid particles with specific proteins, which make it possible to monitor with ease the antigen-antibody type interactions. The obtained results can give a basis for revealing various biospecific interactions in the systems under study.

For theoretical description of this effect we use the model of isolated particle (Kosobkin, 1983). Consider enhancement of electric field by metal sphere with radius $r=a$ with frequency-dependent complex dielectric permeability $\varepsilon(\omega)$; the sphere is placed in the medium with dielectric permeability ε_l .



For this model, the field of dipole vibrations of electric type asymptotically transforms to flat wave with amplitude $E_0(\omega)$; in quasistatic approximation, it has the form:

$$E(r, t) = \exp(-i\omega t) [E_0(\omega) + E_1(r, t)], \text{ where}$$

$$E_1(r, \omega) = \frac{\varepsilon - \varepsilon_1}{\varepsilon + 2\varepsilon_1} \left(\frac{\alpha}{r} \right) \frac{3(E_0 r) r - E_0 r^2}{r^2}, \text{ where } r \geq \alpha,$$

r is calculated starting from the centre of the sphere.

The efficiency of enhancement of the electric field by the sphere is characterised by the maximal value of the coefficient, which can be calculated with the use of the equation:

$$E_a(r, \omega) = g_{\alpha, \beta}(r, \omega) E_{0, \beta}(\omega)$$

in the pole of the sphere ($r = ae_0$, where $e_0 = E/E_0$), we have

$$g^2(\omega) = \left| \frac{E(ae_0, \omega)}{E_0(\omega)} \right|^2 = \frac{9|\varepsilon(\omega)|^2}{[\varepsilon'(\omega) + 2\varepsilon_1]^2 + [\varepsilon''(\omega)]^2}$$

Here $\varepsilon' = \text{Re}(\varepsilon)$, $\varepsilon'' = \text{Im}(\varepsilon)$ and $g(\omega)$ is the coefficient of enhancement.

In Table 2, we present the factor of enhancement from the experiment (Kuhne et al., 1998) in RATR geometry for biological membranes into which colloid particles of silver are introduced (see Figure 4).

Table 2. Dependence of the enhancement factor on wavenumber.

Wavenumber, cm ⁻¹	Factor of enhancement, Experiment	Factor of enhancement, calculation		Assignment
	g^2	g	g^2	
1732	14,9	3,9	15,21	str. C=O
1647	1,4	3,7	13,69	Amid I
1534	1,6	3,5	12,25	Amid II
1455	3,1	3,4	11,56	def. (CH ₃) asym.
1384	-	3,2	10,24	Background
-	-	-	-	def. (CH ₃) sym.
1225	2,8	2,9	8,41	lipid (str. PO ₂)
1053	18,5	2,6	6,76	str. (C-C)

3. Methods and materials.

3.1. PREPARATION OF DNA AND BSA WITH COLLOIDAL GOLD.

Colloidal gold (it was produced by reduction of Au from HAuCl_4 with citrate, concentration 12.1 mg/ml) was mixed with sodium salt calf-thymus DNA (highly polymerised from Servo) aqueous 5×10^{-3} M solution, kept 24 hours in refrigerator, then precipitated on gold substrate as well as on CaF_2 and lyophilic dried. We prepared the samples of DNA with different amount of colloidal gold (1, 2 and 3 drops of colloidal gold per the 10 mkl DNA solution). A drop is about 10 mkl. As reference DNA we used the same DNA aqueous solution without colloidal gold.

Bovine serum albumin (BSA) (Sigma) aqueous solution of 1...40 mg/ml was mixed with colloidal gold, stir and then precipitated on gold substrate.

3.2. FTIR AND SEIRA SPECTRA EVALUATION.

Spectra were collected with IFS-48 Bruker instrument in IR reflectance mode for the DNA on gold substrate. The reflectance attachment used in the experiment has the light incidence angle close to 16.5° in (Dovbeshko, Chegel, et al., 2002). We used Au of 200-500 Å thickness on glass plate as metal substrate. Spectra of DNA with colloidal gold on CaF_2 substrate were collected in transmittance mode. Evaluation of the spectra has been done with Opus 2.2 soft-wear. The position of the bands has been estimated with the use of the method of second derivative and/or standard method. The intensity of the bands was normalised to the band with maximal intensity in each spectrum, namely, to OH-NH-CH stretching vibration in the region $3340\text{-}3400\text{ cm}^{-1}$.

The bands have been assigned to the certain molecular groups in DNA according to references: (Taboury et al., 1985; Taillandier et al., 1985; Tajmir-Riahi et al., 1995; Schrader, 1995; Parker, 1983; Litvinov, 1991) and for proteins according to (Schrader, 1995; Parker, 1983), (Susi et al., 1983; Miyazawa et al., 1958; Byler et al., 1986). For estimation of halfwidth, intensity and real frequencies of overlapping bands, the complex spectral bands in the regions of $3800\text{-}2300\text{ cm}^{-1}$ (region of the OH-NH-CH stretching vibrations), $1800\text{-}1300\text{ cm}^{-1}$ (region of C=O , C=C , C=N stretching, C-H and N-H deformation vibrations) and $1300\text{-}1000\text{ cm}^{-1}$ (region of PO_2^- vibrations) have been decomposed with the option "Curve fit" of Opus 2.2. Shapes of different spectral bands under decomposition have been approximated with Lorenz or Gauss functions. The spectra have been normalised to:

- i) peak intensity of OH vibrations (the most strong line in the spectra) for estimation of the band parameters in the $4000\text{-}700\text{ cm}^{-1}$ region;
- ii) peak intensity of the all bases band at 1650 cm^{-1} for estimation of the bands in the $1800\text{-}700\text{ cm}^{-1}$ region;
- iii) peak intensity of Amid I for estimation of BSA content of different conformations.

Reproducibility of the frequency in the SEIRA spectra was equalled to $\pm 0.5\text{ cm}^{-1}$ and for absorption $\pm 0.0005\text{ a.u.}$

Principal component analysis was applied for SEIRA spectra evaluation. As one principal component was chosen relative intensity of phosphate asymmetrical band (at 1240 cm^{-1}) to

intensity of maximum in the $3400 - 2300 \text{ cm}^{-1}$ region assigned to OH stretching vibration. According to (Shie, 1977) this component multiplied by 5.25 characterises the number of water molecules per 1 nucleotide. The second principal component was ratio of intensity at 1712 cm^{-1} and 1700 cm^{-1} that is a characteristics of conformation state of DNA relating to A, B or Z-form. Earlier we have estimated the contribution of above-mentioned components in principal components and found that they have shown preferential contribution.

3.3. AFM IMAGING.

The microphotograph of the Au surface used as substrate for SEIRA, colloidal particles on gold substrate as well as DNA and BSA was obtained by atomic force microscopy (AFM). We used the tapping mode under AFM imaging, with a commercial Nanoscope IIIa (Digital Instrument, Santa Barbara, CA). Tapping force mode scans were performed using commercially available AFM tips (silicon nitride). The scanning frequency was approximately 1 Hz in all experiments.

3.4. SPR EXPERIMENTAL SET.

Gold thin layer for protein or DNA adsorption and surface plasmon resonance (SPR) measurement was obtained by vacuum deposition of 99.999 pure Au upon glass supports (TF-1 glass, 20x20 mm) via an intermediate adhesive Cr layer. Before Au deposition, glass surface was cleaned by $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ and $\text{HCl}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ solution subsequently, both 1:2:2 by volume concentration during 5 minutes at boiling temperature. Then it was rinsed in bidistilled water and dried in a flow of pure nitrogen. The gold was evaporated from molybdenum heater and deposited at a rate of $1.0\text{-}1.5 \text{ nm}\cdot\text{s}^{-1}$ on room temperature substrate. The thickness of gold surface was within $200\text{-}500 \text{ \AA}$ in the different experiments, for SPR we used gold with $500 \text{ \AA}$ thickness. The Cr interlayer does not exceed $10\text{-}15 \text{ \AA}$. The gold surface just after deposition looks like hydrophobic surface with wetting angle close to 80° and random roughness about $50 \text{ \AA}$ (Figure 5, a). After chemical

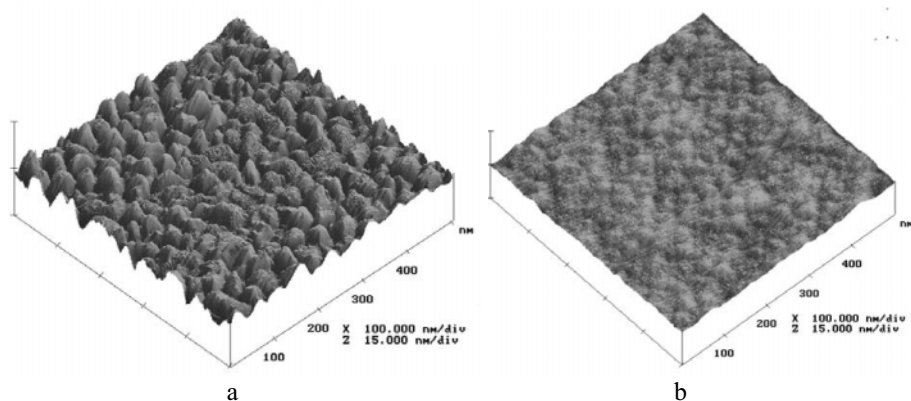


Figure 5. Image of gold surface used in SEIRA and SPR experiment (a) and after chemical polishing by piranha (b).

etching by piranha the surface of gold substrate looks like in *Figure 5, b*. The BSA dissolved in aqueous solution (1 or 10 mg/ml) and freshly prepared have been used for SPR measurement.

The SPR Kretschmann-type spectrometer (Biosuplar-2, Analytical μ -System) with light-emitting diode light source, $\lambda = 6700 \text{ \AA}$ was used for SPR measurement. A high reflection index of the prism ($n=1.61$) and a broad dynamic range (up to 19° in air) of the SPR instrument gives a possibility for analysis of modified surface without change of the initial angle. An open cell of $230 \mu\text{l}$ was used in the case of rapid removal cell content or change content being necessary (Beketov et al., 1998).

4. Results and discussion.

4.1. PECULIARITIES OF STRUCTURE OF DNA IN A AND B-FORM PRECIPITATED ON GOLD SUBSTRATE IN SEIRA EXPERIMENT.

The DNA right-handed helix blocks adopts the C_3' *endo/anti* sugar-base conformation in the A form and C_2' *endo/anti* in the B form (Saenger, 1989). Their spectral band positions are 890 cm^{-1} , 878 cm^{-1} , 860 cm^{-1} and 805 cm^{-1} for the C_3' *endo/anti* (A-form helix) conformation as well as 890 cm^{-1} and 835 cm^{-1} for the C_2' *endo/anti* (B-form helix) conformation (Taboury et al., 1985; Taillandier et al., 1985). In the left-handed helix DNA (Z-form) the positions of the IR bands are $925\text{--}929 \text{ cm}^{-1}$, 868 cm^{-1} , $835\text{--}840 \text{ cm}^{-1}$ and $802\text{--}805 \text{ cm}^{-1}$ in the C_3' *endo/syn* and C_2' *endo/anti* sugar-bases geometry (Taboury et al., 1985; Schrader, 1983).

It is known that DNA conformations in the film and their IR spectra (especially the symmetrical PO_2^- band) strongly depend on the humidity of the film (Taillandier et al.,

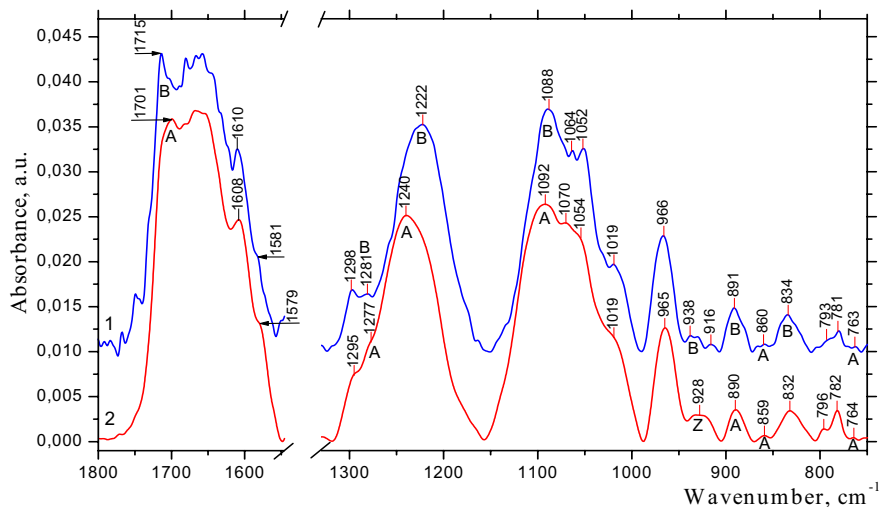


Figure 6. The SEIRA spectra DNA on gold substrate in B (1) and A (2) forms.

1985; Boal et al., 2000; Blagoi et al. 1994; Semenov et al., 1994). Consequently, we repeatedly tested the humidity of the sample (20 times per hour), and repeated the measurements the following days. In all our experiments it was 60% humidity, and we recorded reproducible spectra. However, for Na-DNA from a calf thymus (Servo) on the gold substrate we have observed the main bands in the sugar region at the following frequencies: strong 928 cm^{-1} (Z-form), strong 890 cm^{-1} (both A and B-forms), 859 cm^{-1} (A-form) and strong 832 cm^{-1} (B-form or Z-form) (*Figure 6, curve 2*). If we estimate according to (Taillandier et al., 1985) the contribution of A and B forms, we find a big content the B-form. This seems impossible in our experimental conditions of 60% humidity, where a disordered (a coil) structure could be expected with a much greater contribution from the A-helix form. The majority of the spectral markers for Na salt DNA on the gold substrate is close to the markers of A-form of DNA according to (Schrader, 1983, data are presented in parents), namely, 1092 (1095), 1240 (1240), 1277 (1275), 1370 (1375), 1419 (1418), 1701 (1705) cm^{-1} (*Figure 6, curve 2*). For B-form of DNA on gold (specially prepared by us with 90-100% humidity) its marker positions are close to common markers of B-form, (in parents are presented data from (Schrader, 1983) namely, 1088 (1085), 1222 (1220-1225), 1281 (1281), 1374 (1374-1375), 1425 (1425-1430), 1715 (1714-1718) cm^{-1} (*Figure 6, curve 1*).

We must assume that any substrate can strongly influence the sugar conformation of DNA, even in the case when other structural DNA components do not feel this influence. So, the influence of substrate on the nucleic acid spectra should be estimated separately in every case. In our case, we deduce that the gold substrate induces conformational change of the sugars if they come closely to gold peaks. The band observed at 832 cm^{-1} is presumably due to reformation of intermolecular H-bonding (NH, OH and CH groups) near to the gold substrate (Boal et al., 2000), as the result of the bending DNA at gold peaks. It is also possible that water molecules take active part in this process.

A similar process was discussed in (Gaigeot et al., 2000), in connection with non-coincidence of the data obtained with inelastic scattering of nucleic acid blocks in solid state and calculations with density functional theory for the spectral region under 900 cm^{-1} . They proposed that intermolecular H-bonds were formed in the film involving $\text{N}_1\text{-H}$ and $\text{N}_3\text{-H}$ groups of the bases, giving strong band at the 830 cm^{-1} . In our case the bands at 834 cm^{-1} and 832 cm^{-1} in B and A - form of DNA on gold, correspondingly, have been registered.

It is very difficult to resolute the 1054 and 1070 cm^{-1} C-O deoxyribose vibrations as well 1153 and 1019 cm^{-1} vibrations assigned to $\text{C}_2\text{-O}$ for DNA on transparent substrate. In the DNA on gold substrate we could separate some of this vibrations under changes in nucleic acid structure under internal or external stimuli (Dovbeshko, Repnytska, et al., 2002).

In DNA and RNA from tumour cells we have found numerous structural peculiarities in geometry on gold that clearly manifest them. All these data have been discussed in details in our earlier publications (Dovbeshko, Chegel et al., 2002, Dovbeshko, Repnytska, et al., 2002). We should mention that for nucleic acids for concentration (10^{-2} - 10^{-4} M) dependence of intensity bands on concentration solution and thickness films have not been registered.

4.2. BSA ON GOLD SUBSTRATE.

We have studied a process of adsorption of BSA on gold substrate of different morphology in SPR and SEIRA experiment. As usual, BSA forms single molecular layer on gold substrate (*Figure 7*). In the case of thick layer of BSA, the SEIRA spectra of thick and thin protein layer show some differences in conformational states of protein after decomposition of the bands in the Amid I region (*Figure 8*).

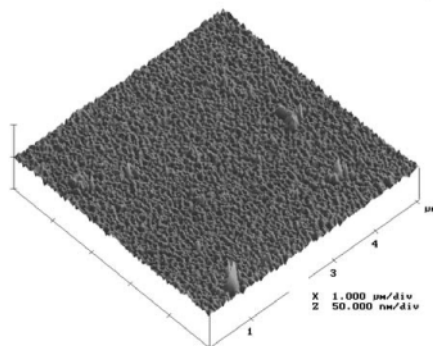


Figure 7. AFM image of amphiphilic bovine serum albumin that forms monolayer on the gold surface rather than polylayers. Sorption from PBS solution of 10 mg/ml.

Thus, the spectra of thin film have been decomposed in 8 components in contrast of thick film, where 10 components have been found, namely, 1602 (in parents the frequency for thick film is indicated) (no band); β -sheet - 1624 (1628), no band (1636); α -helix - 1642 (1643), 1655 (1650); disordering form - no band (1658); turns - 1670 (1669), 1686 (1682); aggregation or side chains - no band (1694), 1702 (1704), 1731 (1712) cm^{-1} . So, in thin film we did not observe disordering form and aggregation of BSA although some changes in orientation of α -helix were observed. In the case of usage of chemically polished Au-surface as substrate for BSA, some decrease of SPR signal and SEIRA (in 2 times) have been registered as well as rearrangement of the conformations.

We have observed dependence of intensity of the bands in absorption for BSA on gold substrate on solution concentration and film thickness in SEIRA (*Figure 9*). The most drastic changes were observed for 1651 cm^{-1} - α -helix. It seems, this occur due to the fact

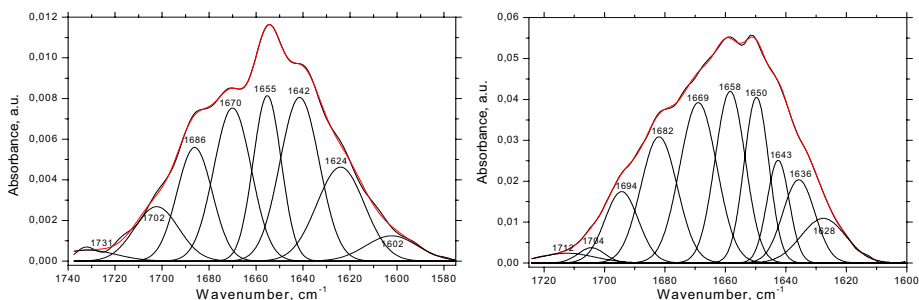


Figure 8. Amid I band in SEIRA spectra of BSA single layer (a) and BSA thick film (b) after decomposition.

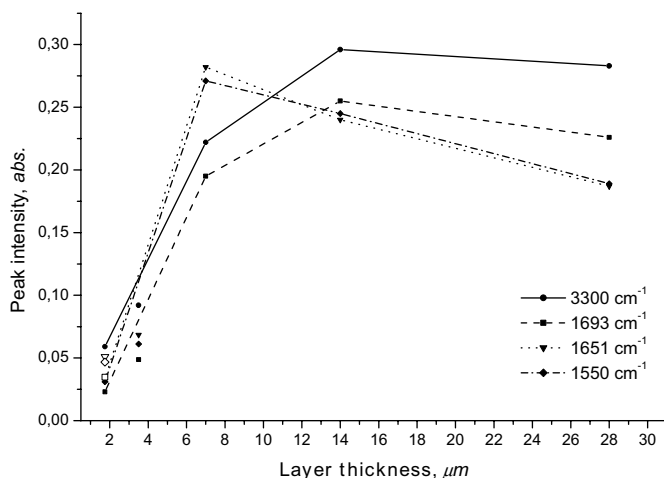


Figure 9. Dependence of peak intensity of BSA bands on film thickness. Solid points – experimental data, open – the data after decomposition.

that other conformational states under increasing of BSA concentration give contribution in this band. We supposed that the process of aggregation, interaction between helix, appearance of new turns, β -sheets, etc. influences the BSA structure in this case. In Figure 9 the open signs refer to the points after correction of intensity of Amid I absorption bands with account of decomposition of Amid I into the same type of the components as it was done for single molecule BSA layer (Fig.7). So, in SEIRA experiment the concentration of BSA should be less than 10 mg/ml.

4.3. DNA-COLLOIDAL GOLD SYSTEM ON GOLD AND CAF_2 SUBSTRATE.

Surface of gold film on SiO_2 and colloidal gold on Au/SiO_2 has some differences (Figure 10): size of particles of colloidal gold (15-40000 Å) is more than this for roughness of Au-surface and they have non-homogenous distribution.

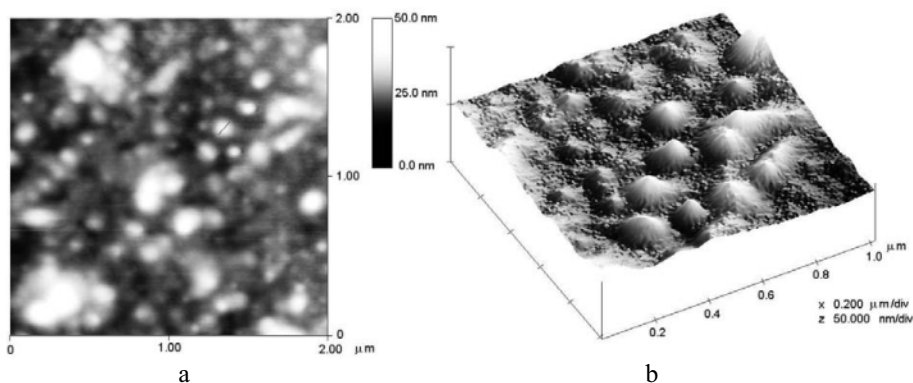


Figure 10. 2-D and 3-D AFM images of colloidal gold on Au/SiO_2 substrate. a – 2-D image, b – 3-D image.

In DNA-colloidal gold system on gold substrate the main spectral features are the followings (*Figure 11*):

- i) decreasing of the intensity of phosphate bands (for sym. band (at 1104 cm^{-1}) in 2.4, for asym. (at 1244 cm^{-1}) – in 2);
- ii) decreasing of the intensity of base band (in the $1800\text{-}1550\text{ cm}^{-1}$ region) in 1.3 (however, the relative intensity of base band to phosphate bands became more in 1.6 (asym. phosphate), 1.8 (sym. phosphate);
- iii) increasing of halfwidth of phosphate bands (for asym. phosphate about $35\text{-}40\text{ cm}^{-1}$);
- iv) high frequency shift of asym. phosphate (from 1240 to 1244 cm^{-1});
- v) high frequency shift of sym. phosphate (from 1093 to 1104 cm^{-1});
- vi) decreasing of shoulder of sym. phosphate at $1050\text{-}1070\text{ cm}^{-1}$;
- vii) increasing of the halfwidth of OH-NH stretching band on 250 cm^{-1} and their high frequency shift about 100 cm^{-1} .

The DNA with colloidal gold has features that are non A, B or Z-form. However, canonical forms of DNA are present here also, especially B and Z-forms (930 cm^{-1}), decreasing of A-form (860 cm^{-1}). The intensity of the band at 960 cm^{-1} decreased about 1.5-2.

We should add that all the spectral features are most prominent for DNA on gold substrate (*Figure 11, curve 1, 3*) in comparison of DNA on CaF_2 substrate (*Figure 11, curve 4*). We suppose that the spectral features of DNA show the process of condensation. Actually we observe here also the spectral features of the process of aggregation, it is impossible to select one of these processes. However, in all the other experiments without adding of polymetal ions we observe an aggregation, but no condensation and the spectral parameters does not influence so drastic characteristic alteration.

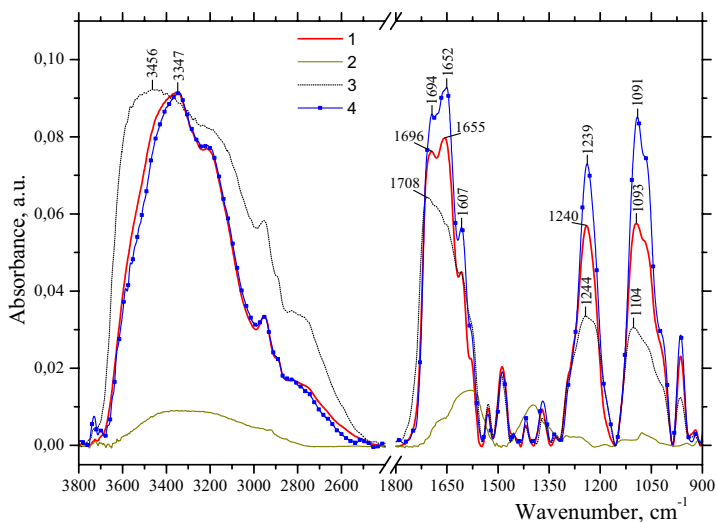


Figure 11. The SEIRA spectra of DNA – colloidal gold system: 1 – reference DNA on Au substrate, 2 – colloidal gold on Au substrate, 3 – DNA-colloidal gold system on gold substrate, 4 – DNA on CaF_2 substrate.

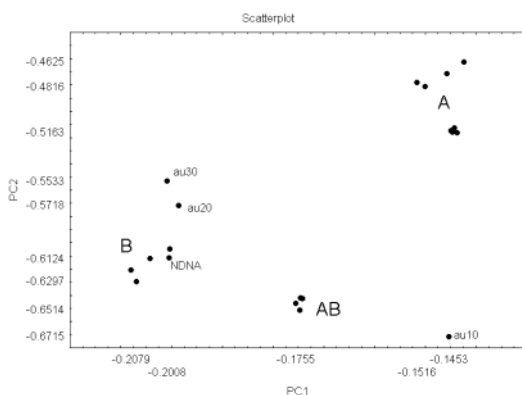


Figure 12. Principal component analysis of DNA.

Principal component analysis in modified form (as described in section 2.1) has been applied for conversion of the different spectra in separate points. We had not enough data for traditional statistic analysis. However, such presentation (Figure 12), shows that the points corresponded to canonical DNA form (A, B) or AB form or condensed DNA (Au10, Au20, Au30) have very small region of localization in principal component plane. In this plane the DNA-colloidal gold is close to B-form, however, our experimental condition impose A-form.

Only using a microscopy it is possible to prove a process of condensation (if we understand the condensation as formation of finite size and orderly morphology structures). Some features of process condensation seem to become visible in our AMF picture for DNA with colloidal gold (Figure 13).

SPR technique is a sensitive tool for characterisation of structure of colloidal gold and colloidal gold – DNA system. The process of DNA-colloidal gold interaction has been studied with SPR by comparison of adsorption of the colloidal gold and its mixture with DNA on gold surface. In Figure 14 the kinetics of adsorption of aqueous solution of colloidal gold of different concentration (Figure 14 a, b, curve 1) and the kinetics of

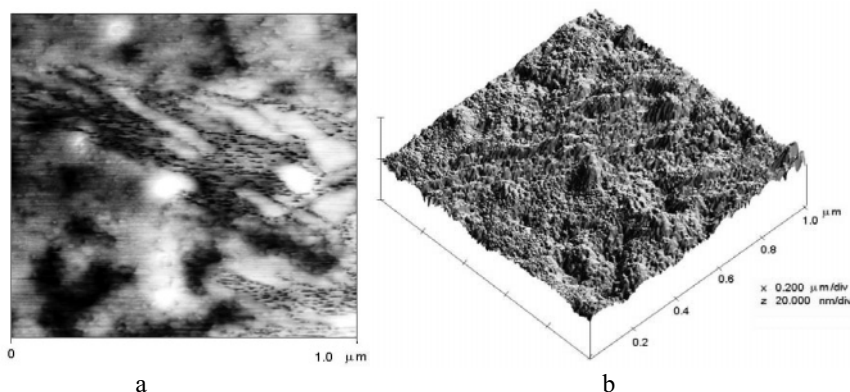


Figure 13. AFM images of DNA with colloidal gold. a – 2-D image, b – 3-D image.

adsorption for mixture of DNA-colloidal gold (Figure 14 a, b, curve 2) are presented. It could be seen that big concentration of colloidal gold revealed the essential difference in SPR response in contrast with small colloidal gold concentration. The SPR spectra show the drastic changes in their position and halfwidth (Figure 14, c) for case of colloidal gold particles adsorbed on gold surface in comparison with bare gold.

It is necessary to note that for small concentrations of colloidal gold the difference in SPR response is less impressed (Figure 14, b). The drastic decrease of the SPR response for DNA-colloidal gold system (big concentration) shows only slight change in SPR position (Figure 14, d).

DNA condensation by colloidal gold causes to drastic decreasing of effective refractive index of adsorbed layer. It could be explained by formation of clusters DNA-colloidal gold as result of condensation processes. Similar decreasing of the SPR response was observed for Ag clusters in the polymer matrix (Steiner et al., 1998). In this case the slowing of the kinetic of the process of adsorption of colloidal gold particles induced by decrease of electrostatic interaction is observed.

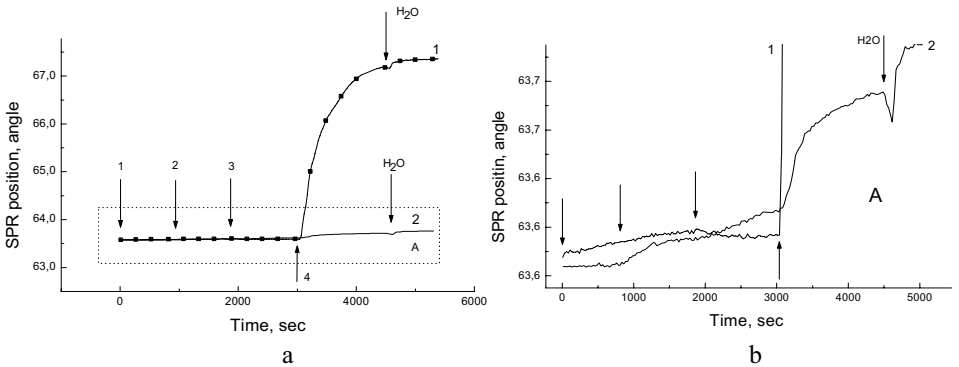


Figure 14. a) Kinetic dependence of the SPR angle position for adsorption of colloidal gold (aqueous solution by concentration of 12.1mg/ml) (1) and for mixture of colloidal gold (the same concentration) with DNA (2); b) the same in Y scaled form. 1, 2, 3, 4 – the points that correspond to aqueous dilution of 1 mg/ml BSA aqueous solution in 1000, 100, 10 and 1 of 12.1 mg/ml initial colloidal gold concentration.

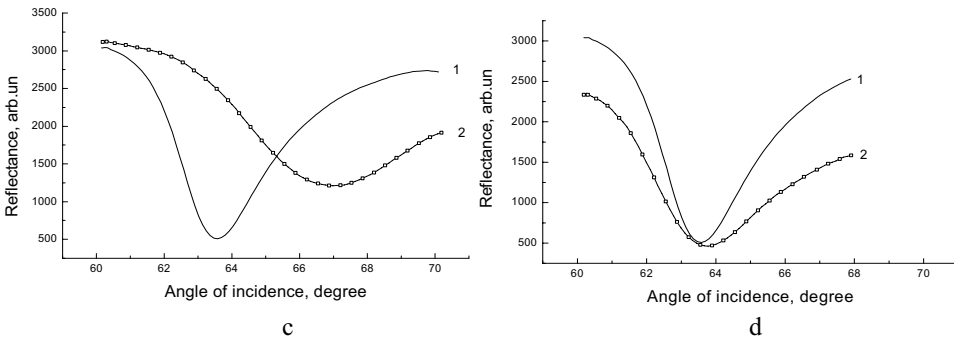


Figure 14. c) SPR curves for bare gold (1) and after adsorption of colloidal gold (aqueous solution by concentration of 12.1mg/ml) (2), d) SPR curves for bare gold (1) and after adsorption of mixture of colloidal gold (the same concentration) with DNA (2).

4.4. BSA – COLLOIDAL GOLD SYSTEM.

Colloidal gold is often used as optical enhancer for IR and SPR. However, in the case of IR, the adding of colloidal gold to protein solution could complicate the FTIR spectra analysis (Figure 15). Intensive absorption of colloidal gold about 1600 cm^{-1} (vibration of COO^- molecular groups) (Figure 15, curve 2) overlaps the Amid I at 1651 cm^{-1} and Amid II bands at 1539 cm^{-1} (Figure 15, curve 1), that lead to difficulties in the spectra interpretation.

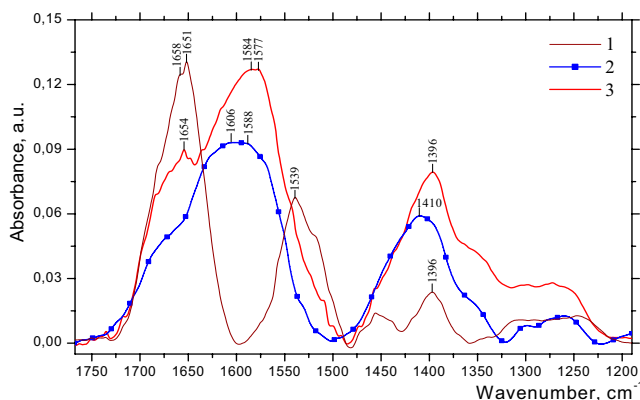


Figure 15. SEIRA spectra of BSA (1), colloidal gold (2) and BSA – colloidal gold system (3) on gold substrate.

Maximum of Amid I band in SEIRA spectra of BSA-colloidal gold system (Figure 15, curve 3) is located at 1654 cm^{-1} in comparison with BSA – 1651 cm^{-1} . So, the 3 cm^{-1} shift is observed in SEIRA spectra of BSA-colloidal gold system and other changes in structure could be studied. So, concentration of colloidal gold should be decreased for SEIRA studies of such systems and sometimes it could be not enough for enhancement. That is why the colloidal gold is not proper enhancer for characterisation of Amid I and Amid II bands.

4.5. FACTOR OF ENHANCEMENT IN SEIRA EXPERIMENT.

Earlier in our experiments (Dovbeshko, Chegel et al., 2002; Dovbeshko, Repnytska et al., 2002) and in literature (Kuhne et al., 1998) we have found that the SEIRA factor is equalled to 3-20 for vibrations of different molecular groups in DNA and membranes (proteins and lipids). As usually, the calculated factor ($g \sim \epsilon'/\epsilon''$) does not coincide with experimentally obtained. The possible reason is the fact that we do not take into account change in polarizability of the molecules absorbed on the metal surface.

From analysis of the formulae presented in chapter 2 the factor of enhancement (g^2) is proportional to $\sim (\epsilon'/\epsilon'')^2$. We estimated g for different metals and could conclude that silver, gold and copper are the best from the enhancers for optical transition in wide IR region (Figure 16). Once our experimental data (Dovbeshko, Repnytska et al., 2003) put a question- could graphite and or carbon nanotube show a property of IR enhancer. Estimation showed that in IR region (10-20 μm) their dielectric properties could give an

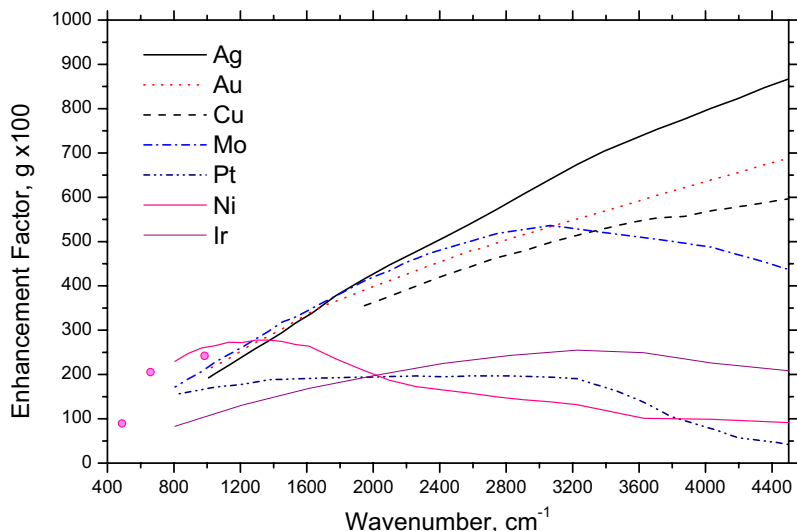


Figure 16. Factor of enhancement for different metals and graphite (indicated by points).

enhancement factor (g^2) in the region of 2-6 (Tomaselli et al., 1981). These data are presented on Figure 16 by separated points. In our experiment we registered the enhancement factor equalled to 1.4- 9 for vibrations of residue graphite on the surface of carbon nanotubes in IR experiment.

5. Conclusion.

SEIRA method is good tool for characterization of conformational state of biological molecules in comparison with conventional IR geometry. Gold substrate does not practically influence the macromolecular conformations of DNA and protein in contrast of colloidal gold. Observed overlapping of the main protein bands - Amid I and Amid II by the bands of colloidal gold could lead to complication of the analysis of protein conformations. We observed the dependence of intensity of absorbance on protein concentration and film thickness for protein on gold substrate that should be taken into account under study. All presented here experimental realization of SEIRA and SPR could be effectively used in the biological experiment. They give complementary information on nature of biological molecule structure and its interaction.

Acknowledgments.

We have greatly indebted to Foundation of Fundamental Research of Ministry of Sciences and Educations of Ukraine and special programme of Academy of Sciences of Ukraine N BII – 99.404/44 for financial assistance.

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CONCERNING SIGNALING IN *IN VITRO* NEURAL ARRAYS USING POROUS SILICON

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1. Introduction

It has been long realized that bidirectional coupling to biological processes requires the passing of information between relatively simple physical devices and highly complex 'living' systems undergoing irreversible processes [1-3]. At the same time, there has been the recognition that the current silicon technology based on 2D composite architectures will soon need to be replaced [4]. There has been, therefore, a widespread drive to create a technology for computing devices for the future.

Many approaches have been investigated to create new computing paradigms, including ones based on development of integrated silicon optoelectronics. One of the most demanding problems of materials' research is the introduction of optical functionality to silicon microelectronics. Notably inefficient at light emission, it was considered rather doubtful that essential optical devices such as lasers would be based on silicon. Various forms of silicon were however developed as potential optoelectronic materials. Of these, nanoporous silicon was, arguably, the key material to realize this technology, because of its room temperature tuneable optical emission [5], waveguiding and detection properties, and because of its potential compatibility with silicon processing.

Porous silicon has, however, had a mixed history in terms of technological applications which have reached the marketplace. The relative ease of its preparation together with its optoelectronic properties certainly paved the way for integrated silicon optoelectronic devices, but ultimately it has been erbium-doped silicon, iron silicide and nanoclustered silicon, and not nanoporous silicon, which have proved the more promising materials for silicon-based lasers. Remarkably, optical gain has now been reported from Si nanoclusters in a silicon dioxide matrix in both transmission and waveguide modes, with silicon quantum dots being the optical amplifying material [6]. Despite these milestones, porous silicon LEDs remain the most convincing and versatile silicon-based optoelectronic devices produced, including porous silicon chemical and pressure sensors.

2. Porous silicon as a bioactive material

Over the past few years porous silicon has been investigated for very different purposes. Despite various reports in the literature suggesting potential toxic effects of silicon-based materials (notably silicone) on living tissue, the porous form of silicon has been found to not show any notable toxic effects and further to have rather surprising tolerance to a range of biological environments [7]. This material therefore is being considered increasingly as a potential biomaterial, and one which could be used in a range of medical applications requiring either passivity (for example for device packaging) or activity (such as for drug delivery). The ability to replace sensory organs with intelligent electronic implants has advantages over tissue transplants in terms of host-graft rejection, the availability of transplantable tissue and the possible transmission of disease. Reliable, sensitive implants would be an undeniable step forward from the 'biochips' available today [8]. *In vitro*, one can envisage the concept of real-time multi-function sensory probes for monitoring and controlling industrial bioreactors. *In vivo* potential applications include implanted intelligent drug delivery systems, sensing devices (ultimately replacement eyes or ears) or electronic prosthesis controllers.

3. Bidirectional coupling to neurons

One of the areas of particular interest for use of porous silicon is as the interface layer for bi-directional coupling of silicon to living neurons. It has been reported recently that porous silicon substrates can be used as a neuron culture substrate for several types of immortalized [9] biological neurons and other cells (such as epithelial cancer and Chinese hamster ovary) [10]. All cell lines studied are viable, respiring and dividing as usual over periods up to weeks, and they adhere surprisingly well to the substrate without requiring the common application of adhesive protein. The focus of this research has been to enable neurons to exist in closer to physiological environments than usually employed, i.e. self-organised and without spatial constraints. Culturing neuron cells without spatial constraint and addressing them via closely situated electrode arrays could give rise not only to sophisticated biomedical devices *in vivo* but also to *in vitro* living neural networks for computational purposes. Purely from a common sense point of view, it might be thought that a plastic (dynamic) environment might allow more normal adaptability and learning processes. Furthermore, despite successes in addressing 'fixed' neurons via patch clamping or separated extracellular contacts [11, 12], the detrimental aspects of patch clamping [13] are avoided.

4. Methodology

In this paper we discuss the methodology issues surrounding investigations of inter- and intra-neuron signaling *in vitro*. We report on B50 rat hippocampal neuronal arrays, cultured on commercial plastic and glass substrates, and on nanoporous silicon. B50s were seeded on a range of substrates with cell densities of 10^6 ml^{-1} , much lower than those reported for forming self-organised clustered networks [14]. B50s are not well-documented in the literature in terms of neuron functionality, and our previous B50

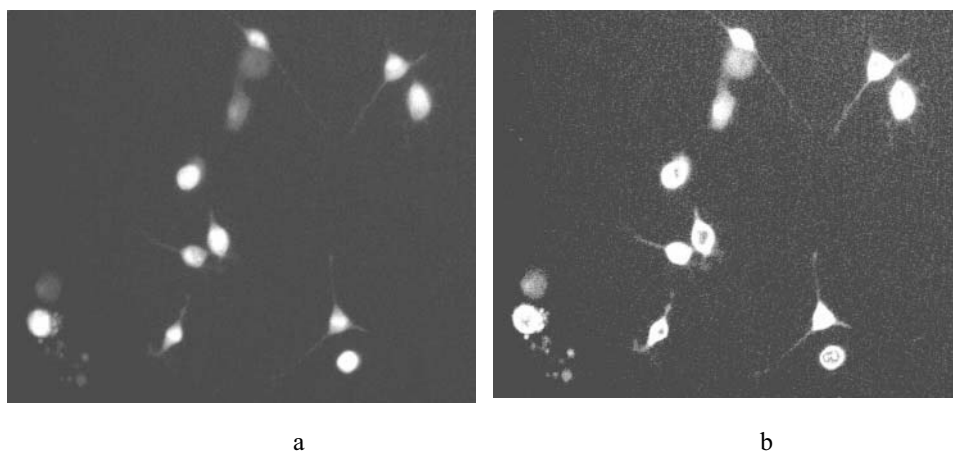


Figure 1. a. Reflection image of differentiated neurons showing extended processes. b. Fura2 fluorescence image from same sample.

stimulation studies have required significant mechanical and chemical stimulation [10]. When cultured in normal solutions B50s appear morphologically to be less elongated than primary neurons, so in the studies reported here the cells here were differentiated biochemically to improve their neuronality [15]. No difference within error in neuron lifecycle has been observed between differentiated and undifferentiated cells apart from morphology (Figure 1a): both types of cells divide, put out processes and survive for days before apoptosis. This means that apart from differences in morphology, the cell cultures are equally healthy.

Calcium imaging was carried out using the Fura2 dual-wavelength probe loaded into B50s in buffered media. Ca ion signals were observed in individual cells in media (Figure 1b). Marked intensity of fluorescence can be seen from cell somas, and there is also indication of calcium in dendrites. However at this stage it was not clear whether the signals were associated with any form of neuron firing whether spontaneous or stimulated, or whether they were associated with other cellular processes not associated with firing. To close in on the mechanism responsible for the fluorescence, spectra were obtained for individual cells as a function of time after microinjection of agonists into the cell culture vessel via a perfusion system. Because the agonists were applied in a series to the same cells, the agonist experiments were repeated with the agonist order changed, to make sure the receptors in the cells in the latter runs were active. The signals were mostly totally reproducible for the particular agonist, whatever the order of agonist microinjection. Particular interest was paid to the response of the cell as a function of cell position with respect to the perfusion chamber geometry, however the cell position did not correlate with cut-on time of the response [15]. Figure 2 shows response as a function of time after microinjection of ATP. It can be seen that the response varies little from cell to cell for a particular agonist apart from cells which show no response. Rather interestingly, multiple responses can be seen from a single cell, and the reasons for this are not clear at present, though multiple firing of the cells has not been ruled out. Measurements are in hand to further understand this behaviour, using receptor identification and microstimulation methods.

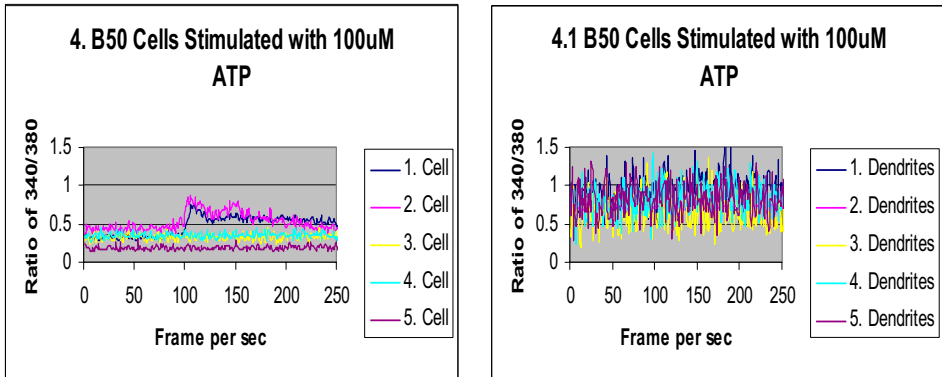


Figure 2: fluorescence intensity of B50 cells as a function of time after microinjection of ATP

5. Future directions

Proteins and nucleic acids have sizes on the nanoscale, so nanostructures are a natural bridge between biology and nanosystems. Using fluorescent semiconductor nanocrystals with diameters smaller than the Bohr radius of their excitons, it is now possible to tag a range of biological systems for imaging [16,17]. At present there are advantages with nanocluster tagging compared to conventional dyes, for example the tags have longer life compared to conventional dyes, and their use has been demonstrated both in vivo and in vitro. The use of such nanocrystals is rather limited at present due to problems of bioincompatibility of the nanocrystals: the individual fluorescent quantum dots typically of CdSe and related materials are encapsulated in phospholipid block-copolymer micelle membranes. In this format they are non-toxic to a variety of cell types and can tag a variety of different proteins or genetic sequences.

Finally, it could be envisaged that the use of *nanosilicon* in the form of silicon-based nanowire nanosensors could eventually lead to transfer of energy and information to and from individual processes and even molecules, to give real-time monitoring of multiple biological variables through the combination of single-molecule fluorescence microscopy and nanoelectronics [18]. This landmark development could result in parallel detection and diagnosis of trace amounts of viruses and proteins etc. It will be interesting to see if in the end such devices are based on porous silicon, with its advantageous optoelectronic properties and biocompatibility. As far as neuron signaling is concerned, studies are in hand at higher cell seeding densities on porous silicon, in particular focusing on the key properties of cell adhesion and migration, and neuron and array morphology. This is of particular relevance to the organization of neurons in the central nervous system, and, along with understanding the role of neuexins in the strength of synaptic connection [19], is likely to shed light on the processes of learning and adaptation.

Acknowledgements

We acknowledge Andrew Mayne, Trevor Clarkson, Jon Robbins, Peter Langlois, Mike Brent, John Taylor, Mike Boarder and Pam White for useful discussions. We should also like to thank the EPSRC, CLRC and the Royal Society for financial support.

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