



NATO Science for Peace and Security Series - B:
Physics and Biophysics

Nanotechnological Basis for Advanced Sensors

Edited by
Johann Peter Reithmaier
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Springer



*This publication
is supported by:*

The NATO Science for Peace
and Security Programme

Nanotechnological Basis for Advanced Sensors

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Published in Cooperation with NATO Emerging Security Challenges Division

Proceedings of the NATO Advanced Study Institute on
Nanotechnological Basis for Advanced Sensors
Sozopol, Bulgaria
30 May – 11 June, 2010

Library of Congress Control Number: 2011926454

ISBN 978-94-007-0905-8 (PB)
ISBN 978-94-007-0902-7 (HB)
ISBN 978-94-007-0903-4 (e-book)
DOI 10.1007/978-94-007-0903-4

Published by Springer,
P.O. Box 17, 3300 AA Dordrecht, The Netherlands.

www.springer.com

Printed on acid-free paper

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Preface

The ever increasing requirements towards safety and security demand the application of *advanced sensors* with greater sensitivity, better specificity, substantially smaller sizes and modest power consumption. Such sensors can be realized with the development of novel functional materials, devices and systems allowing the control of matter on atomic and molecular levels since the performance of the chemical and biological, as well as of most of the physical sensors depends on the interactions that occur at these levels. This can be accomplished only by the application of the recent achievements of *Nanoscience* and *Nanotechnology*. The nanostructured materials possess unique properties – electrical, optical, magnetic, etc. – entirely different from those of the conventional micro- or millimeter sized materials, due to their distinctive size and shape, and predominant surface and quantum effects determining their behaviour. In such a sense the Nanotechnology is the main driving force in the development of advanced sensors. It concerns not only the preparation and investigation of smart nanosized materials for sensor applications, like nanotubes, nanowires, nanoparticles and nanocomposites, but also combination of their performance with ICs, micro- and nanooptics, MEMS and NEMS, leading to higher level of integration and effective processing and transmitting of the sensor signals. Only the common efforts of scientists from different countries and different fields of research – chemistry, physics, biology, materials science and engineering – can bring the complimentary expertise in the development of new generation of sensors taking on the advantages of *Nanoscience* and *Nanotechnology*.

The *NATO Advanced Study Institute on Nanotechnological Basis for Advanced Sensors* took place in Sozopol, a small and charming town in Bulgaria with calm and relaxing atmosphere which has already shown many times to be an excellent place for such events. The first objective of the NATO-ASI was to present to the participants the up-to-date achievements and future perspectives in the preparation and application of novel sensors taking on the advantages of the nanotechnologies. The second objective was the teaching and training of the participants in the scientific and technological background of nanostructures and nanostructured materials used in the preparation of new sensors with improved sensitivity, selectivity,

reliability and response times. The third objective addressed the initiation of transborder and interdisciplinary collaborations between young scientists towards the development and application of new generation of sensors. The overall objective of the ASI was the transfer of competence and technology in the field of nano-enabled advanced sensor systems to meet one of the key priorities of the *NATO Science for Peace and Security Programme*.

The ASI covered several topics connected with the preparation of *advanced sensor elements and devices* taking the advantages of *nanotechnologies* and *nanomaterials* as well as their different applications. The lectures were given by outstanding scientists from universities and research institutes who are experts in nanoscience-based sensor technology. In addition, nineteen thematic seminars on specific topics were included in the programme. Three poster sessions with forty presentations were held, which enhanced the interaction between the participants and the lecturers, enabling them to establish closer contacts and to discuss in less formal atmosphere.

Seventy six participants coming from 13 NATO Countries (Bulgaria, Canada, Czech Republic, Denmark, France, Germany, Greece, Hungary, Italy, Romania, Spain, Turkey, USA) and 5 Partner Countries (Croatia, FYR Macedonia, Moldova, Russian Federation, Ukraine) insured that the overall objective of transfer of competence in the field of nanostructured materials and nanotechnologies for advanced sensors was indeed reached on a high level.

We, the members of the Organizing Committee, would like to thank the NATO Science Committee for the financial support for the organisation of the ASI. The local organisation and the publicity of the ASI in the media (TV, radio, newspapers and information web sites) was actively supported by Mr. Panayot Reyzi, Mayor of Sozopol, whom we gratefully acknowledge.

Kassel – Skopje – Sofia
October 2010

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Group photo of NATO Advanced Study Institute on Nanotechnological Basis for Advanced Sensors

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Part I

Sensors and Nanotechnology

Chapter 1

Nanotechnology-Based Modern Sensors and Biosensors

Wilhelm Kulisch

Abstract In this contribution, basic aspects of modern sensors and especially biosensors are addressed. The most important terms will be defined and a number of transducing principles will be illustrated. For biosensors, the role of the biochemical recognition element and the immobilization of biomolecules on the sensor surface will be emphasized. Glucose sensors will serve as an example to illustrate the development of the past decades. In this context also the roles of nanotechnology and nanomaterials for the development of sensors and biosensors will be highlighted. Thereafter, some examples of label-free optical and electrochemical biosensors are presented. Finally, the possibilities of integrated and miniaturized biosensors are discussed, a development which will eventually result in so-called labs-on-a-chip.

Keywords Sensors · Biosensors · Optical sensors · Electrochemical sensors · Nanomaterials · Lab-on-a-chip

Introduction

Sensors, and with increasing importance also biosensors play a tremendous but often overlooked role in our present everyday's life. This holds for our homes where sensors can be found in every washer, coffee machine, etc., not to speak of security systems. The same is true for our cars which are full of sensors. This list could be expanded to almost every aspect of our life, let it be home, work or recreation.

Similarly, since the first invention of a glucose sensor in 1962 [1] modern medicine and related fields are making increasingly use of biosensors. Here the aim is to replace complex, time and cost-consuming laboratory analyses by rapid

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point-of-care methods to detect diseases or health risks, to monitor industrial or agricultural processes, or to warn for biological, environmental or even military threats [2, 3].

This development has been driven in the past decades by the rapid progression of semiconductor technology since it provides, on the one hand, an ever improving technological base for integrated sensors and biosensors and, on the other hand, an easy method to evaluate the data measured by a sensor and to take appropriate actions based on these data. In the following, these aspects will be discussed in more detail, with an emphasis on biosensors.

The paper is divided into three parts: The first (Sect. 1.2) deals with sensors in general, describing their definition, working principles and characteristics. The second part (Sect. 1.3) is devoted to general aspects of biosensors, their definition, fields of applications, requirements, and sensing principles. Additionally, also biochemical recognition elements and techniques to immobilize biomolecules on the surfaces of sensors are addressed as well as the use of nanotechnology and nanomaterials. The remaining sections deal with more special topics such as optical and electrical biosensors and the integration of biosensors, auxiliary sensors, actuators, electronic devices and microfluidics on so-called labs-on-a-chip.

Sensors: Definitions, Principles and Properties

Human Senses

The term *sensors* is closely related to the word *sense*, which means the ability of living beings to percept their environment. In the case of humans, fives classical senses have been identified, namely sight, hearing, smell, taste, and touch (see Table 1.1), although there are several others such as senses for acceleration, balance, temperature, etc. All human senses are based on the same principles: a physical or chemical signal is detected by receptor cells and converted by an appropriate transduction process to an electrical signal, which is then processed by the nervous system and finally delivered to the brain where it is “displayed”.

Table 1.1 Human senses and their principles

Sense	Name	Organ	Receptor	Transduction
Sight	Vision	Eye	Photoreceptor cell (rods, cones)	Radiant → electrical
Hearing	Audition	Ear	Hair cells	Sound waves → electrical
Taste	Gustation	Tongue	Taste receptor cells	Chem. molecules → electrical
Smell	Olfaction	Nose	Olfactory receptor cells	Odor molecules → electrical
Touch	Haptic perception	Skin	Vater-Pacini corpuscles	Pressure → electrical

To take the visual perception as an example, photons meeting the eye are perceived by the rods and cones located in the retina of the eye. The informations collected by these receptor cells are then transported electrically by the optical nerve to the brain which computes on their basis a picture, thereby taking e.g. into account that the lens of the eye produces an inverted bottom-up picture of reality on the retina.

Table 1.1 lists the classical human senses, the most important receptor cells and the transduction pathways. It can be seen that in all cases the transduction process leads to electrical signals on which the nervous system is based.

Sensors: Definition

Modern technical sensors are based on the same principles as the human senses. According to Ref. [4] they are the technical analogs to human senses together with human intelligence. They can be defined as devices which provide a usable *output* in response to a specified *measurand* [4]. The *output* is usually an electrical quantity since today data processing is based on electronic circuits. In the future, when optical information processing may become important, also optical output signals may become significant. The *measurand* is a physical, chemical or biochemical quantity, property or condition.

Transduction Principles

All sensors are based on a kind of transduction of an input quantity into an electrical (optical) signal, thereby making use of one or more physical or chemical effects. For a comprehensive list of such effects, the reader is referred to Ref. [4]. Table 1.2 lists the most important classes of input signals and some examples for each of them.

A very basic example of such a sensor is the well-known photodiode which converts the intensity of incoming light into an electrical current (or a voltage) as shown schematically in Fig. 1.1. However, in many cases not only one transduction

Table 1.2 Classes of sensor input signals

Input signal	Examples
Mechanical	Length, velocity, acceleration, pressure, force. . .
Thermal	Temperature, specific heat, entropy. . .
Magnetic	Field intensity, flux density, magnetic moment. . .
Electrical	Current, voltage, resistance, capacitance. . .
Radiant	Wavelength, intensity, phase, redox polarization. . .
Chemical	Composition, concentration, pH, redox potential. . .

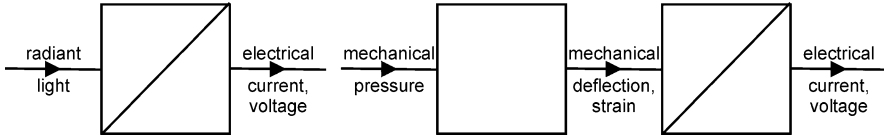


Fig. 1.1 Schematical presentation of a photodiode (*left*) and a pressure sensor (*right*)

Table 1.3 Static and dynamic characteristics of a sensor according to Ref. [5]

<i>Static characteristics</i>		<i>Dynamic characteristics</i>
Accuracy	Non-linearity	Impulse response
Resolution	Hysteresis	Step response
Sensitivity	Repeatability	Response time
Selectivity	Span	Rise time
Minimum detectable signal	Noise	Time constant
Threshold		Recovery time

is used but two or even more. A prominent example are diaphragm pressure gauges. Here the mechanical input signal, the pressure, leads to the bending of a membrane which also induces a strain in it. Thus the first transduction is mechanical (pressure) $\rightarrow$ mechanical (deflection, strain). The second, final transduction is then mechanical $\rightarrow$ electrical: Either the deflection of the membrane is measured capacitively or the strain via the piezoresistive effect.

Sensor Characteristics

There are many properties which can be used to describe the behaviour of a sensor; on the other hand, each of them represents a challenge for the design and realization of a sensor, as a properly working device has to meet strict requirements concerning all of these characteristics. These can be divided into two groups: static and dynamic characteristics [5]. The most important are listed in Table 1.3.

In the following, some examples will be discussed very briefly; for a more comprehensive description the reader is referred to the literature [5].

- The accuracy ε is a measure how closely the true value is approximated:

$$\varepsilon = \frac{X_{meas} - X_{true}}{X_{true}} \quad (1.1)$$

- The sensitivity S is the incremental ratio of output Y to input X :

$$S = \frac{\Delta Y}{\Delta X} \quad (1.2)$$

- The resolution $R_{\max}$ is defined as the smallest detectable increment of the measurand:

$$R_{\max} = \frac{\Delta X_{\min}}{X_{\max} - X_{\min}} \quad (1.3)$$

- The span $X_{\max} - X_{\min}$ describes the operating range of a sensor.
- The selectivity describes the ability of a sensor to differentiate various measurands by separating and quantifying them [6].
- The specificity describes the ability of a method to measure unequivocally the measurand of interest in the presence of other measurands [6].
- The threshold is the smallest initial increment of the measurand that leads to a detectable output.

Figure 1.2 presents three other very important sensor characteristics which describe the response to an input signal: non-linearity, hysteresis and repeatability.

- Step-response: In this figure also one of the most important dynamic sensor properties is included, which describes the behaviour of the output Y on a step increase of the input signal. In the ideal case it is described by the exponential law (where τ is the time constant of the sensor)

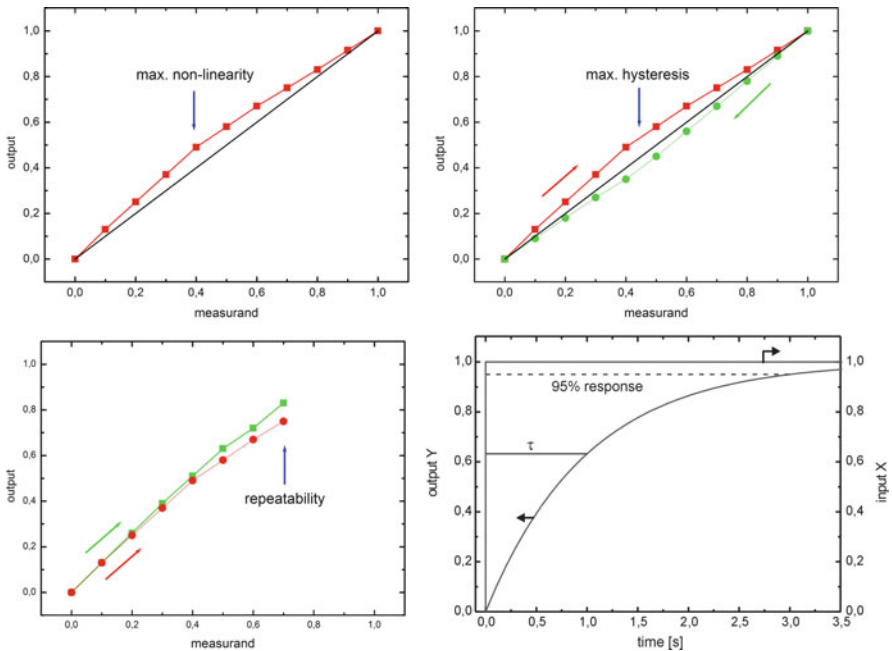


Fig. 1.2 Non-linearity, hysteresis and repeatability of the response of a sensor. Also shown is the response to a step in the input signal

$$Y = Y_0e^{-t/\tau} \tag{1.4}$$

Other important dynamic sensor characteristics are listed in Table 1.3. For further discussions the reader is referred to Refs. [5, 7].

Biosensors

Definitions

Taitt et al. [8] define biosensors as opto/electronic devices that use biological molecules for the detection and quantification of the target of interest. A similar definition is given by Sethi [9]: A biosensor is an analytical device which uses biologically sensitive materials to detect biological or chemical species.

Biosensors are practically identical with sensors as defined above with one important difference: they possess a biochemical recognition element (Fig. 1.3) which transduces the incoming informations (for example the presence of a biomolecule or the occurrence of a biochemical reaction) into a signal which the second major component, the transducer, finally converts into an electrical signal which is processed by the electronic part of the sensor [9].

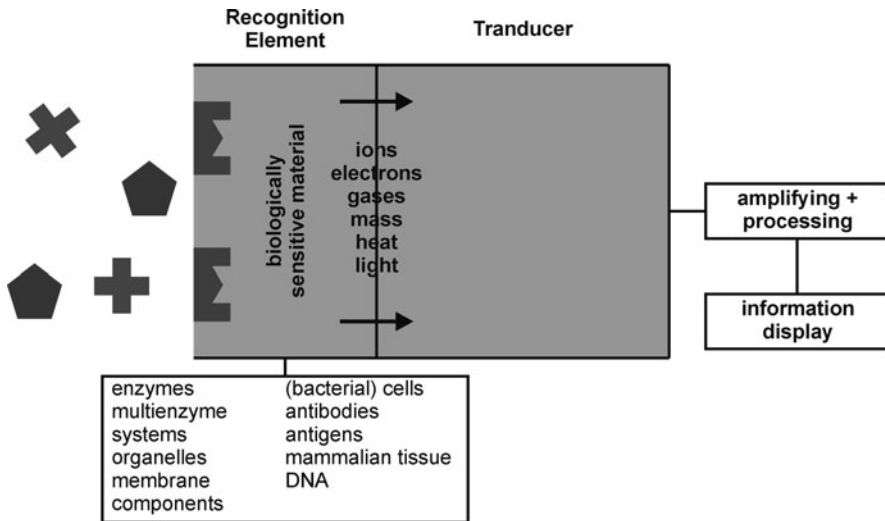


Fig. 1.3 Elements of a biosensor: recognition element, transducer and data processing unit. Also listed are the biological systems which can be used for the recognition element, and possible signals sent by the recognition element to the transducer as a result of the detection of biomolecules or biological reaction (modified from Ref. [9]). The figure also demonstrates the key-lock-principle

Table 1.4 Classification of biosensors [8, 9, 12]

Biosensor Transduction Principles		
Optical	Electrochemical	Other
Labeling Methods fluorescence luminescence radioactive labeling	Conductimetric	Mass SAWS QCM cantilever biosensors
Label-Free Methods surface plasmon resonance grating couplers interferometric sensors	Amperometric enzyme based sensors	Thermal detection of heat of reaction
	Potentiometric FET ISFET	

Sensing Principles

It is convenient to classify biosensors with respect of their basic transduction principles (Table 1.4). Most important at the present time are optical and electrical biosensors although there are also other approaches such as the utilization of the mass change occurring on the recognition of the analyte molecules [10] or the heat of reaction released or consumed in the recognition element [11].

Recognition Elements and the Immobilization of Biomaterials

Biosensors contain – as discussed above – a recognition element in which biomolecules (proteins, peptides, DNA and others (Fig. 1.3)) or biochemical reactions (such as DNA hybridization) are detected. According to Bergveld [13], the most sensitive recognition element in nature is that of the human immune system. Accordingly, most biosensors make use of the so-called “key-lock-principle” which mimics this approach of nature and is schematically shown in Fig. 1.3. Most important in this context are enzymes, on the one hand, and antibody/antigen pairs, on the other hand. The underlying principles are schematically shown in Fig. 1.4.

A very prominent example of an enzymatic biosensor is the well-known glucose sensor which relies on the reaction of glucose with the enzyme glucose oxidase which consumes two electrons [14]. It was invented as early as 1962 by Clark and Lyons [1] and – in many times improved versions – makes up more than one half of present day’s biosensor market.

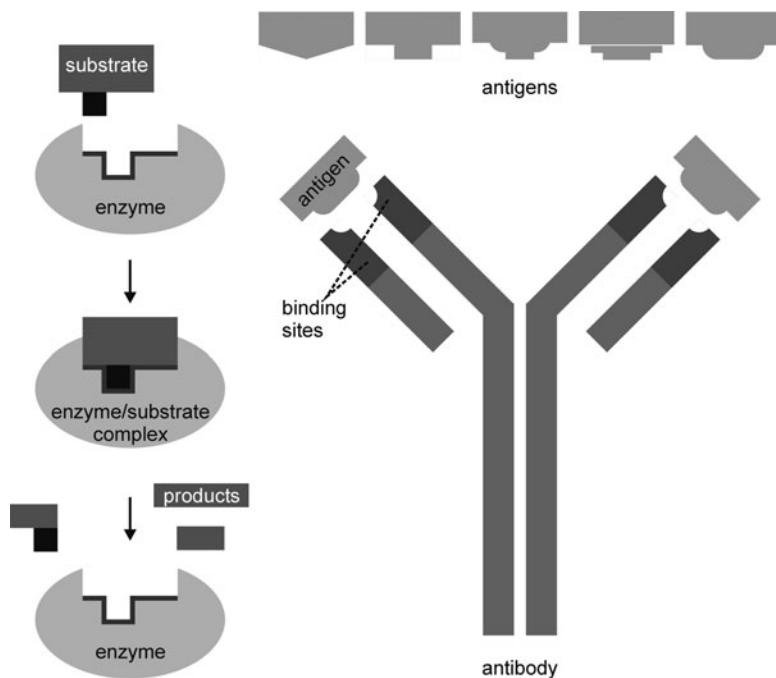


Fig. 1.4 (a) Principle of the use of enzymes as recognition elements in biosensors (in the example given a catabolic (destructive) reaction is shown; there are also anabolic (constructive) enzymatic reaction.); (b) principles of the use of antibody/antigen pairs in biosensors

Thus the fabrication of biosensors requires the immobilization of biomolecules or other biological entities on the sensor surface or another defined place. In addition, making this task more difficult, the biomolecules must retain their shape and especially their bioactivity [15, 16]. Furthermore, the active site must be available for the analyte to allow a reaction [8, 17]. In the past, several approaches have been used to immobilize biomolecules on biosensor surfaces [8, 15].

- Unspecific adsorption (Fig. 1.5a). In this case, the immobilization relies on van der Waals, hydrophobic or ionic forces or on hydrogen bonds. It is the easiest immobilization technique, which however, suffers from variability and reversibility, especially when the ambient conditions fluctuate, and a low density of immobilized biomolecules as compared to other techniques [8].
- Covalent binding. It can be achieved either directly (Fig. 1.5b) or via a heterobifunctional crosslinker (Fig. 1.5c). The latter may become necessary if the surface composition does not allow a direct binding of the molecules. Covalent binding leads to the most stable results [18].
- Entrapment in a membrane or encapsulation in a porous membrane (Fig. 1.5d, e) [19].
- Use of avidin-biotin systems [8].

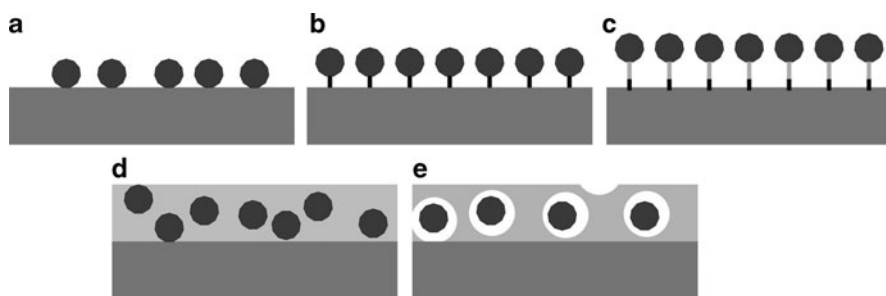


Fig. 1.5 Methods to immobilize biomolecules on a sensor surface: (a) unspecific adsorption; (b) covalent binding; (c) covalent binding using a crosslinker; (d) entrapment in a membrane; (e) encapsulation in a porous matrix

Table 1.5 Requirements of biosensors [9]

High sensitivity	Amenability to miniaturization and integration
High specificity to the target of interest	Internal compensation for drift
Response in the required concentration range	Temperature control
High discrimination ratio	Low production costs
Reasonable response time	Compact design
Multianalyte detection	Re-usability
Reliability	Suitability for practical applications

Requirements

Biosensors, as all technological devices, have to fulfil a long list of requirements to be suited for industrial application. The most important, besides the list of general requirements which apply to all sensors and has been discussed above in 2.4, are summarized in Table 1.5.

Fields of Applications

The applications of biosensors are not restricted to biological research and the clinical/medical field. As can be seen in Table 1.6, there are many different applications proposed or already realized in such diverse fields as agriculture, environment protection or even the defence/security sector.

Use of Nanotechnology and Nanomaterials

The development of modern nanotechnology has had an immense impact on the principles, design and characteristics of sensors and biosensors. This regards at least two aspects: (i) nanotechnology plays a major role in the integration of (bio)sensors together with auxiliary sensors and electronic data processing units

Table 1.6 Present and future applications of biosensors. Modified from Ref. [9]

Clinical/Medical	Industrial	Agriculture	Security/Defence	Environmental
• Diagnosis at ♦ physician's office ♦ clinics ♦ home • Testing of ♦ blood banks ♦ screening labs ♦ medical equipment • Monitoring ♦ therapeutic drugs ♦ surgical and operative	• Fermentation • Food and drug production • Process monitoring • Quality control • Contamination detection • Water and waste monitoring • Hazardous/toxic waste detection • Cosmetic testing	• Diagnosis of ♦ plant diseases ♦ animal diseases • Monitoring of ♦ agricultural chemical ♦ shipping and storage ♦ soil and water • Detection of ♦ hazardous chemicals • Quality control of ♦ meat ♦ plant products	• Detection of ♦ explosive ♦ nerve gases ♦ mycotoxins ♦ viruses ♦ pathogenic bacterial toxins ♦ pathogenic biological toxins	• Detection of ♦ toxic chemical in air, water, soil ♦ personal contaminations

on one chip, a development which in the case of biosensors may lead to so-called labs-on-a-chip. This will be addressed below in Sect. 1.6; (ii) the use of nanoscaled materials leads to new sensing principles and improvement of existing sensor designs due to one or more of the following effects:

- A drastic increase of the surface/volume ratio [20, 21], which can be used to increase the sensitivity of a sensor.
- Reduced distances e.g. between immobilized biomolecules and electrodes lower the response time [20].
- Reduced distances in the sensors lower the response time in diffusion determined processes [22].
- The similarity of size scale between nanomaterials and typical biomolecules makes nanostructures particularly attractive for intracellular tagging and ideal for bioconjugation [20].
- Nanometer sized materials possess electrical, optical, magnetic, etc. properties quite different from the macroscopic properties of the same materials [21, 23–25] which have already been utilized for new sensing principles in biosensors [20, 26–28].

Some examples for the use of nanomaterials for the design of biosensors and the utilization of the principles listed above will be given in the remainder of this paper.

Label-free Optical Biosensors

Concerning optical biosensors, one can generally distinguish between sensors using some kind of labelled molecules which can be easily detected by methods adapted to the labels used, and label-free detection (Table 1.4). In the past decade,

many biosensors have been developed in which the detection of the target of interest (DNA, proteins, etc.) was accomplished by labeling them with a fluorescent, luminescent or radioactive marker. These markers can be easily detected by optical or radiation detection methods. An example can be found in the work of Yang et al. [29] who used DNA oligonucleotides that were modified on the five'end using six-carboxy fluorescein phosphoramidite to prove the hybridization of DNA strands covalently attached to diamond surfaces. Detection methods based on such labeling have been very successfully used to prove the feasibility of a certain immobilization method or to study the interaction of target analytes with specially prepared surfaces. However, for biosensors used in practical/clinical applications such labeling methods are not very practicable as it is necessary to use naturally fluorescent analytes, to label the analyte of interest or to use a sandwich method [16]. Therefore, there is much work currently carried out on the development of label-free optical biosensors.

Evanescent Fields

Almost all label-free optical biosensors make use of evanescent fields which are a common phenomenon at the interface of an optical dense and a less dense material. When light coming from the denser material hits such an interface under an angle lower than the critical angle $\theta_c = \arcsin(n_2/n_1)$ (where n_1 and n_2 are the refractive indices of the two materials), it will be totally reflected (Fig. 1.6). This effect can be used to guide light in planar waveguides and optical fibers. However, according to Maxwell's laws, at the interface the electric field perpendicular to it is not zero; instead there is an exponentially decaying field reaching into the optically less dense material. The penetration depth d of this field depends on the wavelength and the angle of incidence of the light beam and the refractive indices of the materials involved [30, 31]; it is on the order of but lower than the wavelengths of the light,

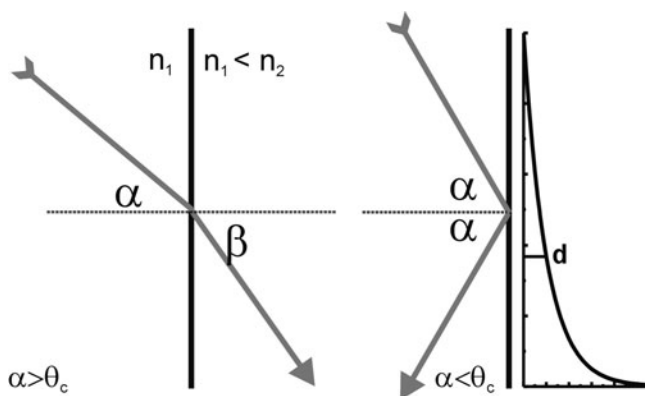


Fig. 1.6 Left: Snell's law; right: total reflection and evanescent fields

i.e. some hundred nanometers. In addition, the properties of the totally reflected wave staying within the optical denser material depends on the optical properties of the region explored by the evanescent wave. It will be influenced by changes in the refractive index as well as by absorption processes taking place within the penetration depth. These effects have been utilized for the design of quite a number of different biosensors.

Surface Plasmon Resonance

Most of the techniques developed up to now making use of evanescent fields in biosensors rely on surface plasmon resonance (SPR). Plasmons are three-dimensional collective oscillations of electrons in a solid; surface plasmons are their two-dimensional analogues. In the case of biosensors they are created in a thin metal layer (usually gold) deposited on a dielectric surface. They propagate parallel to the metal/dielectric interface [32] (Fig. 1.7 left).

In order to create a surface plasmon by an incident photon, both energy and momentum conservation must be fulfilled between photon and plasmon. The latter is fulfilled if the wave vectors of the photon k_{ph} and that of the plasmon k_{pl} are equal in direction and magnitude:

$$k_{ph} = \frac{\omega_{ph}}{c} \sqrt{\epsilon_d} \quad \text{and} \quad k_{pl} = \frac{\omega_{pl}}{c} \sqrt{\frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d}} \quad (1.5)$$

where ω is the angular frequency, ϵ the dielectric constant and the indices d, m stand for the metal and the dielectric, respectively. The surface plasmon created propagates along the metal/dielectric interface over large distances (several μm) and decays exponentially in vertical direction into the adjacent medium (on the order of a few hundred nm). The refractive index of the medium thus has an influence on ϵ_m in Eq. 1.5.

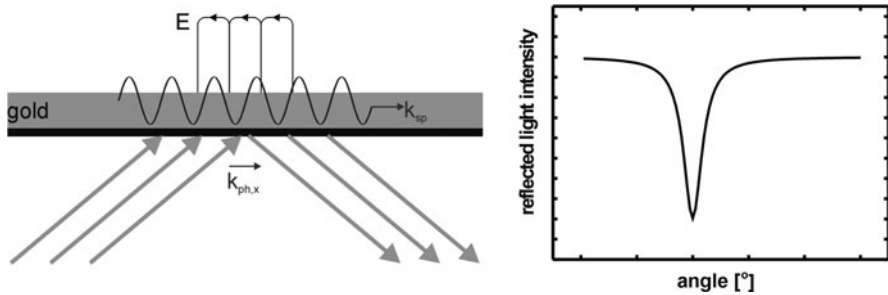


Fig. 1.7 Left: creation of a surface plasmon by a light beam; right: resulting absorption peak in the reflected spectrum

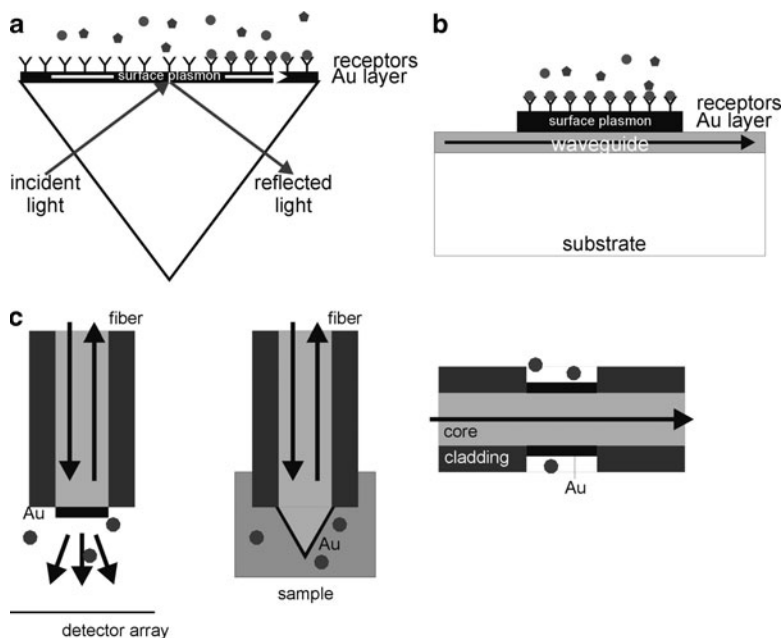


Fig. 1.8 Types of SPR biosensors: (a) prism-coupled sensor [33]; (b) planar waveguide [35]; (c) various designs of fiber-based sensors [34]

There are several principally different configurations of SPR biosensors already realized. The present time standard device is the prism-coupled sensor [33, 34] (Fig. 1.8a). The base of a prism is covered by a thin gold layer onto which receptors have been immobilized. Light is coupled into the prism and reflected at the gold layer on the base. If energy and momentum are correctly chosen, a surface plasmon is excited by the evanescent field in the gold layer which leads to absorption of the incident light. Its momentum depends on the amount of analytes attached to the receptors. There are two modes of operation for prism-coupled SPR sensors [34]: Either the wavelength of the light is varied for a fixed angle of incidence, or the angle is varied for a fixed wavelength (Fig. 1.7 right). These prism-coupled sensors are simple, robust, very sensitive, and the standard design of today's commercially available devices. They possess, however, one major disadvantage: They are not amenable to miniaturization and integration [34].

A solution of this problem are planar waveguide biosensors [34, 35] (Fig. 1.8b). Light is coupled into a planar waveguide, which is partly covered with a thin gold layer with immobilized receptors. Excitation of surface plasmons in the gold layer, the properties of which depend on the amount of analytes on the receptors, will lead to absorption of the light travelling within the waveguide.

A very versatile method to utilize SPR for biosensors are optical fibers. Fig. 1.8c demonstrates three different possible designs of fiber-based SPR biosensors [34].

Further Types of Optical Biosensors

However, utilization of evanescent fields for biosensors is not restricted to SPR-based devices. The attachment of analyte molecules to receptors immobilized on a waveguide surface influences the effective refractive index of the waveguide and thus the propagation of light within it. This can be utilized by:

- Interferometric optical biosensors (Fig. 1.9 left). Light is split by a double slit into two beams travelling parallel through the waveguide. One of the paths possesses a region with immobilized receptors, the other not. At the end of the waveguide the two beams are brought to interference. From the interferogram the differences in the effective refractive index of the two paths and thus the amount of analytes attached to the receptors can be calculated [12].
- Optical grating coupler (Fig. 1.9 right). Light is coupled via an optical grating into a waveguide the surface of which is partly immobilized with receptor molecules. The coupling angle depends on the parameters of the grating, the thickness of the waveguide and its effective refractive index which in turn depends on the amount of analytes attached to the receptors [15, 36].

Finally, not all optical biosensors rely on evanescent fields. At this point, only one example should be mentioned very briefly:

- Optical diffraction gratings formed by self-assembled monolayers of receptor molecules can be used to detect the presence of the corresponding analytes [37, 38].

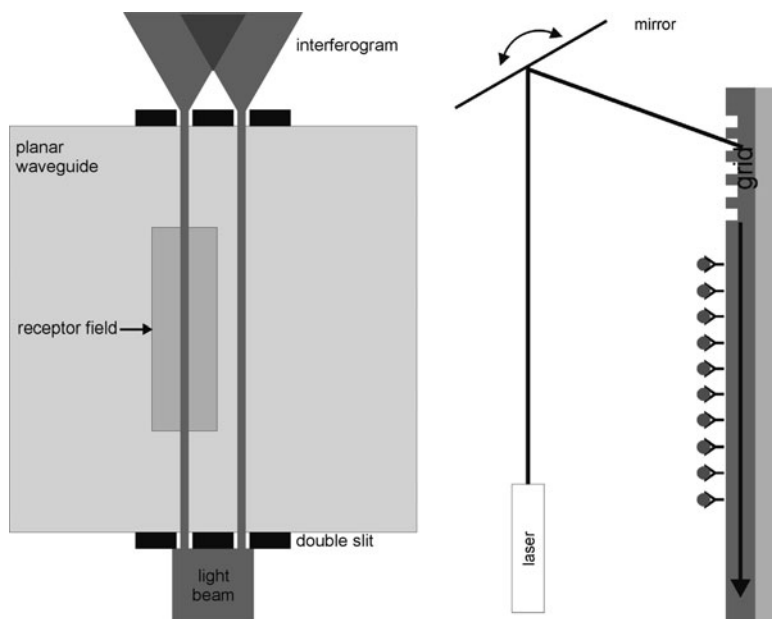


Fig. 1.9 *Left:* interferometric optical biosensor; *right:* optical grating coupler

Electrochemical Biosensors

Types of Electrochemical Biosensors

The second major class of present biosensors are using electrochemical transduction principles [9]. They make use of the fact that most biochemical reactions utilized in biosensors produce or consume charges (electrons, ions). In addition, many biomolecules are (partially) charged. According to the primary electrical signal produced by the sensors, four basic classes of electrochemical sensors can be distinguished (Fig. 1.10):

- In **amperometric biosensors** the charge released by the reaction of receptor and target molecules is measured directly as a current caused by a voltage applied (Fig. 1.10a). In most cases, enzymatic reactions are utilized in this type of electrochemical biosensor [39].
- **Potentiometric biosensors** in contrast utilize the fact that many biomolecules are (locally) charged. Upon immobilization on receptor molecules placed on a thin insulator on a semiconductor surface, the charge density in the vicinity of this surface changes. This can be used in devices based on field effects: either field effect capacitors or field effect transistors (Fig. 1.10b) [9, 42]. They are analogues of the well-known metal-insulator-semiconductor (MIS) devices; but in this case the gate metal is replaced by the electrolyte. Charges accumulated near the semiconductor surface will change the capacity of the capacitor or result in a current change through the transistor by simply changing the flat band voltage of the devices [13, 42]. The transistor depicted in Fig. 1.10b is also known as ion-sensitive field-effect-transistor (ISFET).

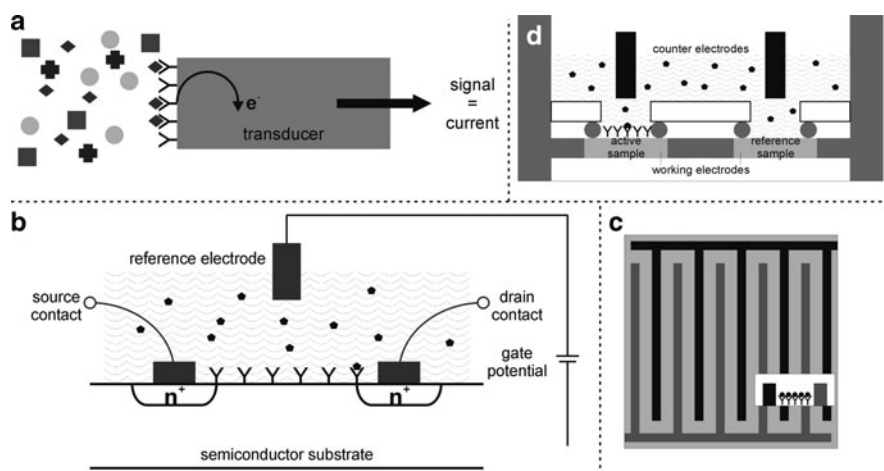


Fig. 1.10 Types of electrochemical biosensors: (a) amperometric; (b) potentiometric; (c) conductimetric; (d) impedimetric. Modified drawings based on Refs. [39–41]

- **Conductimetric biosensors** make use of the fact that many chemical reactions consume or produce ions which changes the conductance of the electrolyte [9]. They consist e.g. of two comb-like electrodes; on the surface in between them receptors such as enzymes are immobilized (Fig. 1.10c). If the specific analyte is present, charges are released or consumed which is easily measured as a change of the conductance. A second pair of identical electrodes without immobilized receptors can be used to compensate for drifts [9, 40].
- **Impedimetric biosensors** make use of the powerful tool of impedance spectroscopy [43]. Here, the complex impedance of a system is measured as a function of frequency over a large frequency range. Assuming an appropriate equivalent diagram for the system under investigation, the changes of the electrical properties upon reaction of the target molecules with the immobilized receptors can be measured quantitatively. The sensor design can be simply the comb-like structure shown in Fig. 1.10c also used for conductimetric measurements, or the vertical design shown in Fig. 1.10d. In this case a reference cell can easily be realized to compensate for drift effects [41].

Electrochemical Detection of DNA Hybridization

Great efforts have been devoted to the task of developing biosensors able to detect specific segments of DNA and RNA [44]. The process of combining two complementary single DNA strands to double stranded molecules is called hybridization (Fig. 1.11). It is fast, highly efficient and extremely specific [45].

DNA molecules are polyanions with negative charges at their phosphate backbone [42]. This means that during the hybridization process negative charges are attached in the near surface region. For this reason, many potentiometric techniques are used to prove a hybridization process to have taken place [42],

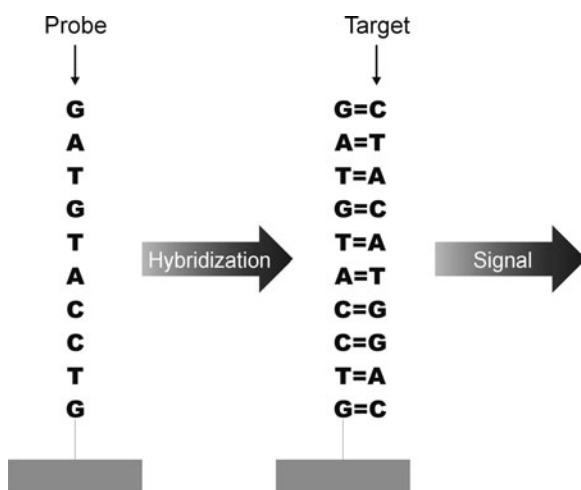


Fig. 1.11 Hybridization of DNA (modified from [46])

partly making use of nanostructures such as Si nanowires [47]. But also impedimetric electrochemical techniques have been used, as well as optical methods based on fluorescence labeling [29].

Lab-on-a-Chip

Today, typical biosensors such as glucose meters¹ are relatively small but still of the size of a hand and thus far from the micrometer scale. In addition such a glucose sensor can measure only one parameter, the glucose concentration in the blood. It is, on the other hand, the aim of the present research in the field of biosensors to develop integrated, multiple-analyte devices with sizes allowing point-of-care analysis of a large number of analytes. Taking into account that each of the sensors requires signal read-out, amplification and processing also to be present on the devices, it follows that every sensor of such a multi-analyte detector should have a size as small as possible, preferably on the micro- or even nanometerscale. To this end, at least two steps are required:

- Miniaturisation of present sensors and their integration with optical and electrical detection systems, auxiliary sensors, data processing units and eventually even actuators to control the detection process on one chip.
- Integration of the necessary flow of analytes and – if required – other liquids or even cells on the same chip.

In other words, the final aim are the so-called labs-on-a-chip [48–50].

Integration and Miniaturization

Modern microelectronics has turned out to be one of the most important forces driving the field of biosensors towards integration and miniaturization [51]. On the one hand, semiconductor technology provides many of the techniques required for such a development. On the other hand, as today's biosensors transduce the incoming signal to an electrical one, it makes sense to use these established technologies to integrate the biosensors together with units for first data processing and amplification on one chip; further steps are then the integration of auxiliary sensors for temperature, pH values and humidity, which are of importance for the evaluation of the data of the biosensor, and even that of actuators which may control the biosensor. A very schematic example of an integrated optical biosensor is shown in Fig. 1.12.

The miniaturization which automatically accompanies such an integration bears, besides the use of established technologies, quite a number of additional advantages. The most important are summarized in Table 1.7.

¹ Glucose sensors are the first biosensors developed as early as 1962 by Clark and Lyons [1]. Their current (2004) share in the world market of biosensors is 85% [48].

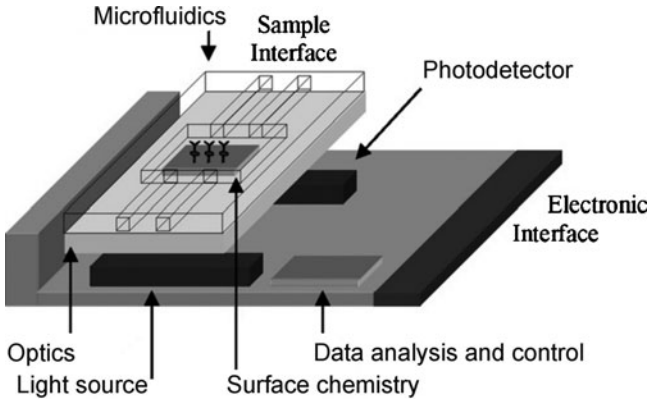


Fig. 1.12 Schematic example of an integrated optical biosensor (modified from Ref. [34])

Table 1.7 Advantages of the miniaturization of biosensors

Performance	Operation	Production
Short reaction times	Low sample consumption	Mass production
Fast analysis	Low power consumption	Reduced costs
Multiple analytes	Less waste	Portable devices
Parallel operation		

It is important to note that miniaturization and integration of biosensors (this also holds for sensors in general) not only possesses advantages with respect to the production of the sensors but also concerning their performance and, even more important, also their operation.

Microfluidics

When the sizes of a biosensor and especially of the recognition elements are reduced down to the micrometer scale, also the sizes of the systems guiding the flows of the analytes to the recognition elements has to be reduced to the micrometer size. Such reduced flow systems have also found applications in other modern fields such as chemical synthesis, cytometry, or photonics [51, 52]. It turned out that the flow of fluids in systems with micrometer dimensions is completely different from that in the macro-world; thus a new field of science has developed which is called microfluidics [51, 53, 54]. The main differences between macro and micro flows are:

The flows in microfluidic systems is always laminar (Fig. 1.13a) [56]. The type of flow in a tube or channel is determined by its Reynolds number

$$\text{Re} = \frac{\rho v l}{\mu} \quad (1.6)$$

where ρ is the density, v the velocity, and μ the viscosity of the fluid. l is the characteristic length determining the flow (e.g. the channel width). As l is on the order of micrometers only, Re is low which means that the flow is always laminar. This also means that mixing of two adjacent flows can only take place by diffusion (Fig. 1.13a) but not by turbulent flow. This can be advantageous but is, on the other hand, a serious problem since in order to mix two fluids, e.g. for a reaction, special devices (mixers) have to be developed. On the other hand, the laminar flow can be utilized e.g. for transportation and sorting of cells and other biological entities as shown schematically in Fig. 1.13b) by a technique which is called laminar fluid diffusion interface (LFDI) [55]. LFDIs are generated when two or more streams flow in parallel in a single microfluidic structure without any mixing of the fluids other than by diffusion of particles across the diffusion interface. It has been established that such structures can be used for diffusion-based separation and detection applications.

Another important effect determining the transport in micrometer channels is (capillary) electrophoresis (Fig. 1.14), which is the transport of ions in a fluid under the influence of an external electrical field. In many cases, the surfaces of the

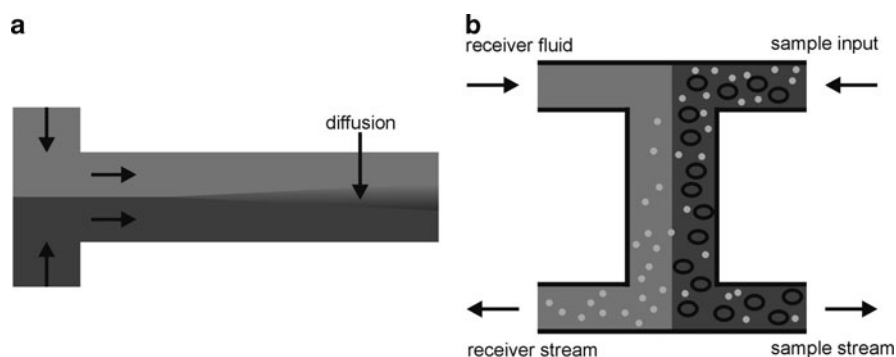


Fig. 1.13 (a) Laminar flow of two adjacent fluids; (b) separation of particles by laminar fluid diffusion interfaces [55]

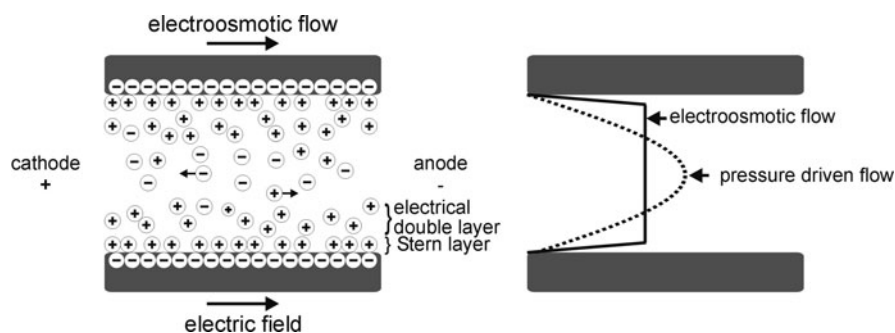


Fig. 1.14 (Left) Basic mechanisms for transport in microchannels by electrophoresis; (right) moving fluid front in the case of pressure driven and electroosmotic flow

microchannels used in microfluidics contain electrically negative functional groups. As a consequence positive counter-ions are attracted to the walls of the channel. Under the influence of an electrical field applied, these counter-ions start to move towards the negative electrode, thereby carrying the solvent molecules with them. As a consequence, the entire fluid starts to move. The most important advantage of this electrophoretic transport is that the moving front is much more defined as in the case of a pressure driven flow through a capillary as shown schematically in Fig. 1.14 (right).

In any case, for such microfluidic systems quite a number of new devices had to be developed such as valves, pumps, mixers, filters and reactors, each of them with dimensions of tens of micrometers only.

Originally, microfluidics devices have been prepared on silicon or glass substrate [56–58], making use of the well-established methods of silicon-micromachining. However, in recent times, elastomers such as polydimethylsiloxane (PDMS) have established themselves as materials of choice, with soft lithography [59] as the most common fabrication technique. Here, a (negative) master of the structure to be created is fabricated by conventional lithography in silicon. The PDMS is casted on this master and cured. Finally, the cast is lifted off from the master and can be used to form (a part of) the microfluidic device which often consists of stacks of several PDMS layers. PDMS has the advantage of being flexible which facilitates the design and operation of components such as pumps, valves, mixers and reactors. In addition it is gas-permeable which allows the provision of living organisms within the microfluidic system with oxygen.

Summary

Aim of this contribution was to outline some general aspects of sensors and especially biosensors. Sensors are devices converting the signal of interest by one or more transduction steps into an electrical (optical) output. They can be classified either according to the measurand or to the transducer principle. A number of static and dynamic characteristics of sensors have been discussed in this contribution.

Biosensors possess in addition a biological recognition element able to detect the presence of the target analyte or the occurrence of a (bio)chemical reaction. Possible recognition elements (e.g. enzymes, antibodies, etc.) have been introduced and their immobilization on the sensor surface was discussed.

The presently most important biosensors are based on optical and electrochemical principles; among the first plasmon resonance devices are most important, among the second field-effect-based devices.

In the final part the need for and the advantages of miniaturization and integration of (bio) sensors have been emphasized. It was shown that these developments may finally lead to so-called labs-on-a-chip. In the course of these development, a completely new field of research has emerged: the so-called microfluidics required to transport fluids and other analytes in micrometer-scaled channels to the miniaturized sensors.

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Part II
Techniques for the Preparation
of Sensor Materials

Chapter 2

Nonlinear Optical Sensors on Metal Nanoparticles Synthesized by Ion Implantation

Andrey L. Stepanov, Alexander Ryasnyansky, and Rashid Ganeev

Abstract Recent results on ion synthesis and nonlinear optical properties of metal nanoparticles in various dielectrics are presented. Copper and silver nanoparticles were fabricated in silica and soda lime glasses by low energy ion implantation. The nonlinear optical characteristics of nanoparticle composite materials, which may be suited for optical sensing, were studied by applying Z-scan transmittance measurements. They were performed in the near IR area at a wavelength of 1,064 nm, using picosecond pulses of a Nd:YAG laser. Optical nonlinearities of the metal nanoparticles in various substrates such as a nonlinear refraction and a nonlinear susceptibility were detected. It was shown that the influence of the dielectric environment (optical constants) around these nanoparticles considerably changes the nonlinear optical response of the composite materials. Ultrafast optical sensors based on nonlinear effects in metal nanoparticles are discussed.

Keywords Metal nanoparticles · Optical-nonlinear absorption · Nanoparticles sensor · Ion implantation

Introduction

Composite materials consisting of metal nanoparticles (MNPs) embedded in dielectrics have arised interest for applications in ultrafast optical sensors and optoelectronics owing to the large values of the nonlinear Kerr susceptibility $\chi^{(3)}$, whose

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real part is related to the intensity-dependent refractive index n_2 [1]. The most conspicuous manifestation of confinement in the optical sensor properties of noble metal nanoparticles is the appearance of surface plasmon resonances (SPR) which strongly enhance their linear and nonlinear responses around the SPR wavelengths [2]. Optical sensor effects rely on the SPR wavelength dependence of the dielectric functions of the composites; the response is much faster (in the picosecond to femtosecond range) in the nonlinear regime. Ion implantation has been shown to produce a high density of MNPs in glasses, polymers and crystalline materials. The high volume fraction and small sizes of the MNP leads to value of $\chi^{(3)}$ larger than those of metal doped solids [3, 4]. This has excited interest in the use of ion implantation to prepare nonlinear optical materials. The impact of a dielectric confinement on the nonlinear optical response of MNPs has been extensively studied using different techniques with wavelengths in the vicinity of the SPR, which are typically in visible range for noble metal nanoparticles. However, for optical applications it is important to have an enhanced nonlinearity of the composite materials at a wavelength of practical use for optical signal propagation, for example, in IR spectral area. Thus, in this paper we concentrate on the study of nonlinear optical refraction of various silicate glasses containing ion synthesized Cu and Ag nanoparticles at the IR wavelength of 1,064 nm.

Experimental Procedure

Soda-lime silicate glasses (SLSG) from Societa Italiana Vetro and SiO_2 from Heraeus were implanted with 50 keV Cu^+ ions at a dose of $8.0 \cdot 10^{16} \text{ cm}^{-2}$ and with 60 keV Ag^+ ions at a dose of $6.0 \cdot 10^{16} \text{ cm}^{-2}$ for a beam current density of $10 \mu\text{A/cm}^2$. The details of the ion implantation are described in Ref. [5]. The samples were analyzed by small-angle x-ray scattering under grazing incidence. Some samples were characterized by transmission electron microscopy (TEM). Optical transmittance spectra were measured from 300 to 900 nm using a dual beam Perkin Elmer Lambda spectrophotometer. All spectra were recorded in the standard differential mode in order to eliminate substrate effects. For nonlinear experiments the Z-scan technique was applied [5]. A mode-locked Nd:YAG laser was used which generated picosecond pulse trains. Single pulses ($\tau = 35 \text{ ps}$) from such a train were amplified up to 1 mJ at $\lambda = 1,064 \text{ nm}$. The maximum laser intensity at the focal point was selected to $8 \cdot 10^{10} \text{ W/cm}^2$ which is lower than the intensity of optical breakdown of the glasses. An experimental set-up with a closed aperture allowed to determined the sign and magnitude of n_2 and $\chi^{(3)}$.

For the calculation of the values of n_2 of the samples the equations of the Z-scan method were applied [6]:

$$\Delta T_{\text{pv}} = 0.406(1 - S)^{0.25} |\Delta \Phi_0| \quad (2.1)$$

$$|\Delta \Phi_0| = (2\pi/\lambda) n_2 I L_{\text{eff}}, \quad (2.2)$$

where the quantity ΔT_{pv} is the difference between the normalized peak and valley transmittance: $T_p - T_v$, I is the radiation intensity, S is the linear transmittance of the aperture, and $\Delta\Phi_0$ is the phase distortion of the radiation process through the sample. $L_{\text{eff}} = (1 - \exp(-\alpha L))/\alpha$ is the effective length of the analyzed material with the real thickness L of the nonlinear layer with ion-synthesized MNPs and the linear absorption coefficient α . In the experiments $\Delta\Phi_0$ is defined as a temporally integrated peak-on-axis phase shift.

Fabrication of Metal Nanoparticles by Ion Implantation

X-ray and optical spectroscopic measurements proved the formation of MNPs in the silicate glasses. These studies (x-ray scattering under grazing incidence) have shown the average sizes of the Cu nanoparticles to be 3.5–4.5 nm. The silver-ion implanted samples were characterized by a broader size distribution of nanoparticles (from 2 to 18 nm) as observed by TEM measurements. The depth of the location of the nanoparticles in the irradiated glasses was about 60 nm. The formation of MNPs was recognized by the appearance of selective absorption bands in the optical transmission spectra with transmission minima in the ranges of 400–450 nm for silver-doped glasses and 550–600 nm for copper-doped glasses, corresponding to the SPRs of silver and copper nanoparticles (Fig. 2.1). Radiation defects stimulate additional light absorption in the glasses in the shorter wavelength spectral range close to the

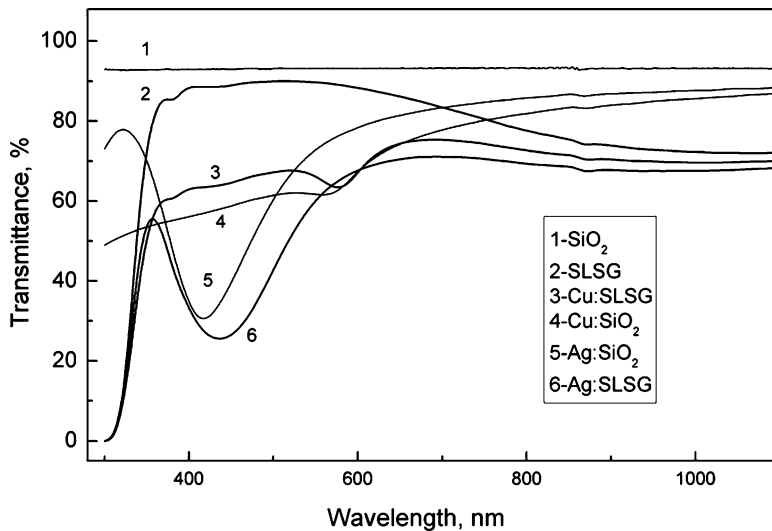


Fig. 2.1 Optical transmittance spectra of Cu and Ag nanoparticles synthesised in SiO₂ and SLSG by ion implantation

UV region. However, it should be noted that present nonlinear optical study was performed using radiation with a wavelength of 1,064 nm, which lies far from both SPRs and intra-band transitions of MNPs.

Nonlinear Refraction of Metal Nanoparticles

The Z-scan method was used for the determination of both the value and the sign of the n_2 and the Kerr nonlinear susceptibility responsible for the self-action of laser radiation. The characteristics of normalized transmittance dependences $T(z)$ of the Cu-ion implanted glasses in a closed-aperture scheme as a function of the sample position with respect to the focal point z are shown in Fig. 2.2. The two glasses with Cu nanoparticles have a different sign of n_2 ; it is negative for Cu:SiO₂ but positive for Cu:SLSG. In particular, this means that the Cu:SiO₂ sample shows self-defocusing behaviour, while Cu:SLSG is characterised by self-focusing one. The values of n_2 calculated using Eqs. 2.1 and 2.2 are presented in Table 2.1.

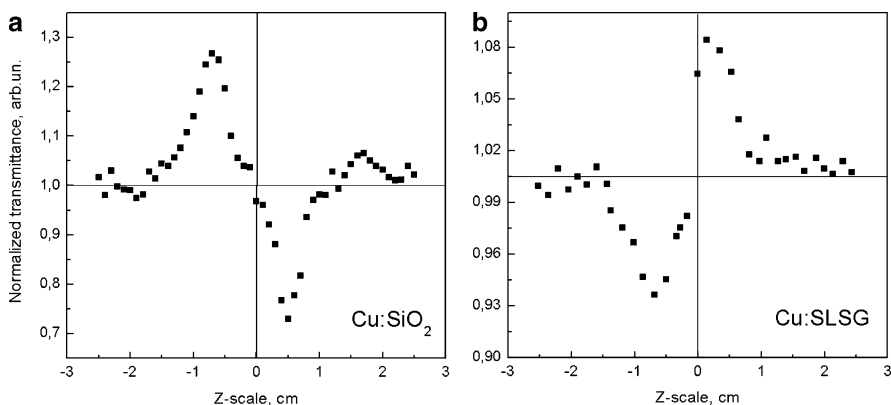


Fig. 2.2 The dependences of the normalized transmittance of implanted glasses on z . (a) Cu:SiO₂ and (b) Cu:SLSG

Table 2.1 The nonlinear optical characteristics of glasses with implanted MNPs (esu = electrostatic unit)

Sample	n_2 , 10^{-8} esu	$\text{Re}\chi^{(3)}$, 10^{-9} esu	Nonlinear self-action
Cu:SiO ₂	-13.7	-32	Self-defocusing
Cu:SLSG	3.6	8.3	Self-focusing
Ag:SiO ₂	1.5	2.5	Self-focusing
Ag:SLSG	3.5	5.7	Self-focusing
SLSG	$8.1 \cdot 10^{-6}$	$1.4 \cdot 10^{-6}$	Self-focusing

It was observed that there were no changes in the $T(z)$ curves of pure SiO_2 . The SLSG matrix shows optical nonlinear features with a positive sign, but as can be seen in Table 2.1 this value is smaller than the nonlinear refraction of SLSG with Cu nanoparticles.

The real part of $\chi^{(3)}$ (Table 2.1) was calculated using the following equation [6]:

$$\text{Re}\chi^{(3)} = n_0 n_2 / 3\pi, \quad (2.3)$$

where n_0 is the linear refractive index.

Another important peculiarity of the nonlinear optical properties of copper-doped glasses is that the wavelength of 1,064 nm is situated close to the two-photon excitation of SPRs of copper nanoparticles (Fig. 2.3). The value of the nonlinear refraction index n_2 can be varied over a large range depending on the type of interaction (resonant or non-resonant). Non-resonant contributions to the refractive index are usually positive [7]. In the case of quasioresonant (one- or two-photon) interactions, the sign of the nonlinear refraction index is determined by the correlation between the fundamental frequency, the doubled frequency (in the case of two-photon quasi-resonance) and the resonant frequency of the medium investigated.

The optical properties of a material containing nanoparticles can be considered in the framework of an effective medium approximation [2] since the wavelength of the laser radiation used in the present study was much larger than the sizes of MNPs. A two-level model for homogeneous condensed matter was considered [8]. According to this, the sign of the nonlinear refractive index is determined by the sign of the detuning of the laser radiation frequency (or their harmonics) by the SPRs of the MNPs. $\text{Re}\chi^{(3)}$ can be written as follows:

$$\text{Re}\chi^{(3)} \propto (\omega_{i0} - \omega_p)^{-3}, \quad (2.4)$$

where ω_p and ω_{i0} are the frequencies of the SPR and the laser radiation. The index i denotes one- or two-photon processes.

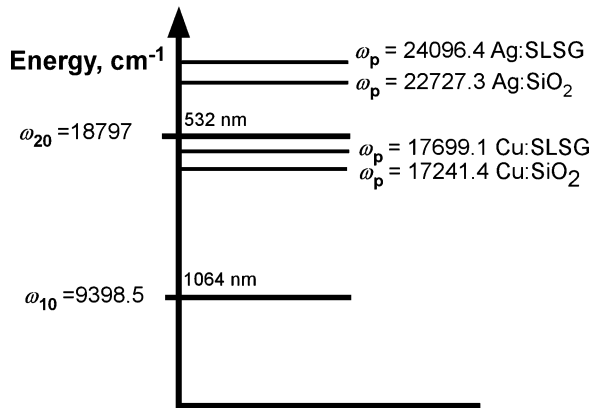


Fig. 2.3 Energy diagram of glasses with copper and silver nanoparticles (SiO_2 – SG)

Differences of the spectral locations of the SPR in copper nanoparticles were observed for the two glass matrices (Fig. 2.1). The SPR maxima in the cases of Cu:SLSG and Cu:SiO₂ were located at 580 and 565 nm, respectively. A two-photon excitation of the samples at the frequency of the laser radiation can be considered. Taking the doubled laser frequency $\omega_{20} = 18,797 \text{ cm}^{-1}$ (Fig. 2.3), one gets a negative sign of the frequency detuning for both SPRs, which predicts a negative sign of $\text{Re}\chi^{(3)}$ for both composites. These conditions correspond to the self-defocusing phenomenon observed in the case of the Cu:SiO₂ sample (Fig. 2.2a). However, in reality for the Cu:SLSG sample self-focusing was observed (Fig. 2.3b). In order to understand this peculiarity the nonlinear contributions from the glass substrates without MNPs have to be estimated. The dependences of $T(z)$ in the closed-aperture arrangement were studied for both non-implanted glasses. In the case of SiO₂ there were no changes in the $T(z)$ curve at the intensities used. This means that the nonlinear effect observed for Cu:SiO₂ was solely due to the copper nanoparticles. At the same time self-focusing was observed for an undoped SLSG matrix (Table 2.1). Therefore the nonlinear optical effect in the Cu:SLSG composite is determined by some specific superposition of the contributions from the MNPs and the glass itself.

Figure 2.4 presents the dependences $T(z)$ in the closed-aperture arrangement for the Ag:SiO₂ and Ag:SLSG samples. As can be seen, a positive nonlinearity (self-focusing effect) was observed for both samples. The composites containing silver nanoparticles are, as in the case of copper nanoparticles, characterized by different spectral locations of the SPR maxima, depending on the type of substrate (Fig. 2.1). The SPRs of Ag:SiO₂ and Ag:SLSG were at 415 nm ($\omega_p = 24096.4 \text{ cm}^{-1}$) and 440 nm ($\omega_p = 22727.3 \text{ cm}^{-1}$), respectively. Thus the doubled frequency of the laser radiation is smaller than that of the SPRs of Ag nanoparticles

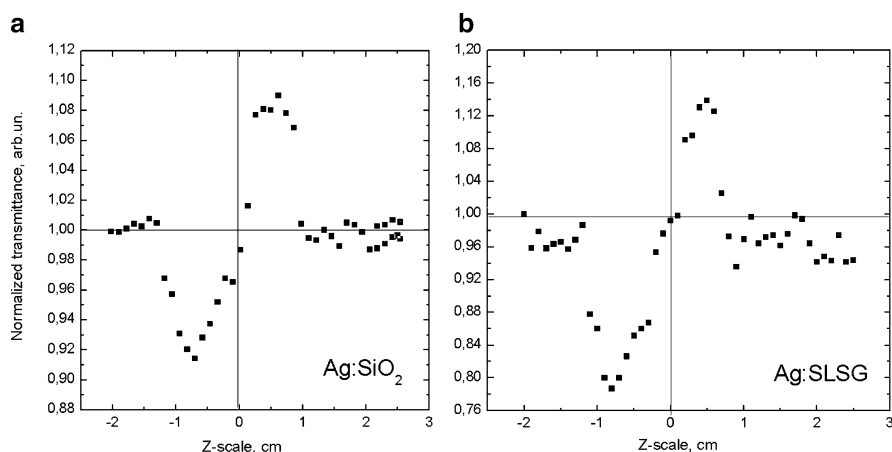
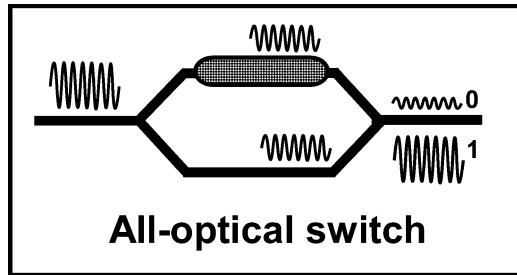


Fig. 2.4 The dependences of the normalized transmittance of implanted glasses on z . (a) Ag:SiO₂ and (b) Ag:SLSG

Fig. 2.5 All-optical switch in the Mach-Zehnder geometry. The phase shift is induced by the nonlinear (intensity-dependent) index of refraction in the upper arm. Part of a diagram from Ref. [3]



in both matrices which corresponds to the positive sign of the refractive nonlinearity (Eq. 2.4). The results of the nonlinear optical parameter measurements of silver-doped glasses are presented in Table 2.1.

The third-order nonlinear effects described above can be used to design optical switches. For example, consider the schematic optical switch shown in Fig. 2.5 [3], based on a Mach-Zehnder interferometer geometry. It operates by inducing an index change – and hence a phase shift – between the two arms of the interferometer. Thus an input signal, evenly divided between the two arms, can give either a 0 or a 1 output depending on the phase shift. The same effect can be achieved in an all-optical configuration using a material with an intensity-dependent index of refraction n_2 in one arm of the interferometer; here the switching effect is set by the size of the nonlinear index and the intensity of the input signal.

Conclusions

Composite materials consisting of noble metal nanoparticles embedded in linear or nonlinear dielectrics are attracting growing interest for applications in photonics and sensors. Well-established for their useful linear optical SPR absorption at wavelengths depending on the dielectric environment, these materials have also interesting nonlinear optical refraction properties which are the result of classical electromagnetic effects in the MNPs. These classical effects arise from the time-dependent dipole field induced by an electromagnetic wave acting on the electrons in the immediate vicinity of the MNPs. This feature is of critical importance for the performance of the sensor. The nonlinear optical response exhibits ultrafast switching speeds, a large nonlinearity and modest switching energies which are all of advantage for sensor applications. The experiments presented above have demonstrated that silicate glasses with MNPs synthesized by ion implantation appear to be potentially interesting for applications of these materials in photonic devices for optical switching and sensors.

Acknowledgments The author is grateful to the Alexander von Humboldt Foundation (Germany) and the Austrian Scientific Foundation in the frame of the Lise Meitner program for financial support. This work was partly supported by the Russian State Contract No. 02.740.11.0797.

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Chapter 3

Laser Ablative Deposition of Polymer Films: A Promise for Sensor Fabrication

Jadranka Blazevska-Gilev, Jaroslav Kupčák, Jan Šubrt, and Josef Pola

Abstract There is a continuing interest in the use of polymer films as insulating components of sensors; a number of such films have been prepared by polymer sputtering or vacuum deposition processes involving gas phase pyrolysis/photolysis and by plasma decomposition of monomers. An attractive and rather new technique for the deposition of novel polymer films is IR laser ablation of polymers containing polar groups. We have recently studied this process with poly(vinyl chloride) (PVC), poly(vinyl acetate) (PVAc) and poly(vinyl chloride-co-vinyl acetate) P(VC/VAc) to establish its specific features and differences to conventional pyrolysis.

Keywords Laser ablation · Laser-induced polymer films · PVC · PVAc · P(VC/VAc) · Metal-PVC composites

Introduction

The thermal degradation of the very useful poly(vinyl chloride) (PVC) has been extensively studied for many years [1–4] and was shown to involve two stages, which are the initial elimination of HCl (yielding conjugated polyene units) and the subsequent formation of aromatic structures and carbonaceous residues. Slow heating of PVC by heat delivered from the reactor walls carried out in previous

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studies allowed a thermodynamical control of the polymer degradation, which was possibly affected by heterogeneous steps. Conventional decomposition of poly (vinyl chloride-co-vinyl acetate) [5–8] by side-group elimination yielded acetic acid and hydrogen chloride in a proportion remaining constant during the degradation and corresponding to that in the initial copolymer. Thermal degradation of poly (vinyl acetate) [9–13] has been shown to be dominated by elimination of acetic acid and to lead to the formation of a carbonaceous residue containing conjugated C=C bonds along with cyclic and aromatic units [14].

A completely different mode of thermal degradation of polymers can be achieved through heating by IR laser pulses [15, 16]. This specific thermal process occurs within a temperature jump and is controlled by kinetic rather than by thermodynamic degradation. It is feasible through multiple-photon absorption of low energy infrared photons, which leads to a high vibrational excitation density in the polymer and high heating and cooling rates ($\sim 10^{6-11}$ and $\sim 10^{3-6}$ K s⁻¹, respectively) [17–19]. This process is currently of high interest for two different reasons. First, it allows a feasible fabrication of various polymer films which are deposited near the irradiated original polymer target due to facile ejection of large macromolecules and/or fragments which efficiently recombine to form various polymeric structures [20–23]. Second, the elimination of heterogeneous steps and the kinetic control of the polymer decomposition can result in decomposition pathways different from those observed in conventional degradation [24].

Composite materials, especially thin films containing metal nanoparticles embedded in a polymer matrix, have recently attracted much attention (e.g. [25–27]) due to possible applications in optical and magnetic devices. In this paper, we therefore report also on infrared laser-induced ablative decomposition of metal (Cu and Fe)/polymer (PVAc) composites and compare this process to the IR laser ablative degradation of pure PVAc. We show that the metal loading of the polymer leads to the formation of gaseous products similar to those observed in the ablative decomposition of pure PVAc, and that the ablation results in the deposition of thin crosslinked, acetoxy-group-containing polymer films which incorporate metal particles. The latter finding demonstrates ablative transfer of metal particles encapsulated by a polymer to be feasible.

Experimental

The irradiation of PVC, PVAc, metal (Cu and Fe)/polymer (PVAc) composites and copolymer (0.5–0.8 g samples compressed in a tablet) with a transversely excited atmosphere CO₂ laser (Plovdiv University) using the P(20) line of the 00°1–10°0 transition (944.19 cm⁻¹) was performed with an incident fluence of 0.6–25 J cm⁻² and a repetition frequency of 1 Hz. The tablet was housed on the bottom of an evacuated (10⁻² mbar) Pyrex vessel (42 ml in volume) equipped with a side arm with a rubber septum, a PTFE valve and a NaCl window and connected to a

vacuum manifold with a vacuum meter. The vessel contained a holder for quartz, KBr and copper substrates. The properties of the films deposited onto these substrates and the vessel surface in total amounts of ~10–15 mg were evaluated by FTIR spectroscopy (Nicolet Impact spectrometer), X-ray photoelectron spectroscopy (XPS), UV/VIS spectroscopy (Shimadzu UV/VIS 1601 spectrometer) and electron microscopy. Volatile products were identified through their mass spectra (Kratos MS 80 mass spectrometer) and were also monitored by FTIR spectroscopy. Quantification of the volatile products was performed through their mass spectra and calibrations with reference samples. SEM analyses were performed using a Philips XL30 CP scanning electron microscope equipped with an energy-dispersive analyzer (EDAX DX-4) of the X-ray radiation. A PV 9760/77 detector in low vacuum mode (0.5 mbar) was used for quantitative determination of the elements [C, O and Cl]. The XPS spectra were measured using an ESCA 310 (Gammadata Scienta, Sweden) electron spectrometer equipped with a high-power rotating anode, a wide-angle quartz crystal monochromator, and a hemispherical electron analyzer operating in the fixed transmission mode.

PVC (average MW 62,000), PVAc (average MW 167,000), P(VC/VAc), $([-CH_2CH(Cl)-]_x[-CH_2CH(O_2CCH_3)-]_y, x/y=9, MW \sim 44,000)$, copper nano powder (99.8%, particle size ~100 nm) and iron powder (97%, particle size ~44 μm) were purchased from Aldrich. The orange Cu/PVAc and gray Fe/PVAc composites were prepared by simple blending polymer and metal powder in the weight ratio of 5:1 in acetone. The mixture was stirred vigorously to obtain homogeneity. Thereafter, the solvent was removed using a rotary evaporator and the residual solid was dried at 40°C for 72 h in vacuum (10^{-3} mbar).

Results and Conclusions

IR Laser Irradiation of PVC

The pulsed IR laser irradiation of PVC at 0.6–25 J cm⁻² yields vinyl chloride, HCl, C₁₋₄ hydrocarbons, benzene, H₂ and toluene and causes the deposition of a polymeric films that contains conjugated C=C bonds and less Cl than the initial PVC. The ablative deposition is affected by the laser fluence.

Irradiations at higher fluences result in larger portions of the solid deposit (and lower amounts of volatile products), increase the fraction of vinyl chloride among the volatile products, and practically do not affect the Cl content in the deposits. The deposited polymeric films do not contain aromatic fragments and become intractable upon prolonged storage, which is explained by polymerization of the conjugated C=C bonds leading to crosslinking. The films fabricated at medium fluences contain nanosized fibres and necklaces whose Cl content becomes lower at higher fluences (Fig. 3.1).

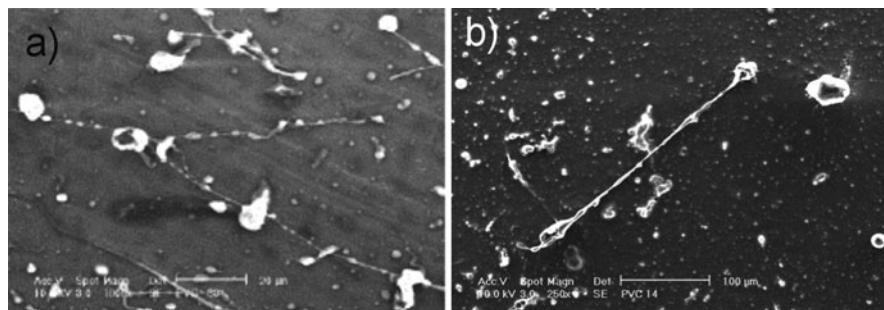


Fig. 3.1 SEM images of the deposits obtained by irradiation of PVC at fluences of 6.5 J cm^{-2} (a, bar=20 μm) and 11 J cm^{-2} (b, bar=100 μm), respectively

These features may improve [28, 29] the mechanical properties of the deposited films. The thermal degradation (TGA) of the films differs from that of PVC and involves two equally important stages of decomposition. The ablative deposition of PVC can be considered as a suitable technique for the fabrication of intractable crosslinked polyhydrocarbon films containing nanofibers and different contents of C—Cl bonds. The laser degradation of PVC into vinyl chloride represents the first example of thermal degradation of PVC into a monomer.

IR Laser Irradiation of P(VC/VAc)

IR laser-induced ablative degradation of P(VC/VAc) yields gaseous and solid products whose formation can be explained by cleavage of both pendant groups of the copolymer chain. The former reactions are assumed to occur as radical chain steps, the latter to take place as homolysis of near and distant C—C bonds. The molar ratio of vinyl chloride/HCl increases at higher laser fluxes; this increase is more pronounced than that observed in the laser degradation of PVC. The ablative degradation of the copolymer is in the fluence range of $7\text{--}15 \text{ J cm}^{-2}$ faster than that of poly(vinyl acetate) and poly(vinyl chloride). The process allows to control the ratio of Cl— and $\text{CH}_3\text{C}(\text{O})\text{O}$ groups in the deposited films by the irradiating conditions. The deposited films contain carbonaceous microfibers that are more distinctive than those produced by IR laser-induced ablative degradation of PVC (Fig. 3.2).

IR Laser Irradiation of PVAc

Three previously unobserved thermal pathways of IR laser-induced decomposition of PVAc were detected. These are the formation of vinyl acetate, the formation of acetone and the ablative deposition of polar polymeric films. The formation of

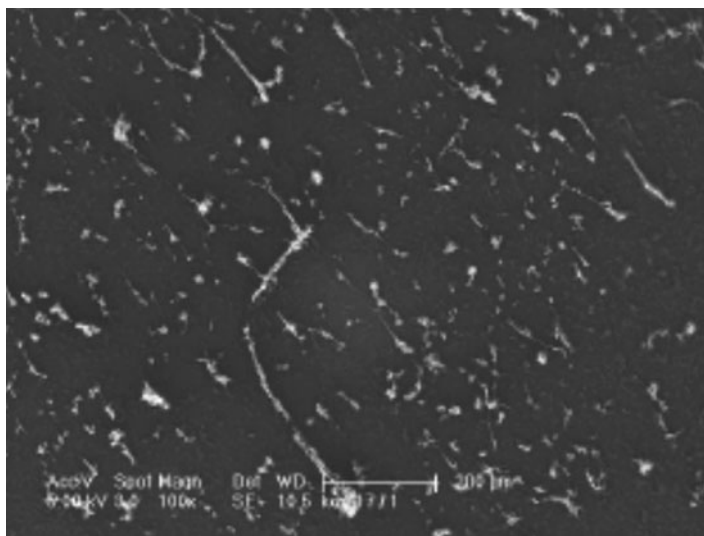


Fig. 3.2 SEM image of a film obtained by irradiation of P(VC/VAc) at 13 J cm^{-2}

vinyl acetate is the first example of thermal degradation of poly(vinyl acetate) into the monomer. The specific features of the laser-induced decomposition of PVAc are attributed to a kinetic control of the decomposition and the absence of heterogeneous contributions to the decomposition. The relative extents of these pathways depend on the laser fluence. Low-fluence irradiation of PVAc yields vinyl acetate (main product) along with acetone and H_2 . High fluence irradiations result in the formation of a multitude of volatile compounds (vinyl acetate, acetone, acetic acid, CO , CO_2 , methane, ethane and H_2) and lead to the ablative deposition of polymeric films containing conjugated $\text{C}=\text{C}$ bonds and half of the acetate groups initially present (Fig. 3.3). The deposited polymer films become intractable upon prolonged staying, which is explained by polymerization at the conjugated $\text{C}=\text{C}$ bonds leading to crosslinking. The ablative deposition of PVAc allows the fabrication of intractable crosslinked PVAc-based films and suggests intensive use of IR laser-induced treatment of solid linear chain polymers with pending polar groups.

IR Laser Irradiation of PVAc/Metal Composites

IR laser ablation of bulk PVAc loaded with Fe microparticles and Cu nanoparticles leads to the formation of gaseous products (hydrocarbons, acetic acid, carbon oxides) and the ablative deposition of polar, metal particles-containing polymeric films (Fig. 3.4).

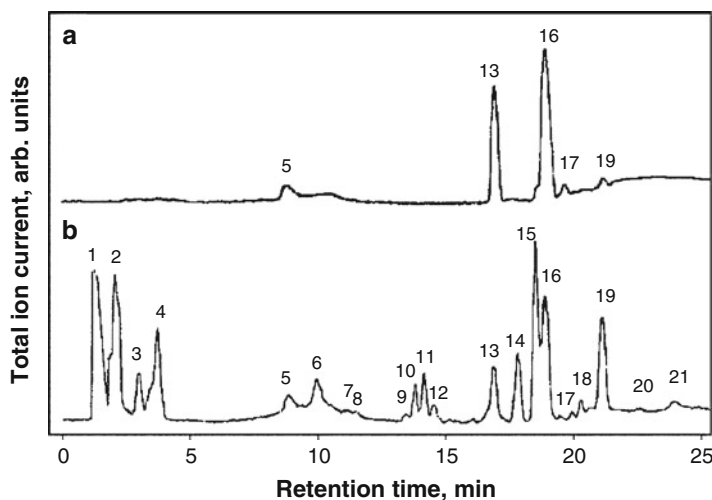


Fig. 3.3 Typical GC/MS traces of volatile products obtained upon irradiation of PVAc at fluences lower (a) or higher (b) than 2 J cm^{-2} . The examples given relate to the products distribution observed for 1.6 and 5.2 J cm^{-2} . Peak assignment: 1: CH_4 ; 2: CO_2 ; 3: C_2H_4 ; 4: C_2H_6 ; 5: H_2O ; 6: $\text{CH}_3\text{CH}=\text{CH}_2$; 7: $\text{CH}_3\text{C}\equiv\text{CH}$; 8: $\text{CH}_2=\text{C}=\text{CH}_2$; 9: CH_3CHO ; 10: C_4H_8 ; 11: C_4H_6 ; 12: $\text{CH}_2=\text{CH}-\text{C}\equiv\text{CH}$; 13: $\text{CH}_3\text{C}(\text{O})\text{CH}_3$; 14: cyclopentadiene; 15: $\text{CH}_3\text{CO}_2\text{H}$; 16: $\text{CH}_2=\text{CHOC}(\text{O})\text{CH}_3$; 17: $\text{C}_2\text{H}_5\text{OC}(\text{O})\text{CH}_3$; 18: C_6H_8 ; 19: C_6H_6 ; 20: C_6H_{10} ; 21: $\text{CH}_3-\text{C}_6\text{H}_5$

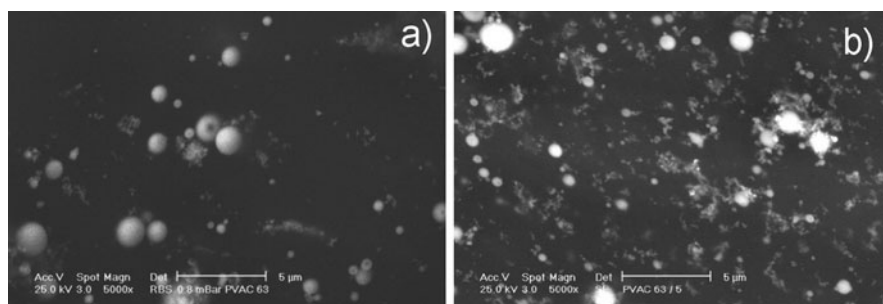


Fig. 3.4 SEM images of (a) the irradiated PVAc/Cu target and (b) a film deposited there from at a fluence of 4 J cm^{-2} (the bars correspond to $5 \mu\text{m}$)

These films possess ca. 50% of the initially present acetate groups; initially they contain $\text{C}=\text{C}$ bonds which undergo reactions leading to polymer cross-linking. The crosslinked PVAc-based films incorporating metal particles are thermally less stable than similar crosslinked PVAc-based films ablatively deposited from pure PVAc. The distribution of the volatile products and the structure of the deposited films from pure- and metal particles-loaded PVAc

are very similar. The process reported reveals that ablation of metal particles embedded in a polymer body is feasible and shows that it will be possible to fabricate films of metal/polymer composites in which the metal particles are completely protected by the polymer.

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Chapter 4

Fabrication of Porous and Dense Ceramics from Transitional Nano-Alumina

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Abstract Porous alumina ceramics (density 0.75 TD) with a typical vermicular microstructure were obtained from transitional nano-alumina powder by cold isostatic pressing ($P = 500$ MPa) and sintering at non-isothermal conditions from RT to $1,500^{\circ}\text{C}$. Mechanical activation, realized by attriting, was used to reduce the $\alpha\text{-Al}_2\text{O}_3$ transformation to a temperature of $1,038^{\circ}\text{C}$. Conventional pressing ($P = 500$ MPa) and sintering at $1,500^{\circ}\text{C}$ were used to fabricate 0.96 TD dense alumina ceramics. Electrophoretic deposition was applied to the mechanically activated powder followed by isostatic pressing and sintering. Compacts with a density of 0.94 TD were obtained at $1,400^{\circ}\text{C}/30$ min. The microstructure was homogenous with grain sizes of 300 ± 100 nm.

Keywords Transitional alumina · Vermicular microstructure · Mechanical activation · Electrophoretic deposition

Introduction

Fabrication of advanced ceramic materials from nanosized powders has received increased attention in the last years due to the new properties (mechanical, optical, electrical and magnetic) of nanostructured ceramics [1]. The major difficulty in

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the fabrication of uniform and high density nanostructured ceramics is the extremely large specific surface area of the nanosized particles which result in high agglomeration in the green bodies obtained after pressing. The agglomeration causes a low relative density and inhomogeneity in the green body, both of which hinder densification during sintering [2].

Theoretical predictions by Frenkel [3] and Herring [4] clearly suggest that the rate of densification is inversely proportional to the cube of the particle size. Thus, as the particle size decreases from micrometer to nanometer, a substantial decrease of the sintering time can be expected at a given temperature. Many experimental investigations support this theoretical prediction. Skandan et al. [5] sintered nanosized titania at 800°C, well below the sintering temperature for conventional titania powders. Rhodes [6] produced densely packed compacts of nanosized zirconia particles and observed sintering of the compacts nearly to the theoretical density at much lower temperatures than used for sintering coarse zirconia particles.

Studies on producing nanostructured ceramics from nanopowders have highlighted the problem of achieving high densities without excessive grain growth. It is known that nanopowders have a large specific surface area and a high defect density, specially in mechanically activated powders, which can act as additional driving forces during sintering [7, 8]. Bossert and Fidancevska [9] gave details of the effect of mechanical activation on the sintering of transition alumina. Ref. [10] describes a method to obtain dense alumina starting from nanoscaled transitional alumina. Konig et al. [11] described the effect of particle size and morphology of alumina powders on green bodies prepared by electrophoretic deposition.

This paper presents the fabrication of alumina ceramics from transitional nanoalumina powder by using isostatic pressing, slip casting and electrophoretic deposition followed by sintering of the alumina ceramics.

Experimental

The nano aluminium oxide powder (99.78%) used in this study was obtained from IBU-Tech, Germany. The powder was obtained from aluminium tri-sec-butylat at 850°C by the pulsation reactor technique. The powder morphology was observed via transmission electron microscopy (TEM). The specific surface area was measured using nitrogen gas adsorption (multipoint BET method, Gemini, Micromeritics, USA). Phase analysis of the alumina was carried out by X-ray diffraction (XRD) with Ni-filtered CuK_α radiation. Shrinkage during sintering was followed by dilatometry (NETSCH TMA 402E) in air atmosphere, using a heating rate of 10 K min^{-1} in the temperature interval from RT to 1,500°C. The final density of the sintered compacts was determined by the Archimedes displacement method. A high resolution scanning electron microscope (Leica IS 110, Germany) was employed to observe the microstructure of the sintered samples.

Mechanical activation (wet milling) of the starting powder was performed by a NETZSCH attritor mill using alumina balls at pH 5 for 0.5 h. A suspension with a alumina solid load of 20 wt% was used. Conventional pressing ($P = 500$ MPa) and sintering at $1,500^{\circ}\text{C}$ were used to fabricate alumina ceramics.

The electrophoretic deposition (EPD) technique applied in ceramics processing has been discussed by Sarkar and Nicolson in a review article [12]. In the present work, a EPD cell containing two platinum electrodes connected to a power supply was used to obtain alumina deposits. The pH of the transition alumina suspension was 11. The content of alumina in the suspension was 7.5 wt%. The EPD experiments were conducted under a constant voltage of 24 V and a current of 35 mA for 30 min, resulting in the formation of a deposit thickness of about 3 mm. The EPD-formed green deposits were dried in air atmosphere for 48 h and at 105°C for 4 h. The EPD compacts were cold iso-statically pressed (CIP) at 500 MPa (WEBER PRESSEN KIP 500 E) and sintered at $1,400^{\circ}\text{C}/30$ min.

Slip casting was used for the fabrication of alumina ceramics where the solid load was ca. 40 wt%. Sintering was performed at $1,500^{\circ}\text{C}/4$ h.

Results and Discussion

The morphology of the powder presented in Fig. 4.1 shows the spatial arrangement of the nanoparticles. The size of the primary alumina particles was 5–10 nm. The specific surface area was $95\text{ m}^2/\text{g}$. One part of these nanosized primary particles form aggregates in the as-received powder with sizes around 100–200 nm.

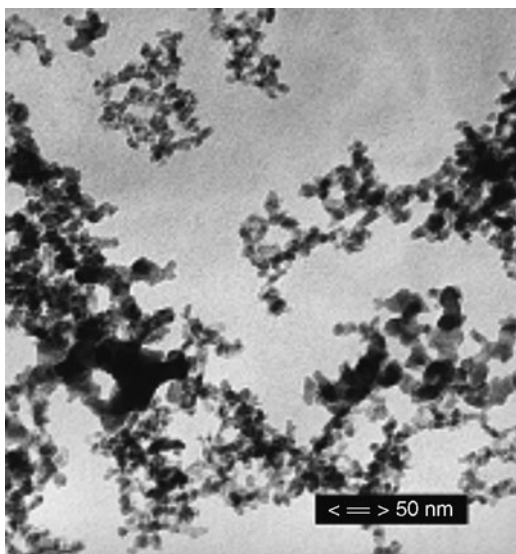


Fig. 4.1 TEM photograph of the starting transition alumina powder (the bar represents 50 nm)

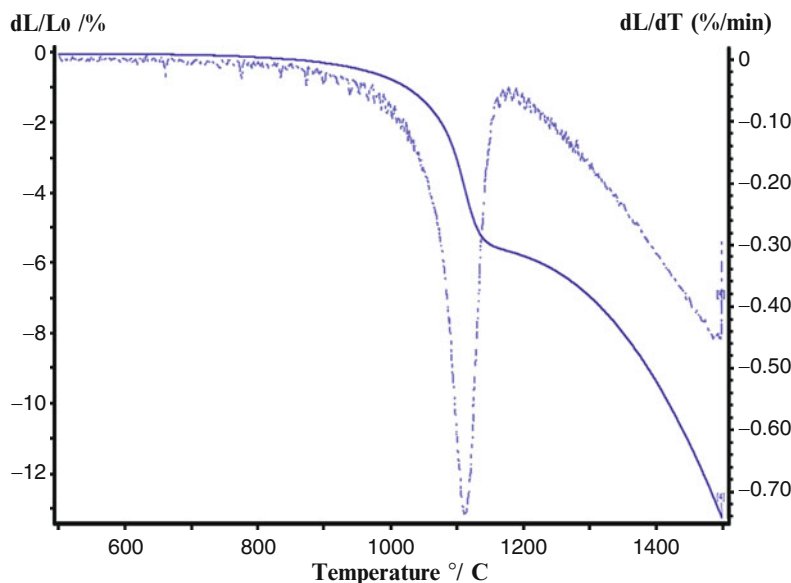


Fig. 4.2 Shrinkage ($\Delta L/L_0$) and shrinkage rate of a compact formed from as-received powder during sintering at 10 K min^{-1} to $1,500^\circ\text{C}$

The powder was first uniaxially pressed at 20 MPa and then isostatic pressed at 500 MPa. The green density of the compact was 0.57 TD. As a result of aggregation and subsequent agglomeration of the primary particles, compacts of nano-sized particles usually have low densities after cold pressing. The low density is due to two factors: (1) the presence of large voids in the green state and (2) inefficient packing of particles in the structure of the green state.

The sinterability of the compacts formed from the starting powder is shown in Fig. 4.2, where $\Delta L/L_0$ is plotted as a function of the temperature ($\Delta L = L_0 - L$); where L_0 is the initial length of the sample and L the instantaneous length. The temperature at which measurable shrinkage begins is 970°C . At a temperature of $1,500^\circ\text{C}$ the shrinkage value was $\Delta L/L_0 = 13\%$, where a density of 0.75 TD was achieved. Transition nanoalumina shows two regions of densification during the course of sintering with a constant heating rate.

The first one is a distinctive feature of sintering kinetics with a rapid shrinkage in the temperature region of $1,010\text{--}1,148^\circ\text{C}$, with a maximum shrinkage rate at $1,107^\circ\text{C}$. This densification is associated with the phase transformation of $\gamma\text{-Al}_2\text{O}_3$ via the δ - and the θ - to the stable α -phase. The second shrinkage region above $1,148^\circ\text{C}$ is the densification of the $\alpha\text{-Al}_2\text{O}_3$ at higher temperatures.

The microstructure of the sample sintered at $1,500^\circ\text{C}$ is shown in Fig. 4.3. It consists of a vermicular network in which the pores and the pore channels are the same scale as the $\alpha\text{-Al}_2\text{O}_3$ grains. The elongated pores have sizes of $0.5\text{--}1.5 \mu\text{m}$.

After mechanical activation by attriting, the specific surface area was increased from 95 to $99 \text{ m}^2/\text{g}$, which means that a new surface was created, which provides

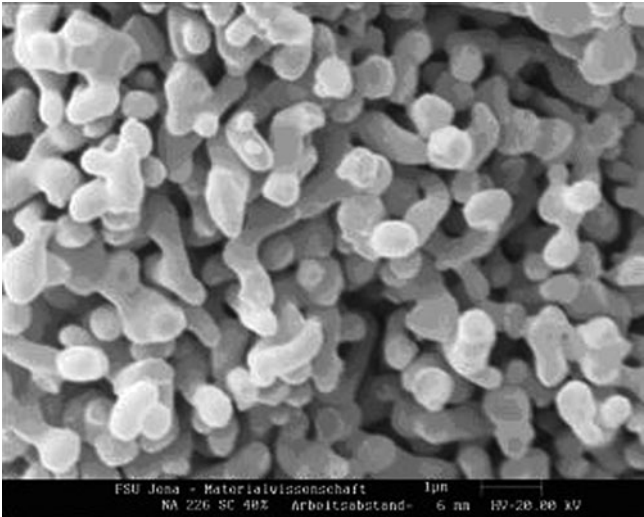


Fig. 4.3 SEM micrograph of the fractured surface of a sample sintered at 1,500°C (the bar represents 1 μm)

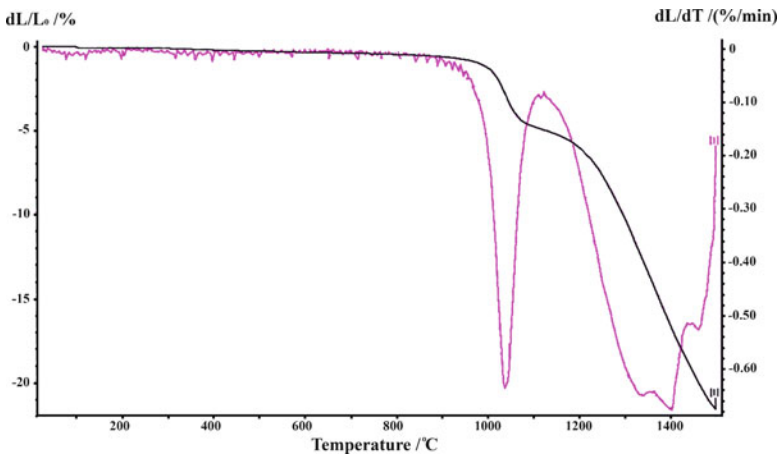


Fig. 4.4 Shrinkage ($\Delta L/L_0$) and shrinkage rate of a mechanically activated systems during sintering at 10 K min^{-1} to 1,500°C

potential sites for nucleation. The shrinkage during sintering of the compacts formed from activated powder is shown in Fig. 4.4. $\alpha\text{-Al}_2\text{O}_3$ transformation after mechanical activation was reduced to a temperature of 1,038°C. Alumina ceramics with density of 0.96TD was fabricated after sintering.

Mechanically activated powder was further used for electrophoretic deposition to produce alumina ceramics. The microstructure of a sample is shown in Fig. 4.5.

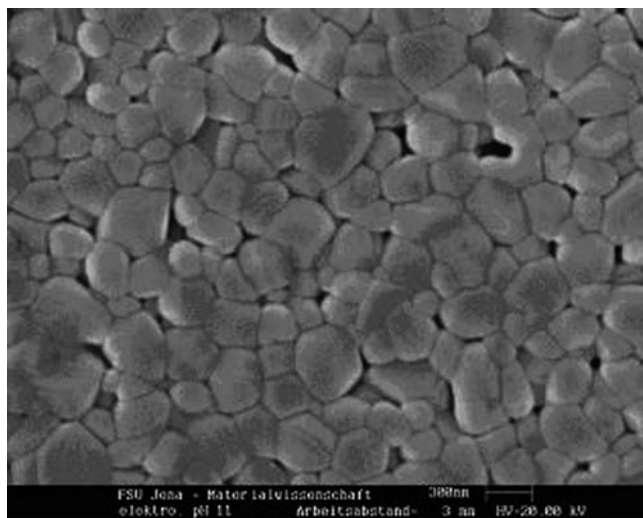


Fig. 4.5 SEM micrograph of a sintered sample fabricated by mechanical activation and electrophoretic deposition at 1,400°C for 30 min (0.94 TD) (the bar represents 300 nm)

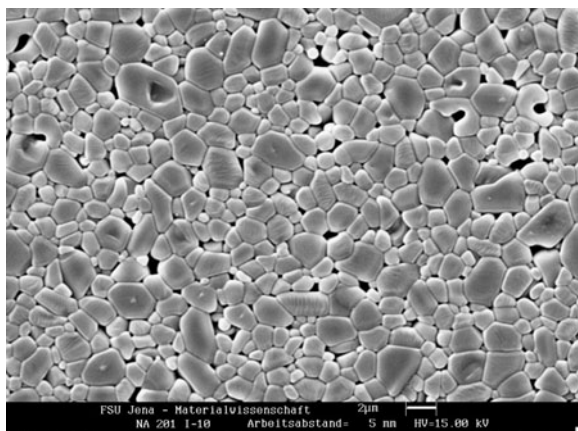
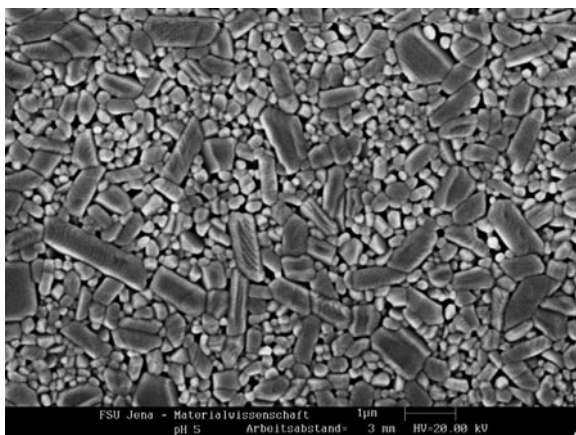


Fig. 4.6 SEM micrograph of the polished and thermally etched surface of a sample sintered at 1,500°C (the bar represents 2 μm)

It is relatively homogenous with grain sizes of 300 ± 100 nm. There is no intra-granular pore formation which indicates that the densification rate may have been faster than the grain growth rate at the processing temperature [13]. Increasing the sintering temperature up to 1,500°C without soaking time yielded a sample with evident grain growth. The grain size is 1–3 μm (Fig. 4.6).

Fig. 4.7 SEM micrograph of a bimodal structure of a compact fabricated by slip casting sintered at 1,500°C for 4 h (the bar represents 1 μm)



A bimodal microstructure (Fig. 4.7), with a density of 0.90 TD was fabricated by slip casting. One part of the grains possesses dimensions of 150–200 nm, the other sizes of 500–2,000 nm.

Conclusion

Transition nano-alumina powder obtained by the pulse reactor technique contains γ -, δ -, θ - and α - Al_2O_3 . Consolidation was achieved by applying an isostatic pressure of 500 MPa and by non-isothermal sintering at RT to 1,500°C, leading to compacts with a vermicular structure and a density of 0.75 TD. In order to reduce the sintering temperature and to obtain nano-alumina ceramics, mechanical activation was employed. Electrophoretic deposition of the mechanically activated transition alumina enables to obtain compacts with a density of 0.94 TD and a grain size of 300 ± 100 nm at 1,400°C for 30 min soaking time at the final temperature.

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Chapter 5

Modification of Nanosilica Surface by Methyl Methacrylate Silane Coupling Agents

Igor Telegeev, Evgenij Voronin, and Evgenij Pakhlov

Abstract Composites based on silicas and methyl methacrylate silane coupling agents are advanced materials for sensor technologies. The purpose of the present research is to combine silica-organic compounds with inorganic constituents to tailor the binding properties. It deals with a new method of covering silica nanoparticles by methyl methacrylate silanes in a pseudo-liquid state. The adsorption process and the chemical reactions of methacrylate-containing silanes and the surface of nanosized silica were examined by means of infrared spectroscopy, thermal analysis and transmission electron microscopy (TEM). The study confirmed the total modification of the silica surface with silanes.

Keywords Nanosized silica · Surface modification · Methacrylate coatings

Introduction

Highly-dispersed nanosized silica has been extensively used as support or carrier in catalysis, drug delivery, nanomedicine, nanobiotechnology, and bioanalysis. From the different types of entities that can be incorporated in silica nanoparticles, silane coupling agents have emerged as one of the most interesting subjects, with applications in bioanalysis, optical sensors, and photoactive materials [1].

In order to impart essential chemical properties such as polymerophily, adhesion, ability to effective cross-linking, etc. to nanosilica, chemical modifications of the surface are used, i.e. converting the surface silanol groups into organic or silica-organic ones by chemical reactions.

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There are many factors affecting the result of silica surface treatment, including the type of coupling agent, its concentration and the time and temperature of the treatment. Since these factors might interact with each other in determining the final result of the surface treatment, a design of experiment (DoE) is needed to achieve the optimal conditions for the treatment. Gas-phase modification techniques applied to disperse oxides are considered as the most progressive [2]. The purpose of this study was the development of a modification method for nanosilica by low-volatility silane coupling agents in a pseudo-liquid state. The nanosilica modification results were studied by means of characterization techniques such as Fourier transform infrared (FTIR) spectroscopy, thermal analysis and TEM.

Experimental

A-300 nanosilica (SiO_2 powder, average diameter 9.5 nm, with a surface area of $310 \text{ m}^2/\text{g}$) was used as received. 3-(Diethoxymethylsilyl) methylmethacrylate, 3-(trimethoxysilyl) propyl methacrylate (γ -MPTS), 3-(trimethoxysilyl) propyl acrylate, triethoxy (octyl) silane and methyltriethoxy silane were used as coupling agents for the silica surface modification.

According to the design of experiment, four independent variables were examined: the type of coupling agent, the concentration of the coupling agent (0.28, 0.56 and 0.7 mmol/g), the treatment time (1, 3 and 6 h) and the treatment temperature (20°C , 50°C , 75°C , 100°C , 150°C). The nanosilica modification was performed in a reactor of intensive mixing, which consists of a flask and a high-intensive blender. When rotated at $300\text{--}500 \text{ min}^{-1}$, the nanosilica transforms into a pseudo-liquid state. An amount of 10 g nanosilica was mixed for 10 min. Then a specific amount of the coupling agent was added to the mixture. The mixture was heated to different temperatures for a specific duration of time.

To prepare samples for transmission electron microscopy (TEM) analyses, a drop of nanosilica colloid solution was placed on a copper grid coated with a carbon membrane. The solvent then evaporated at room temperature, leaving the nanosilica on the grid. The samples were examined with a TEM (SEMI PEM-125 K, 100 kV).

To study the functionalization of the silane coupling agent on the nanosilica surface, Fourier transform infrared (FTIR) spectroscopy was used (Thermo Nicolet, Nicolet Instrument Corporation). The nanosilica and the silica-covered substrates were scanned in the transmittance mode in the wavelength range from $1,200$ to $4,000 \text{ cm}^{-1}$ [3].

A thermal gravimetric analyzer (TGA) was used to measure the surface absorption of the nanosilica before and after surface treatment. The nanosilica powder was heated from room temperature to $1,000^\circ\text{C}$ with a ramping rate of $20^\circ\text{C}/\text{min}$. The weight loss of the nanosilica powder was recorded as a function of temperature.

Results and Discussion

The FTIR analysis confirmed the successful introduction of functional groups onto the nanosilica surface. A reduction of the absorption peak at $3,750\text{ cm}^{-1}$, which is related to the presence of silanol groups [4] in the untreated silica, indicates a total surface modification (Fig. 5.1). The ratio of the parent free silanol and the grafted organosilyl groups was determined to be 1.4:1, i.e. 55% of the silane molecules react with the surface silanol groups in a monofunctional and 45% in a bifunctional way.

The particle dispersion after treatment was evaluated by transmission electron microscopy (TEM). A reduced filler–filler interaction is manifested by the mono-dispersion of the silica filler as shown in (Fig. 5.2).

The surface treatment of the nanosilica was also characterized by TGA. It can be seen that untreated nanosilica had a weight loss (about 2 wt%) below 200°C , which is related to the elimination of physically absorbed water on the surface.

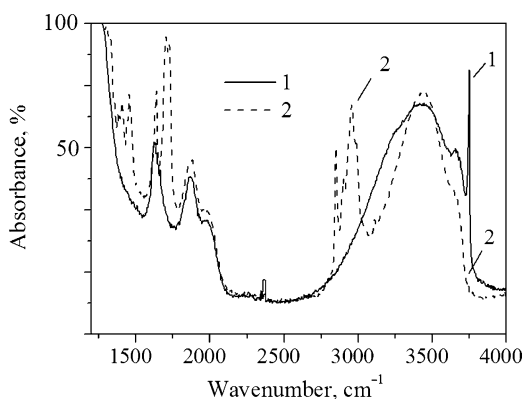


Fig. 5.1 FTIR spectra of the initial nanosilica (1) and after treatment with γ -MPTS (2)

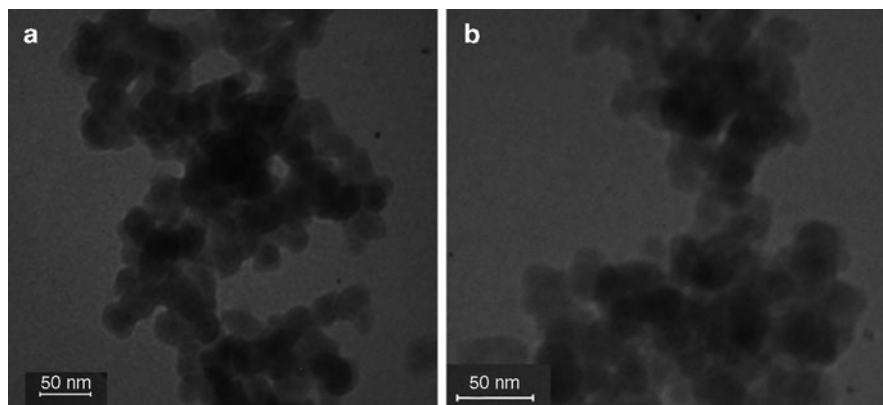
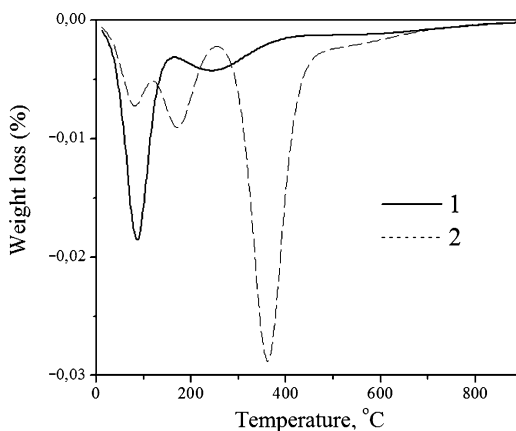


Fig. 5.2 TEM pictures of nanosilica (a) and treated with γ -MPTS (b)

Fig. 5.3 TG curves of the initial nanosilica (1) and after treatment with γ -MPTS (2)



The nanosized silica possesses a large surface area which makes it easy to pick up moisture in a typical laboratory environment even after they were dried. On the contrary, after silane surface treatment the nanosilica evidently does not pick up water because of the changes in the hydrophilic behavior (Fig. 5.3). The treated nanosilica steadily loses weight starting in the range of 300–500°C, which is caused by the debonding and degradation of the grafted functional silane groups on the surface.

The DoE gave the following optimum experiment condition: concentration of the coupling agent 0.7 mmol/g, treatment time 1 h and treatment temperature 100°C. The results showed that nanosilica treatment by low-volatility alkylacrylate-containing trialkoxysilane at atmospheric pressure in the pseudo-liquid state using a reactor of intensive mixing with a longer reaction time at a specific temperature achieve mono-dispersed silica, as confirmed by TEM pictures. Transmittance FTIR showed that the silane functional groups were grafted to the silica surface. TGA results indicated that the modification of the nanosilica surface reduces the water adsorption.

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Chapter 6

Microstructures Produced by Chemical Etching of Finely Scratched Silicon

Eugen Harea

Abstract Today, microstructures produced by mechanical forming of various materials are widely used in micro- and nanotechnology. Frequently the mechanical forming is combined with chemical etching of surfaces [Grabco et al., Phys. Stat. Sol. (c), 6:1295, 2009]. To improve the behaviour of indium tin oxide/silicon photosensors (ITO/Si), it is desirable to increase the ITO/silicon contact area. For this purpose the (001) surface of the Si substrates was scratched in different directions by abrasives. Thereafter, the specimens were subjected to selective chemical etching. The etch-pit patterns obtained were rectangular or square, with the sides oriented along the $\langle 100 \rangle$ direction. The dimensions of etch-pit patterns depended on the chemical treatment duration; they enlarge with increasing treatment time.

Keywords Mechanical forming · Microstructures · Chemical etching · Etch-pit patterns · Surface modification

Introduction

The rise of the efficiency and the lowering of the fabrication price is important in the manufacture of sensors. One of the ways to increase the efficiency of photo-sensors on silicon is to structurize the surface of the substrate, which can significantly increase the active area as well as the absorption of light. In many cases the microstructure fabrication is combined with chemical etching of the surfaces [1].

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The present paper used the following technique: to achieve a structured substrate surface, silicon was mechanically polished and then chemically etched. During the process, anomalous etching was found at separately placed scratches.

Experimental

To obtain structured substrate surfaces, Si was mechanically polished by Cr_2O_3 powder and then chemically etched in a boiling solution of KOH and H_2O in the ratio 1:3 for 20 s. In this process, unusual anomalous structures were observed for separately placed scratches (Fig. 6.1).

To further study this phenomenon, scratches were made in the $\langle 110 \rangle$ direction. The results of the chemical etching are shown in Fig. 6.2. The etch-pits form periodically repeated structures, whose dimensions and shape can be varied by the etching duration and the direction of the scratch.

Results and Discussion

The creation of surface structures by chemical etching of scratches can be compared to the chemical etching of the photolithographically prepared patterns. In this case, the selective etchant reacts with the substrate in places free from the photoresist.

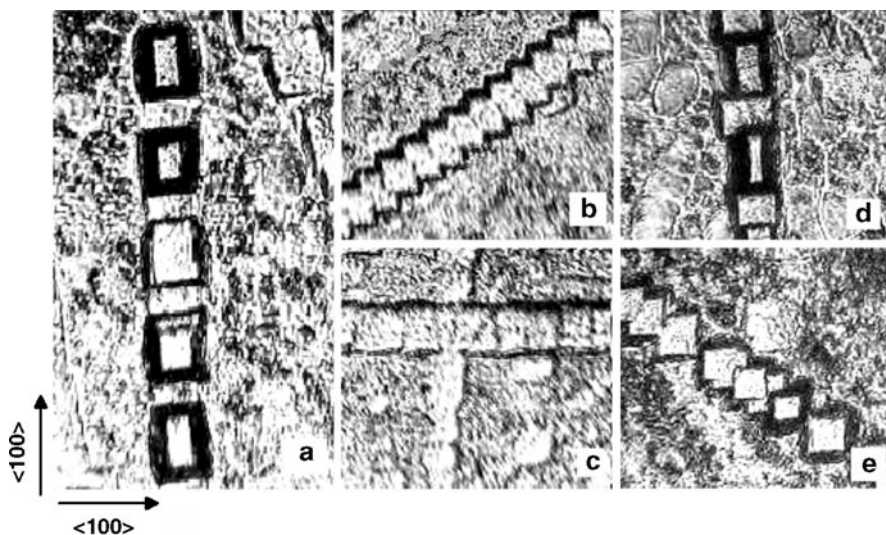


Fig. 6.1 Etch-pit patterns resulting from scratches made on Si surfaces in different directions with different applied loads. Each image presents a width of 50 μm

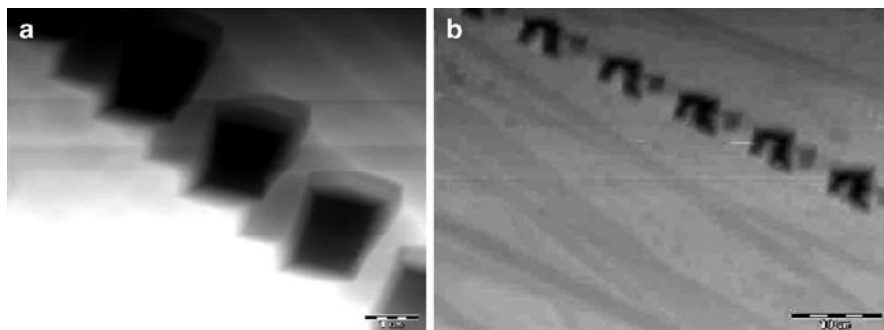


Fig. 6.2 AFM image of etch-pit patterns resulting from scratches made on Si surfaces in $\langle 100 \rangle$ direction. The bars represent 1 μm for (a) and 10 μm for (b)

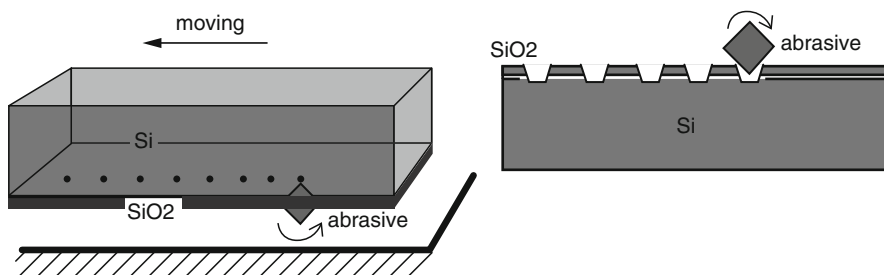


Fig. 6.3 Formation of SiO_2 pattern on Si during the abrasive treatment

In our experiment, the native SiO_2 film always formed under normal conditions, can be considered as a mask. It can be assumed that separate abrasive particles with a specific shape, while rolling on the surface of the sample, will regularly perforate the silica film, thus forming the pattern on Si (Fig. 6.3).

During the selective chemical etching the Si reacts with the KOH only in places where the SiO_2 film was mechanical deformed. This model accounts for the complex shape of the microstructures in Fig. 6.4b.

At the same time such a model is hardly valid if one takes into account the fact that the width of the scratches before the chemical treatment is 0.5–1 μm , while the thickness of the SiO_2 film is only 1–3 nm.

Another explanation of the phenomenon under discussion can be found when analyzing the mechanical action of the abrasive particles on Si. The existence of strongly ordered dislocation zones at scratches on single crystals is known for a long time [2], the dislocations being chemically more active due to the lattice defects. It is also well known that dislocations created by mechanical deformation of Si at room temperature are strongly localized [3]. Hence, it can be supposed that the whole surface area of the scratch should be more easily etched than the untouched surface, which took place in our case at scratches with a certain depth.

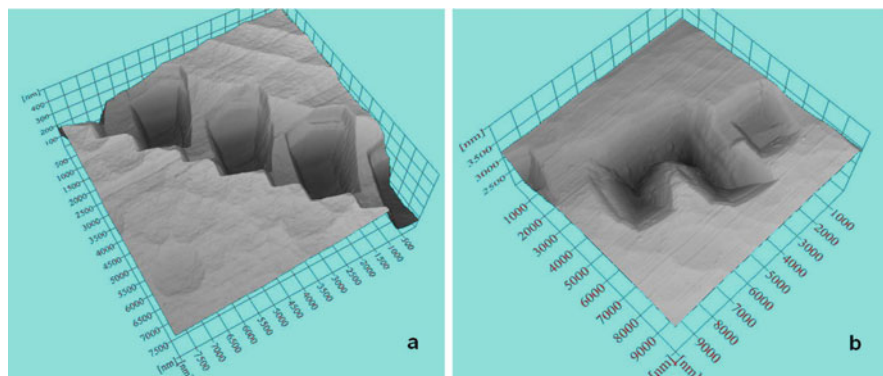


Fig. 6.4 3-D image of etch-pit patterns resulting from scratches made on Si surfaces in $\langle 100 \rangle$ direction

However, the model given does not explain why at small deformations of the Si (scratching in our case), under selective chemical treatment certain etch pits are formed that are well identical in shape and highly periodical within the area of an individual scratch.

Conclusions

The present paper discusses a novel, quick and cheap way to obtain certain structures on Si by mechanical activation of the required direction of the selective chemical treatment. Further studies of the effect as well as of the dependence of the shape of the etch pits on the crystallographic direction, the depth of the scratches, and the shape and size of the abrasive particles will allow one to get required microstructures of a given shape and with the necessary quantity.

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Chapter 7

Multilayer Films and Capsules of Sodium Carboxymethylcellulose and Polyhexamethylenguanidine Hydrochloride

Nataliia Guzenko, Oleksandra Gabchak, and Evgenij Pakhlov

Abstract The complexation of polyhexamethylenguanidine hydrochloride (PHMG) and sodium carboxymethylcellulose (CMC) was investigated for different conditions. Mixing of equiconcentrated aqueous solutions of the polyelectrolytes was found to result in the formation of an insoluble interpolyelectrolyte complex with an over-weight of carboxymethylcellulose. A step-by-step formation of stable, irreversibly adsorbed multilayer film of the polymers was demonstrated using the quartz crystal microbalance method. Unusually thick polymer shells with a large number of loops and tails of the polyanion were formed by the method of layer-by-layer self-assembly of PHMG and CMC on spherical CaCO_3 particles. Hollow multilayer capsules stable in neutral media were obtained by dissolution of the inorganic matrix in EDTA solution.

Keywords Multilayer polyelectrolyte films and capsules · Polyhexamethylenguanidine hydrochloride · Sodium carboxymethylcellulose · Layer-by-layer adsorption · Interpolyelectrolyte complex

Introduction

Polyelectrolyte multilayer films and capsules prepared by deposition of oppositely charged polyelectrolytes on various templates (layer-by-layer self-assembly technique) are promising for diverse applications, including drug delivery, diagnostics, coating of textiles or paper, sensors, catalysts, microreactors, construction materials etc. [1–4]. The versatility of this technique by using different combinations of polyelectrolytes and templates together with the possibility to control the characteristics of

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the materials obtained by variation of a wide number of factors (pH, ionic strength, solvent nature, structure of the polymers and inclusion of additional functional components) draw attraction of investigators in different scientific fields [5–7].

This paper deals with the formation of an interpolyelectrolyte complex (IPEC) between oppositely charged polyhexamethylenguanidine hydrochloride and sodium carboxymethylcellulose either by simple mixing them in solution or by layer-by-layer adsorption on the surface of a piezo-quartz crystal as well on the surface of micro-sized spherical calcium carbonate particles.

Experimental

Materials. Sodium carboxymethylcellulose (CMC) with a viscosity of 5,000–8,000 mPa·s (1% aqueous solution) and a degree of substitution of 0.8–0.95 was purchased from Akucell (Sweden). CMC is a weak acid with $pK_a \approx 5.1$ (measured by potentiometric titration) and has a substantial negative charge at pH values higher than 6. Polyhexamethylenguanidine hydrochloride (PHMG) with a molecular weight of $M_w \approx 5$ kDa was obtained from Biocid (Ukraine). PHMG is a strong polymer base with $pK_a \approx 13.5$.

Calcium carbonate microparticles ($d = 4\text{--}5\ \mu\text{m}$) were synthesized according to Ref. [8]. Briefly, CaCl_2 and Na_2CO_3 solutions (0.33 M) were mixed under vigorous stirring for 30 s leading to the precipitation of CaCO_3 particles. Subsequently, three centrifugation and washing steps with pure water were performed in order to remove the unreacted species.

Multilayer assembly of the polyelectrolytes was accomplished by their adsorption at a concentration of 1 mg/ml in aqueous 0.15 M NaCl solutions. Oppositely charged polyelectrolyte species were subsequently added to the suspension of CaCO_3 particles followed by repeated centrifugation cycles. After the intended number of layers was adsorbed, a solution of ethylenediaminetetraacetic acid (EDTA) was used to remove the core which resulted in the formation of hollow polyelectrolyte capsules.

Infrared spectrometry. The IR spectra of the samples diluted in KBr have been recorded with a ThermoNicolet FTIR spectrophotometer (Nicolet Instrument Corporation, USA) in the reflectance mode.

Differential thermal analysis and thermogravimetry were performed with a Q-1500D Paulik-Paulik-Erdey type thermobalance (MOM, Budapest, Hungary) under the following conditions: $m \approx 8$ mg, reference material Al_2O_3 , ceramic crucible, heating rate $10^\circ\text{C}/\text{min}$ in air under static conditions in the temperature interval $10\text{--}800^\circ\text{C}$.

Quartz crystal microbalance measurements were performed with a home built apparatus; detailed information on the set-up can be found in [9].

ζ -Potential Measurements. The ζ -Potential of the microcapsules dispersed in pure water was determined with a Malvern Zetasizer 3000 (UK) and the ζ -potential value was the average of three successive measurements.

Optical Microscopy. An optical microscope PZO Warszawa SK 14 (Poland) was used for the determination of the morphology of the template microparticles, covered CaCO_3 spheres and the hollow capsules obtained. A sample suspension was dropped on the glass plate of a hemocytometer and then examined regarding the following parameters: diameter, size, form and uniformity of microparticles. The images observed were taken with a digital camera DCM 300 TREK attached to the microscope.

Results and Discussion

The mixing of equiconcentrated aqueous solutions of PHMG and CMC was found to result in the formation of an insoluble IPEC with an overweight of carboxymethylcellulose. The insolubility of the complex proves the compensation of the total charge of both polymers. The infrared spectrum of the IPEC shows more expressively the absorption bands characteristic for CMC (900, 1,020, 1,320, 1,419, 1,585 cm^{-1}), while a mechanical mixture of equal masses of both polymers yielded an IR spectrum with comparable contributions from both polymers (Fig. 7.1). This could be evidence for a CMC mass excess within the complex. The polyanion is supposed to form loops to neutralize the polycation charge because of the low charge density of the CMC.

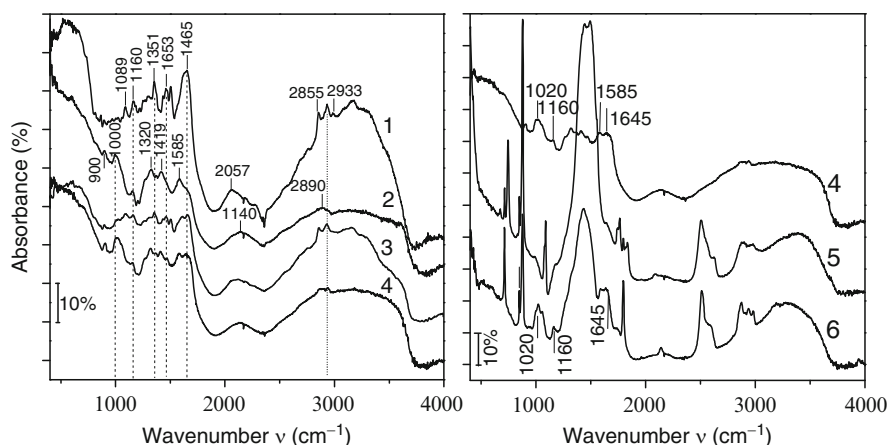


Fig. 7.1 IR spectra of (1) PHMG; (2) CMC; (3) a mechanical mixture of the polymers; (4) an IPEC of PHMG and CMC; (5) CaCO_3 spheres; (6) CaCO_3 spheres after adsorption of 20 PGMG-CMC layers

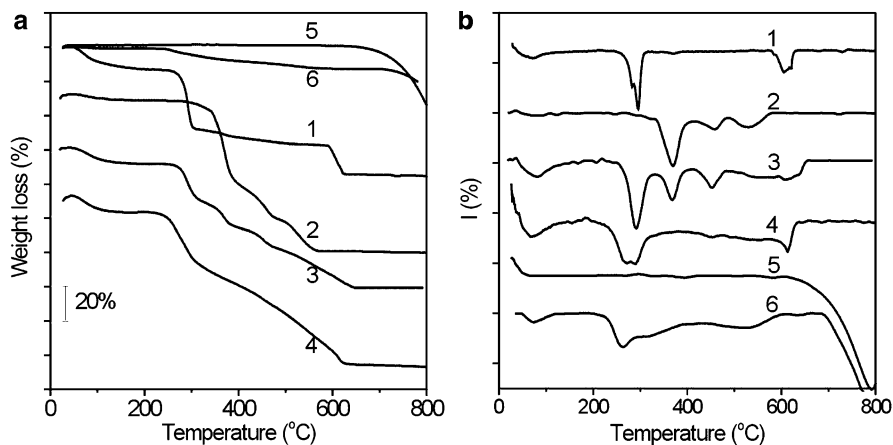


Fig. 7.2 Thermal gravimetry (a) and DTG curves (b) of: (1) sodium carboxymethylcellulose; (2) polyhexamethylenguanidine hydrochloride; (3) a mechanical mixture of CMC and PHMG (1:1); (4) an interpolyelectrolyte complex of the polymers; (5) CaCO_3 (5); (6) CaCO_3 spheres after adsorption of 20 PHMG and CMC layers

The interaction between PHMG and CMC resulting in complex formation was also confirmed by thermal analysis (Fig. 7.2). The differential thermal gravimetry (DTG) curve of the mechanical mixture contains the peaks typical for both polymers, whereas the thermal decomposition of the IPEC takes place in different degradation stages with different weight losses.

The process of multilayer PHMG/CMC film formation was investigated using the quartz crystal microbalance method. Step-by-step adsorption of four double layers of the polyelectrolytes resulted in a persistent reduction of the resonance frequency of the quartz crystal resonator, equal to 1,000 Hz, which corresponds to a mass increase of 0.05 g/m^2 for the polymer coating formed (Fig. 7.3).

Furthermore, the layer-by-layer self-assembly of PHMG and CMC during their alternate adsorption from 0.1% polymer solutions (in 0.15 M NaCl) on micro-sized calcium carbonate spheres was studied. Charge overcompensation after the adsorption of the oppositely charged polyelectrolytes was observed using the electrophoresis method by an alternating change of the ζ -potential of the particles (Fig. 7.4).

A microscopic study showed the formation of $5 \text{ }\mu\text{m}$ thick polymer shells after the adsorption of 20 polyelectrolyte layers (Fig. 7.5). The mass of the multilayer shells was evaluated from the TG curves in the temperature interval $200\text{--}650^\circ\text{C}$, (where an organic component destructs) as the difference between the mass losses of pure CaCO_3 and CaCO_3 spheres after the adsorption of 20 PHMG and CMC layers (Fig. 7.2a, curves 5, 6). This value amounted to 13.6% of the core mass. The density of the multilayer, which was calculated from the analysis of the thickness and the mass of the shells formed amounted to about $4 \cdot 10^4 \text{ g/m}^3$, which

Fig. 7.3 Increase of film mass as a function of the number of polymer layers

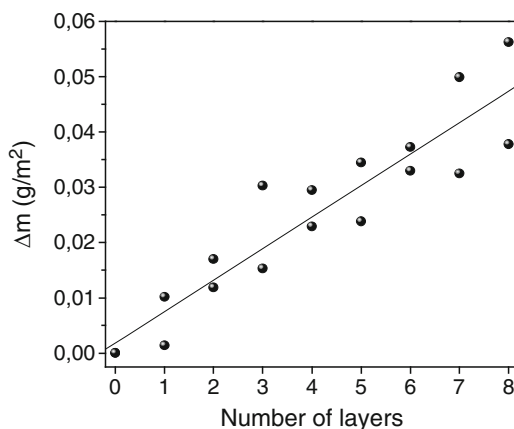
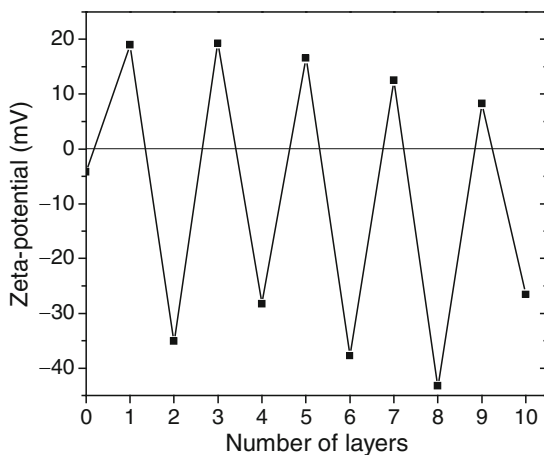


Fig. 7.4 ζ -Potential as a function of polyelectrolyte layer number. Even numbers: CMC; odd numbers: PHMG



testified the formation of loose, strongly hydrated polyelectrolyte films in aqueous medium.

The IR spectrum of the polymer capsules showed absorption bands at 1,020, 1,160, 1,585, 1,645 cm^{-1} and also near 2,850–2,980 cm^{-1} , which are characteristic for the interpolyelectrolyte complex of PHMG and CMC, obtained by simple mixing of the polymer solutions (Fig. 7.1). Moreover, the thermal decomposition of the films formed on the surface of the spherical templates by the layer-by-layer technique goes through the same stages as that of the complex formed in solution (Fig. 7.2). Dissolution of the inorganic matrix with ethylenediaminetetraacetic acid (EDTA) resulted in the formation of hollow multilayer capsules which were stable in neutral media (Fig. 7.5).

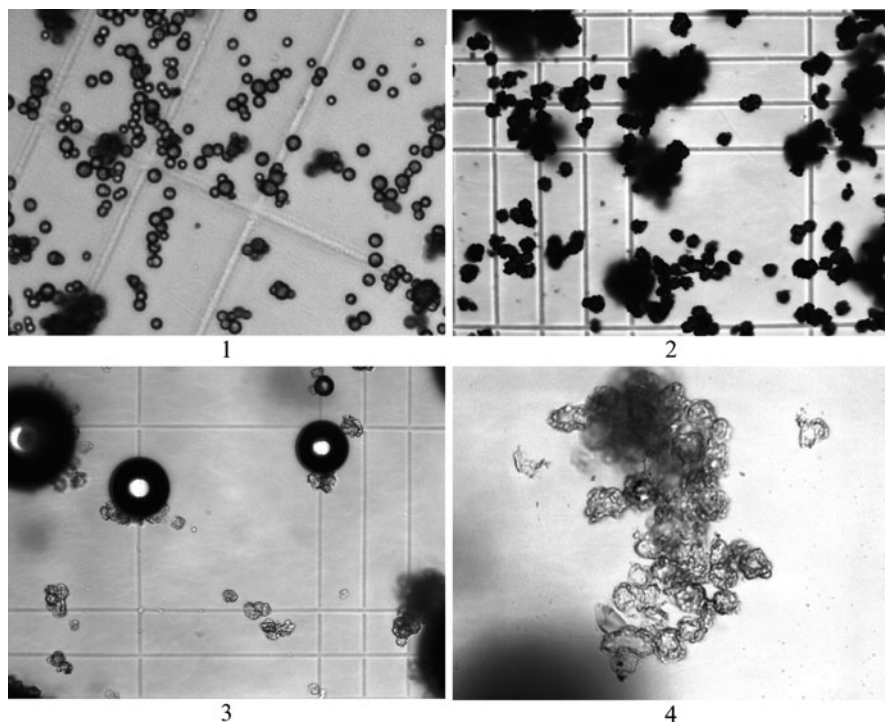


Fig. 7.5 Optical microscopy images showing the formation of hollow polyelectrolyte capsules of PHMG-CMC: (1) synthesized carbonate matrix with a spherical morphology; (2) CaCO_3 spheres after adsorption of 20 layers of PGMG and CMC by layer-by-layer self-assembly; (3) process of inorganic core dissolution with EDTA; (4) hollow multilayer microcapsules (the side of small square of hemocytometer is 50 μm)

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Chapter 8

Preparation and Characterization of TiO₂-Based Photocatalysts by Chemical Vapour Deposition

Goran Nacevski, Mirko Marinkovski, Radmila Tomovska,
and Radek Fajgar

Abstract In the present work, a novel technique for the preparation of TiO₂-based photocatalysts modified with SiO₂ is presented, using a pulsed ArF laser to induce a chemical vapor deposition process. The irradiated gas mixture was composed of TiCl₄/SiCl₄ precursors in excess of oxygen. Laser irradiation at 193 nm with a repetition frequency of 10 Hz induced the deposition of thin nano-sized mixed oxide films. In order to improve the photocatalytic activity of the catalysts and to expand the activity from the UV to the visible part of the spectrum, doping of the catalysts with chromium oxides was performed. For that aim, the same technique of catalyst preparation was used, irradiating the same gas mixture with the addition of chromyl chloride as Cr precursor. The thin films prepared were annealed up to 500°C in order to remove crystal defects, which could be responsible for poor photocatalytic activity. The dependence of structure and properties on reaction process and irradiation conditions (laser energy and fluence, precursors pressure) were examined. The main aim was to find the best conditions for the production of highly photoactive catalysts and to decrease deactivation processes during the photo-oxidation. The composition, structure and morphology of the oxide catalysts prepared were studied by various spectroscopies, electron microscopy and diffraction techniques.

Keywords TiO₂-based photocatalysts · TiO₂/SiO₂ mixed oxides · Laser induced CVD

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Introduction

The system $\text{SiO}_2/\text{TiO}_2$ possesses interesting material properties and possibilities for important industrial applications such as low thermal expansion glasses, fatigue resistant optical fiber claddings, catalysts and catalyst supports, chalk resistant paint pigments (SiO_2 usually in combination with Al_2O_3) [1] and also self-cleaning glasses [2]. It was shown that the inclusion of a SiO_2 barrier layer into the TiO_2 system can hinder the diffusion of substrate components into the photoactive TiO_2 film, and consequently improve the photoactivity of titania films when compared to those films deposited directly onto a substrate [2]. On the other hand, the introduction of chromium into the photocatalyst system will ensure a shift of the absorptivity of the catalyst toward visible light wavelengths, as well as a transformation of chromium from the hexavalent to the trivalent state [3–5]. Hexavalent chromium is toxic and carcinogenic [6].

Experimental

Laser photolysis experiments were conducted with gaseous mixtures of $\text{TiCl}_4/\text{SiCl}_4/\text{O}_2$, $\text{TiCl}_4/\text{CrO}_2\text{Cl}_2/\text{O}_2$ and $\text{TiCl}_4/\text{SiCl}_4/\text{CrO}_2\text{Cl}_2/\text{O}_2$ in vacuum using an ArF laser (ELI model 94) operating at 193 nm with a repetition frequency of 10 Hz. The samples were irradiated in a Pyrex reactor consisting of a tube of 4 cm length equipped with a quartz window. The reactor has two sidearms, one fitted with a rubber septum and the other connecting to the vacuum line. It consists of metals (Al, Cu), stainless steel, tantalum, and glass substrates, which, covered with the deposited solid material in the course of photolysis, were transferred for measurements of their properties by UV and RAMAN spectroscopy. Laser photolysis of the above mixtures were carried out using pulse energies of 50–80 mJ incident on an area of 2.3 cm^2 . Experiments were carried out with ratios $\text{Ti/Si} = 8:1$, $\text{Ti/Si} = 4:1$, $\text{Ti/Cr} = 9:1$, $\text{Ti/Cr} = 4:1$, $\text{Ti/Si/Cr} = 9:1:1$ and $\text{Ti/Si/Cr} = 9:4:1$. All experiments were performed in excess of oxygen. The mixtures prepared were irradiated for 5 min by the ArF laser.

Results and Discussions

During the irradiation, for all systems investigated, a white fog appeared and slowly descended on the reactor walls and on the substrates as a white deposit. As – deposited materials were annealed in order to remove crystal defects in the TiO_2 -based materials or to transfer them from the amorphous to the crystalline anatase phase. The annealing temperature for all TiO_2 films was $400^\circ\text{C}/2 \text{ h}$, except for: (i) Ti/Si/O , for which the temperature needed for crystallization is $430^\circ\text{C}/2 \text{ h}$, and

(ii) Ti/Cr/Si/O, for which the crystallization temperature is 500°C/2 h. This reveals that the presence of SiO₂ in the photocatalytic systems increases the temperature needed for crystallization and phase transformation, very probably because of the fact that SiO₂ is covering the TiO₂ surface and provide it with a higher thermal stability. The chromium content in the TiO₂ lattice has no influence on the crystallization temperature.

In Figs. 8.1, 8.2 and 8.3 UV-VIS spectra are shown for all three systems for as-prepared deposits and annealed materials. Figure 8.1 reveals that an increasing SiO₂

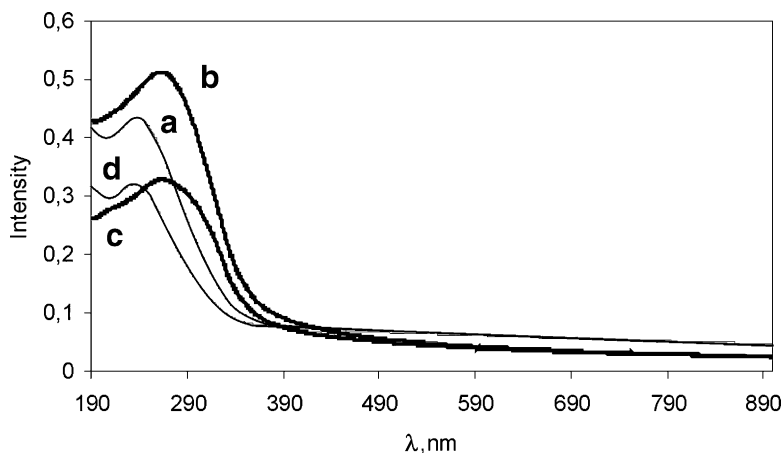


Fig. 8.1 UV-VIS spectra of TiO₂ deposits for the system Ti/Si: (a) Ti:Si = 8:1 as-prepared; (b) Ti:Si = 8:1 annealed at 430°C/2 h; (c) Ti:Si = 4:1 as-prepared; (d) Ti:Si = 4:1 annealed at 400°C/2 h

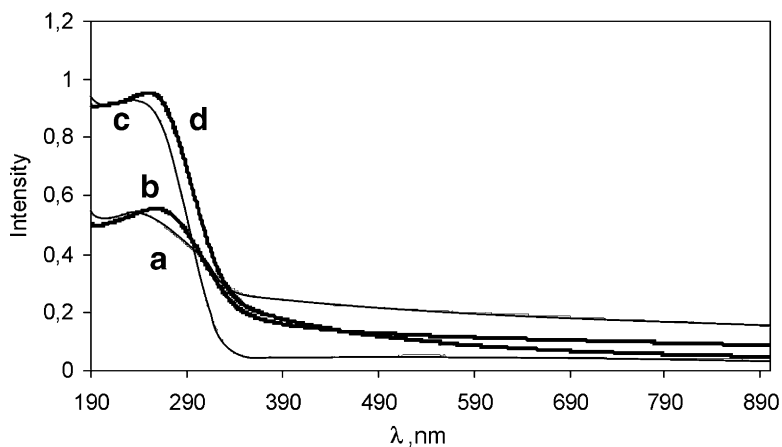


Fig. 8.2 UV-VIS spectra of TiO₂ for the system Ti/Cr: (a) Ti:Cr = 9:1 as-prepared; (b) Ti:Cr = 9:1 annealed at 400°C/2 h; (c) Ti:Cr = 4:1 as-prepared; (d) Ti:Cr = 4:1 annealed at 400°C/2 h

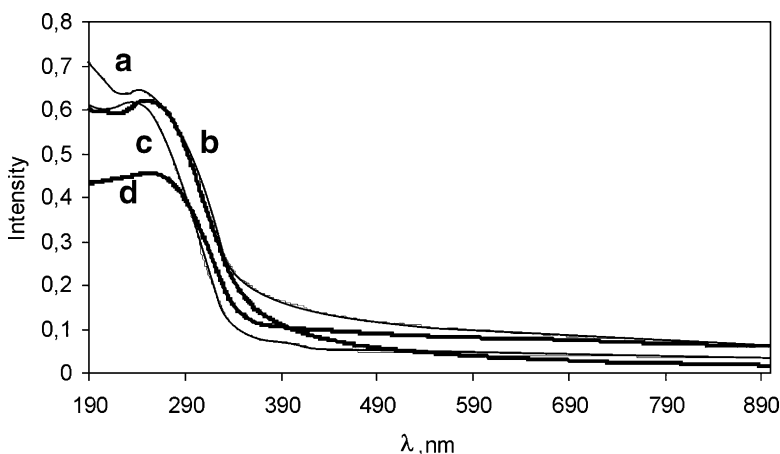


Fig. 8.3 UV-VIS spectra of TiO_2 for the system Ti/Si/Cr : (a) $\text{Ti:Si:Cr} = 9:4:1$ as-prepared; (b) $\text{Ti:Si:Cr} = 9:4:1$ annealed at $400^\circ\text{C}/2\text{ h}$; (c) $\text{Ti:Si:Cr} = 4:1:1$ as-prepared; (d) $\text{Ti:Si:Cr} = 4:1:1$ annealed at $400^\circ\text{C}/2\text{ h}$

content slightly decreases the absorptivity of the photocatalysts. It is very probably that the TiO_2 nanoparticles are partially covered with SiO_2 during the CVD process, which would block the active centers of the photocatalysts and reduce their absorptivity. In Fig. 8.2 the influence Cr doping of TiO_2 with on the UV absorption of the materials is presented. The shift of the absorptivity is obvious for the annealed materials (the samples absorb up to around 600 nm); the effect is more pronounced for the samples with a ratio $\text{Ti:Cr} = 9:1$, e.g. for a lower amount of the dopant in the TiO_2 . Regarding the doping on the SiO_2 -modified TiO_2 system, the effect of absorptivity shifting is less pronounced (the materials absorb light up to around 500 nm, Fig. 8.3). This less pronounced effect can be explained by the presence of SiO_2 material and the covering effect.

Raman spectra for all systems (Ti/Si/O , Ti/Cr/O and Ti/Si/Cr/O) are given in Figs. 8.4, 8.5 and 8.6. The deposits were examined on Ta substrates with a 473 nm laser, a pinhole aperture of 100 μm and 100% laser energy.

From Fig. 8.4 it can be seen that as-prepared deposits show no peaks in the Raman spectra (lines (a) and (c)), which confirm their amorphous structure. Spectra (b) and (d) in Fig. 8.4 show peaks centered at 634, 516, 392 and 142 cm^{-1} which appeared after annealing of the materials and are characteristic Raman shifts for the anatase structure [7].

Similar findings are obtained from Fig. 8.5; as prepared deposits do not show any peaks (lines (a) and (c)), while characteristic anatase Raman shifts could be seen for spectra (b) and (d). The presence of dopant Cr atoms in this systems is obvious from the small Raman peaks appearing at 570 cm^{-1} and in the region 700–900 cm^{-1} [8].

Lines (a) and (c) in Fig. 8.6, similarly, hint at amorphous structures of the as-deposited materials in the system Ti/Si/Cr/O , while lines (b) and (d) possess characteristic anatase Raman shifts. Additionally a new and quite strong shift has

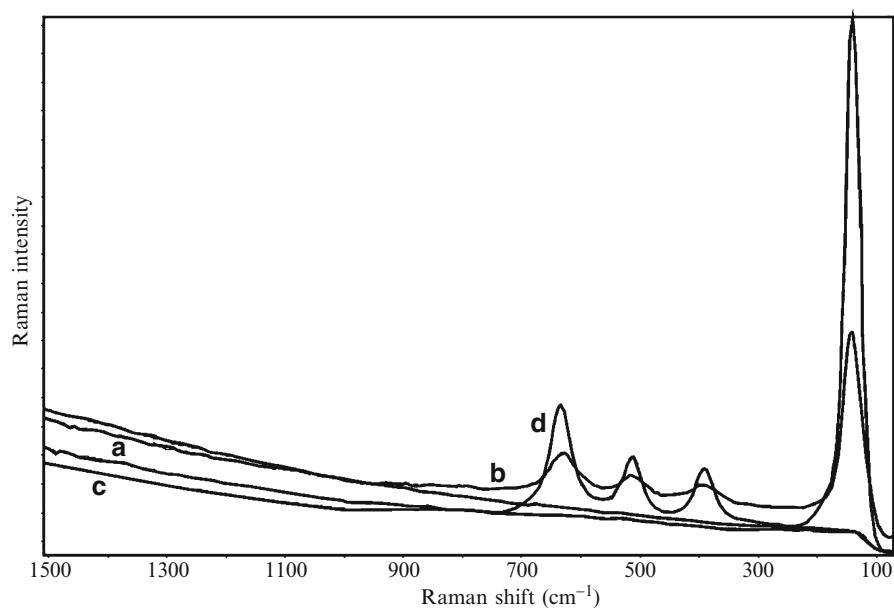


Fig. 8.4 Raman spectra of TiO_2 deposits for Ti/Si systems: (a) Ti:Si = 8:1 as-prepared; (b) Ti:Si = 8:1 annealed at $430^\circ\text{C}/2\text{ h}$; (c) Ti:Si = 4:1 as-prepared; (d) Ti:Si = 4:1 annealed at $400^\circ\text{C}/2\text{ h}$

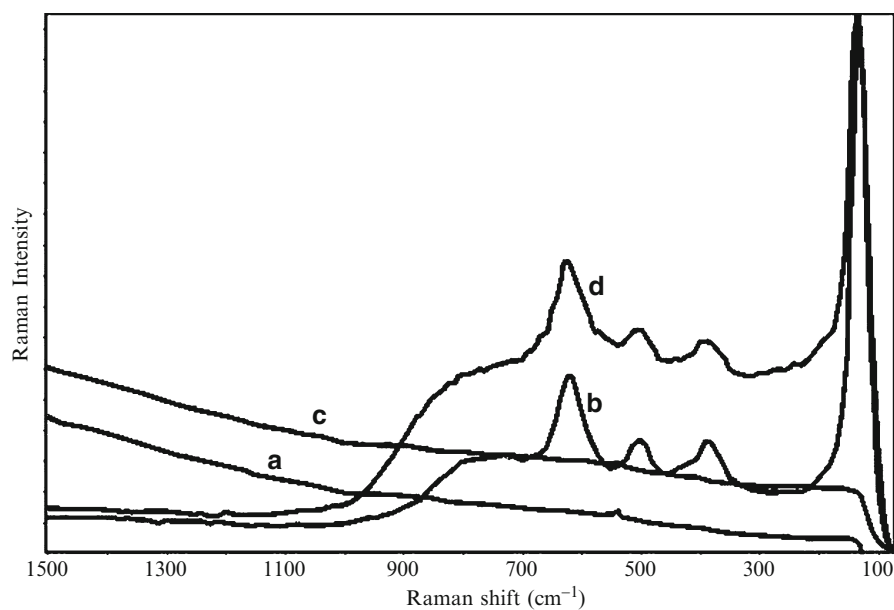


Fig. 8.5 Raman spectra of TiO_2 deposits for Ti/Cr systems: (a) Ti:Cr = 9:1 as-prepared; (b) Ti:Cr = 9:1 annealed at $400^\circ\text{C}/2\text{ h}$; (c) Ti:Cr = 4:1 as-prepared; (d) Ti:Cr = 4:1 annealed at $400^\circ\text{C}/2\text{ h}$

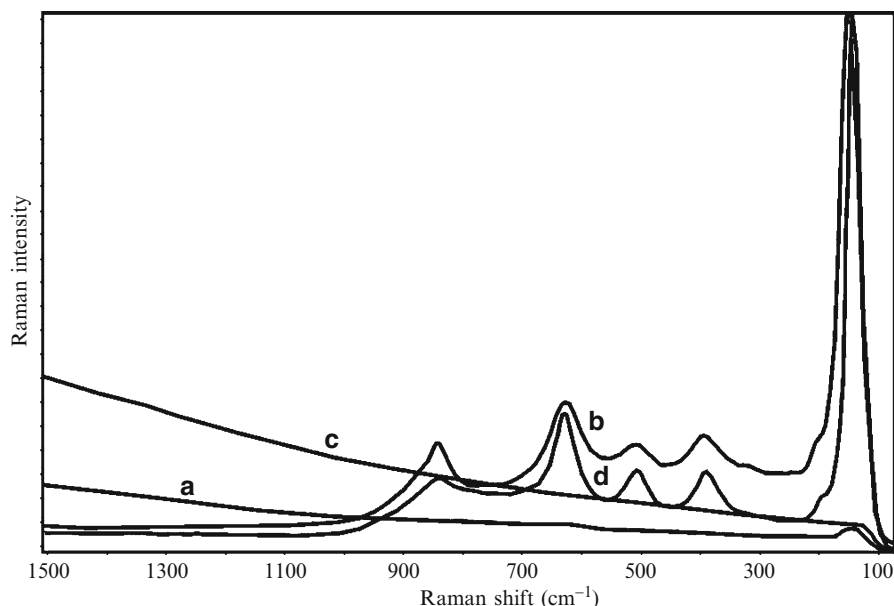


Fig. 8.6 Raman spectra of TiO_2 deposits for systems Ti/Si/Cr: (a) Ti:Si:Cr = 9:4:1 as-prepared; (b) Ti:Si:Cr = 9:4:1 annealed at $500^\circ\text{C}/2$ h; (c) Ti:Si:Cr = 4:1:1 as-prepared; (d) Ti:Si:Cr = 4:1:1 annealed at $500^\circ\text{C}/2$ h

appeared at around 820 cm^{-1} , very probably revealing the presence of higher amounts of Cr in the structure, since the intensity of this band is sensitive to the content of Cr [8].

Conclusions

ArF laser induced chemical vapor deposition in the systems $\text{TiCl}_4/\text{SiCl}_4/\text{O}_2$, $\text{TiCl}_4/\text{CrO}_2\text{Cl}_2/\text{O}_2$ and $\text{TiCl}_4/\text{SiCl}_4/\text{CrO}_2\text{Cl}_2/\text{O}_2$ has resulted in the deposition of white films consisting of Ti/Si/O, Ti/Cr/O and Ti/Si/Cr/O, respectively. The as deposited films were annealed at temperatures between 400°C and 600°C for 2 h. According the Raman spectra, "as-prepared" deposits are amorphous for all investigated systems. After annealing a phase transformation has occurred and anatase structures were obtained: for TiO_2 modified with SiO_2 the phase transformation occurred at $430^\circ\text{C}/2$ h, for TiO_2 doped with chromium at $400^\circ\text{C}/2$ h, and for TiO_2 modified with SiO_2 and doped with Cr at $500^\circ\text{C}/2$ h. The presence of SiO_2 has been found to increase the crystallization temperature and decrease the UV absorptivity compared to bare TiO_2 , according to the UV spectra. These effects of SiO_2 modification were explained as a result of SiO_2 layering on the TiO_2 surface, leading to decreasing absorptivity and increasing temperature stability.

The Cr dopant in TiO_2 lattice has no influence on the crystallization temperature, while it shifts the absorptivity of the catalysts toward the visible light.

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Chapter 9

Porous Mullite Ceramics for Advanced Sensors

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and Milosav Milosevski**

Abstract Porous mullite ceramics were fabricated by activated reaction sintering a mixture of rice husk ash and technical alumina as precursors for SiO_2 and Al_2O_3 , respectively. MgO was used as a catalyst. The mixture was attrition milled to particles sizes ranging from 10 to 30 nm. Green compacts were prepared by uniaxial pressing at 50 MPa. Two types of porous mullite ceramics were fabricated. The first one was prepared by sintering the green bodies at $1,300^\circ\text{C}$ for 3 h. An apparent porosity of 20% was achieved, with pore sizes ranging from 100 to 500 nm. Mechanical properties such as E-modulus and bending strength were 80 ± 2 GPa and 130 ± 7 MPa, respectively. The second one was fabricated at $1,500^\circ\text{C}$ for 3 h by using powdered active coal as pore creator. It possessed an apparent porosity of $26 \pm 1\%$, the pore sizes ranged from 5 to 50 μm . Anisotropic grain growth occurred, resulting in needle like mullite structures. The E-modulus and bending strength were 63 ± 3 GPa and 49 ± 2 MPa, respectively.

Keywords Rice husk ash · Reaction sintering · Porous mullite ceramics · Advanced sensors

Introduction

The basic properties of mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), such as chemical composition, phase stability, crystalline structure, microstructure, stability at elevated temperatures, and high resistivity make it a suitable material as a substrate for advanced sensors. Porous mullite ceramics with good mechanical properties and the ability

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J.P. Reithmaier et al. (eds.), *Nanotechnological Basis for Advanced Sensors*,
NATO Science for Peace and Security Series B: Physics and Biophysics,
DOI 10.1007/978-94-007-0903-4_9, © Springer Science+Business Media B.V. 2011

to withstand higher gas flow rates can be utilized for this purpose. A literature survey suggested the application of clays, natural kaolin, fly ashes, Al_2O_3 , $\text{Al}(\text{OH})_3$, and aluminium powders for the fabrication of porous mullite [1–7]. The use of wastes, such as various kinds of waste aluminium oxide and silica from rice husk ash for the synthesis of mullite have also been reported [8,9]. Different process routes and techniques can be applied, such as the reaction-bonding technique [1], the in situ decomposition pore-forming technique [2], the aerated concrete technology [3], a calcination treatment followed by a leaching treatment [4], reaction sintering [5,6], and gel-casting [7]. The present investigation deals with the fabrication of porous mullite ceramics by activated reaction sintering of a mixture of rice husk ash and technical alumina as precursors for SiO_2 and Al_2O_3 , respectively, with the addition of MgO as a catalyst, as a potential support for advanced sensors applications.

Experimental

Rice husk ash (RHA) obtained by combustion at 600°C of acid treated rice husk from the region of Kocani, Republic of Macedonia, and technical alumina (TA), a commercial product from “Kombinat Aluminijuma Podgorica”, Monte Negro, were used as precursors for SiO_2 and Al_2O_3 . A mixture (MX) of RHA and TA with the addition of 2 wt.% MgO (Merck, purity > 99.99%) as a catalyst, was used for the synthesis of porous mullite ceramics. Scanning electron microscopy (SEM) (Leica S 440i) was used to examine the morphology of the raw materials and the microstructure of the fabricated porous mullite ceramics. Energy dispersive X-ray spectroscopy analysis (EDX) was used to determine the composition of the RHA, TA and MX. The specific surface area was determined by BET analysis (Gemini, Micromerit USA). The phase composition of the powders and of the sintered samples was determined by X-ray diffraction analysis (XRD) (Bruker D8 Discover). Mechanical activation of the MX was performed in an attrition mill (Netzsch 4V1M) for 3 h in water. Transmission electron microscopy (TEM, Jeol 3010) was used to investigate the morphology of the mechanically activated MX. Green bodies were fabricated by uniaxial pressing of the MX at 50 MPa (Weber Pressen KIP 100). After optimization, two types of porous mullite ceramics were fabricated. The first one was obtained by sintering the green bodies at $1,300^\circ\text{C}$ for 3 h. The second one was obtained by applying 40 wt.% powdered active coal as a pore creator. Sintering was realized in two steps: a treatment from RT to $1,200^\circ\text{C}$ to combust the organic matter, and at $1,500^\circ\text{C}$ for 3 h. The density of the sintered samples was measured according to Archimedes’ principle. The mechanical properties (E-modulus and bending strength) were determined for polished samples (8 pieces, $50 \times 5 \times 5 \text{ mm}^3$) at room temperature (3-point bending tester Netzsch 401/3).

Results and Discussion

A SEM micrograph of the RHA is shown in Fig. 9.1a. From the figure it can be seen that the RHA particles possess an expressed relief structure. Also, there are protuberances present attached to the base of the RHA. The interior of the RHA is porous, contributing to the high specific surface area of $298.0 \text{ m}^2/\text{g}$. According to EDX and XRD analysis, the RHA was composed of pure silica in the amorphous state.

The morphology of the TA can be seen in Fig. 9.1b. The TA possesses a granulated form. The granulates consist of particles with dimensions ranging from 5 to $30 \text{ }\mu\text{m}$. The specific surface area is $2.3 \text{ m}^2/\text{g}$. According to EDX and XRD analysis, the TA mainly consists of Al_2O_3 (more than 99%) in its α -form.

A TEM micrograph of the mechanically activated MX is shown in Fig. 9.2. A considerable refining was achieved; the powder particles have sizes ranging from 10 to 30 nm .

A SEM micrograph of the first type of porous mullite ceramic is shown in Fig. 9.3. At the temperature/time of consolidation ($1,300^\circ\text{C}/3 \text{ h}$), the major part of the reaction of mullitization ($3\text{Al}_2\text{O}_3 + 2\text{SiO}_2 \rightarrow 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) has taken place, as is evident from the XRD pattern in Fig. 9.4. Only a small amount of the α -alumina phase was detected besides mullite as the main constituent. On the other side, the densification at this temperature was very slow. The porous mullite ceramics contain pores with shapes changing from spherical to irregular, with pore sizes ranging from 100 to 500 nm . The pores are interconnected, and the porosity is 20%. The contacts between the mullite grains are well established, yielding good mechanical properties. The E-modulus and bending strength were $80 \pm 2 \text{ GPa}$ and $130 \pm 7 \text{ MPa}$, respectively.

By increasing the temperature of sintering to $1,400^\circ\text{C}$, the porosity decreased and the pores were no longer interconnected. At $1,400^\circ\text{C}/1 \text{ h}$ pure mullite was formed (Fig. 9.4). At a temperature of $1,500^\circ\text{C}$ a liquid phase is formed in MX [10], enabling liquid phase sintering and thus conditions for anisotropic grain growth. As Chen et al. reported [6], anisotropic grain growth of mullite improves the mechanical properties of porous mullite ceramics by a factor of 2. As by sintering the MX

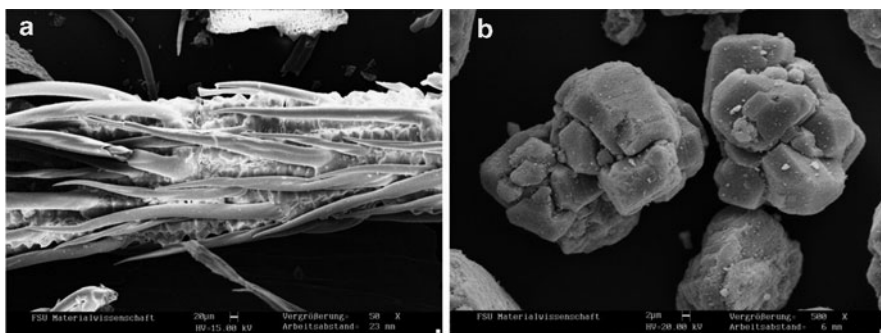


Fig. 9.1 SEM micrograph of the raw materials: (a) RHA (bar $20 \text{ }\mu\text{m}$); (b) TA (bar $2 \text{ }\mu\text{m}$)



Fig. 9.2 TEM micrograph of the mechanically activated mixture for the synthesis of porous mullite ceramics after 3 h attriting (bar 10 nm)

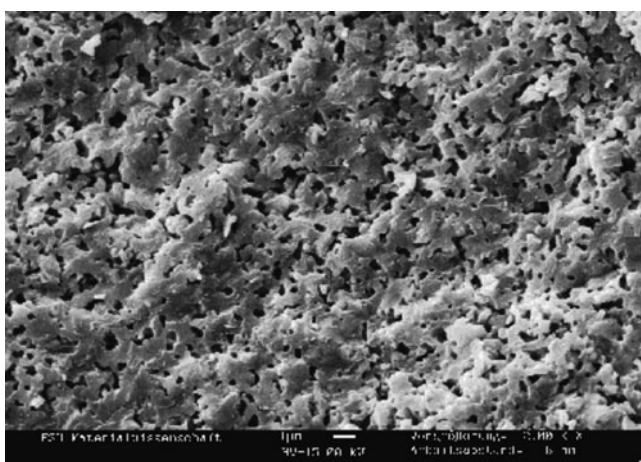


Fig. 9.3 SEM micrograph of porous mullite ceramics obtained by sintering a MX sample at 1,300°C for 3 h (bar 1 μm)

samples at 1,500°C high densities were achieved, a possible approach to fabricate porous mullite ceramics with anisotropic grain growth is to apply a pore creator.

Fig. 9.5 shows SEM micrographs of the second type porous mullite ceramic. From Fig. 9.5a it can be seen that the mullite possesses a relatively homogenous microstructure. The pores are elongated, with sizes ranging from 5 to 50 μm . They are interconnected, and the porosity is 26%. Fig. 9.5b shows the microstructure of the walls of the pores in Fig. 9.5a. As can be seen, the pore walls are dense with a

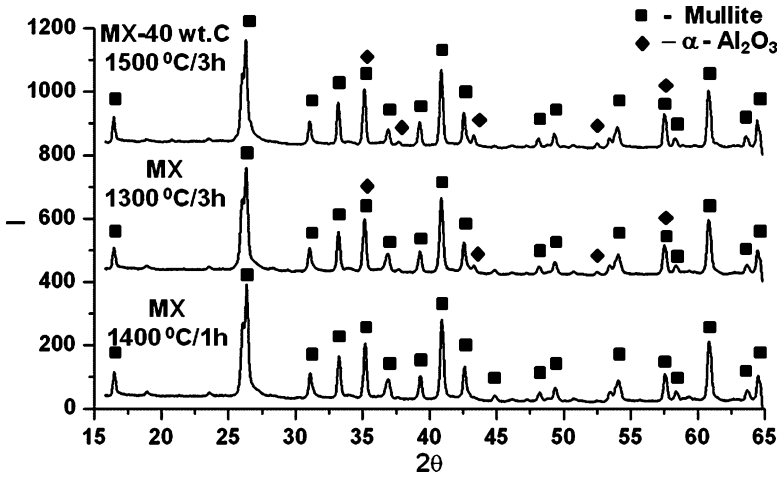


Fig. 9.4 Figure 9.1: XRD patterns of pure mullite (MX 1,400°C/1 h), the first type of porous mullite ceramic (MX 1,300°C/3 h), and the second type of porous mullite ceramic (MX-40 wt.% C 1,500°C/3 h)

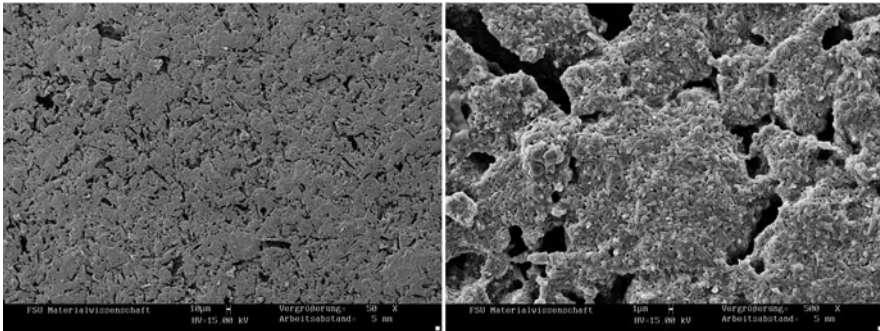


Fig. 9.5 SEM micrographs of a porous mullite ceramic obtained from MX by sintering at 1,500°C/3 h and applying active coal as a pore creator: (a) (bar 10 μm), (b) (bar 1 μm)

homogenous microstructure. An anisotropic mullite grain growth occurred. Mullite needles with length up to 3 μm were obtained, contributing to the good mechanical properties of the fabricated porous mullite ceramic. The E-modulus and bending strength were 63 ± 3 GPa and 49 ± 2 MPa, respectively.

Both porous mullite ceramics obtained were stable in aggressive media. Regarding their physical and mechanical properties, they can find potential applications in the fabrication of advanced sensors, as protective material in temperature sensing applications, as insulating ceramic substrate layer in layered sensors, and as membrane material in solid electrolyte gas sensors.

Conclusions

A mixture of rice husk ash and technical alumina, with the addition of MgO as a catalyst, was used to directly prepare porous mullite ceramics through in situ reaction sintering. Mechanical activation was performed on the mixture, resulting in a considerable refining after 3 h attrition milling, with particles sizes ranging from 10 to 30 nm. After optimization, two types of porous mullite ceramics were fabricated. The first one was prepared by sintering the mixture at 1,300°C for 3 h. An interconnected porous microstructure with a porosity of 20% and pores size ranging from 100 to 500 nm, was obtained. The second type of porous mullite ceramic was obtained by sintering the mixture at 1,500°C for 3 h and adding 40 wt.% active coal as a pore creator. A microstructure with elongated pores was obtained. The pores were interconnected, and the pore size ranged from 5 to 50 μm . The porosity was 26%. Regarding the physical and mechanical properties, both porous mullite ceramics can find potential application in the fabrication of advanced sensors.

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Part III
Techniques for the Characterization
of Sensor Materials

Chapter 10

Surface Analytical Characterization of Biosensor Materials

Giacomo Ceccone, D. Gilliland, and Wilhelm Kulisch

Abstract The development of materials for applications in biosensors and other fields of modern biotechnology critically depends on the characterization of the surfaces of these materials. In this contribution, two major techniques for this purpose are introduced, namely X-ray photoelectronspectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). First, the principles, advantages but also shortcomings of both techniques are described. But it is also shown that the application of both techniques to the same surface can lead to synergetic effects overcoming the shortcomings of each technique by the strengths of the other. Examples will be presented from our recent work on biomaterials such as Ta₂O₅, TiO₂, and TiC/a-C, which are promising candidates for applications in biosensors and other field of biotechnology. Finally it will be shown that in any case care has to be taken in the interpretation of XPS and ToF-SIMS results as there are several sources of artefacts caused by the measurements themselves.

Keywords Biosensors · Surface characterization · XPS · ToF-SIMS

Introduction

The development and optimization of (new) materials play a crucial role in the developing field of modern nanotechnology-based sensors and biosensors. This requires in turn the application of advanced techniques to characterize these

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materials, e.g. to determine their composition and bonding environment, especially for the utmost surface region. In this contribution, two methods will be introduced and discussed to some extent, namely X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). In z-direction perpendicular to the surface, their resolution is on the nanometer scale; for XPS it is, depending on the element to be detected, on the order of some nm, while with ToF-SIMS only the utmost surface layer is analyzed. However, the lateral resolution is only in the micrometer range, for XPS it is on the order of some micrometer unless synchrotron radiation is used for excitation, while for ToF-SIMS a lateral resolution in the submicron range can be reached. Nevertheless, both methods are complementary in the sense that XPS can easily be quantified but possesses a limited concentration resolution of about 0.5%, while ToF-SIMS has a resolution down to the ppb range but it is difficult to impossible to obtain quantitative results.

In this contribution, first the principles, possibilities and limitations of both techniques are discussed, and the synergy of the two methods is highlighted. In the remaining sections some examples are presented on the development and characterization of Ta₂O₅, TiO₂ and TiC/aC thin films for applications in biosensors and other biotechnological fields. In the final section, possible problems and limitations of the use of XPS and ToF-SIMS for the characterization of biosensor materials are addressed.

Surface Analysis

XPS

X-ray photoemission spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), is a qualitative and quantitative spectroscopic technique that measures the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within a material. The technique was developed by the group of K. Siegbahn at Uppsala, Sweden, in the 1960s [1] on the basis of Einstein's [2] theory of the photoelectric effect and basic concepts published in 1914 [3].

A schematic of the XPS principle is presented in Fig. 10.1a whereas in Fig. 10.1b a schematic diagram of an XPS system is illustrated.

The basic XPS experiments involves the bombardment of a material in vacuum (usually of the order of 10^{-9} to 10^{-10} mbar) with soft X-rays. The typical X-ray excitation lines are Mg $K\alpha$ ($h\nu = 1256.6$ eV) and Al $K\alpha$ ($h\nu = 1486.6$ eV). X-ray absorption by an atom in the solid leads to the ejection of an electron either from deep shell levels (Fig. 10.1a) or from the valence band levels. A fraction of these electrons, which are generated close to the sample surface, escape into the vacuum system and can be collected by an electron analyzer (Fig. 10.1b). The overall process is known as photoelectric effect, and the spectrum of the electron intensity presented as function of energy is called the X-Ray photoelectron spectrum. A typical spectrum (usually referred to as survey-scan or wide-scan) for a Ta₂O₅ film acquired with

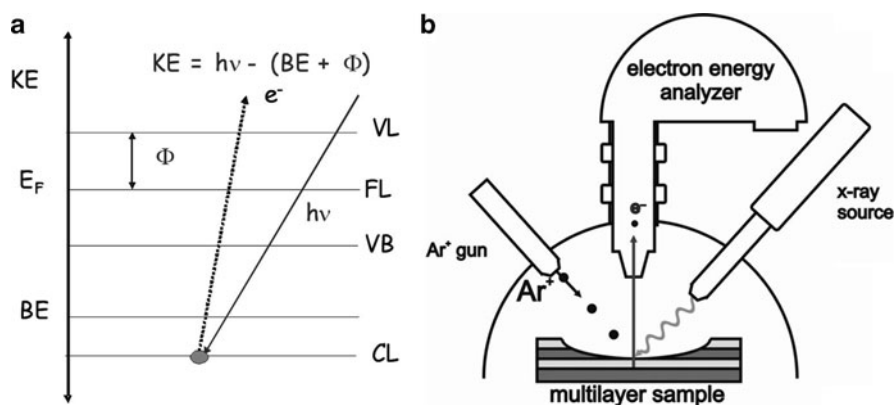


Fig. 10.1 (a) Principles of XPS; (b) schematic diagram of a XPS system

an Axis Ultra instrument (KRATOS, UK) [4] with monochromatic Al $K\alpha$ radiation and a pass energy of 160 eV is shown in Fig. 10.2. Besides the different peaks related to photoelectrons emitted by Ta, C and O atoms, also the peak at about 970 eV indicated as OKLL should be noticed. This peak corresponds to the Auger lines of oxygen that derive from the de-excitation process after the photoemission [5]. All elements (except H and He) can be detected by the XPS technique.

For a conducting sample in electrical contact with the spectrometer, conservation of energy leads to the formula presented in Fig. 10.1a, where KE is the measured kinetic energy of the photoelectron, $h\nu$ is the energy of the exciting X-ray photon, BE is the electron binding energy relative to the Fermi level (E_F) of the sample (defined as $E_F = 0$), and ϕ is the work function of the spectrometer (normally about 4.5 eV). For this, in order to obtain reliable information about the BE of emitted photoelectrons, the spectrometer must be carefully calibrated. This is achieved using clean metal standards (usually Ag, Cu and Au) [6]. In the case of insulating specimen the situation is complicated by the fact that the sample does not have a well defined Fermi level and cannot be in electrical contact with the spectrometer. In this case the term ϕ in the equation accounts for these uncertainties implying that a common reference point needs to be established. Usually this is done by referring all peaks to that of hydrocarbon species always present at the sample surface, which is set to 285.0 eV [7].

Moreover, photoemission from an insulator leads to the build-up of a positive surface charge that has to be dissipated in some way. Of course this problem is very important in the case of application of XPS for the analysis of biosensing platforms and surfaces, due to the presence of highly insulating materials such as polymers and biomolecules.

For non-monochromatic sources, charge neutralization can be achieved through a “flood gun” that delivers low energy electrons to restore surface neutrality. The problem is more complex in the case of monochromatic X-ray sources, where the surface charging can vary within the sample surface due to the non-uniformity of the photon flux. Although the use of flood guns with a potential adjustable between

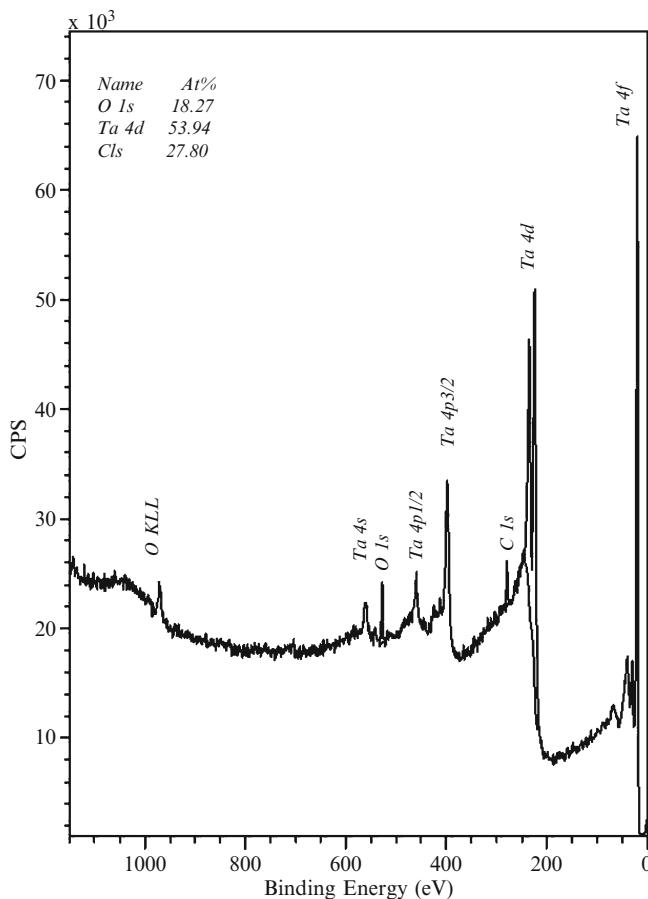


Fig. 10.2 Wide spectrum of a Ta₂O₅ oxide film deposited onto a clean silicon wafer

1 and 10 V is still a valid solution, other advanced techniques providing good and reproducible charge compensation for nearly all insulating samples have become available in the recent years [8]. In particular, the use of a magnetic immersion lens (snorkel lens) and a flood of low-energy ions (below 50 eV) are the most effective.

As mentioned above, from XPS spectra one can extract both quantitative and qualitative information about the surface under analysis. In particular, from a quantitative point of view, since the intensity of the emitted photoelectrons is proportional to the concentration of the element present on the sample surface, the surface atomic concentration of an element A in a homogeneous solid or film can be extracted from the following formula:

$$X_A = \frac{\frac{I_A}{S_A}}{\sum \frac{I_i}{S_i}} \quad (10.1)$$

where I_i is the measured intensity and S_i are the relative sensitivity factors (RSF), which are usually established experimentally for every spectrometer by using standard samples. In Fig. 10.2 the surface composition of a Ta_2O_5 film deposited on silicon is reported as example. Here, the following peaks and RSFs were used: O 1s (532 eV, 0.78), C 1s (285 eV, 0.278) and Ta 4d (224 eV, 5.158). The detection limit achievable with the XPS technique is of the order of parts per thousand. In special cases (concentration at the top surface and long acquisition times), a detection limit of parts per million can be attained.

Besides this quantitative information, XPS can also provide valuable information about the chemical bonds present at the surface. For instance, by acquiring high resolution spectra of the C 1s transition one can identify the different types of carbon present at the surface. For example, in Fig. 10.3, high resolution C 1s spectra of acrylic acid films spin-casted or deposited by plasma polymerization are presented.

As can be seen the spectra presents remarkable differences. In the case of pure acrylic acid (Fig. 10.3a) three components are identified. These components correspond to the different chemical bonds of carbon in the acrylic acid (formula $\text{CH}_2\text{—CH—COOH}$). In particular the component at 285.00 eV is attributable to hydrocarbon moieties CH , whilst the component at 289.2 eV is related to the carboxylic functions COOH . The component at 285.55 eV is due to the carbon backbone atom bonded to the carboxyl group, C—COOH , and is referred to as “beta” carbon [9].

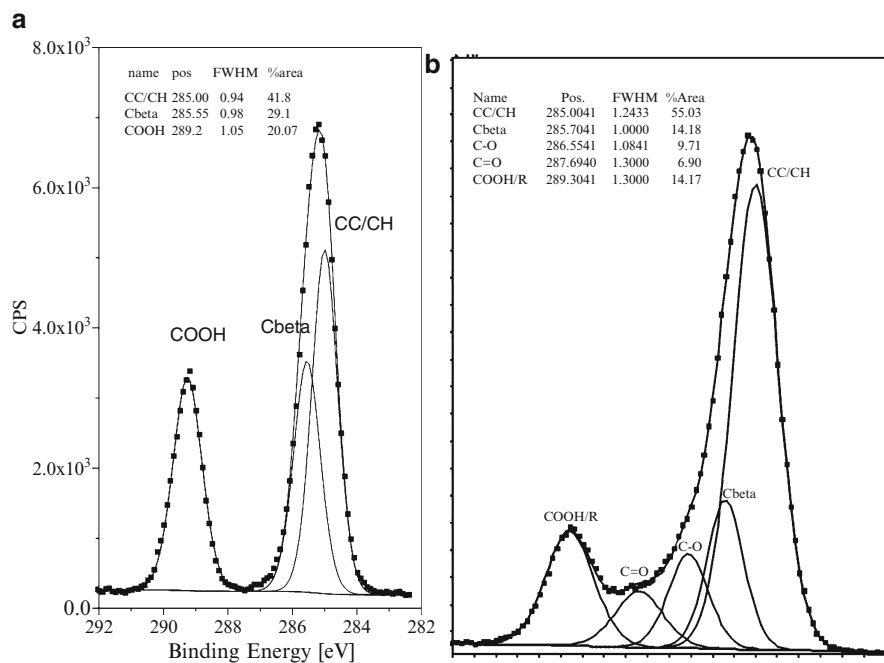


Fig. 10.3 C 1s core level spectra of (a) spin-casted acrylic acid and (b) plasma polymerized acrylic acid film

Taking into account the chemical formula, one should expect a equal contribution from the three different carbon atoms; however an excess of hydrocarbon is noticed. This is most likely due to some hydrocarbon contamination present at the film surface; it should be underlined that these results are in excellent agreement with published XPS databases [10].

In the case of the plasma polymerized film (ppAA), the situation gets more complex. In fact two additional components are detected in the C 1s envelope: one at about 286.5 eV attributable to C–O bonds and the other at about 287.7 eV which is related to C=O moieties [11]. Moreover, the amount of retained COOH functionalities is strongly reduced (from 29% to 15%). These effects are a consequence of the cross-linking of the polymer chains due to the plasma process. Thus, although plasma polymerization is able to stabilize acrylic acid polymers rendering them insoluble in water and in biological fluids, one should carefully select the process parameters in order to maintain enough carboxylic functionalities that are important for the linking of biomolecules to the surface.

Apart from the spectral information, modern XPS instruments allow the possibility of performing photoelectron microscopy and micro-spectroscopy analysis. In this case the analyzer is tuned to a particular energy of the photoelectric peak of the element of interest, and the sample is mapped to obtain the distribution of such an element on the surface by acquiring a so-called “parallel” image [12]. This possibility is of a great importance when analyzing heterogeneous or micro-patterned surfaces. In fact, photoelectron imaging allows locating specific areas on a sample surface for small-spot spectral analysis. XPS imaging has been applied successfully to study polymer blends [13], segregation effects in polymer systems [14], surface treatments of polymers by UV and plasmas [15,16], and to investigate corrosion and oxidation [17]. However, the limitations of the XPS imaging is the spatial resolution that is limited to the micron range (about 10 μm with the AXIS ULTRA spectrometer used in this study). Although recently an instrument with a resolution of 650 nm has been commercialized [18], the only possibility of obtaining spatial resolution at the nanometer level is to use a synchrotron radiation source [19]. For this, the XPS imaging techniques is more and more coupled with other microscopic and spectroscopic techniques, such as AFM, confocal microscopy, imaging FTIR and ToF-SIMS to correlate XPS results with other imaging techniques which have comparable field of view but contain different information [20].

The XPS analysis depth ranges between 2–3 and 10 nm, depending on the angle between the surface and the analyzer axis (take-off-angle, TOA). This allows the possibility of performing angle resolved-XPS analysis to obtain both quantitative and qualitative information at different depths of the sample. This procedure has proven to be a relatively simple method to determine several parameters of the sample surface, such as the thickness of an oxide or contamination layer [21]. ARXPS has two main advantages: it is a non destructive technique, preserving the chemical state information present, and it has very good absolute depth resolution. However, if the upper layer exceeds 10 nm or in the case of multilayered films, the ARXPS technique is not anymore able of providing valuable information. In this case, depth profiling methods have to be applied. This is usually achieved by

combining the XPS analysis with a sputtering (or etching) process via an Ar^+ ion beam with energies between 0.5 and 5 keV [22]. The ion beam is also used to clean sample surfaces prior the analysis. However, in order to extract reliable information from a ion etching depth profile, careful calibration of the etching rate is needed. Furthermore, if the sample is composed of elements with different etching rates, this must be taken into account. Another effect that must be accounted for is the modification of the surface chemistry by the ion beam. An example of this effect is presented below (see section [Measurements induced artefacts](#)).

TOF-SIMS

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a surface-sensitive analytical method that uses a pulsed ion beam (Cs^+ , microfocused Ga^+ or clusters of Au and Bi) to remove molecules from the very outermost surface of a sample. The particles (secondary ions) are removed from atomic monolayers on the surface as illustrated in Fig. 10.4a.

These particles are then accelerated to a constant kinetic energy and injected into a “flight tube”; then their mass is determined by measuring the exact time at which they reach the detector (i.e. time-of-flight). In Fig. 10.4b a schematic diagram of a ToF-SIMS spectrometer is illustrated.

ToF-SIMS is the dominant variant of the *static* SIMS technique that emerged as a powerful technique in surface analysis as a consequence of the work of Benninghoven and his group at the University of Münster in the late 1960s [23]. In recent years ToF-SIMS has become one of the most powerful techniques for characterizing the surfaces of organic materials encompassing automotive paints, CD coatings, amino acid and protein layers, frozen cells and tissues [24].

The basic concept of the process is relatively simple: when a high energy ion beam (1–25 keV) bombards a surface, the particle energy is transferred to the atoms

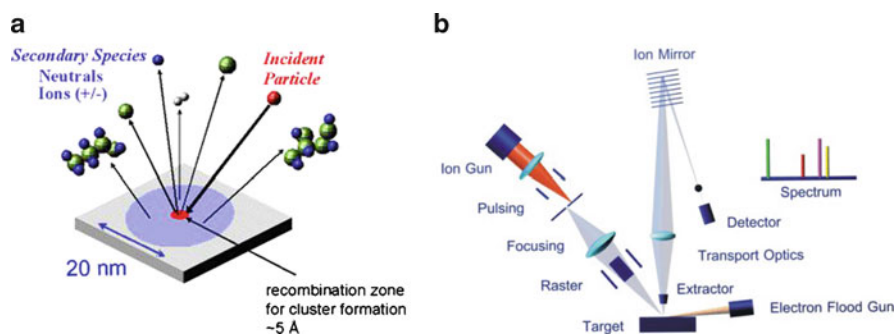


Fig. 10.4 (a) Principles of ToF-SIMS; (b) schematic diagram of a TOF-SIMS system

of the solid via billiard-ball type collisional processes. A *cascade* of collision occurs between the atoms in the solid; some of them return to the surface and give rise of an emission of atoms and molecular fragments, some of which (less than 5–10%) are ionized (Fig. 10.4a). Even if the technique looks apparently destructive, the essence of the *static* mode is to use very low primary ions doses (below 10^{13} ions cm^{-2}). Under this condition, less than 1% of the surface atoms or molecules receive an ion impact, and the species are generated from an area smaller than 10 nm^2 leaving the vast majority of the surface unaware of the removal event. Thus the spectral information arises from a surface that can be considered undamaged.

Three operational modes are available using ToF-SIMS: surface spectroscopy, surface imaging and depth profiling. In the last case, a second ion gun (O_2 , Cs^+ and more recently C_{60}^+ ions) is used to remove materials from the surface while analyzing with the first gun. In this case the technique is called *dynamic* SIMS and becomes destructive [25].

The ToF-SIMS technique allows the acquisition of mass spectra between 0 and 10,000 amu with a high mass resolution ($M/\Delta M = 7,000$ amu) and high sensitivity (in the ppm range). This features permits to distinguish easily particles with the same nominal mass (e.g. Si and C_2H_4 , both with amu = 28). Moreover, ions (positive or negative), isotopes, and molecular compounds (including polymers, organic compounds, up to ~amino acids) can be detected. In addition, ToF-SIMS has a much higher lateral resolution than XPS, allowing sub-micron imaging to map any mass number of interest. Finally, because every pixel of a ToF-SIMS map represents a full mass spectrum, it is possible for an analyst to retrospectively produce maps for any mass of interest, and to interrogate regions of interest (ROI) for their chemical composition via computer processing after the dataset has been instrumentally acquired.

An example of ToF-SIMS imaging analysis is presented in Fig. 10.5. It shows a silicon sample on which a protein-resistant polymer (polyethylene glycol) has been grown in selected areas (dark regions of the optical image) on a silicon substrate. The growth method was a atom transfer radical polymerization of polyethylene glycol methacrylate (PEGMA) starting from a bromine containing initiator (α -bromoisobutyryl group $(\text{CH}_3)_2\text{BrC}-$, see Fig. 10.6) immobilized on the epoxide functionalized silicon substrate. To create a patterned surface the bromine functionalized silicon was exposed to UV light through a metal mask such that the initiator was eliminated or deactivated locally in the areas exposed to the UV light. This was followed by a wet chemical step in which a protein resistant-brush polymer (40–80 nm) of polyethylene glycol was grown from the initiator on the remaining unexposed areas of the sample. Finally the PEG patterned sample was immersed in a protein solution, then rinsed and analyzed by ToF-SIMS.

The optical image shows the area of analysis with the darker regions showing the areas where the polymer has been grown (40–80 nm). The ion images show the distribution of certain key ions which show the position of the exposed substrate (SiO_2), the PEG polymer ($\text{C}_2\text{H}_5\text{O}_2^-$ and $\text{C}_4\text{H}_7\text{O}_2^+$), the residual initiator ($\text{Br}(-)$), and arginine from the protein ($\text{C}_5\text{H}_{10}\text{N}^+$).

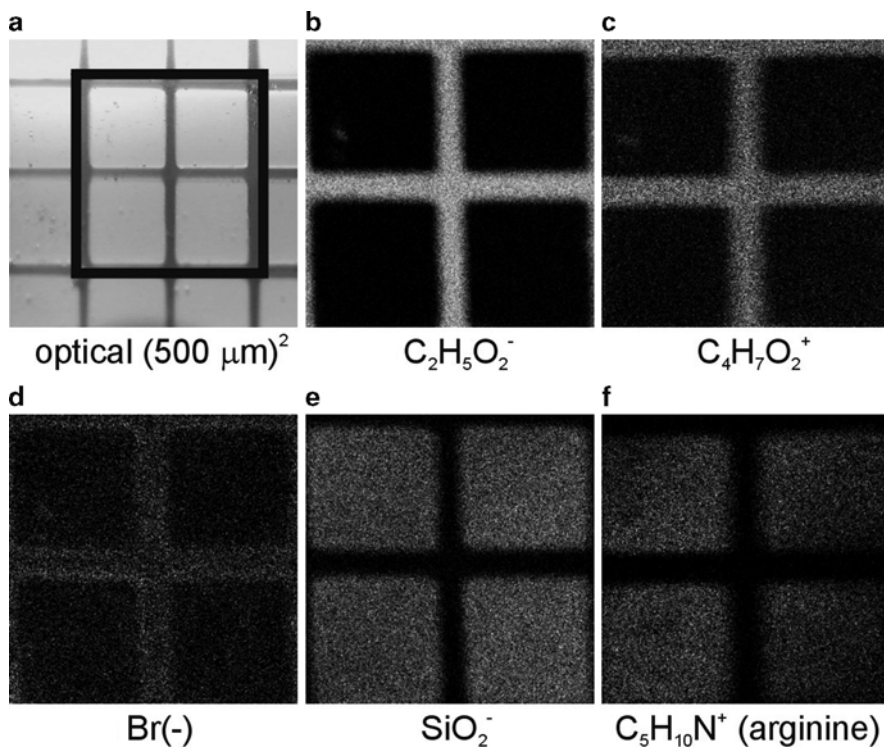
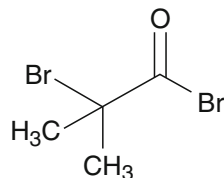


Fig. 10.5 Optical and ToF-SIMS ion images of micropatterned surfaces

Fig. 10.6 α -Bromoisobutyryl bromide (BIB)



XPS and TOF-SIMS: Synergetic Effects

From the description of the XPS and ToF-SIMS techniques given in the previous paragraphs, it is quite evident that the two techniques are complementary in providing information about the chemical states of the surfaces. In particular, the combination of the quantitative analysis obtained by the XPS with the TOF-SIMS molecular information is of paramount importance for the study of surface functionalization processes and biosurfaces [26].

For example, in the development of biosensors platforms, the development of surface treatments methods able to reduce or eliminate non-specific binding of

biomolecules on the wetted surfaces of the micro-fluidics part of the sensor is a quite challenge task. For instance, several methods such as PECVD [27,28] and self assembling monolayers (SAMs) [29,30] can be successfully used for depositing protein-resistant layers on different substrates (glass, polymers, silicon, Au, etc.). However, the modification of surfaces to modulate proteins and biomolecule adsorption still remain a challenge for a number of reasons. For instance, in the case of glass, the formation of SAMs is complicate by their sensitivity to humidity and their propensity in forming multilayers. On the other hands, the PECVD technique can be difficult to use in complicated geometries (such as microfluidics channels). A possible solution could be obtained by using a chemical route named atomic transfer radical polymerization (ATRP) [31]. In this method the material to be coated is firstly treated to immobilize a polymerization initiator on the surface. In this case the initiator rich surface is produced by exposing it to the vapour from reactive α -bromoisobutryl bromide(BIB) which serves to immobilize the ATRP active bromoisobutryl group ($(\text{CH}_3)_2\text{BrC}-$).

This surface is then immersed in a deoxygenated solution containing a catalyst and macromonomers of poly(ethylene glycol) methacrylate. When this solution contacts the initiator treated surface a series of chemical reactions result in the growth of a polymer brush outward from the sample surface. This liquid-based method has a number of advantages in that there are fewer difficulties in coating complex structures or thin capillaries and that it requires only low-cost equipment and inexpensive chemicals reagents. Furthermore, the method once optimized should be relatively simple to scale-up. When the polymerization process is carried out from a surface, the method is called surface initiated atomic radical polymerization (SI-ATRP) [32].

The ATRP process has been already applied to grow protein-resistant coatings on silicon oxide wafers [33,34]. In our case we have applied this technique to grow protein-resistant poly(ethylene glycol) methyl methacrylate (PEGMA) films not only on silicon wafers as in the example described previously (Fig. 10.5) but on different substrates, namely poly(oxyethylene) (POM), poly(ethyleneterephthalate) (PET) and silica glasses. The use of ToF-SIMS and XPS allowed us to control the surface chemistry at each step of the process. The data from XPS provided an accurate quantification of the elements present at the surface while ToF-SIMS could confirm the presence of the desired molecular groups.

In Table 10.1 the surface composition, obtained by XPS, of POM at different step of the process is presented.

Table 10.1 Surface composition of SI-ATRP process on POM substrate

Sample	C (at%)	O	N	Br	Rest (Cl, Ca, Si. . .)
POM as-received	52.2	47.4	0.33		
POM + BSA	59.7	34.4	4.79		1.1
POM/PGMA	56.8	43.1	–		0.1
POM/PGMA/BIB	56.6	43.0	0.10	0.3	
POM/PGMA/PEGMA	64.1	35.9	0.06		
POM/PGMA/PEGMA + BSA	64.8	35.0	0.07		

As can be seen, the POM surface is not antifouling as result from the high nitrogen content detected after immersion in 1 mg/mL BSA solutions for 1 h. The presence of the protein, as indicated by the appearance of nitrogen in the XPS spectra was confirmed by ToF-SIMS which showed numerous amino acid specific molecular fragments.

With regard to the coating process, the chemical composition is strongly affected by the different steps of the SI-ATRP process; in particular, the O/C ratio can be used to follow the steps related to the poly(glycidyl methacrylate) (PGMA) and PEG deposition, whilst the detection of the presence of Br indicates that the BIB initiator has been immobilized on the surface. For instance, the O/C ratio of the as received POM is 0.94 very close to the theoretical value of 1; the deposition of PGMA and immobilization of BIB do not change this value much, in agreement with the fact that the deposited films are in the monolayer range and quite thin with respect to the XPS analysis depth. In this specific example, the appearance of bromine in the XPS spectra after exposure to the initiator precursor is not a definitive proof that the α -bromoisobutryl group ($\text{Br}(\text{CH}_3)_2\text{C}-$) is bound to the surface by since the precursor group also contains the acid bromide. However, a detailed examination of the ToF-SIMS spectra obtained after exposure to BIB showed that in addition to the expected $\text{Br}^{(-)}$ peaks there were also peaks directly attributable to the $(\text{Br}(\text{CH}_3)_2\text{C})^+$ molecular fragment. This data served to confirm unequivocally that the correct initiator species for ATRP polymerization had been fixed on the surface and could be used in a semi-quantitative manner to optimize the initiator immobilization step.

In contrast to this, after the polymerization of the PEGMA the O/C ratio drops to about 0.54, which is again very close to the theoretical value of 0.5 which would be expected for pure PEG. This indicates that the deposited PEGMA d layer is able to mask completely the underlying layers (BIB, PGMA) of the sample. Moreover, the O/C ratio does not change after immersion in BSA solution (1 mg/mL, 1 h) thus demonstrating the excellent protein repellent character of the deposited coating. These non-fouling properties were further confirmed by the more sensitive ToF-SIMS analysis which showed the absence of amino acid fragments.

In a variation of this process, already described in the previous section, a silicon surface made active towards ATRP by treating with PGMA and BIB was additionally patterned by exposure to UV light through a metal mask before the ATRP polymer growth step. From ToF-SIMS analysis it was shown that the areas exposed to the UV light were rapidly modified, losing bromine and effectively deactivating these areas toward ATRP. When such modified samples were treated with the ATRP growth solution the effect was to produce a chemically contrasted surface where the anti-fouling PEG brush would grow only from the areas of the surface unmodified by the UV. In this case the UV modification step occurred to very thin layer (1–2 nm) and with a lateral features of a 10–20 μm both of which are factors which create difficulties for XPS analysis. In contrast, the use of ToF-SIMS was better suited to this providing a high spatial resolution chemical maps and spectra which permitted the optimization of the UV deactivation step of the patterning process. Furthermore, the analysis of the samples after polymer growth and

exposure to a protein solution showed the desired distribution of amino acids on the surface (Fig. 10.5) which confirmed the fouling/non-fouling contrast of the surface with a resolution below that reasonably possible for most XPS systems.

In these two examples which have as a common element the growth of ATRP polymer films it can be seen that XPS and ToF-SIMS can be highly complimentary to each other. Each method has a series of strengths and weaknesses which can in many cases be compensated by the use of the alternative technique: XPS is very powerful in obtaining quantitative elemental analysis data but with moderate sensitivity and spatial resolution while ToF-SIMS is highly sensitive with high spatial resolution but in most circumstances is unsuited to quantitative analysis.

Example 1: Ta₂O₅ Films for Waveguides in Biosensors

Owing to their outstanding optical properties [35,36] such as a high refractive index (2.1–2.2), a very low optical absorption over a large part of the spectrum (300 nm to 2 μ m) and a large optical bandgap (4.2 eV), and also due to their high chemical resistance [37,38] and biocompatibility [39], tantalum pentoxide (Ta₂O₅) thin films have found widespread applications in various fields and especially in biosensors [40–44].

We have used (dual) ion beam sputtering ((D)IBS) to deposit Ta₂O₅ films on silicon, glass and thermoplast substrates at room temperature as waveguides for biosensors with the aims of a high refractive index and a very low absorption (<3 dB/cm) [45,46]. In the course of these investigations, surface analytical techniques such as XPS and ToF-SIMS played a decisive role.

Figure 10.7 (left) shows the composition of IBS Ta₂O₅ films as revealed by XPS as a function of the oxygen partial pressure during the process (the gas mixture used was Ar/O₂). It can be seen that a partial pressure $p_{O_2} \geq 3 \times 10^{-2}$ Pa is required to

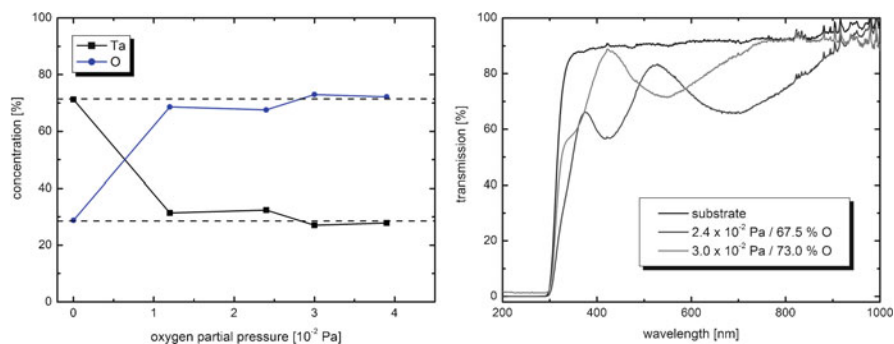


Fig. 10.7 *Left:* Composition of Ta₂O₅ films as a function of the oxygen partial pressure during IBS deposition. The dashed horizontal lines represent stoichiometry. The surfaces were etched for 3 min with 3 keV Ar⁺ ions prior to the measurements. *Right:* UV-Vis spectra of an understoichiometric and a stoichiometric Ta₂O₅ film. Also shown is a spectrum of an uncoated glass substrate

reach stoichiometry (which is indicated by the dashed vertical lines in the figure). These differences in the composition turned out to be significant for the optical properties of the films as is evident from the UV/VIS spectra shown in the right side of Fig. 10.7. The absorption edge is determined by the glass substrate; experiments performed on quartz slides revealed that the absorption edge of the films is about 260 nm; a Tauc plot yielded an optical band gap of 4.0 ± 0.1 eV. Most striking in the spectra in Fig. 10.7 is the fact that considerable absorption up to at least 500 nm is observed for the understoichiometric film, whereas for the stoichiometric layer there is no absorption down to 400 nm. This shows that stoichiometry is a sine qua none to achieve absorption-free Ta_2O_5 films. Further experiments have shown that with the IBS process it is possible to deposited stoichiometric Ta_2O_5 films with an absorption below 3 dB/cm at 500 nm [46].

Further informations were obtained from the XPS Ta 4f and O 1s core level spectra of a stoichiometric film shown in Fig. 10.8. The Ta 4f spectrum consists of a doublet at 27 and 28.9 eV which can be assigned to Ta 4f_{7/2} and Ta 4f_{5/2} transitions. This means that only one state of tantalum bonding exist, which from the peaks positions can be identified as stoichiometric Ta_2O_5 . The presence of suboxides (see section [Sputter induced damage](#)) can be excluded.

Interestingly, the O 1s spectrum of the same film shows two contributions indicating two bonding states of oxygen at the sample surface (Fig. 10.8, right). The main peak can be assigned to stoichiometric Ta_2O_5 . The small peak at 532.8 eV may hint at the presence of suboxides which, however, can be excluded from the Ta 4f spectrum. Thus it is very likely that this peak can be assigned to oxycarbon surface contaminations which are always observed for as-grown Ta_2O_5 films as will be discussed below.

The XPS results on DIBS Ta_2O_5 thin films presented hitherto gave considerable insight into the surface composition of the films. However, it is well known that such as-grown films are very prone to rapid surface contamination. Thus, before

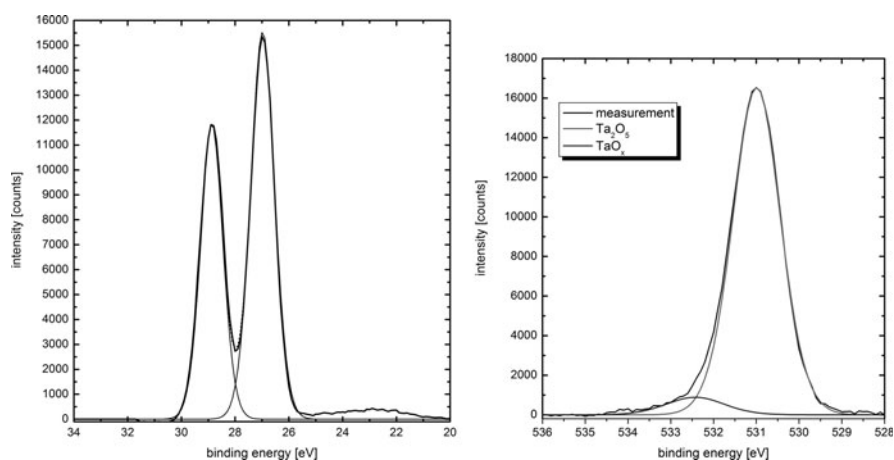


Fig. 10.8 Ta 4f (*left*) and O 1s core level spectra (*right*) of a stoichiometric Ta_2O_5 film

functionalization of any biomolecules onto Ta_2O_5 surfaces it is common to clean them by an appropriate process. Three techniques were employed for this purpose: (i) a 10 min treatment in a microwave O_2 plasma; (ii) a photochemical treatment employing the so-called UV/ O_3 process; and (iii) a pure chemical treatment with the co-called piranha solution ($\text{H}_2\text{O}_2\text{:H}_2\text{SO}_4$ 1:3). Details of these treatments can be found in Ref. [46].

Directly after these treatments, the surfaces were investigated by XPS. It has to be mentioned, however, that they were exposed to air between treatment and characterization. The results are summarized in Table 10.2. It can be seen that all surfaces are heavily contaminated by oxycarbon species; this regards the “cleaned” surfaces also. The tantalum content is about 15.5–17.5% for all surfaces; for stoichiometric Ta_2O_5 it should be 29%. Table 10.2 also lists the contact angles against purified water measured directly after the treatments. Here a clear trend is observable: the as-grown surface is highly hydrophobic; all three treatments render it hydrophilic. For the piranha and UV/ O_3 treatments, the contact angles are below 5° . These contact angles are in good agreement with data reported by de Palma et al. [39]. The most striking observation from Table 10.2 is that these obvious changes of the nature of the surface do not reflect at all in the surface composition revealed by XPS.

To investigate these discrepancies, the surface of the samples after these treatments have been assessed by ToF-SIMS. Two examples of such measurements are presented in Fig. 10.9. The diagram on the left side shows normalized count rate ratios of the form $\text{Ta}_x\text{O}_y\text{H}/\text{Ta}_x\text{O}_y$. Normalization has been carried out with respect

Table 10.2 Surface composition (XPS) of an as-grown Ta_2O_5 film and after various surface treatments. Also given are the contact angles θ_c of these surfaces and, for comparison, the θ_c values reported by De Palma et al. [39]

Sample	As grown	O_2 plasma	Piranha	UV/ O_3
Ta [%]	15.5	14.7	17.4	16.5
O [%]	62.4	66.9	69.4	64.4
C [%]	22.1	18.5	13.2	19.1
θ_c [$^\circ$]	85 ± 2	26 ± 1	4.5 ± 1	4.5 ± 1
θ_c [$^\circ$] [39]	≈ 90	...	< 5	< 5

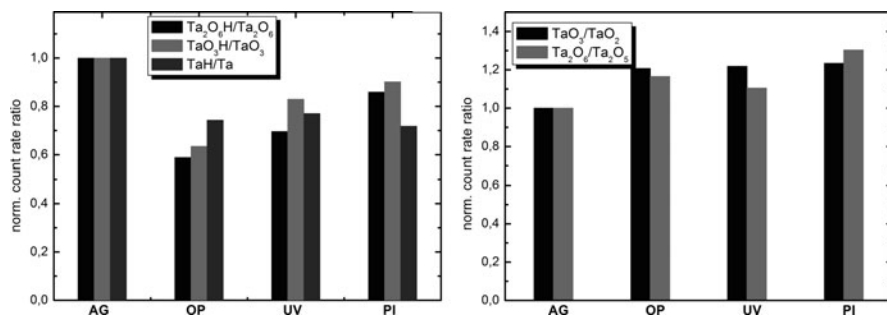


Fig. 10.9 Normalized ToF-SIMS count rate ratios of (left) hydrogen containing over hydrogen free Ta species and (right) $\text{TaO}_3/\text{TaO}_2$ and $\text{Ta}_2\text{O}_6/\text{Ta}_2\text{O}_5$ for differently treated tantalum pentoxide surfaces. Normalization was performed with respect to the as-grown surface

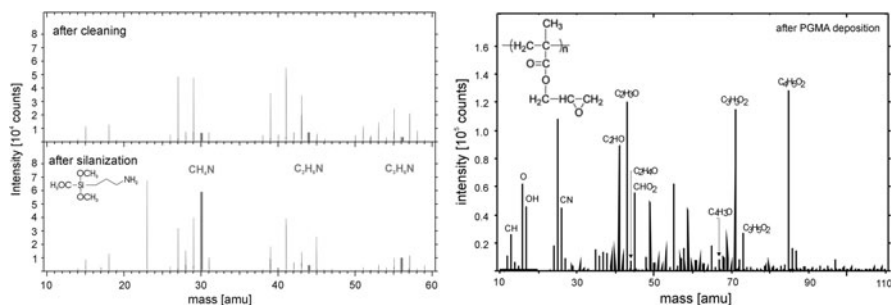


Fig. 10.10 ToF-SIMS spectra of a Ta_2O_5 film after UV/ O_3 treatment (*left, upper panel*) and after exposure to APTMS (*left, lower panel*) and to PEGMA (*right*)

to the as-grown surface. It can be seen from the diagram that all three treatments lead to a reduction of the concentration of hydrogen containing species on the surface. In a similar way, the right diagram in Fig. 10.9 shows the normalized count rate ratios $\text{TaO}_3/\text{TaO}_2$ and $\text{Ta}_2\text{O}_6/\text{Ta}_2\text{O}_5$ assessed for these samples. It can be seen that both ratios increase after the treatments. Thus these ToF-SIMS measurements show that – although no changes in the overall surface composition of the samples are evident from the XPS data in Table 10.2 – these surface treatments lead to distinct surface modifications such as a reduction of the surface hydrogen content and a stronger oxidation of the surface material but more work is required to correlated these results with the contact angles reported in Table 10.2.

In order to use these Ta_2O_5 films as waveguides in biosensors it is necessary to immobilize biomolecules on the surface of the films. This in turn requires the functionalization of the surfaces with specific chemical groups. A common method is silanization, making use of the O and OH containing groups on the surface of the films [39–41]. In order to investigate the viability of this route for our films, a silanization with 3-aminopropyl trimethoxysilane (APTMS) was carried out after a UV/ O_3 treatment step [46]. The resulting surfaces have been investigated by ToF-SIMS; the results are presented in the left diagram of Fig. 10.10. In the lower panel of this diagram it is evident that the count rates of nitrogen containing groups of the form $\text{C}_x\text{H}_y\text{N}$ have increased considerably which may be taken as a prove that amine bearing groups have successfully introduced to the surface.

In a second series of experiment we have used the spin-casting of a poly(glycidyl methacrylate) (PGMA) layer to introduce epoxy groups to the surface of Ta_2O_5 films. A ToF-SIMS spectrum of such a layer is shown in the left diagram of Fig. 10.10 which clearly demonstrates the successful deposition of a layer which is rich in $\text{C}_x\text{H}_y\text{O}_z$ species.

Example 2: TiO_2 Films for Applications in Biosensors

Like Ta_2O_5 , titanium dioxide (TiO_2) possesses a high refractive index and a very low absorption over a large part of the spectrum [47–49]. Thus, like tantalum pentoxide, there are many possible or already realized applications in various fields

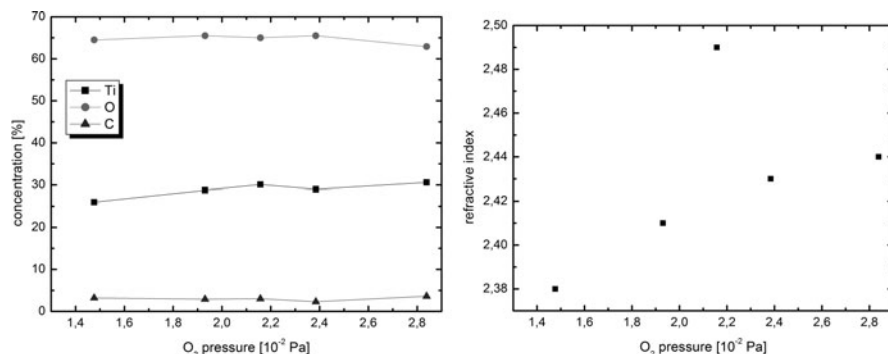


Fig. 10.11 Composition (*left*) and refractive index (*right*) of TiO₂ films as a function of the oxygen partial pressure

and especially in biosensors. Moreover, TiO₂ has been recognized to be an effective photocatalyst [50].

Figure 10.11 shows on the left side the dependence of the surface composition as a function of the oxygen partial pressure during IBS deposition of TiO₂ films. There is no great variation of the concentrations with p_{O_2} . The stoichiometric composition of TiO₂ is 33.3% Ti and 66.7% O. From the diagram in Fig. 10.11 it can be seen that due to surface contaminations (especially carbon) neither the concentration of Ti nor that of oxygen reach these values. But for all samples investigated the ratio O/Ti is larger than two. Probably the surplus oxygen is due to oxyhydrocarbon species on the surface.

The right diagram in Fig. 10.11 shows the refractive index n of the TiO₂ films as a function of p_{O_2} . The index increases with the oxygen partial pressure but there is also a very high value observed for $p_{O_2} = 2.15 \times 10^{-2}$ Pa. However, neither the increase of n with p_{O_2} nor this exceptionable value are reflected in any way by the XPS data shown in the left diagram of Fig. 10.11.

Example 3: TiC/a-C Nanocomposite Films for Biomedical Applications

TiC/a-C nanocomposite films consisting of titanium carbide nanocrystallites embedded in an amorphous carbon matrix possess excellent mechanical and tribological properties such as a high hardness, a low friction coefficient and a high thermal and corrosion resistance [51–54] and can, depending on the structure, designed to be either superhard [55] or supertough [51]. As titanium and its compounds are highly biocompatible [56,57], TiC/a-C nanocomposite films are thus promising candidates for the coating of orthopaedic implants. Doping of such films with Ca may serve to stimulate the formation of new bone tissue [57].

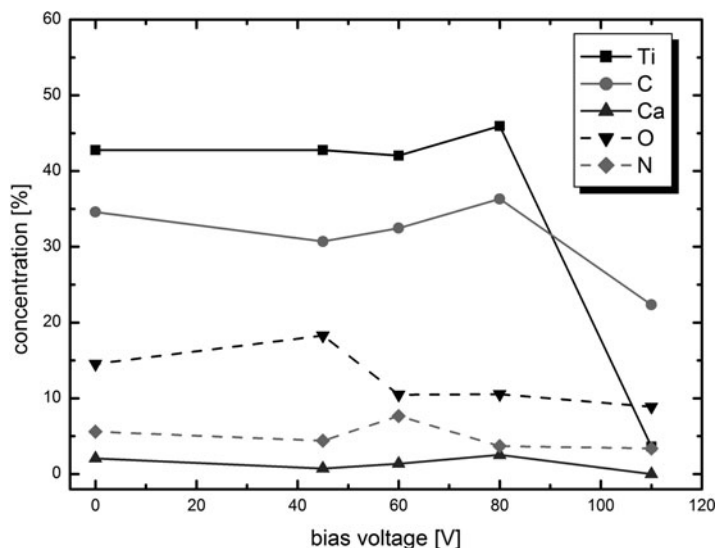


Fig. 10.12 Surface composition of TiC/a-C films as a function of the bias voltage applied

We have prepared Ca-doped TiC/a-C films by a hybrid deposition technique consisting of dc sputtering of a $\text{TiC}_{0.5} + 10\%$ Ca target, combined with a high density inductively coupled plasma to excite and ionize the sputtered species [58–60]. The films consisted of TiC nanocrystallites of 5–15 nm diameter embedded in an amorphous carbon matrix [60].

The composition of the films was determined by XPS. Fig. 10.12 shows data as a function of the bias voltage applied during the deposition. No clear influence of the bias can be detected in Fig. 10.12. The decrease of all concentration values for $V_B = 110$ V can be explained by the fact that this film has delaminated from the substrate due to the high compressive stress caused by the high bias voltage.

Figure 10.13 shows C 1s and Ti 2p core level spectra of such a TiC/a-C film, which gave considerable insight into its bonding structure. Both peaks consists of four contributions each.¹ The peak positions and their assignments are summarized in Table 10.3. It has to be mentioned that the film has been sputter etched for 1 min with 3 keV Ar^+ ions prior to the measurement.

The main peak of the C 1s spectrum at 181.2 eV stems from carbon atoms bound as carbides, i.e. TiC. The peak at 282.1 eV is due to distorted carbon in TiC, i.e. C atoms knocked into the TiC lattice by the ion bombardment during the deposition or during the sputter etching. The broad peak at 286.4 eV stems from C–C bonds. Its presence is of great importance for the structure of these films as it proves the

¹ Please note: The Ti 2p peaks are doublets Ti 2p_{1/2} (above 459 eV) and Ti 2p_{3/2} (below 459 eV). Thus the eight peaks in the spectrum stem from four different contributions.

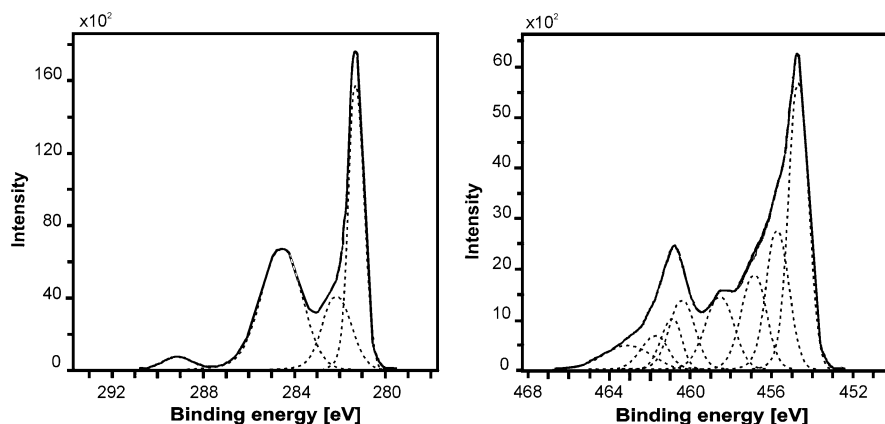


Fig. 10.13 C 1s (*left*) and Ti 2p core level (*right*) of a TiC/aC nanocomposite film deposited at $V_B = 100$ V

Table 10.3 Positions and assignments of the C 1s and Ti 2p peaks observed in Fig. 10.13

C 1s				Ti 2p _{3/2}		
Peak	Position	Assignment	Ref.	Position	Assignment	Ref.
1	281.2	TiC	[61,62]	454.7	TiC	[62]
2	282.1	Distorted C	[54]	455.6	Ti–O in TiC lattice	[62]
3	284.6	C–C		456.9	Ti–O–C, Ti–O–N	[59]
4	287	C–O		458.6	TiO ₂	

existence of an amorphous carbon matrix. The small peak at 287 eV, finally, is due to some oxycarbon bonds on the surface,

The four peaks of the Ti 2p spectrum can be assigned to as follows: The main peak at 454.7 eV stems from TiC, in agreement with the C 1s spectrum. The next one is due to Ti–O bonds in groups where O replaces carbon in the TiC lattice. The remaining two Ti 2p peaks can be assigned to oxygen containing groups, namely Ti–O–N and Ti–O–C (456.9 eV) and TiO₂ (458.6 eV), respectively.

Measurement Induced Artefacts

No physical/technological technique is perfect; this holds for deposition methods and characterization techniques likewise. In the course of the investigations presented above two major problems associated with XPS were encountered. Both are closely related. In most cases, and also in the examples discussed above, the vacuum has to be broken between deposition and surface characterization, i.e. the samples are exposed to laboratory air. Even if this exposure lasts only a few minutes, it will lead to contamination by oxyhydrocarbon species. It is common in surface analysis to etch these surface contaminations by a slight Ar⁺ ion

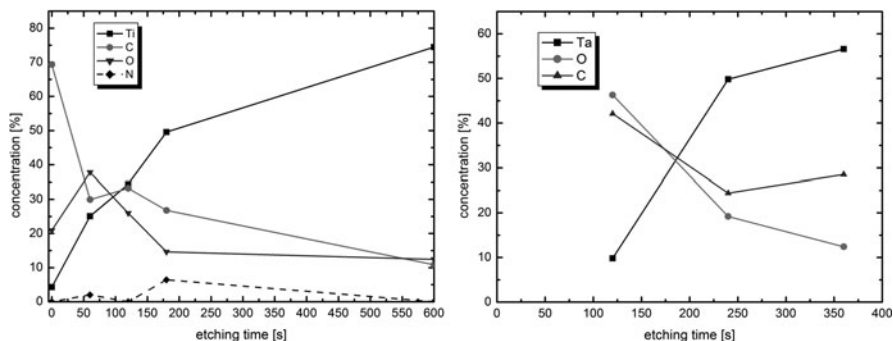


Fig. 10.14 Surface composition as a function of etching time for a Ti (*left*) and a Ta foil (*right*)

bombardment for a couple of minutes. However, this necessary surface etching can lead to significant artefacts, the most important of which are preferential sputtering/knock-on effects and ion induced damages.

Preferential Sputtering

Figure 10.14 shows the surface composition of pure Ti (left) and Ta foils (right) as a function of the etching time (3 keV Ar^+). Both samples had been stored for several years in air and were thus expected to be heavily contaminated with oxyhydrocarbon species (among others). Indeed the metal surface content without etching is very low. On a first view surprising is the fact that even prolonged Ar^+ etching does not lead to a pure metallic nature of the sample surfaces. This can be explained by the mechanisms of the sputtering effects taking place during the 3 keV Ar^+ etching process. The sputter yield depends on the masses of the elements involved. Sputtering is most effective for equal masses; in the cases discussed above Ar (40 amu) can easily sputter Ti (47.9 amu) and to a lesser extent also Ta (180 amu). But the light elements C (12 amu), N (14 amu) and O (16 amu) are “knocked-on” by forward sputtering deeper into the material by the heavier Ar^+ ions. These effects are known as preferential sputtering and knock-on effect.

Sputter Induced Damage

A second major effect which has to be taken into account is that the etching (although “mild” conditions are used) may lead to changes in the bonding environment of the samples to be investigated. An example stemming from our work with Ta_2O_5 films is shown in Fig. 10.15. It is well-known that ion etching of Ta_2O_5 films leads to the formation of suboxides at the film surface [63–65]. On the left side of Fig. 10.15 a Ta 4f spectrum of the same stoichiometric film as in Fig. 10.8 is shown

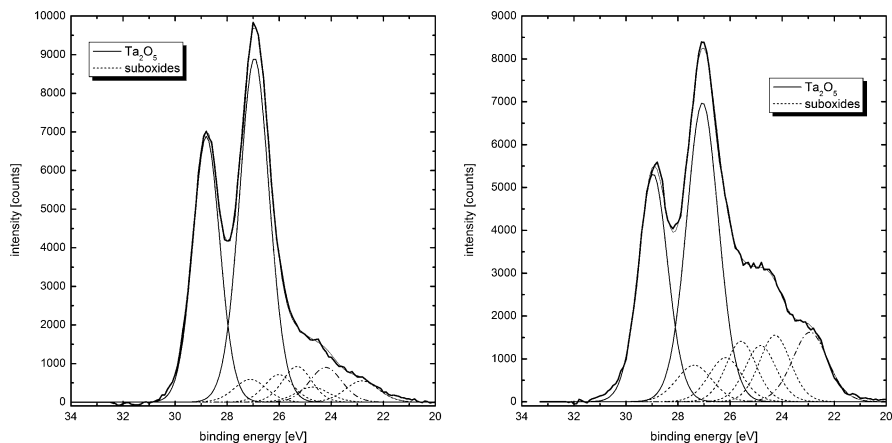


Fig. 10.15 Ta 4f spectra of a stoichiometric (*left*) and an understoichiometric Ta_2O_5 film (*right*) after 3 keV Ar^+ etching

but this time after 3 min 3 keV Ar^+ etching. Whereas for the unetched film only one of the typical Ta 4f doublets is present, there are at least four of these doublets present for the etched surface in Fig. 10.15, hinting at four different bonding states of tantalum, in contrast to only one for the unetched film. These additional states can be assigned to Ta suboxides which have been created by ion induced damage during the etching step.

On the right side of Fig. 10.15 the Ta 4f spectrum of an understoichiometric film is shown, also obtained after 3 min 3 keV Ar^+ etching. Again, there is a shoulder on the low energy side of the main peak hinting at the presence of suboxides at the film surface which is, however, much higher than that of the stoichiometric film. Therefore, as both films in Fig. 10.15 have been subjected to the same ion etching conditions it can be concluded that the understoichiometric film must have contained Ta suboxides already after deposition, in agreement with the results presented in section [Example 1: \$\text{Ta}_2\text{O}_5\$ films for waveguides in biosensors](#).

Conclusion

In this contribution, the importance of surface analytical techniques for the development of novel materials for modern biosensors has been highlighted. Emphasis has been laid on two most important methods, namely X-ray photoelectron spectroscopy and time-of-flight secondary ion mass spectrometry. Both techniques have unique advantages but also shortcomings. XPS is quantitative but has a limited concentration resolution; ToF-SIMS is not quantifiable but has an extremely high resolution almost down to the ppb region. Combined application using a thorough experimental design can thus lead to synergetic effects providing results not obtainable with a single techniques.

The possibilities of a combined application of XPS and ToF-SIMS have been demonstrated using three examples of materials important for biosensors and other biomedical applications, namely Ta₂O₅, TiO₂ and TiC/a-C nanocomposites. Finally, it was shown that – as for every experimental technique – also for surface analytical techniques care has to be taken in the interpretation of the results and artefacts must not be overlooked.

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Chapter 11

Nanovoids in Glasses and Polymers Probed by Positron Annihilation Lifetime Spectroscopy

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Abstract Nanovoids in As_2S_3 -based glasses (As_2S_3 , $(\text{As}_2\text{S}_3)_{85}\text{Ag}_{15}$, and $(\text{As}_2\text{S}_3)_{85}(\text{AgI})_{15}$), a polymer and a As_2S_3 -polymer nanocomposite were studied using the positron annihilation lifetime spectroscopy (PALS) technique. After computer treatment of the PALS data recorded, it was found that only two components τ_1 (short-lived) near 0.2 ns and τ_2 (long-lived) near 0.4 ns are resolved for the As_2S_3 -based glasses. At the same time, in the case of the polymer sample two components τ_2 near 0.3 ns and τ_3 (pick-off annihilation of *ortho*-positronium) near 2.8 ns were detected, while for the As_2S_3 -polymer nanocomposite three components τ_1 near 0.2–0.3 ns, τ_2 near 0.4–0.5 ns and τ_3 near 2.4 ns were established.

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The volume of nanovoids in the materials studied was determined, and the fractional free volumes of the As_2S_3 -polymer nanocomposite and the polymer matrix were compared. The results obtained are important to utilize As_2S_3 -based glasses and polymer nanocomposites for advanced sensor applications.

Keywords Chalcogenide glasses · Polymers · Nanovoids · Positron annihilation lifetime spectroscopy

Introduction

The concept of the free-volume structure of solids and subsequently the correlation between the free volume and the atomic structure and the physical properties of solids and its interpretation is a very useful and actual idea in the physics of disordered systems and especially of polymers [1]. Positron annihilation lifetime spectroscopy (PALS) is known as a powerful experimental tool for the investigation of free-volume defects in solids despite their structural hierarchy; it possesses a high sensitivity to the pore size in the range of 1–10 nm and is nondestructive. In the last few years, the study of the free volume using PALS has significantly increased for metals, polymers and topologically disordered materials (glasses, fine-grained ceramics, thin films). The method is based on the fact that the lifetimes of a positron and its bound form, positronium (Ps), is very sensitive to the presence of defects and structural inhomogeneities in the matrix. Thermalized positrons can be trapped and annihilated in vacancy-type defects with the surrounding electrons, giving information on the local electronic environment around the defects. The purpose of the present work is the investigation of nanovoids in As_2S_3 -based glasses, a polymer and an As_2S_3 -polymer system using the PALS technique.

Experimental

Preparation of As_2S_3 -Based Glasses

Bulk As_2S_3 -based glasses (As_2S_3 , $(\text{As}_2\text{S}_3)_{85}\text{Ag}_{15}$, and $(\text{As}_2\text{S}_3)_{85}(\text{AgI})_{15}$) were prepared by the conventional melt-quenching technique in evacuated quartz ampoules from appropriate mixtures of high purity precursors [2]. From the ingots, bulk samples in form of disks of about 1–1.5 mm thickness were cut and subsequently polished to yield high optical-quality surfaces for the measurements. To remove mechanical strains developed during synthesis, cutting and polishing procedure, the samples were annealed for 1 h at a temperature 20–30 K below the glass transition temperature. The amorphous state of the prepared samples was verified by XRD measurements.

Polymer Preparation

O,O'-bis(2-Aminopropyl)-polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol-500 (Jeffamine ED-600, Fluka) was dried under vacuum for 30 min. 3-Isocyanatopropyltriethoxysilane (ICPTES, Aldrich), tetraethoxysilane (TEOS, 98%, Aldrich) and n-butyl amine were used as received. 0.875 mmol of Jeffamine (535 μL) was added to 1.76 mmol of ICPTES (464 μL) in order to obtain a liquid ureasilicate monomer. Thereupon 1.05 mmol of TEOS (251 μL) and 300 μL of n-butyl amine were added to the mixture, which was kept under stirring for more than 10 min. The mixture was transferred into a plastic Petri dish and jellified under appropriate conditions. Then the obtained gels were heated in a vacuum furnace at 60°C at 0.1 Pa. A non-rigid, homogeneous and highly transparent stiff gel in form of a disk with a diameter of 40 mm and a thickness of 0.25 mm was obtained within 1 day. The schematic network of the polymer obtained is shown in Fig. 11.1.

As₂S₃-Polymer Nanocomposite Preparation

The starting materials for the preparation of As₂S₃ ingots were As (5 N) and S (5 N). The melting of the components was carried out in sealed quartz ampoules at 650°C and a residual pressure of 0.1 Pa. The melt was quenched to room temperature, and the obtained glassy samples were finely grounded in powder form and dissolved in n-butylamine. The final concentration of the As₂S₃ clusters containing solution was about 0.1 M. Incorporation of the chalcogenide phase was realized by mixing the preliminary obtained ureasilicate monomer with the chalcogenide nanoclusters, dispersed in the organic solvent. For this purpose 300 μL of freshly prepared As₂S₃ in n-butyl amine solution was added drop by drop to the mixture under vigorous stirring. The stiff gel was obtained as described above.

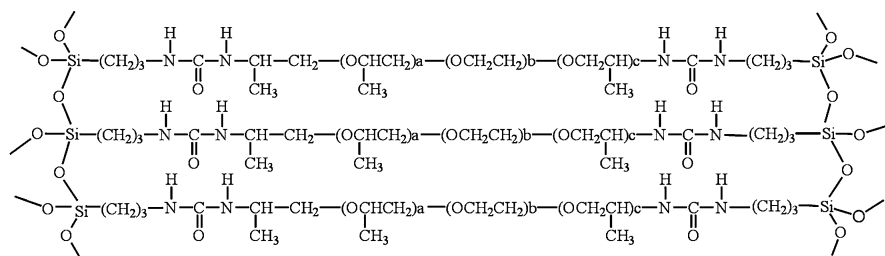


Fig. 11.1 Schematic representation of the organic-inorganic ureasilicate (ureasil) hybrid network

PALS Measurements

The PALS measurements were performed at room temperature using a conventional fast-fast coincidence system with an ORTEC spectrometer and radioactive ^{22}Na isotopes with an activity of 0.74 MBq, placed between two sandwiched samples, as a positron source. The time resolution of the system was 0.270 ns (full width at half maximum) as monitored using of the lifetime spectrum measured for a ^{60}Co source which seems to contain no positron yield, i.e. has no long-lived components. In general, each PAL spectrum was recorded with a total number of 10^6 counts, which is high enough to get a good analysis and repeated four to five times to check its reproducibility. The lifetime spectra were analysed using the LT-9.0 program of Kansy [3].

The best results of the mathematical treatment of the PAL spectra were obtained by resolving them into two lifetime components with characteristic lifetimes less than 0.5 ns (τ_1 near 0.2 ns and τ_2 near 0.4 ns; positron trapping modes) and a slight mixing of a third component with character lifetimes τ_3 near 1.9–3.0 ns (the so-called positronium decay modes). In all cases, the experimental errors did not exceed ± 0.01 ns in the lifetime data and $\pm 1\%$ in the intensity data. Each of the spectra measured was multiply treated owing to slight changes in the number of final channels, the annihilation background and the time shift of the spectrum. The variance of statistically weighted least-squares deviations between the experimental and theoretical data was taken into consideration. Assuming that the most optimal results deviate in the range from 0.95 to ~ 1.1 – 1.2 [4], only results with a deviation close to 1.0 were included for analysis. In such way, we obtained the number of PALS data (positron lifetimes τ_1 , τ_2 , and τ_3 and corresponding intensities I_1 , I_2 and I_3 , where $I_1 + I_2 + I_3 = 1$) which correspond strongly to the annihilation of positrons in the materials investigated.

Results and Discussion

Table 11.1 shows the values of the resolved lifetime components τ_i ($i = 1, 2, 3$) with relative intensities I_i obtained by the LT-9.0 computer program with two-component fitting, along with the component input $\tau_i I_i$ for the As_2S_3 -based glasses investigated, the polymer and the As_2S_3 -polymer nanocomposite. According to the two-state positron trapping model, the first PALS input component reflects mainly the structural specificity of a material and determines partly the average electron density distribution (or structural compactness) of the network examined, while the second one corresponds directly to more extended free-volume positron traps (free-volume defects, vacancy-like clusters, etc.) [4,5].

After the LT computer treatment of the PALS data recorded, it was found that only two components τ_1 (short-lived) near 0.2 ns and τ_2 (long-lived) near 0.4 ns are resolved for the As_2S_3 -based glasses (As_2S_3 , $(\text{As}_2\text{S}_3)_{85}\text{Ag}_{15}$, and $(\text{As}_2\text{S}_3)_{85}(\text{AgI})_{15}$) [6]. At the same time, in the case of the polymer sample two components

Table 11.1 Fitting parameters of the LT program describing the positron annihilation in the materials studied

Sample	Fitting parameters					
	τ_1 (ns)	I_1 (a.u.)	τ_2 (ns)	I_2 (a.u.)	τ_3 (ns)	I_3 (a.u.)
As ₂ S ₃	0.19	0.25	0.36	0.75	—	—
(As ₂ S ₃) ₈₅ Ag ₁₅	0.18	0.33	0.35	0.68	—	—
(As ₂ S ₃) ₈₅ (AgI) ₁₅	0.19	0.24	0.35	0.76	—	—
Polymer	—	—	0.31	0.81	2.8	0.19
As ₂ S ₃ -polymer	0.27	0.66	0.49	0.26	2.4	0.08

	Component input		
	$\tau_1 I_1$ (ns)	$\tau_2 I_2$ (ns)	$\tau_3 I_3$ (ns)
As ₂ S ₃	0.05	0.27	—
(As ₂ S ₃) ₈₅ Ag ₁₅	0.06	0.24	—
(As ₂ S ₃) ₈₅ (AgI) ₁₅	0.05	0.27	—
Polymer	—	0.25	0.53
As ₂ S ₃ -polymer	0.18	0.13	0.19

τ_2 near 0.3 ns and τ_3 near 2.8 ns were detected, while for the As₂S₃-polymer nanocomposite three components τ_1 near 0.2–0.3 ns, τ_2 near 0.4–0.5 ns and τ_3 near 2.4 ns were established.

One can clearly see that significant changes in the PALS parameters for the Ag/AgI-As₂S₃ investigated glasses have occurred for the Ag-containing alloy, as compared to the pure As₂S₃, whereas the AgI-containing alloy does not show such an effect. On the basis of PALS data it was established in Ref. [6] that hole-like defects with a volume larger than or comparable to the size of the Ag⁺ ions (18–20 Å³ [7]), but smaller than the size of the AgI clusters present in the structure of the host glass matrix As₂S₃; they form effective positron traps. In other words, the atomic volume of Ag⁺ ions (18–20 Å³) may be considered as a minimum size of open-volume defects corresponding to the defect-related component τ_2 near 0.4 ns in chalcogenide glasses.

In the case of the polymer and the As₂S₃-polymer nanocomposite, the component τ_3 related to the positronium (Ps) formation is typical for amorphous polymers [4]. *Positronium* is the bound state of a positron and an electron, having an atomic radius comparable to that of the hydrogen atom. Ps (e⁺, e[−]) exists in two spin states: one is called *para*-positronium (*p*-Ps) in which the positron (e⁺) and electron (e[−]) spins are antiparallel; the other state, *ortho*-positronium (*o*-Ps), corresponds to parallel particle spins. Positronium appears in the *para* and *ortho* spin states with a relative formation rate of 1:3, i.e. 25% *p*-Ps:75% *o*-Ps. Para-Ps annihilates with a lifetime $\tau_1 = 0.125$ ns in vacuum, while the triplet *ortho*-Ps with parallel spins has a lifetime $\tau_3 = 142$ ns in vacuum. In condensed matter, a positron in *o*-Ps predominantly annihilates during collisions with atoms and molecules, with an electron other than its bound partner and possessing an opposite spin. This process, the so-called *pick-off annihilation*, reduces the *o*-Ps lifetime τ_3 to a few nanoseconds. The *o*-Ps formation probability and lifetime are extremely sensitive to the electron

density of the immediate surrounding around the *o*-Ps. Thus, an *ortho*-Ps prefers surroundings with a low electron density, i.e. free volumes, and it cannot form in materials with a high electron density.

In polymers, the *o*-Ps localises in the space between and along the polymer chains and at the chain ends (free volume holes), and its lifetime gives an indication of the mean radii of these holes [8]. The well-known semi-empirical Tao-Eldrup (TE) equation is usually applied to estimate the size of free-volume voids in different polymer materials in the literature [1,8–11]. In the TE model the *o*-Ps particle resides in a spherical potential well, having an infinite potential barrier of radius R_0 . It is assumed that an electron layer forming a thickness ΔR is present on the wall of the hole, the effective radius of which is consequently $R = R_0 - \Delta R$, and that the lifetime of the *o*-Ps in the electron layer is the spin-averaged Ps lifetime of 0.5 ns. The relationship between the *o*-Ps lifetime τ_3 and the void radius R is the following:

$$\tau_3 = \tau_0 [\Delta R / (R + \Delta R) + 1 / 2\pi \sin (2\pi R / (R + \Delta R))]^{-1}, \quad (11.1)$$

where $\tau_0 = 0.5$ ns and $\Delta R = 0.166$ nm is the fitted empirical electron layer thickness. By fitting the above equation with the measured τ_3 values, the values of the hole radius R and the free volume size in a spherical geometry $V_f = (4\pi/3)R^3$ can be evaluated. The relative intensity of the longest component, I_3 , is generally correlated to the density of the holes, which can be considered as a kind of trapping centres for Ps. A semi-empirical relation taken from Ref. [8] can be used to determine the fraction of free volume (f_V) in polymers as

$$f_V = CV_f I_3, \quad (11.2)$$

where V_f is the free volume calculated from τ_3 with a spherical approximation, I_3 (in %) is the intensity of the respective component, and C is a constant.

Following Table 11.1, one can see that the component τ_3 is related to the pick-off annihilation of *ortho*-positronium, and the volume of voids in the polymer and the As₂S₃-polymer nanocomposite can be evaluated. By fitting Eq. (11.1) with the measured τ_3 values, one can estimate that the void volume V_f for the polymer sample is about 160 Å³ and for the As₂S₃-polymer sample about 125 Å³. The fractional free volume is proportional to $V_f \times I_3$, because C in Eq. (11.2) is constant. Hence, the fractional free volume $V_f \times I_3$ is found to be 3,040 a.u. for the polymer and 1,000 a.u. for the As₂S₃-polymer nanocomposite, i.e. the fractional free volume is reduced three times when As₂S₃ nanoclusters are added to the polymer matrix. Thus, we can assume that the As₂S₃ nanoclusters are randomly distributed in the polymer matrix in the places of low density fluctuations or free volumes. The density fluctuations present in the As₂S₃-polymer nanocomposite and the amorphous polymer are small volumes of about 125–160 Å³ as deduced by PALS in the present work, in good agreement with the literature data [8–11]. David et al. [12] came to similar conclusions, studying density fluctuations in amorphous systems using synchrotron radiation small angle x-ray diffraction (SAXS) and positron annihilation lifetime spectroscopy (PALS).

Finally, the results reported in this study on the minimum size of open-volume defects in chalcogenide glasses and the effect of a chalcogenide phase on the fractional free volume in polymer nanocomposites should be taken into account for progress in advanced applications of the investigated chalcogenide-based materials as active media for gas sensors [2], infrared sensors [13,14] and infrared biosensors [15,16].

Conclusions

The results obtained in this PALS study of nanovoids in As_2S_3 bulk glasses, a polymer and an As_2S_3 -polymer nanocomposite revealed that:

1. Only two components τ_1 (short-lived) near 0.2 ns and τ_2 (long-lived) near 0.4 ns are resolved for the As_2S_3 -based glasses (As_2S_3 , $(\text{As}_2\text{S}_3)_{85}\text{Ag}_{15}$, and $(\text{As}_2\text{S}_3)_{85}(\text{AgI})_{15}$); but in the case of the polymer sample two components τ_2 near 0.3 ns and τ_3 (pick-off annihilation of *ortho*-positronium (*o*-Ps)) near 2.8 ns are detected, while for the As_2S_3 -polymer nanocomposite three components τ_1 near 0.2–0.3 ns, τ_2 near 0.4–0.5 ns and τ_3 near 2.4 ns are established;
2. *o*-Ps is not detected in the As_2S_3 -based glasses studied, but it is clearly identified in the case of the polymer sample and the As_2S_3 -polymer nanocomposite;
3. The atomic volume of the Ag^+ ion ($18\text{--}20 \text{ \AA}^3$) can be considered as a minimum size of open-volume defects corresponding to the defect-related component τ_2 near 0.4 ns in chalcogenide glasses;
4. The density fluctuations that are present in the As_2S_3 -polymer nanocomposite and the amorphous polymer are small volumes of about $125\text{--}160 \text{ \AA}^3$ as deduced by PALS, in good agreement with literature data;
5. The fractional free volume $V_f \times I_3$ is determined to be three times lower for the As_2S_3 -polymer nanocomposite compared to the pure polymer;
6. The results reported on the minimum size of open-volume defects in chalcogenide glasses and the effect of a chalcogenide phase on the fractional free volume in polymer nanocomposites should be taken into account during applications of the investigated materials in sensor electronics.

Acknowledgments This work is partly supported by the Ministries of Education and Science of Ukraine and Bulgaria in the framework of the Bilateral Ukrainian-Bulgarian Cooperation on Science and Technology (2009–2010). One of the authors (TK) also gratefully acknowledges an International Visegrad Fund for the award of scholarship (Ref. No. 50810672) and Dr. M. Hyla and Prof. J. Filipecki for their kind assistance with the PALS set-up. K.K. and V.B. are grateful to the financial support of project BG051PO001/07/3.3-02/58/17.06.2008.

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Chapter 12

Detection of Structural Units of Nanocrystalline Diamond Surfaces Using Surface-Enhanced Raman Scattering

Miklos Veres, S. Tóth, E. Perevedentseva, A. Karmenyan, and M. Koós

Abstract The usability of different configurations of surface-enhanced Raman scattering (SERS) on nanocrystalline diamond was examined. SERS spectra were measured using gold colloid, a sputtered gold film and a patterned gold surface as SERS agents with near-infrared excitation, and the general features of the spectra were compared. The enhancement factor of the three methods was tested with monodispersed polymer particles as model materials. The highest enhancement was obtained for the patterned gold surface SERS agent.

Keywords Ultra-nanocrystalline diamond · Grain boundary · Surface-enhanced Raman spectroscopy

Introduction

Detailed surface characterization of nanocrystalline (NCD) and ultra-nanocrystalline diamond (UNCD) is of great importance for many emerging applications of these materials. While mechanical characteristics, adhesion and smoothness were the key parameters earlier [1, 2], when these materials were used as protective coatings, the utilization of their biocompatibility [3], surface chemistry [4], electrochemical [5] and other advantageous properties require the knowledge of their surface structure, preferably grain by grain, on the nanoscale.

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Versatile application possibilities of nanodiamonds are strongly related to their unique structure. In these materials the intergrain region between the diamond crystallites consists of an amorphous carbon phase, which is usually treated as or together with the surface region of crystallites (called grain boundaries). The entire nanodiamond film is build up of carbon atoms (and hydrogen): the diamond grains contain only sp^3 hybridized C atoms, while the amorphous carbon phase consists of both sp^3 and sp^2 hybridized carbon atoms. Because of their π bonds the latter are not randomly distributed in the matrix, but couple together, forming sp^2 “islands” (or clusters) surrounded by the “ocean” (or matrix) of sp^3 C atoms. These sp^2 clusters have π and π^* states much closer to the Fermi level than the σ and σ^* states of sp^2 and sp^3 hybridized carbon atoms, so they will determine the optical and electronic properties of nanodiamonds. The surface chemistry will also be controlled by the grain boundaries [6, 7]. This is the reason why the characterization of the grain boundaries, and particularly the bonding configuration of sp^2 carbon atoms here is so important. But since both grains and grain boundaries built of the same element which has a small volume and are, in addition, sandwiched between the crystallites, the realization of this task is rather difficult.

Raman Spectroscopy of NCD

Raman spectroscopy was found to be a very sensitive tool for the characterization of carbon-based materials, including nanocrystalline diamond [8–10]. Many macroscopic parameters are correlated with the features of the Raman spectrum. But because of the many crystallites falling into the probing volume, this method gives mainly generalized information on the nanodiamond structure.

In general, the Raman spectrum of nanocrystalline diamond consists of five bands, including one narrow peak at $1,333\text{ cm}^{-1}$ and four wide bands located around $1,150$, $1,350$, $1,450$ and $1,570\text{ cm}^{-1}$. The first of these peaks is assigned to the diamond grains (the narrow line), all others to the amorphous carbon (grain boundaries) [11, 12].

Because of resonant Raman scattering (a significant increase of the scattering cross-section when the excitation energy is close to the energy of a real electronic transition of the sample), the intensity of the bands related to sp^2 C clusters is a few orders of magnitude higher than that of the sp^3 C atoms in the matrix and in the diamond grains. The sp^2 C clusters in the structure have different sizes and topologies and thus different band gaps and characteristic vibrational frequencies (usually the larger the size of the cluster, the smaller is its band gap). Therefore, whatever (visible) excitation is used for the Raman measurements, it will excite resonantly a set of sp^2 clusters having band gaps close to the energy of the probing photons, and the spectrum will be dominated by the peaks of these structural units. Due to the different characteristic frequencies of the clusters their Raman peaks will overlap, resulting in broad bands. By changing the excitation wavelength, vibrations of a different set of sp^2 C clusters will be enhanced selectively.

Earlier we found [13, 14] that by using near-infrared excitation and lowering the excitation volume it is possible to suppress the broad bands of the amorphous phase in the Raman spectrum of nanocrystalline diamond and the characteristic peaks of the structural units on grain boundaries can be enhanced selectively. The method was found to work well for NCD samples with average grain size above 100 nm. It was shown also that for UNCD thin films with crystallite sizes below that limit these vibrations can be enhanced selectively using surface-enhanced Raman spectroscopy.

Experimental

Nanocrystalline diamond powder having average grain size of 10 nm and the gold colloid were purchased from Sigma-Aldrich, Klarite patterned gold surfaces from Renishaw Diagnostics. Monodisperse polymer particles were prepared using γ -radiation induced polymerization from diethylene glycol dimethacrylate (purchased from Sigma-Aldrich).

For the SERS measurements with the gold colloid the NCD powder was added to the colloidal gold (in aqueous solution) and sonicated in an ultrasonic bath for 10 min. In case of patterned surfaces the NCD crystallites were dissolved in distilled water by sonication for 10 min. After that the solution was dropped onto a Si wafer. The measurements were carried out after evaporation of the water. An island type gold film was sputtered on top of the NCD powder on a Si wafer. The sputtering time was 15 s.

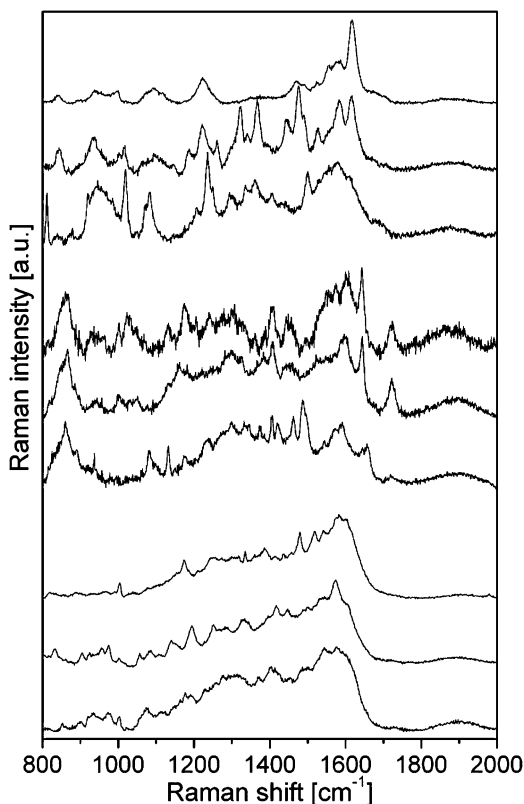
Raman spectra were recorded with a Renishaw 1000 Raman spectrometer attached to a Leica DM/LM microscope. The excitation beam was focused into a spot having a diameter of 1 μm . A diode laser operating at 785 nm served as excitation source. The integration time was 10 s.

Results and Discussion

Figure 12.1a compares typical near-infrared excited SERS spectra of NCD powder measured with colloidal gold, the patterned gold substrate and the sputtered gold configurations. The narrow peaks seen in the spectra indicate that the surface enhancement occurs in each configuration. The variation in the peak positions and intensities indicate that the method is highly sensitive to changes of the bonding configuration of the sample [13] (the spectra were taken at different points of the systems). The assignment of the bands was discussed earlier [13, 15].

The spectra recorded with colloidal gold and the patterned substrate show similar features: they contain narrow peaks sometimes appearing on the background of broad bands related probably to the amorphous carbon phase in the

Fig. 12.1 Typical SERS spectra recorded with a gold colloid (*upper three curves*), a patterned gold substrate (*three curves in the middle*) and sputtered gold (*lower three curves*)



sample. The background is more intense in the spectra measured with sputtered gold. It also has a different shape, possibly because of the amorphization of the nanodiamond structure during the sputtering process. The low relative intensity of the SERS peaks implies that the enhancement is lowest for this configuration.

To evaluate the enhancement and compare the different configurations more objectively, the SERS set-ups were tested also using monodisperse polymer particles. These polymer spheres were found to have a uniform size and structure; therefore their spectra are expected to be similar in different SERS configurations. The particle size was 200 nm, and the measurements were performed in places where only one particle fell into the excitation spot.

Figure 12.2a, b compare the as-measured and normalized SERS spectra of polymer particles with their normal Raman spectrum measured under the same conditions. The highest intensity was obtained when using the patterned surface (the enhancement ratio was found to be around 1,300), the lowest for the sputtered gold (the enhancement ratio was 40). The enhancement ratio with the gold colloid was around 350.

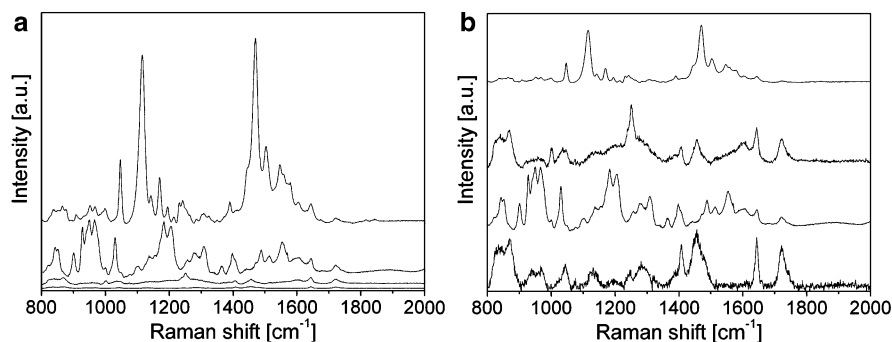


Fig. 12.2 (a) Normal Raman and SERS spectra of monodisperse polymer particles recorded in different configurations: (from bottom to top) normal Raman, with sputtered gold, with gold colloid and with patterned gold substrate. (b) Normalized spectra of (a)

Summary

Surface-enhanced Raman spectroscopic measurements with colloidal gold nanoparticles, a patterned gold surface and sputtered gold were performed on nanocrystalline diamond powder. All three configurations were found to be usable for this material. The enhancement of the different set-ups was compared using polymer particles. The highest enhancement was found for the patterned gold surface, the lowest for sputtered gold islands.

Acknowledgements This work was supported by Hungarian-Korean Intergovernmental S&T program KR-6/2009.

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Part IV

Sensor Materials

Part IV.1

Carbon-Based Materials

Chapter 13

Production, Purification, Characterization, and Application of CNTs

Aleksandar T. Dimitrov, Ana Tomova, Anita Grozdanov,
and Perica Paunović

Abstract Nanomaterials and nanotechnologies play a significant role in many fields of modern science: material science, chemistry, catalysis, molecular biology, and medicine. They exhibit novel, better physical and chemical properties than the bulk materials. This is a result of the change in the electronic structure, which is responsible for electroconductivity, optical absorption, chemical reactivity, catalytically activity and mechanical properties. The subject of this work is the production, characterization, purification and application of carbon nanotubes (CNTs).

Keywords Carbon Nanotubes (CNTs) · Purification · SEM · TEM · Raman · TGA

Introduction

Until 1985 only two types of all-carbon crystalline structures were known to the scientists, namely the naturally occurring carbon allotropes diamond and graphite. In 1985 Harry Kroto and his group from the University of Sussex carried out a set of experiments involving graphite vaporization by means of a high-power laser. Using mass spectrometry, they discovered a new allotrope of carbon, the fullerenes, with C_{60} as a dominant species. Fascinated by the work done by Kratschmer, Iijima set pursuit on a detailed high resolution transmission electron microscopy (HRTEM) study of the soot produced by their experiments. In 1991 he discovered that the hard, cylindrical residue, which formed on the graphite cathode after evaporation (usually discarded as waste), contained a whole range of novel graphitic structures. These new structures were later on named multi-wall carbon nanotubes. Almost 2 years

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after his discovery of MWCNTs, Iijima and his group discovered single-wall carbon nanotubes (SWCNTs), which are considered as the fundamental structure of CNTs as they consist of a single sheet of graphite rolled-up to form a cylinder which is then end-capped by a C_{60} hemisphere. The small diameter (nano-scale) and long length (micro-scale) of CNTs lead to such large aspect ratios that they can be considered as ideal one-dimensional systems. The nano-scale size of CNTs makes them the host of quantum effects which, combined with their symmetries, has led to their unique electronic, optical, magnetic and mechanical properties.

CNTs are mainly produced by evaporation of pure carbon by using strong energetic sources (electric arc, laser or solar heating) or by catalytic decomposition of hydrocarbons. The treatments that are used for their production are rather expensive and not very productive.

The large scale use of CNTs is still limited due to the high production costs and the low productivity. The use of CNTs requires a production method that combines growth control with low costs and scalability. The method we proposed recently (Dimitrov, Fray, and Schwandt) based on electrolysis of molten salts, is considered as a more advantageous and economical method when compared with arc-discharge, CVD and laser ablation methods due to the lower cost of energy, the set-up simplicity required and the large scale production of CNTs.

Because their unique mechanical electrical and thermal properties, CNT are identified as possible components in various applications, including nano-electronics devices, tips for scanning probe microscopes, power applications, field emitters, and sensors, amongst other.

Carbon

Carbon was discovered in prehistory and was known to the ancients. The allotropes of carbon are the different molecular configurations that pure carbon can take. The three relatively well-known allotropes are amorphous carbon, graphite and diamond. Several exotic allotropes have also been synthesized or discovered, including fullerenes and carbon nanotubes.

Graphite

Graphite is a conductor and can be used as material for the electrodes of an electrical arc lamp, or as the lead in pencils. Each carbon atom is covalently bonded to three other surrounding carbon atoms. Each carbon atom possesses a sp^2 orbital hybridization (Fig. 13.1). The π -orbital electrons delocalized across the hexagonal atomic carbon sheets of contribute the conductivity of graphite.

Fig. 13.1 sp^2 orbital hybridization within the carbon atom

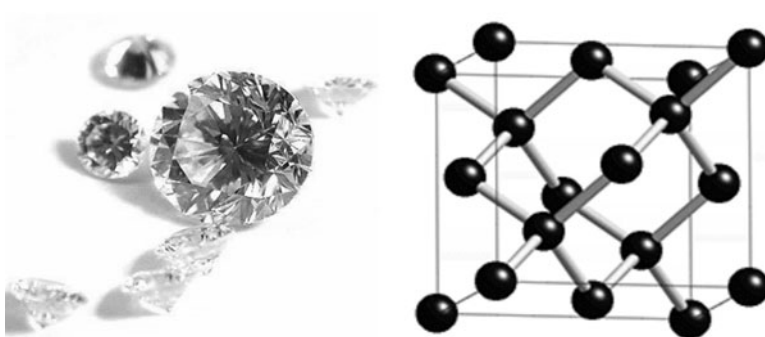
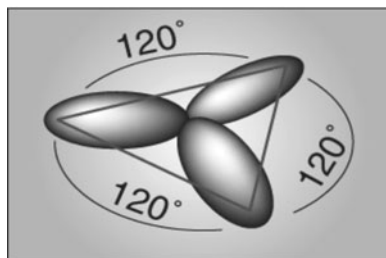


Fig. 13.2 Crystalline structure of diamond

Diamond

Diamonds typically crystallize in the cubic crystal system and consist of tetrahedrally bonded carbon atoms (Fig. 13.2). The tetrahedral arrangement of atoms in a diamond crystal is the source of many of diamond's properties; graphite has a rhombohedral crystal structure; as a result shows dramatically different physical characteristics—contrary to diamond, graphite is a very soft, dark grey, opaque mineral.

Fullerenes

The molecule on the stamp in Fig. 13.3 is a “fullerene” molecule called C_{60} , created from 60 carbon atoms arranged in the same structure as a football. This was first discovered by a group of scientists from the US and Sussex University in the 1980s, and in 1996 Professor Sir Harry Kroto from Sussex received the Nobel prize for the discovery. After balls came tubes of carbon, and the nanotech revolution began.

Fig. 13.3 The stamp with application of fullerene molecule (C₆₀)



Carbon Nanotubes

Carbon nanotubes, discovered by Iijima [1], are supposed to be a key component of many technologies because of their outstanding structural, mechanical and electronic properties. Almost every week a new potential application of CNTs is identified. They are finding applications in molecular electronics, chemical sensors, scanning probes and special capillaries. Furthermore, CNTs have a great potential to be used as fillers in polymer composites replacing carbon fibers and carbon blacks. Several applications for CNTs have been suggested in energy production and energy storage devices [2–5]. They also could be used as an electrode material in lithium ion batteries, as an electrode material in electrochemical capacitors or as a support material for electrocatalysts used in fuel cells.

At the present time, nanotubes are fabricated by various methods which are generally expensive and provide a low yield of material. The main routes currently used in the production of carbon nanotubes are: (1) electric arcs and lasers, (2) catalytic decomposition of hydrocarbons over a transition metal (e.g. acetylene over Fe), and (3) electrolysis in molten salt [6,7].

In 1995, Hsu and co-workers discovered one of the most promising ways of producing carbon nanotubes [8,9]. They electrolyzed molten lithium chloride using graphite electrodes. The cathode eroded during the electrolysis, and nano-scaled products including multiwalled nanotubes (MWCNTs) were found in the electrolyte.

Chen et al. [10,11] connected the erosion of the cathode and the formation of the products with the intercalation of alkali metals into graphite. This was further extended by Fray [12,13] who realized that the cathodic carbon/graphite erosion was similar to that found in the Hall-Heroult cell where alkali metals also intercalate into graphite.

Dimitrov et al. [14] reported that the constant voltage electrolysis, as opposed to the constant current electrolysis, which had been applied in most previous cases, could improve and increase the yield of CNTs produced.

Structure of CNTs

Discovered by the electron microscopist Sumio Iijima in 1991, these ‘molecular carbon fibres’ consist of tiny cylinders of graphite, closed at each end with caps which contain precisely six pentagonal rings. There are three possible high symmetry structures for nanotubes, known as ‘zig-zag’, ‘armchair’ and ‘chiral’. The terms ‘zig-zag’, ‘chiral’ and ‘armchair’ refer to the arrangement of the hexagons around the circumference. They are illustrated in Fig. 13.4. In practice, it is believed that most nanotubes do not have these highly symmetric forms but possess structures in which the hexagons are arranged helically around the tube axis. Experimentally, the tubes are generally much less perfect than the idealized forms shown in Fig. 13.5, and may be either multilayered or single-layered.

Nanotubes range in length from a few tens of nanometers to several micrometers, and in outer diameter from about 2.5 nm to 30 nm. Usually, they consist of one or more tubes of graphite carbon. The ends of the tubes are usually capped. Single-walled carbon nanotubes (SWCNTs) are formed from one tube; they often aggregate together in bundles of several tens of nanotubes. Multi-walled carbon nanotubes (MWCNTs) consist of two or more graphitic layers concentrically stacked with a common longitudinal axis, as in a Russian doll (Fig. 13.5).

The distance between the layers in a MWCNTs is ~ 3.4 Å, similar to the interlayer spacing in graphite. MWCNTs typically have between 2 and 50 layers. SWCNTs can be found individually dispersed in bundles (or ‘ropes’) containing approximately 3–100 SWCNTs. Typically, the nanotubes in the bundles vary in helicity but occasionally all the nanotubes within a bundle are of the same helicity.

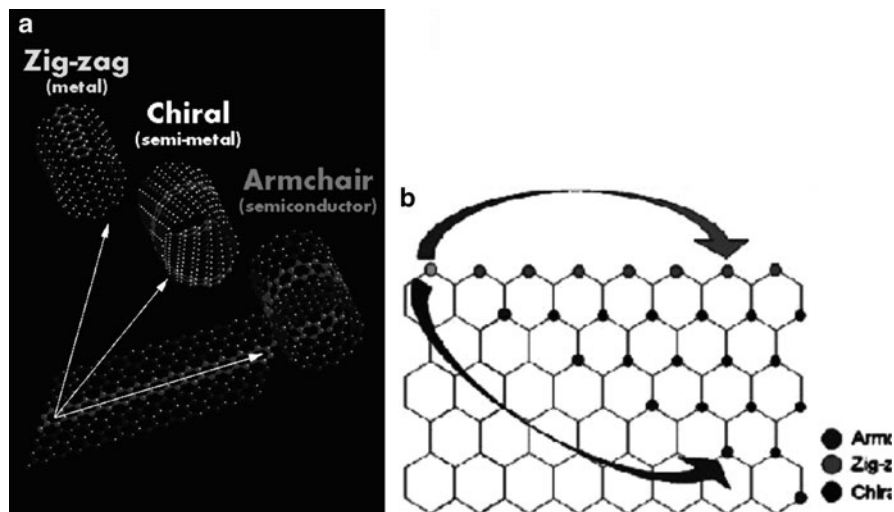


Fig. 13.4 (a) Zig-zag structure, chiral structure and armchair structure; (b). The graphene sheet can be rolled more than one way, producing different types of carbon nanotubes [15]

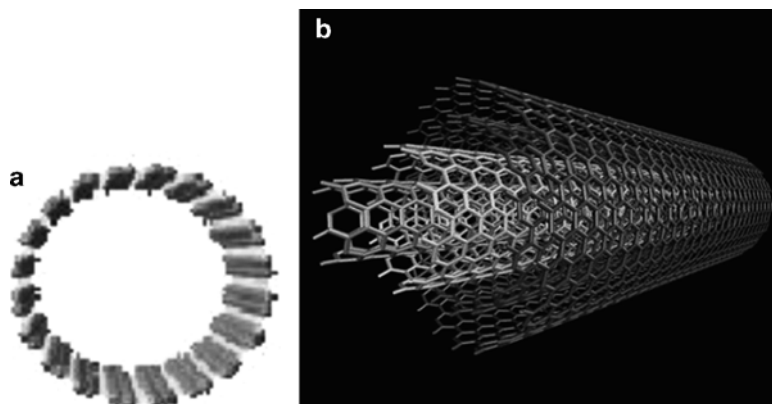


Fig. 13.5 (a) Single-walled and (b) Multi-walled carbon nanotubes

Properties of CNTs

Carbon nanotubes are a very promising material in wide field of applications. They are strong, stiff, and electrically conductive. After they were discovered, extraordinary mechanical and electrical properties were predicted theoretically. Experimental measuring of the properties of CNTs is difficult. But novel techniques like scanning probe microscopy improved and facilitated this.

The investigated mechanical properties were the Young's Modulus E , the breaking stress $\sigma\chi$, and changes in structure under large strain. The results obtained from different testing techniques showed that the Young's Modulus of SWCNTs and MWCNTs is in the range of 0.1–5 TPa and 0.5–1 TPa, respectively. It should be pointed out that the Young's Modulus may vary for MWCNTs produced and prepared by different methods. This is because different production methods may cause different lattice defects in CNTs.

The electronic properties of CNTs may also vary depending on the diameter and structure of the CNTs. Because of that, nanotubes can be either metallic, a narrow band-gap semiconductor or a moderate band gap semiconductor.

It is well known that diamond and graphite have the highest thermal conductivities of all materials at moderate temperatures. A high thermal conductivity was therefore also expected for CNTs.

Heat conduction experiments show that the thermal conductivity of CNTs increases with temperature. A highly-aligned SWCNTs rope has a thermal conductance of $\sim 250 \text{ Wm}^{-1}\text{K}^{-1}$ while for an unaligned SWCNTs rope it is $\sim 30 \text{ Wm}^{-1}\text{K}^{-1}$ at room temperature. Further experiments showed that MWCNTs have a thermal conductance of only $28 \text{ Wm}^{-1}\text{K}^{-1}$ [16].

Production Methods of CNTs

At the present time, nanotubes are made by various methods which are generally expensive and provide low yields of the material. All the production methods for carbon nanotubes involve breaking down a source of carbon and then reforming the carbon into nanotubes.

The following section outlines the main routes currently used in the production of carbon nanotubes (chemical vapor deposition, arc-discharge and laser ablation) and the electrolysis in molten salts.

Arc Discharge

The most widely used technique to produce nanotubes is the electric arc discharge, the same method as is used to prepare fullerene molecules. Notably, carbon nanotubes were firstly discovered in the examination of fullerene materials produced by the arc technique [1]. A variety of different arc-evaporation reactors have been used for the synthesis of nanotubes. A typical example is illustrated in Fig. 13.6.

The principle of this method is based on an electric arc discharge generated between two graphite electrodes under an inert atmosphere of helium or argon. The high temperature occurring between the two rods during the process allows the sublimation of carbon.

In short: The chamber must be connected both to a vacuum line with a diffusion pump and to an inert gas supply. A continuous flow of inert gas at a given pressure is usually preferred over a static gas atmosphere. The pressure of gas is 0.6–0.8 atm. The electrodes are made from graphite. The anode is 6–10 mm in diameter, the cathode twice the diameter of the anode. The distance between the electrodes is 1–3 mm. Efficient water-cooling of the cathode is very important in producing good quality nanotubes, and the anode is also frequently cooled. The position of the anode should be adjustable from outside the chamber, so that a constant gap can be maintained during arc-evaporation. The current depends on the diameter of the

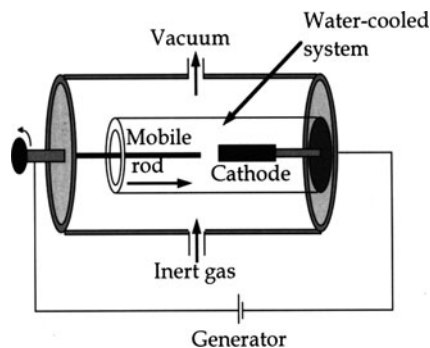


Fig. 13.6 Schematic illustration of an arc-evaporation apparatus [17]

rods, their separation, the gas pressure and so on, but is usually in the range 50–100 A. The voltage applied is between 25 and 50 V. The plasma formed in between the electrodes has a temperature of 3,700°C, and the current density at the surface of the anode is 150 A cm⁻².

The electric-arc process allows the production of SWCNTs and MWCNTs at the same time. These tubes are often covered with amorphous carbon which contains metallic particles in the case of metal/carbon co-evaporation. The yield of nanotubes is not very high, whereas with the laser ablation method the yield is much higher, but the quantities are still small. The shape and composition of the deposit which forms on the cathode following arc-evaporation depends strongly on the conditions used.

Laser Ablation

A second very useful and powerful technique for producing carbon nanotubes is the laser ablation method. The method is very similar to the arc-vapor method. A piece of graphite is vaporized by laser irradiation under an inert atmosphere. Historically, laser ablation was the first technique used to generate fullerene clusters in the gas phase. Figure 13.7 shows a laser oven apparatus used to make CNTs.

Carbon is vaporized from the surface of a solid disk of graphite into a high-density helium (or argon) flow, using a focused pulsed laser. A graphite target is placed in the middle of a long quartz tube mounted in a temperature-controlled furnace. After the sealed tube has been evacuated, the furnace temperature is increased to 1,200°C.

The tube is then filled with a flowing inert gas and a scanning laser beam is focused onto the graphite target by way of a circular lens. The laser vaporization

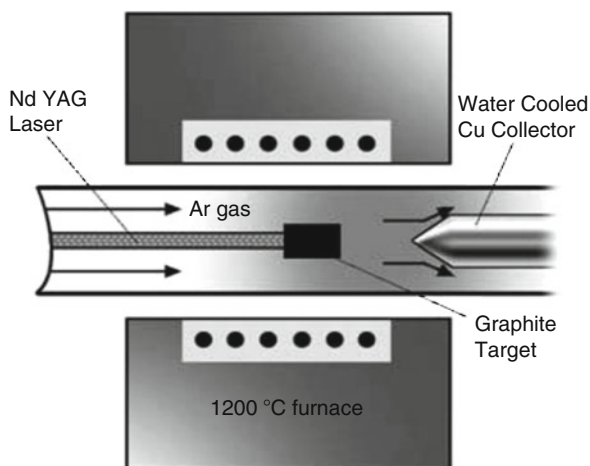


Fig. 13.7 Schematic illustration of a laser oven apparatus [8]

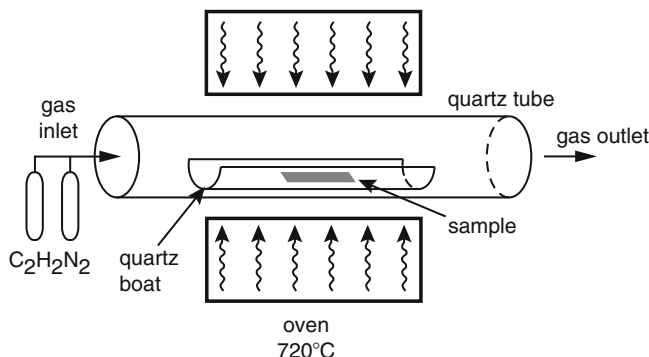


Fig. 13.8 Schematic illustration of the catalytic vapor method [17]

produces carbon species, which are swept by the flowing gas from the high-temperature zone and deposited on a conical water-cooled copper collector. As with the arc-vapor method, a pure graphite target will produce MWCNTs but mixed graphite-metal target will produce SWCNTs.

Chemical Vapor Deposition (CVD)

The catalytic vapor method is illustrated in Fig. 13.8. Generally the production is carried out in a flow furnace at atmospheric pressure. The production of CNTs by this method is very effective and enables the production of both, MWCNTs and SWCNTs. The catalyst is placed in a ceramic boat which is put into a quartz tube. A hydrocarbon is reacted with a metal catalyst at moderate temperatures. The production can be carried out either in a single zone furnace or in a two-zone furnace.

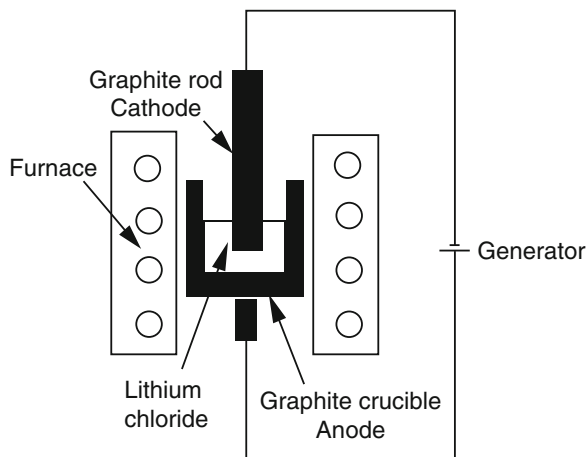
Using a two-zone furnace, the catalyst precursors and/or hydrocarbon are vaporized in the first stage and then swept by a carrier gas to the second stage where the MWCNTs are formed. The reaction temperature is typically 600–900°C; the hydrocarbon used are acetylene, benzene, ethylene, methane or xylene diluted with Ar, N₂ or H₂ [18,19].

The purity of MWCNTs depends on the elements used as the catalyst, the preparation of the catalyst and the temperature of the reaction.

Molten Salt Electrolysis

An electrochemical method for the synthesis of multiwalled nanotubes was described by the Sussex group. It involved the electrolysis of molten lithium chloride using a graphite cell in which the anode was a graphite crucible and

Fig. 13.9 Schematic illustration of the molten salt electrolysis method [17]



the cathode a graphite rod immersed in the melt. It was the first example of producing CNTs in a condensed phase [8]. The method is presented in Fig. 13.9.

The nanotubes are formed by passing a constant current through a molten alkali metal salt using graphite electrodes. The cathode erodes during the electrolysis and CNTs form within the electrolyte. The carbonaceous material produced was found to contain large amounts of rather imperfect multiwalled nanotubes which are similar in appearance to catalytically formed tubes. This method can produce MWCNTs with diameters of 10–50 nm and lengths of 100 nm–20 μm [10]. As yet, no SWCNTs have been produced using this method. The highest purity obtained by this method is 50 vol% [10].

A wide range of other nanoparticles are also produced. These include carbon fibres, encapsulated particles, amorphous carbon and tambourines [9,10].

Hsu et al. [20] reported later that the electrolytic method could also be used to make carbon coated metal nanowires by adding a low melting temperature metal or salt in small concentrations to the electrolyte. For example, SnCl_2 added to LiCl resulted in the production of nanotubes filled with Sn. Thus, the technique could be proven to be a useful method of preparing filled carbon nanostructures.

The Mechanisms of CNTs Formation by Molten Salt Electrolysis

Several mechanisms have been suggested for nanotube formation in the high temperature production routes introduced above. The common basis of these mechanisms is the formation of carbon dimers and trimers on vaporization which combine and form a graphitic structure. These structures include pentagonal rings, which allow the formation of the end caps of the nanotubes, from which the nanotubes grow. The hypotheses then diverge: one proposes that nanotubes grow from a closed fullerene by addition of carbon species into the existing

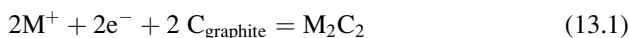
graphite structure, the other that the nanotubes grow with one end open. The latter is now favored, especially as simulations have shown that there is bonding between the graphitic layers at the open ends of MWCNTs [21]. This could stabilize the open end during growth, while its high chemical activity would facilitate addition of carbon species to the tube.

The conditions for nanotubes formation in molten salt electrolysis are radically different from those in the high temperature methods. The erosion of the cathode has to be a source of carbon used for the formation of nanotubes. In the literature there are two possible causes of this erosion, chemical attack and intercalation.

Oxidation Mechanism

The theory of oxidation mechanism was proposed by Hsu et al. [20]; it is shown in Fig. 13.10.

First step: Reduction of alkali ions and dissolution of graphite into the salt and formation of carbides:



Second step: Entrance of the carbides into the electrolyte, their oxidation by chlorine gas generated at the anode, and formation of graphitic carbon and releases of the alkali metal.



Third step: Electrons can transfer through the conducting graphite layer to the encapsulated carbide, and chlorine can oxidize the carbide inside the particle through the graphite. Thus, oxidation forms more graphite layers, creating the inner wall of the nanotubes.

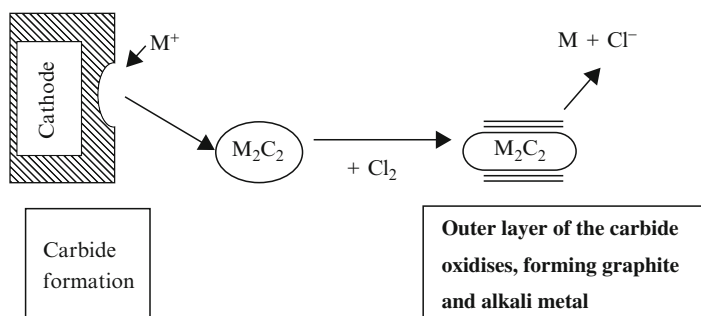


Fig. 13.10 The oxidation mechanism for nanotubes (Adapted from [20])

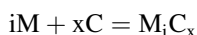
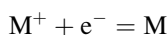
Fourth step: After deposition of graphite onto the surface the M_iC_x is extruded forming a fresh surface for graphitisation. The growth of the nanotubes continues with more carbide particles joining the nanotubes and being then oxidized.

Intercalation Mechanism

Chen et al. [11] proposed a theory based on the decomposition of M_xC_y species. In this case the intercalation of alkali metals into the graphite layer structure of the cathode causes the observed erosion [16].

The mechanism is shown in Fig. 13.11 and summarized below:

- Intercalated alkali metal atoms react with the graphite cathode to form carbide or graphite intercalation compounds.



$$x \geq i \geq 2$$

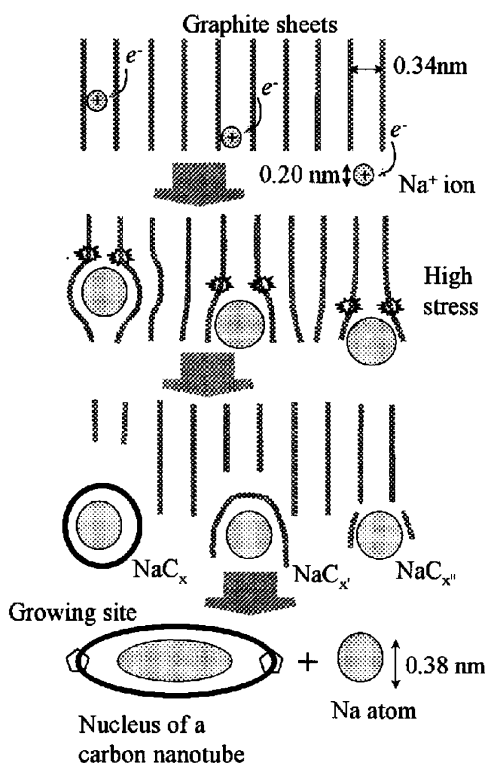


Fig. 13.11 The intercalation mechanism for nanotubes (Adapted from Chen [11])

- The fast and continuous intercalation of the alkali metal into the layered structure of graphite leads to an expansion and disintegration or erosion of the cathode. This causes the formation of a metastable M_iC_x compounds.
- These compounds will then combine in the molten salt to produce the nucleus of a nanotubes, with a simultaneous release of the alkali metal from the compound. It is suggested that this occurs as the M_iC_x compounds tend to regain the more stable graphite structure.

It is proposed that only M_iC_x compounds tend to adopt the more stable graphite structure. It is also believed that only M_iC_x compounds with particular values of i and x will behave in this way.

Nano-Nozzle Mechanism

An alternative mechanism was proposed by Hsu et al., involving the formation of nanotubes at the cathode via a carbide ‘grid’ [22]. The mechanism is illustrated in Fig. 13.12.

First step: Reduction and deposition of alkali atoms at the cathode surface.

Second step: Electrodeposited metal combines with carbon at the cathode surface and forms carbides.

Third step: The alkali carbides form an array which acts as a grid. The grid is composed of small crystallites, which are in a ‘quasi-fluid state’ at the temperature of electrolysis. This allows carbon atoms from the cathode to pass through the crystallites via the d-spacings.

Fourth step: Order is imposed on the incoming carbon atoms by their passage through the array. The ordered carbon atoms aggregate on the outside of the crystallites to form nanotubes, and the nanotubes formed extrude from the surface.

Kaptay Mechanism

Kaptay et al. did research on the molten salt electrolysis to produce CNTs. They use the intercalation mechanism of sodium into the cathode to explain the formation of the species observed [23]. They proposed a mechanism of formation of nanotubes as summarized below:

First step: Deposition of alkali or alkaline earth metals at the graphite/molten salt interface.

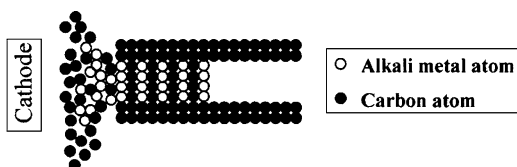


Fig. 13.12 The nano-nozzle theory (Adapted from [22])

Second step: Diffusion of these metals into the space between the graphite layers. The driving force of fast diffusion is the formation of stable intercalation compounds.

Third step: Intercalated atoms cause mechanical stress and the ablation of one or several graphite layers from the bulk graphite. These graphite layers will be suspended in the molten salt and sooner or later rearrange to form tubes.

Purification and Functionalization of CNTs

The carbon nanotubes could be contaminated with catalyst particles, carbon clusters and smaller fullerenes (C_{60}/C_{70}). There are several techniques for purification: (1) removal of the catalyst by acidic treatment (+ sonication), thermal oxidation or magnetic separation (Fe); (2) removing of small fullerenes by micro filtration or extraction with CS_2 ; and (3) removal of other carbonaceous impurities by thermal oxidation, selective functionalization of nanotubes or by annealing.

Also, for CNTs it is very important to be pretreated and functionalized before they are applied. In order to make the dispersion in liquids easier, it is necessary to physically or chemically attach certain molecules, i.e. functional groups, to the carbon nanotubes.

Methods for functionalizing are cutting, oxidation, wrapping etc. For biological purposes, carbon nanotubes can be functionalized with lipids, proteins or biotins.

Application of CNTs

Due to their unique electrical, mechanical and chemical properties CNTs are a very promising material. Many applications have been proposed for carbon nanotubes and CNT composites (Fig. 13.13).

Their chemical stability, high thermal conductivity and high mechanical strength are beneficial properties. They are ideal for field emitters due to their small diameters and high aspect ratio, the main interest being their use in flat screen displays.

Furthermore, CNTs have a great potential to be used as fillers in polymer composites. They could replace carbon fibers used for mechanical reinforcement and carbon blacks used for anti-static applications. A major advantage of the nanotubes is their process ability. They could also be used as filler in electrically conducting polymers, and more recently they have been successfully used as fillers in conducting epoxy polymers and polyvinyl alcohol (PVOH) matrices. This increases the mechanical strength and electrical conductivity of the polymer. The high stiffness and breaking stress of nanotubes make them suitable for high performance composites.

Several applications for CNTs have been suggested in energy production and storage. The development of fuel cell systems for transport applications may

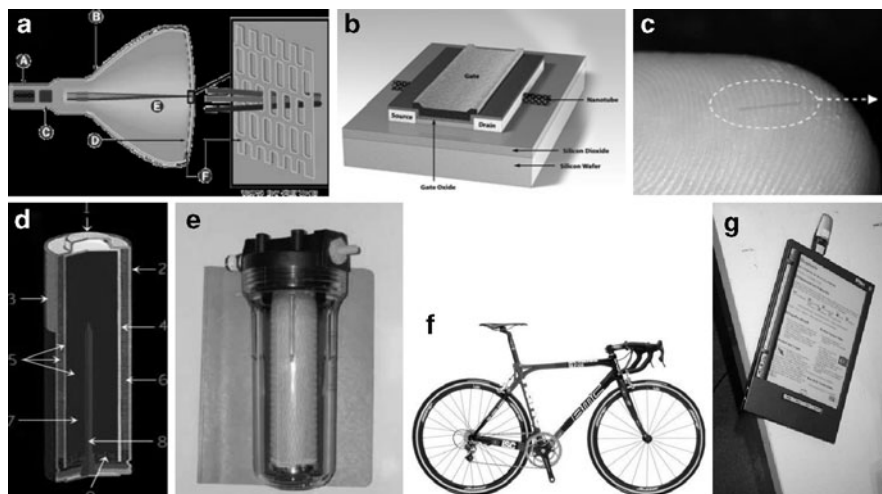


Fig. 13.13 Different applications of CNTs

require the storage of hydrogen. In particular, fuel cells could replace combustion engines in vehicles. Adsorption of hydrogen onto a porous material provides a safer and more compact system than the storage of gaseous hydrogen. The hydrogen storage of 6.5 wt% at reasonable pressures and temperatures is the target set by the U.S. Department of Energy for the technology to be useful [24]. Carbon nanostructures are a potential storage medium because hydrogen can be absorbed on their surface and possibly intercalate into their interlayer spacing [25].

CNT composites could be used as electrode materials in lithium ion batteries, where the intercalation of lithium ions into the electrode materials is required. They could also be used as electrode materials in electrochemical capacitors, which require very high specific surface area materials.

Finally, CNTs could be used as individual molecules in components of miniaturized electronic devices.

Production of CNTs by Electrolysis in Molten LiCl

MWCNTs were produced in an alumina crucible as the container of the molten salt electrolyte. Commercial graphite rods (type EC4) were used as an anode and cathode material [14]. Molten LiCl was used as the electrolyte.

The cell was used inside a sealable Inconel tube reactor with a water-cooled jacket heated to 1,600°C by a vertical Lenton furnace which was equipped with a programmable controller.

The samples extracted from the solidified electrolytes were inspected by scanning electron microscopy (SEM), using a JEOL 6340F (10 kV), transmission electron

microscopy (TEM, JEOL 200CX, 200 kV), thermogravimetric analysis (TGA), and Raman spectroscopy (Renishaw Ramascope 1000).

SEM and TEM Analyses

Electron microscopy was mainly used for identifying and evaluating different constituent and the concentration of CNTs in the products. In general, the products obtained surprisingly contain a large quantity of MWCNTs, more than 80%. The morphologies of the products obtained by electrolysis in molten LiCl are very similar to those reported previously [8–11,14]. Figure 13.14 shows low and high magnification SEM images, respectively, of the CNTs obtained by electrolysis at a constant overpotential.

Furthermore, the TEM images in Fig. 13.15 also show CNTs produced under the same conditions. The material was found to be aggregated with the aggregates always containing nanotubes and nanoparticles.

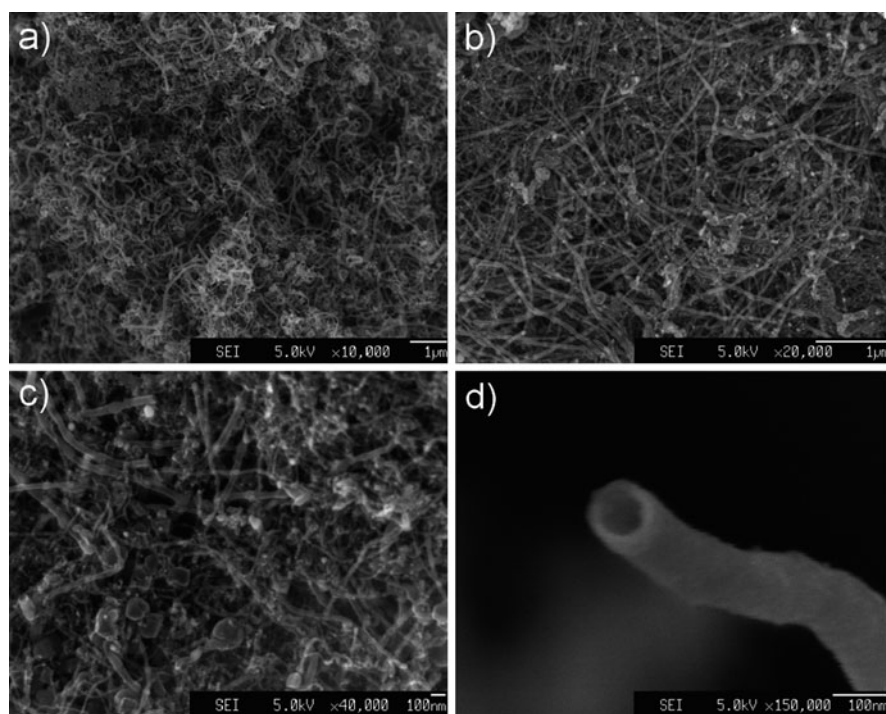


Fig. 13.14 EM images of CNTs produced by electrolysis in molten LiCl. Magnification: (a) $\times 10,000$; (b) $\times 20,000$; (c) $\times 40,000$; and (d) $\times 150,000$

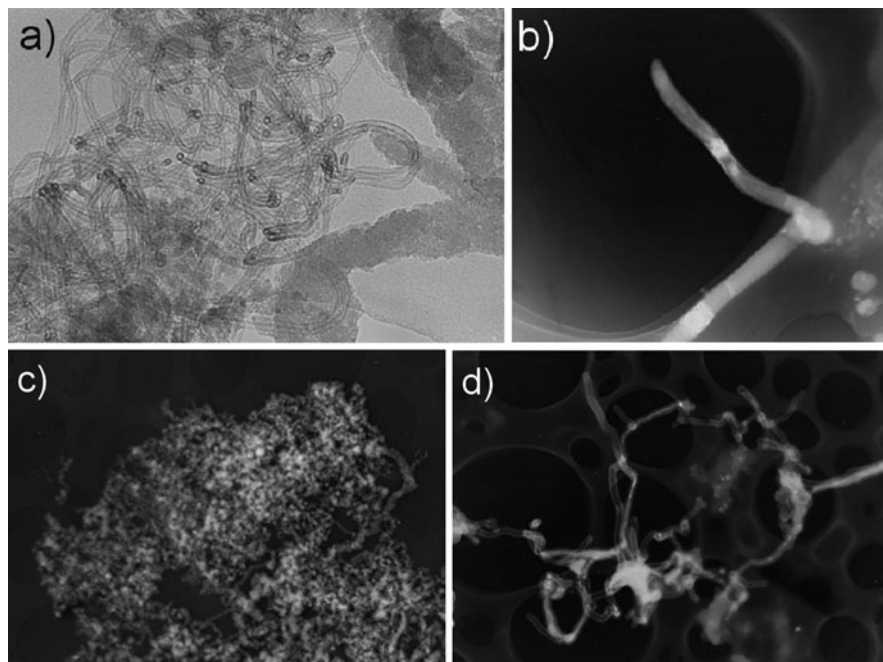


Fig. 13.15 TEM images of CNTs produced by electrolysis in molten LiCl

As one can see the nanotubes are highly entwined, similar to the nanotubes produced catalytically using a floating catalyst. The SEM and TEM observations also show that the nanotubes could stretch between two separate aggregates, with one end in each of them. But normally a great deal of them start and end in the same aggregate with some exceptions curving out of the aggregates.

Typically, the observed samples show that most of the examined carbon nanotubes are curved and multiwalled (Fig. 13.14); their sizes range between 50 nm and 3 μm in length and 10–80 nm in diameter. In addition to nanotubes, the other constituents in the product were some aggregated carbon nanoparticles and some small pieces of non-reacted graphite particles.

The TEM observations in Fig. 13.15 show that some of these tubes and particles contain foreign materials. These fillings could be either lithium or lithium carbide, if the latter is formed. The images also show that most of the material (more than 80%) are MWCNTs. There are small amount of impurities, as metal particles, carbon fibers, amorphous carbon structures, and impurities originating from the salt.

Single walled carbon nanotubes (SWCNTs) were not found in the material produced and inspected during this study. This fact may lead to the conclusion that under those circumstances the production of SWCNTs is not possible.

The SEM and TEM images presented in Figs. 13.14 and 13.15 also show that the yield of the MWCNTs is very high. In comparison with our first results

reported in our previous paper [14], the results presented in this study show that the yield of carbon nanotubes is more than three times higher.

Thermogravimetric Analysis

Thermogravimetric analysis includes heating the raw graphite material and carbon nanotube samples produced by electrolysis in molten salt under oxygen flow, thus oxidizing the various components at different temperatures. TGA analysis of the thermal stability of the carbon nanotubes is a good measure for the determination of the overall quality of the carbon nanotubes obtained.

The TGA thermograms are presented in Figs. 13.16 and 13.17, where the blue lines show the weight loss as a function of temperature from 0°C to 1,200°C; the green lines are the corresponding differential thermal analysis (DTA) curves. Since the DTA curves directly reflect variations in the weight with temperature, we will focus on them.

The DTA curve obtained when commercial EC4 graphite was heated under oxygen flow shows two peaks at about 500°C and 950°C indicating that the oxidation process of the graphite consist of two stages. The DTA curve obtained when a carbon nanotube sample produced by electrolysis in molten salt was heated under oxygen flow, shows that the process of thermal oxidation occurs also at two stages, and with peaks at 450°C and 720°C (Fig. 13.17).

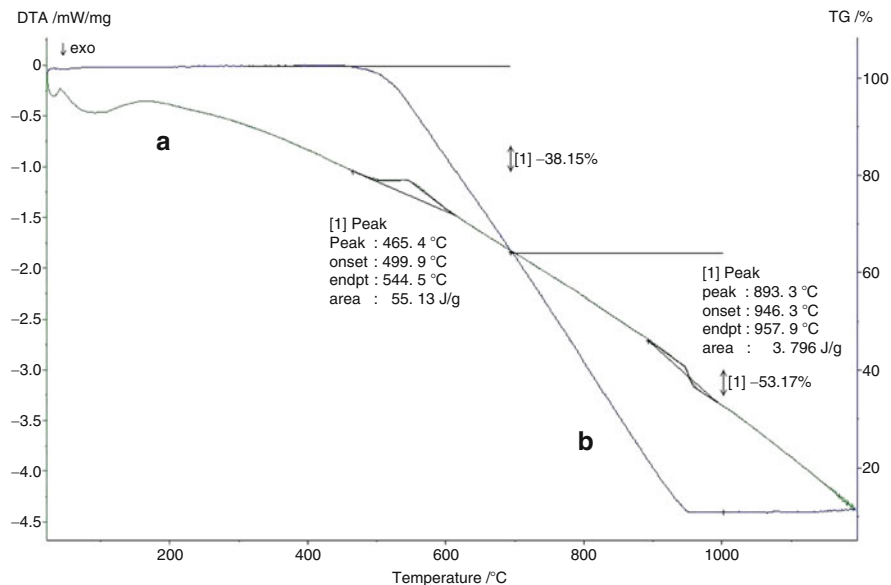


Fig. 13.16 Thermogravimetric analysis of a graphite sample obtained for the commercial graphite used as a cathode. *a*-line: data obtained by differential thermal analysis. *b*-line: weight loss as a function of temperature

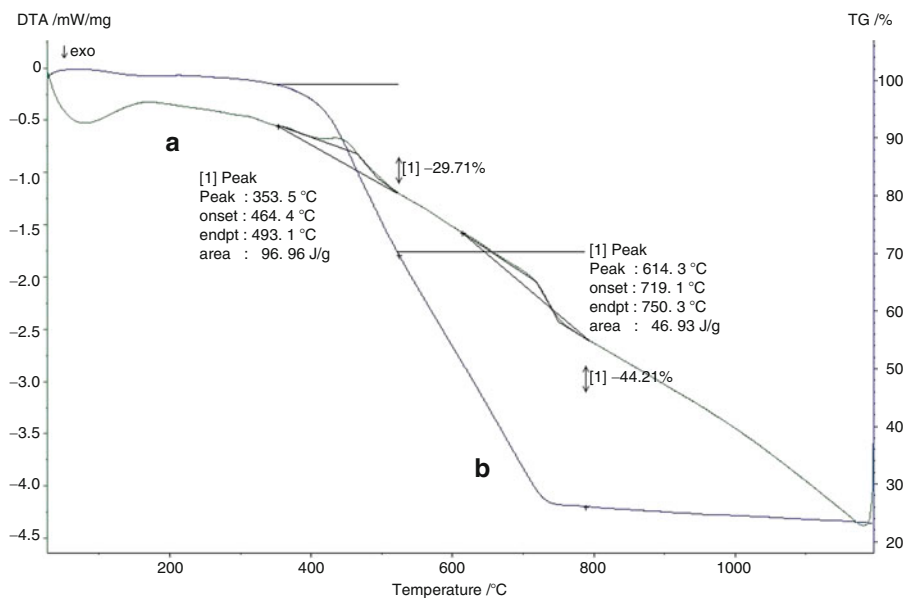


Fig. 13.17 Thermogravimetric analysis of carbon nanotube samples obtained by electrolysis in molten salt. *a*-line: data obtained by differential thermal analysis. *b*-line: weight loss as a function of temperature

The curve indicates that MWCNTs probably oxidize at temperatures below 450°C: the first peak can be attributed to the oxidation of amorphous carbon, the second peak at 720°C corresponds to the oxidation temperature of carbon fullerenes and non-reacted graphite particles. The lower oxidation temperatures registered for the MWCNTs indicate that some defects and derivatization moieties are present in the nanotubes walls that can cause the lower thermal stability.

The thermogravimetric study performed by D. Boom and his coworkers [26] has shown that graphite has a higher thermal stability than MWCNTs and oxidize at higher temperatures. Based on this study and the curves shown in Figs. 13.16 and 13.17, we can say that our results are in contradiction with the result obtained by Boom et al. It is obvious that the raw EC4 graphite material used as a electrode material oxidize at a temperatures which does not correspond with any of two temperatures of burning of carbon nanotubes sample.

Raman Spectroscopy

Raman spectroscopy has been used to determine the degree of crystallinity of the carbon materials produced. The MWCNTs produced in this study gave Raman spectra typical for multi-walled carbon nanotubes and graphitic particles.

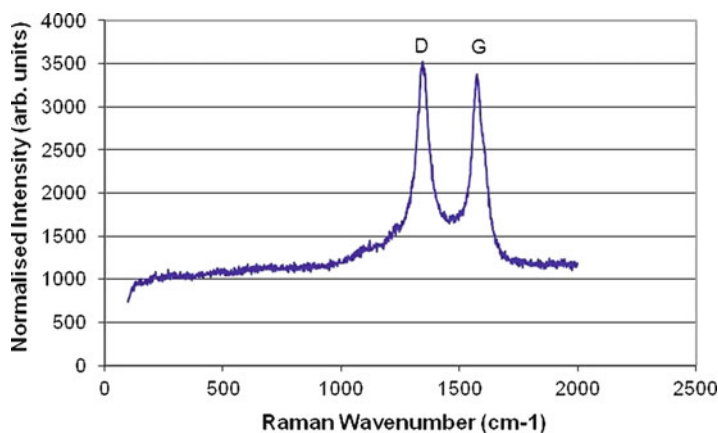


Fig. 13.18 Normalised Raman spectrum taken from MWCNTs produced by electrolysis

They had a G peak at $\sim 1,585 \text{ cm}^{-1}$ from the in-plane vibration of the C–C bonds, and a D peak at $\sim 1,350 \text{ cm}^{-1}$ due to the disorder in the crystals.

By comparing the intensities or areas of the D and G peaks, the extent crystallinity of the material can be assessed. The intensities ratio of the G and D bands (I_G and I_D) gives an indication of the crystal size within the sample. Smaller I_D/I_G ratios indicate larger crystals [27,28]. Highly oriented pyrolytic graphite (HOPG) has an I_D/I_G ratio approaching zero, while amorphous carbon has a value of ~ 3.3 . HOPG is a high quality graphitic material consisting of planes of carbon atoms, which are highly oriented between each other.

A normalized Raman spectrum obtained from MWCNTs produced by electrolysis in molten LiCl are shown in Fig. 13.18. By observation of the spectrum it is clear that two characteristic very sharp peaks for nanotubes appear: the D and G bands.

The D-peak with its maximum near $1,350 \text{ cm}^{-1}$ indicates disordered carbon atoms refers to defects such as pentagons and heptagons in graphite, edges of the graphite crystal and mostly amorphous carbon [29,30]. The G-line with its maximum at $1,585 \text{ cm}^{-1}$ is related to highly oriented graphite [31]. On the right side of the G-line a shoulder appears near $1,620 \text{ cm}^{-1}$; it is denoted as D'-peak. The appearance of this D'-peak points out that these carbon nanotubes are multiwalled [32]. So, the ratio of intensities of the characteristic peaks (I_D/I_G) indicates the extent of defects and impurities in the nanotubes.

A peak analysis yielded an I_D/I_G ratio of ~ 1 . The spectra and also the TEM and SEM analysis confirmed that there were no single-walled nanotubes present in the sample.

Conclusion

In summary, we can conclude that instead of constant cell potential electrolyses as reported in our previous work [14], constant cathode potential electrolysis

ensures better conditions for the production of MWCNT. The results show that EC4 is a proper material for the present purpose.

The material produced by this method was investigated with SEM and TEM. The data obtained by these techniques give sufficient evidence that the observed samples may amount more than 80% MWCNTs. The nanotubes are mostly of curved shape.

Observation of normalized Raman spectra gained from CNTs produced with constant cathode potential showed clearly two peaks. The peaks are very sharp, and the intensity analysis showed that the ratio I_D/I_G has a value ~ 1 . The position and intensities of the D and G peaks are an indication that the produced MWCNTs are of good quality.

Finally, it should be underlined that the results presented give sufficient evidence that the production of CNTs by constant overpotential electrolyses in molten LiCl is very promising.

Acknowledgments The authors gratefully acknowledge the financial support from the Royal Society of the United Kingdom and the NATO. Great thanks to Professor D. J. Fray and Dr. K. Schwand for their extensive help and advice throughout this project.

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Chapter 14

Graphene: 2D-Building Block for Functional Nanocomposites

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Abstract In this article we present a general introduction to the field of graphene and in particular of graphene-based composites. The opportunities for achieving novel high performance composite materials with enhanced properties are highlighted and the challenges to be overcome discussed. As the application of graphene as a nanofiller in composite materials is imminent, the availability of processable graphene sheets in large quantities seems essential to the success of exploiting composite and other applications of graphene. In addition, our work on the synthesis of electroactive graphene-polyaniline composites is presented.

Keywords Graphene · Nanocomposites · Polyaniline

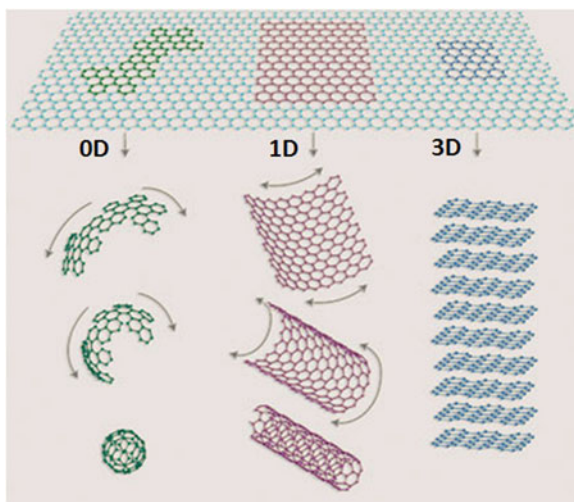
Introduction

Graphene is defined as a two-dimensional nanostructure of hexagonally arranged sp^2 hybridized carbon atoms. Considered the parent of all graphitic forms of carbon (Fig. 14.1), it has become one of the most exciting topics of research in the last years [1–4], providing a unique combination of physicochemical properties of ever-increasing interest in materials science. Important properties of graphene are a quantum Hall effect at room temperature [5–7], an ambipolar electric field effect along with ballistic conduction of charge carriers [8], a tunable band gap [9], and a high elasticity [10], giving rise to a vast field of potential applications.

In this article we provide the reader a background knowledge on the production of graphene and graphene-based composite materials, essential for exploiting composites and other applications of graphene.

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Fig. 14.1 Graphene: the parent of all graphitic forms [3]: 0D-fullerene, 1D-carbon nanotubes and 3D-graphite



Synthesis of Graphene

Since graphene samples were first obtained by micro-mechanical cleavage of graphite by Geim et al. in 2004 [8], several strategies have been developed for the production of graphenes. The most important methods employed to produce graphene samples in a large-scale can be divided into two categories:

1. Techniques starting with graphite (or a comparable starting material) not containing any oxygen functionalities: epitaxial growth on an insulator surface (SiC), arc discharge of graphite, conversion of nanodiamond, chemical vapor deposition (CVD) on the surfaces of single crystals of metals (Ni), use of intercalated graphite as the starting material, dispersion of graphite in solvents.
2. Techniques involving the exfoliation of graphite oxide followed by reduction [11], yielding sheets of reduced graphene oxide (they must be considered as chemically modified graphenes since they generally contain some oxygen functions such as $-\text{OH}$ or $-\text{COOH}$ groups).

Liquid-Phase Production of Graphene

Among all these methods special attention must be paid to the production of graphene in the liquid phase, as it constitutes an important aspect for their posterior processing into films and composites:

1. Single-layer graphene suspensions have been produced by exfoliating graphite in surfactant water solutions [12] or in organic solvents such as N-methylpyrrolidone (NMP) [13]; exfoliating alkali-metal intercalated graphite in NMP [14]

or lithium-intercalated multiwalled carbon nanotubes [15]. It has been reported that the use of a solvothermal procedure and subsequent sonication [16] leads to graphene flakes and that two-dimensional linear graphene ribbons can be prepared by oxidative cyclodehydrogenation of polyphenylene precursors [17].

2. As-prepared graphite oxide formed by Hummer's method undergoes full exfoliation into single-layer graphene oxide under sonication forming stable dispersions in water [18] or in several organic solvents [19].

The most popular method for large-scale production of graphenes appears to be the one based on graphite oxide [20], followed by thermal [21], electrochemical or chemical [22–24] reduction to restore its electronic properties.

Graphene has been characterized by a variety of microscopic and other physical techniques including atomic force microscopy (AFM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and Raman spectroscopy [25–27]. Single-layer graphene placed on a silicon wafer with a 300 nm thick SiO₂ layer, becomes visible in an optical microscope [11,28]. While AFM directly gives the number of layers [11], scanning tunneling microscopy (STM) [29], scanning electronic microscopy (SEM) and TEM [30,31] images are useful in determining the morphology and structure of graphene.

Approaches for the Preparation of Graphene-Polymer Composites

Significant work on the synthesis of graphene-polymer composites has been done [32]. The interlayer spacing in graphite oxide (GO) is much larger (0.61–1.1 nm) than in pristine graphite and several functional groups (e.g. hydroxyl, carbonyl, epoxide, etc.) are associated with GO layers, constituting an ideal material for monomer intercalation and polymerization in inter-layer spaces prior to exfoliation, or in interflake spaces after exfoliation. For example, several polar organic compounds and polymers have been intercalated [33–37].

Three procedures for the preparation of graphene-based composite materials are distinguished:

1. Intercalation of a monomer into inter-layer spaces of graphite or GO (before or after exfoliation), followed by in-situ polymerization. The most studied systems are polystyrene- and poly(methyl methacrylate)-based composites [38–40], and nanocomposites based on matrices such as nylon [41], polypropylene [42], poly(arylene disulfide) [43], and epoxy resins [44].
2. Dissolution of a polymer in a solution in which graphene or graphene oxide sheets are already dispersed.
3. Preparation of isolated graphene or graphene oxide sheets, which are then mixed with a polymer (e.g. using a twin-screw extruder).

In these approaches, GO may be reduced to graphite before or after polymer addition to restore the graphene structure and its conductive properties through a thermal [21], electrochemical or chemical treatment [22–24].

Chemical compatibility between filler and matrix is a critical factor to consider in the preparation of a nanocomposite material. Graphene oxide and reduced graphene oxide sheets are known to have very active surfaces or edge functional groups enabling them to disperse in water or in a polar solvent forming stable colloidal suspensions and, hence, to be mixed with water-soluble [33–35,45,46] or organic media soluble-polymers [47,48].

Graphene-Polyaniline Composites

Electroactive polymers show the electrical, electronic, magnetic, and optical properties of a metal while retaining the mechanical properties (flexibility and toughness) and processibility associated with a conventional polymer [49,50]. Besides, the backbone of a conducting polymer consists of a truly conjugated and delocalized π – electron system and is thus highly compatible with both carbon nanotubes and graphene derived materials. Highly synergetic effects leading to improved properties can be expected by properly compounding electroactive polymers with graphene. Between the members of this family we choose polyaniline (PANI), due to its easy synthesis and tunable redox characteristics [49], for the synthesis of graphene-based composites.

Similarly to the work of Jiménez et al. with carbon nanotubes [51], we prepared graphene-PANI composites. Graphite oxide, prepared using a modified Hummer's method [17], was exfoliated into graphene oxide sheets by sonication in water, followed by mild centrifugation to remove unexfoliated material [18]. An in-situ polymerization of aniline monomers (HCl, 1 M) led to the formation of a graphene oxide-PANI composite (PANI-GO). Afterwards, this composite was reduced by a chemical treatment using hydrazine. During reduction both the graphene oxide sheets and the emeraldine salt form of PANI got transformed into reduced graphene oxide sheets (RGO) and a more reduced state of PANI, respectively, forming R(PANI-GO) composite, as it is schematically shown in Fig. 14.2.

We showed that the incorporation of graphene into this polymeric matrix has a strong effect on the material: during the in-situ polymerization process graphene acts as a template for the growing PANI backbone, changing its typical nanofibrillar morphology into a planar one.

Additionally, upon reduction we observed highly synergetic interactions leading to improved processing properties and enhanced physical properties [52]: (1) water dispersibility, (2) ambient stability, (3) thermal stability, (4) higher conductivity, and (5) higher capacitance of the material. The integration of graphene in the polymeric matrix provides a high conductivity as well as some exceptional redox properties, making this composite a suitable electrode material to be used as a supercapacitor.

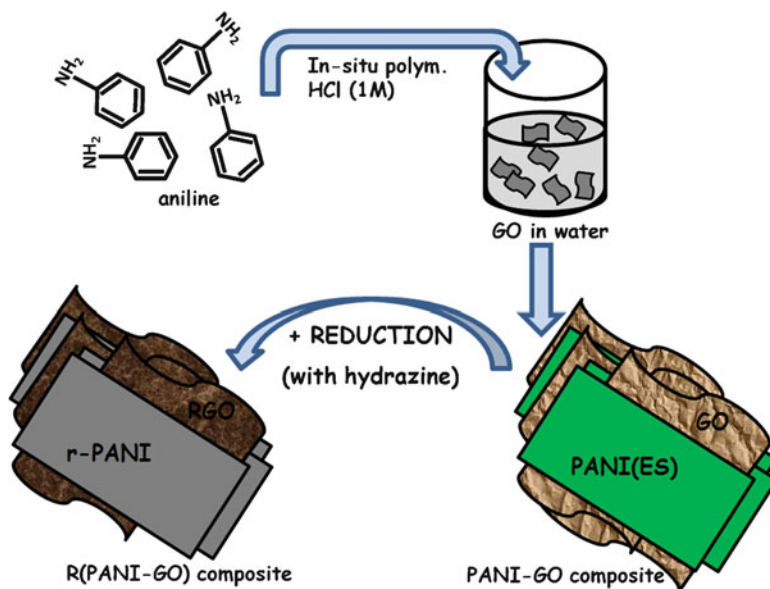


Fig. 14.2 Scheme showing the in situ polymerization of aniline in the presence of graphene oxide sheets in HCl (1 M) medium and the posterior chemical reduction

Summary and Outlook

A general introduction into the field of graphene, its production methods, processing techniques and technological applications has been presented. Focusing on the development of graphene-based composites in general, critical issues and compounding strategies were discussed. We presented the particular preparation of graphene-polyaniline nanocomposites by an in-situ polymerization process, showing the achievement of enhanced properties and processing characteristics. Further progress towards novel high performance graphene-based nanocomposite materials is being performed, using other electroactive polymers.

Acknowledgements The authors acknowledge financial support from MICINN under project MAT2007-66927-C02-01 and from DGA under projects PI086/08 and T66.

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Chapter 15

PCL/MWCNT Nanocomposites as Nanosensors

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Maria E. Errico, and Gennaro Gentile

Abstract Due to the unique electronic, metallic and structural properties of carbon nanotubes (CNTs) as compared to other materials, researchers focused on utilizing these characteristics for engineering applications such as actuators, hydrogen storage materials, chemical sensors and nanoelectronic devices. Many papers have been published utilizing CNTs as the sensing material in pressure, flow, thermal, gas, optical, mass, strain, stress, chemical and biological sensors. Amongst many of their superior electro-mechanical properties, the piezoresistive effect in CNTs is attractive for designing strain sensors. When CNTs are subjected to a mechanical strain, a change in their chirality leads to modulation of the conductance. In this paper, a novel carbon nanotube/biopolymer nanocomposite was used to develop a piezoresistive strain nano bio-sensor. A biocompatible polymer matrix has been used to provide good interfacial bonding between the carbon nanotubes. Multi-walled carbon nanotubes (MWCNT, diameter $d = 30\text{--}50$ nm, purity $>95\%$) have been used for the preparation of polycaprolactone (PCL)-based nanocomposites (PCL/MWCNT). The nanocomposites were prepared by mixing the MWCNTs and PCL in a tetrahydrofuran solution for 24 h. Characterization of the PCL/MWCNTs nanocomposite films was performed by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), Fourier-transform infrared (FTIR) and scanning electron microscopy (SEM), as well as by mechanical and electrical measurements.

Keywords Multi-wall carbon nanotubes · Nanocomposite · Nanosensor

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Introduction

Chemical and mechanical multi-nanosensors can be described as devices composed of a sensitive part which, interacting with the surrounding environment, collects and concentrates molecules and structural elements at or within the surface which thereupon undergoes physical changes, and of an appropriate transducer that converts these changes of the sensing part into an interpretable and quantifiable signal. The heart of the multi-nanosensor is the sensitive element, which is the interface between transducer and external environment, so that the nature and the selectivity of the sensor depends upon these interactive materials. The list of most promising materials for multi-nanosensors includes polymers, ceramics, metals, nano-structured materials and nanocomposites, molecular sieves, sol-gels, biomaterials and their combinations [1–7]. Thus, for design and development of multi-nanosensors and their performances, proper and detailed physical, chemical and structural characterization of the sensing materials are essential for a complete understanding of their properties.

The design of novel multi-nanosensors based on carbon nanotubes (CNTs) is facilitating new research directions in the area of nanostructured materials science, device engineering and circuits. Amongst many of their superior electro-mechanical properties, the piezoresistive effect in CNTs is attractive for designing strain sensors. When CNTs are subjected to a mechanical strain, a change in their chirality leads to a modulation of their conductance.

It is well known that carbon nanotubes have a great potential for industrial applications due to their unique structure and properties. They have also many distinct properties that can be exploited to develop the next generation of sensors [1]. However, among the major limitations of the application of the unique properties of carbon nanotubes in this field have been their high costs and the lack of availability. Today, there are already different types of MWCNTs commercially available on the market. The FP6 CANAPE project has been related to the production of nanotubes within Europe [1]. In the frame work of this European Commission project, applications of CNTs in electronics, catalysis, composites and nano-biology have been studied. In order to prepare CNT/polymer nanocomposites, several problems had to be overcome. Namely, one is to obtain uniform dispersions of CNTs in a polymer matrix despite the insolubility of CNTs and the inherently poor compatibility between the CNTs and the polymers. In direct blending of CNTs and polymers, the nanotubes tend to aggregate; such nonuniform dispersions in the polymer matrix often results in deteriorious effects. The second main approach is utilization of biodegradable polymeric materials from renewable sources such as polylactide (PLA), poly(ϵ -caprolactone) (PCL) and poly(3-hydroxybutyrate) (PHB). Biocompatible nanocomposites based on CNTs and biopolymer matrices are still subject of great research interest, especially with respect to the effects of carbon nanotubes on the thermal and mechanical behavior of the composites, as well as the utilization of piezoresistive effects in CNT/polymer nanocomposites, which opens up the field of biomedical/biomechanical applications of these hybrids.

Most of the sensors based on carbon nanotubes are field effect transistors, since in the past great interest has been focused on the study of the changes in their electrical properties as a consequence of the interaction with gaseous species; these electrical properties are extremely sensitive to the effects of charge transfer and chemical doping by various molecules. Fujiware et al., studied the N_2 and O_2 adsorption properties of carbon nanotubes bundles and their structures [2]. The effect of the adsorption of several gases on carbon nanotubes was also described by Zahab et al. [3]. Sumanasekera et al. have created a thermoelectrical chemical sensor to measure reversibly thermoelectrical power changes of carbon nanotubes in contact with He, N_2 and H_2 [4]. Kang et al. from the University of Cincinnati have worked on polymethylmethacrylate (PMMA) based CNT/PMMA strain sensors for structural health monitoring [5]. Bio-nanocomposite sensors have been a research topic also at the Florida Advanced Center for Composite Technologies. Here MWCNT/PMMA strain sensors were studied, comparing solution prepared sensors with dry-blended ones. Zhang et al. from the Rensselaer Polytechnic Institute have studied MWNT/polycarbonate strain sensors and published gauge factors 3.5 times larger than that of typical strain gauges (5% MWNTs).

In this paper, a novel carbon nanotube/biopolymer nanocomposite was used to develop a piezoelectric multi-nanosensor. A polymer matrix has been used to provide good interfacial bonding with the carbon nanotubes. A biopolymer matrix of poly-(ϵ -caprolactone) (PCL) acts as host polymer matrix for transferring the load to the CNTs. Multi-walled carbon nanotubes are used in order to reduce the cost for real application. They can be integrated into the material (composite) and serve both sensor and structural functions.

Experiment

PCL/MWCNTs nanocomposite films have been prepared by the solution casting method, via mixing of the MWCNTs and PCL in a tetrahydrofuran solution for 24 h. MWCNTs ($d = 30\text{--}50$ nm, purity $>95\%$) have been used for the preparation of polycaprolactone based nanocomposites. Characterization of the PCL/MWCNTs nanocomposite films was performed by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), Fourier-transform infrared (FTIR) and scanning electron microscopy (SEM), as well as by mechanical measurements.

DSC measurements were performed with a DSC system (Mettler Star) under nitrogen atmosphere in the non-isothermal regime (heating rate = 10 K/min, cooling rate: 40, 20, 10 and 5 K/min). All specimens were weighted to be in the range of 8–9 mg. TGA was performed in the range of $50\text{--}800^\circ\text{C}$ with heating rate of 20 K/min (in nitrogen) using a Perkin Elmer Pyris DIAMOND TGA/DTA system. FTIR spectroscopy was used to characterize the structure of the PCL/MWCNT

nanocomposites. FTIR spectra were recorded with a Perkin Elmer Paragon 500 analyzer, using 64 scans and a resolution of 2 cm^{-1} . SEM microphotographs were recorded with a Cambridge Stereoscan microscope model 440.

Results

Characteristical non-isothermal crystallization data such as the onset crystallization temperature T_o , the end temperature of crystallization T_c , and the exothermic peak temperature T_p of the crystallization were determined from DSC curves; the results are shown in Table 15.1. It is evident that as the cooling rate increased, all the parameters (T_o , T_c and T_p) were shifted to lower temperatures. The lower the cooling rate, the earlier the crystallization starts. The PCL/MWCNT nanocomposites have higher T_p values than the pure PCL at all cooling rates (except for PCL/0.5% MWCNT at 40 K/min). This phenomenon can be explained by the heterogeneous nucleation of the MWCNTs suggesting that the melted PCL macromolecule segments can be easily attached to the surface of the rigid nanotubes, which leads to the crystallization of PCL macromolecules at higher temperatures.

Themogravimetric analysis has shown that the temperature of thermal decomposition for PCL/MWCNT nanocomposites was slightly shifted to lower temperatures compared to the pure PCL ($T_{d\text{PCL}/1\%\text{MWCNT}} = 393^\circ\text{C}$, $T_{d\text{PCL}} = 395^\circ\text{C}$).

To evaluate the state of dispersion of CNTs within the polymer matrix, the nanocomposites films have been observed by scanning electron microscopy. The characteristic morphology of the nanocomposites is presented in Fig. 15.1 (a: pure PCL, b: PCL/0.5% CNT, c: PCL/1% CNT). The SEM images clearly show that

Table 15.1 The nonisothermal parameters for PCL and PCL/MWCNT nanocomposites determined by DSC exotherms. T_o : onset crystallization temperature [$^\circ\text{C}$]; T_c : end temperature of crystallization [$^\circ\text{C}$]; T_p : exothermic peak temperature of crystallization [$^\circ\text{C}$]

Cooling rate [K/min]	Crystallization parameter [$^\circ\text{C}$]	PCL/ 0.25% MWCNT			
		PCL	PCL/0.5% MWCNT	PCL/1.0% MWCNT	
5	T_o	34.2	39.7	40.0	44.6
	T_c	26.1	32.1	29.5	34.9
	T_p	30.3	36.7	36.0	39.9
10	T_o	31.2	37.2	37.7	42.3
	T_c	20.8	26.7	23.9	29.6
	T_p	27.4	33.3	31.7	36.9
20	T_o	28.8	34.1	35.1	39.7
	T_c	15.4	19.2	16.3	21.9
	T_p	24.9	28.9	27.2	33.3
40	T_o	26.8	30.5	31.8	37.1
	T_c	8.0	7.7	5.4	9.3
	T_p	22.7	28.9	21.6	28.3

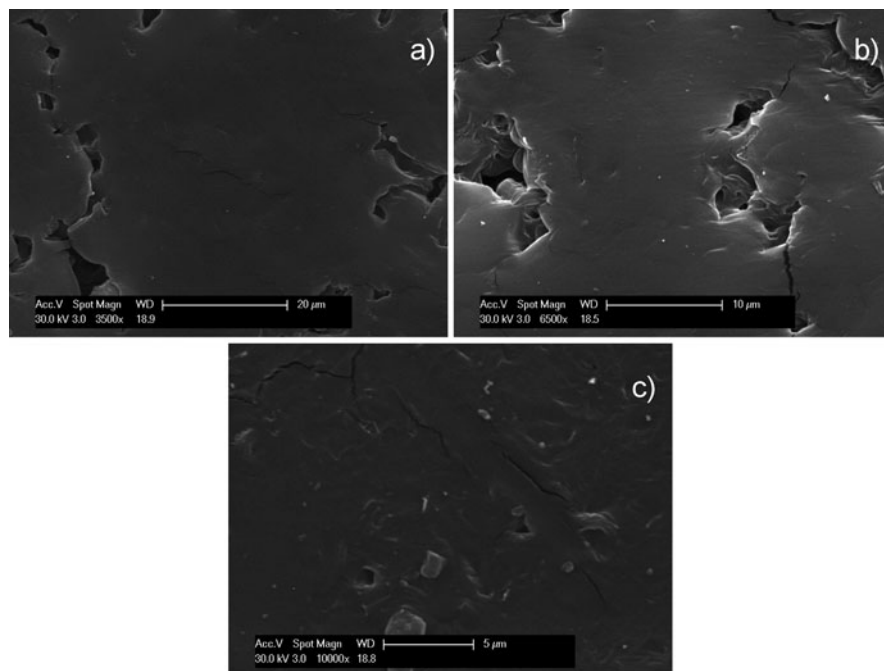


Fig. 15.1 SEM microphotographs of the prepared PCL/CNT nanocomposites. **a:** pure PCL ($\times 35,00$), **c:** PCL/1% CNT ($\times 10,000$), **b:** PCL/0.5% CNT ($\times 6,500$)

Table 15.2 Linear growth rate G and activation energy ΔE_a for PCL and PCL/MWCNT nanocomposites

Parameter	PCL	PCL/0.25% MWCNT	PCL/0.5% MWCNT	PCL/1.0% MWCNT
ΔE_a [kJ/mol]	308.6	250.2	257.9	317.0
G [min^{-1}]	3.60×10^3	1.19×10^3	2.06×10^3	3.01×10^3

homogeneous dispersions of MWCNTs (well-dispersed bright dots) throughout the PCL matrix are achieved at all CNT contents.

For the PCL/MWCNT nanocomposites obtained, also the linear growth G and the activation energy ΔE_a were determined (Table 15.2). Generally, for increasing MWCNT contents, the values of both parameters increase. A higher content of MWCNTs means more steric hindrance and a reduction of the transportation ability of the polymer chains (higher ΔE_a).

The FTIR spectra of the pure PCL matrix and PCL/MWCNT nanocomposites are shown in Fig. 15.2. Besides small peak shifts, there are no new peaks which suggests that there are no remarkable structural changes in the nanocomposites obtained.

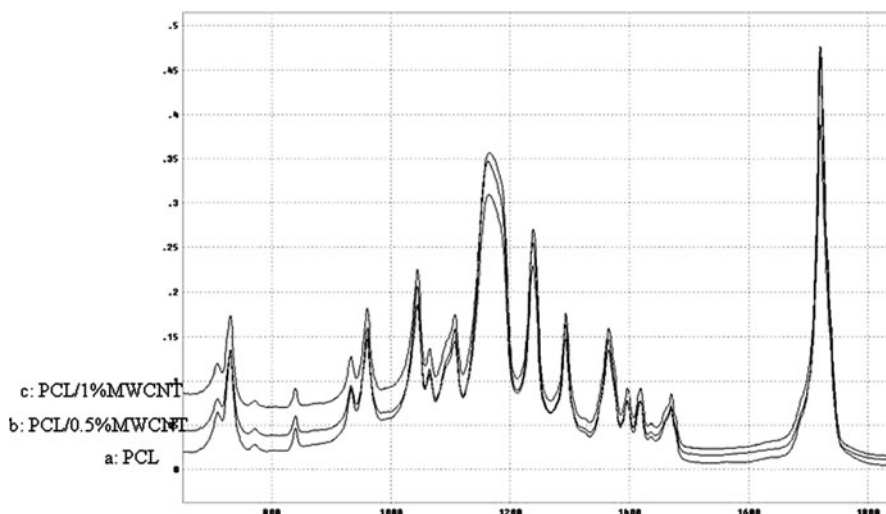


Fig. 15.2 FTIR spectra of **a:** PCL and PCL/MWCNT (**b:** 0,5 wt.% CNT; **c:** 1 wt.% CNT) nanocomposites

Conclusions

The results presented above indicate that introducing MWCNT into PCL significantly changes the properties of the obtained nanocomposites. SEM images shown that a homogeneous dispersion of MWCNT was achieved throughout the PCL matrix at all CNT contents. Nonisothermal crystallization of the PCL/MWCNT nanocomposites depended significantly on the MWCNT content and the cooling rate. The crystallization temperature for the PCL/MWCNT nanocomposites decreased with increasing cooling rate for a given MWCNT content. The incorporation of MWCNT accelerates the mechanism of nucleation and crystal growth of PCL. The resulted crystalline structure clearly indicate that this type of nanocomposites could be used in sensor devices.

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Part IV.2

Oxide Materials

Chapter 16

Nanostructured ZnO Thin Films: Properties and Applications

Doriana Dimova-Malinovska

Abstract Zinc oxide has been recognized as one of the most important semiconductor materials for optoelectronics, solar cells, piezoelectricity, gas sensing, bio- applications etc. ZnO has been an object of intensive investigation, particularly in its low dimensional structures – thin layers with nanometer crystallites, nano-wires, nano-rods or nano-tubes, nano-bells and others. In thi contribution the optical and structural properties of ZnO thin films are discussed. The application of ZnO thin films as a transparent conductive electrode for solar cells and light emitting diodes, as well as for gas sensors is demonstrated. The possibility for bio-application of ZnO films is also discussed.

Keywords ZnO · Nanomaterials · Gas sensors

Introduction

ZnO is a material widely used in industry for decades, which experiences a scientific and technical renaissance in the last few years. ZnO is a wide band gap semiconductor (3.37 eV at room temperature) with direct electron transitions, a large exciton energy (60 meV) and a hexagonal close packed structure (wurtzite). Its unique chemical, surface and nanostructured properties give opportunities to find various new applications of ZnO in optoelectronics. This includes ZnO application as transparent conducting electrode for photovoltaics (solar cells) and light emitting diodes, and also as phosphorescent and luminescent material in the visible (blue-green) and ultraviolet regions [1, 2]. ZnO is one of the first oxide materials,

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which have attracted attention for their potential application as gas sensors due to their chemical sensitivity to different gases, high chemical stability, non-toxicity and low cost [3–6]. The material properties are determined mostly by the structure and surface morphology, which strongly depend on the preparation method. In the last few years, ZnO has been an object of intensive investigations, particularly in low dimensional structures – thin layers with nanometer crystallites, nano-wires, nano-rods or nano-tubes, nano-bells and others [7–9]. In these species, the charge carriers are restrained to defined energy levels leading to amplification of the exciton oscillator strength and the intensity of light emission. On the other hand, the increased specific surface area in nanocrystalline structures increases the sensitivity to different gaseous media [10, 11].

ZnO as a Transparent Conductive Material

Al or Ga doped ZnO has found wide applications as transparent electrodes for thin film solar cells based on a-Si:H, CdS/CdTe, CdS/CIS etc. The requirements are the same as for the semiconductors in the cells, namely a low-cost, large-scale technology of preparation, high conductivity and optical transmission, and good stability. ZnO has an energy gaps of 3–3.4 eV, depending on the deposition process. It has an optical transmission in the range 80–85% in the visible/near infrared range and a sheet resistance of 5–10 $\Omega/\square$. Recently, ZnO films have attracted interest as transparent conductive coatings. They offer various advantages: i) they consist of cheap and abundant elements; ii) they can be produced by large-scale coating; iii) they allow tailoring of the ultraviolet absorption; iv) they have a high stability in hydrogen plasma; v) they can be deposited at low growth temperatures. The most frequently used preparation methods of Al or Ga doped ZnO are sputtering [12], reactive evaporation of Zn in an O₂ atmosphere, CVD etc.

Figure 16.1 shows optical transmission spectra of ZnO:Al films deposited by magnetron sputtering with different r.f. powers [12]. The average transmission in the range 400–900 nm is about 0.85, i.e. the transmission of the films is about 90% of that of the substrate, and does not appear to decrease with increasing r.f. power. The free carrier concentration n and the mobility μ decrease with the r.f. power and reach saturation at 150 W. The increase of ρ with r.f. power could be related to the increase of defects in the films due to the high growth rate and bombardment with energetic ion and neutral species during the deposition and hence to increased electron trapping at the grain boundaries that can reduce the mobility and concentration of free carrier and thereby limit the conductivity of the films.

ZnO thin films have been applied as a transparent electrode in light emitting structures on the bases of porous silicon (Fig. 16.2) [13]. Electroluminescence (EL) from the device structure in the visible region was detected under forward bias conditions, when field-assisted tunnelling was observed.

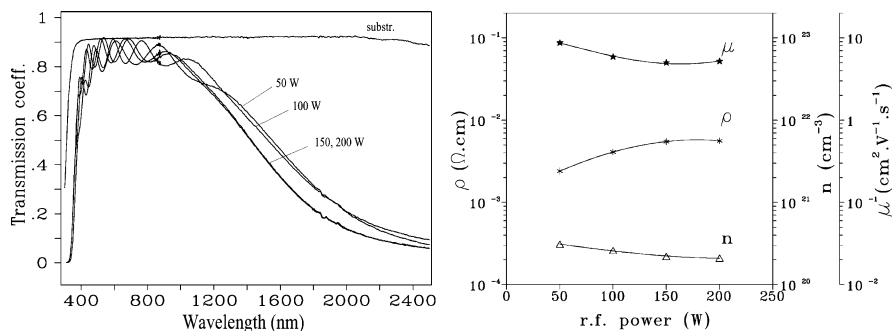


Fig. 16.1 Optical transmission spectra (*left*) and film resistivity ρ (asterisks), mobility μ (stars) and concentration n (triangles) of free carriers (*right*) for ZnO:Al deposited at different r.f. power. The substrate transmission spectrum is also shown [12]

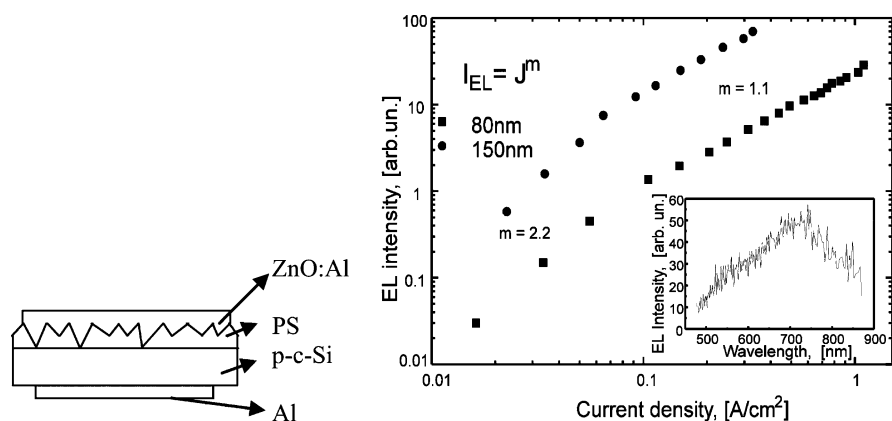


Fig. 16.2 Scheme of a light emitting diode (LED = with ZnO as transparent conductive oxide (TCO) (*left*), and dependence of the EL intensity on the forward current the LED (*right*). The insert displays the spectral dependence of the EL [13]

ZnO for Gas Sensor Application

The ability of undoped and Er, Ta or Co doped ZnO thin films to sorb ammonia vapour was demonstrated by the quartz crystal microbalance (QCM) method. For this purpose, the resonance frequency shift was measured. The sorption process was investigated over an aqueous ammonia solution with a concentration of 100 ppm. The change in the frequency f of the QCM as a function of its mass loading was detected. Surface morphology and cross section images of the ZnO film used for this purpose (deposited by rf magnetron sputtering in Ar atmosphere) are shown in Fig. 16.3. The columnar structure of the film is clearly visible with sizes of the

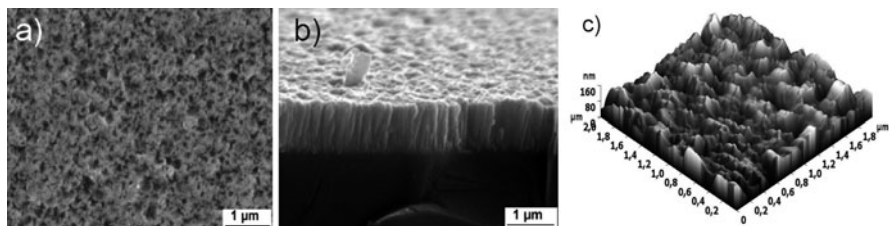


Fig. 16.3 Top surface (a) and cross section (b) SEM images and AFM picture (3D image 2×2 μm) (c) of a ZnO film deposited by rf magnetron sputtering of a ZnO target in an Ar atmosphere

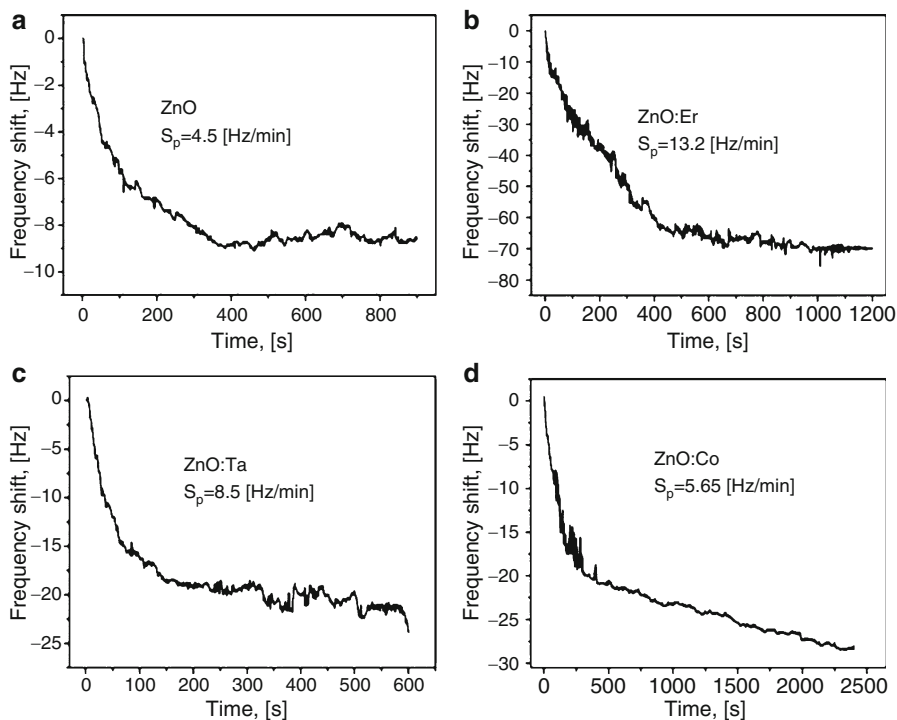


Fig. 16.4 Time-frequency shift characteristics of a quartz crystal microbalance with: (a) ZnO, (b) ZnO:Er, (c) ZnO:Ta, (d) ZnO:Co films over a 100 ppm NH_3 solution [11]

nanocrystallites of about 100 nm. Fig. 16.4 shows the frequency change Δf as a function of the exposure time over a 100 ppm ammonia solution for different samples. The highest rate of the frequency change S_p is registered in the first 2 minutes for all samples investigated. Thereafter, the rate slowly decreases and the frequency approaches to a constant value.

The rate of change for the first 2 min was calculated in order to estimate the sensitivity of each kind of ZnO layer. The S_p value and the total sorbed mass Δm

Table 16.1 Values of the optical band gap E_g , the average grain size D , the rate of sorption Sp , and the sorbed mass Δm , over 100 ppm NH_3 for different kinds of samples. The values of D are calculated using values of 2θ (given in the brackets) and the corresponding FWHM

Samples	E_g , eV	D , Å; (2θ), deg	Sp , Hz/min	Δm , ng
ZnO:Er	3.30	102; (31.50°) 98; (34.30°) 90; (35.80°)	13.20	32.20
ZnO:Co	3.352.95	105; (34.04°)	5.65	12.78
ZnO:Ta	3.46	131; (33.10°)	8.50	8.76
ZnO	3.30	160; (31.60°) 177; (34.40°) 110; (36.21°)	4.50	4.86
ZnO:H	3.31	173; (34.37°)	80	37.7

was evaluated using the relationship between Δf and Δm for a rotated Y-cut (AT-cut) of the quartz crystal, given by the Sauerbrey equation [14]:

$$\Delta f = -(2.26 \times 10^{-6} f^2 \Delta m / A), \quad (16.1)$$

where f (MHz) is the frequency of the QMB before exposure to ammonia, Δm (g) is the mass of the sorbed gas on the surface of the ZnO films and A (cm²) is the surface area of the electrodes.

The total sorbed mass on the samples was calculated for the whole period until saturation was achieved. The data are presented in Table 16.1. The lowest rate of sorption and the smallest total sorbed mass (4.5 Hz/min and 4.86 ng, respectively) are registered for ZnO. In the case of films doped with Ta and Co, values of 8.5 Hz/min and 8.76 ng, and 5.65 Hz/min and 12.78 ng for sorption rate and mass, respectively, were obtained. It has to be noted that the largest rate of frequency change (13.2 Hz/min) was measured in the case of sorption on ZnO:Er layers, which corresponds to a total sorbed mass of 32.20 ng, and on ZnO:H layers (80 Hz/min and about 37.7 ng). However in the case of ZnO:H the rate of absorption decreased to 2.47 Hz/min after the first 2–3 min. Thus, higher sensitivities were observed for H and Er doped ZnO films, as compared to undoped, ZnO:Co and ZnO:Ta films. Differences in the grain size of the deposited films could be one of the reasons for the different behaviour of the QCM sensors. Higher sorbed masses are detected for samples with smaller grain size.

ZnO for Bio-Applications

ZnO belongs to a group of metal oxides which are characterized by a photooxidizing capacity versus chemical and biological species; in addition they are anti-microbial and self-sterilizing [15]. Moreover, ZnO is generally regarded as a safe material for human beings and animals, and it has been used extensively in the fabrication of personal care products [16, 17].

The pioneering paper of Yamamoto [18] reports on the effect of the particle size on the antibacterial activity of ZnO particles in water. The targeted bacteria were *Escherichia coli* (Gram-negative) and *Staphylococcus aureus* (Gram-positive). Measuring the electrical conductivity of the ZnO suspension with bacterial growth assessed its antibacterial activity. An increase of the incubation time, at which the electrical conductivity starts to increase, means that the respective ZnO slurry inhibits the bacterial growth. It was observed that decreasing the particle sizes increases the antibacterial activity of ZnO with respect to both *E. coli* and *S. aureus*. The inhibition of bacterial growth is mainly due to the generation of hydrogen peroxide (H_2O_2) from the ZnO surface, which creates radicals destroying the cell walls of the bacteria. Very recent studies confirmed these effects and revealed the role of different factors on the antibacterial activity of ZnO/water suspensions [19, 20]. There is only one report until now on the use of ZnO thin films for the detection of bacteria in a water droplet placed on the film surface [21]. The coating of ZnO nanorods, prepared by a hydrothermal method, has an antibacterial effect with respect to *E. coli* and *Bacillus atrophaeus* (a Gram-positive bacterium). It was proven that in this case H_2O_2 may not play an important role for the cell-membrane destruction. Instead, the release of Zn^{2+} ions from the ZnO surface and their interaction with the membranes was suggested as alternative mechanism of antibacterial activity.

Nanowires on a SnO_2 :F coated glass substrate have been prepared by an electrochemical process using a three-electrode potentiostatic system with a saturated calomel electrode as reference. An aqueous solution containing ZnCl_2 and KCl at pH = 4.00 under flowing air or/and additional supplement of H_2O_2 was employed [22]. Different substrates were used for deposition: SnO_2 :F-coated glass and carbon tissue.

SEM micrographs show that the ZnO films consist of nanowires (Fig. 16.5). Raman spectra of the ZnO films with nanowires possess the vibrational bands typical for ZnO. They are most pronounced for the sample deposited with the highest H_2O_2 concentration. The ZnO layers exhibit a high diffuse reflection in the near IR and visible ranges of the spectrum. ZnO layers with such a surface morphology could also be applied as a back contact for increased light trapping in thin film solar cells.

It was shown that by this method it is possible to deposit ZnO nanowires on biomedical carbon tissue. The SEM images of the deposited ZnO pillars are presented in Fig. 16.6. The pillars have sizes of about 200–500 nm and grow perpendicular to the surface of the tissue fibers.

Detection of different chemical species was performed by the method of surface assisted laser desorption ionization (SALDI) [22]. SALDI is a novel method of ionization of organic and bioorganic compounds, which is under intensive development over the last decade. In SALDI ionized species are formed in the gas phase from analytes deposited on the surface of a specially designed SALDI-active substrate which is irradiated with a pulsed laser.

Figure 16.7a shows a typical SALDI mass spectrum of 400 pg atenolol deposited on a nc-ZnO surface from a 200 ng/ml solution. It can be seen that the base peak in the spectrum is associated with the protonated atenolol molecule at $m/z = 267$.

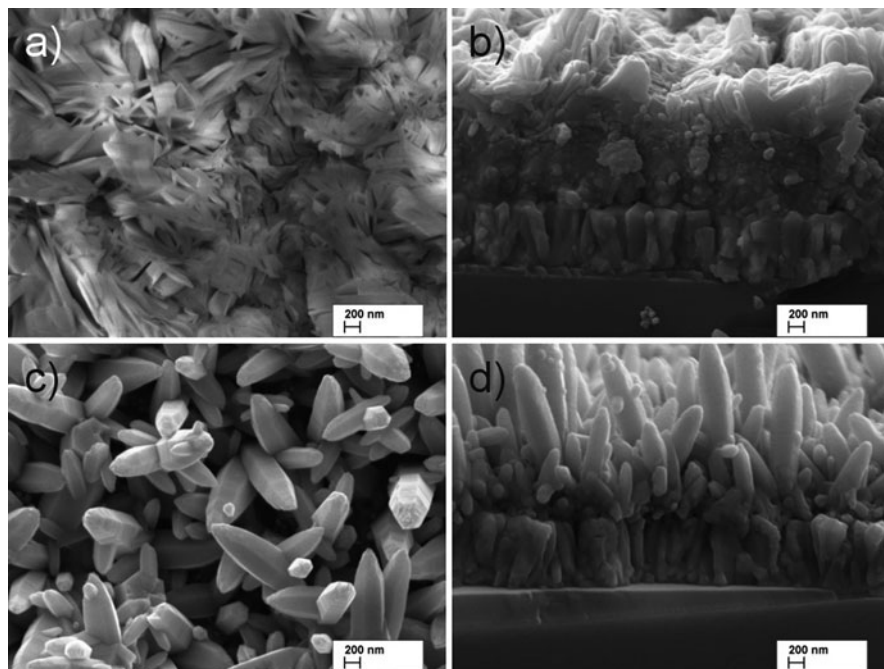


Fig. 16.5 SEM images of the surface (a,c) and cross section (b,d) of ZnO films prepared by electrochemical deposition with low (a,b) and high (c,d) H_2O_2 concentration [22]

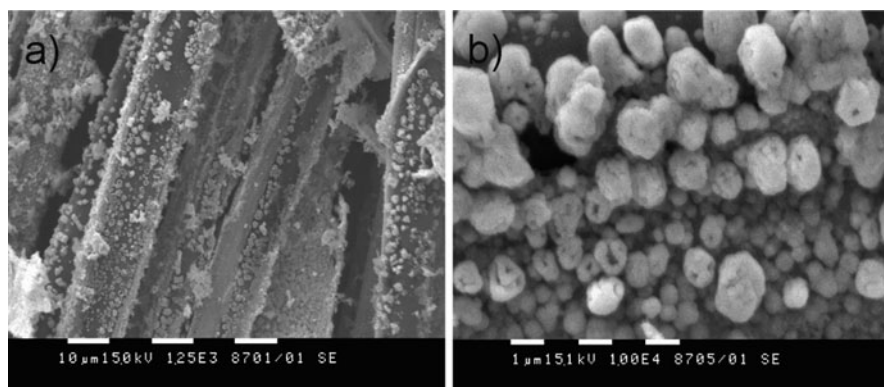


Fig. 16.6 SEM images of ZnO pillars on a carbon tissue surface. Note the different magnification in the two pictures [22]

No fragment ions are observed in the spectrum. The minor background peaks result from surface contaminations, possibly from vacuum pump oil. In general, however, the obtained mass spectra are “clean” with a low chemical background. This property of nc-ZnO surface minimizes the need for sample clean-up.

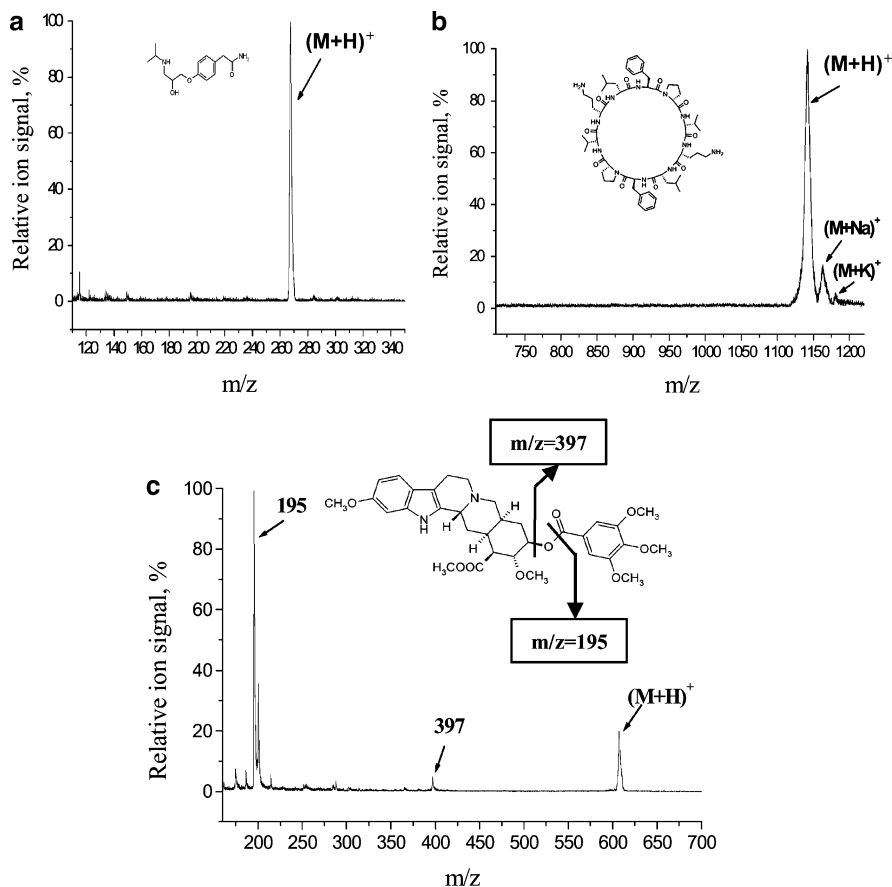
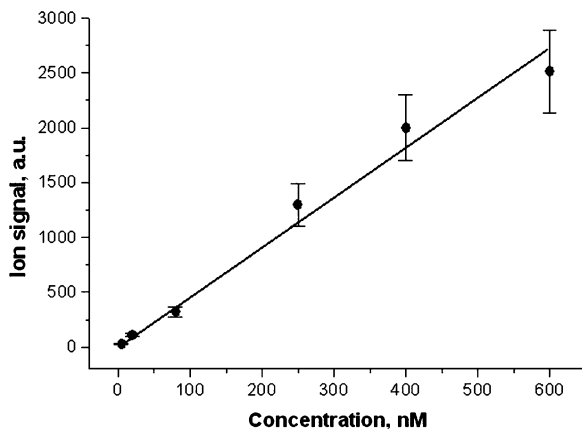


Fig. 16.7 SALDI mass-spectrum of atenolol (a), gramicidine S (b) and reserpine (c) deposited on the ZnO thin film surface [23]

Figure 16.7b shows a SALDI mass spectrum of 1 ng (0.9 pmole) of gramicidine S measured for a 500 ng/ml solution of this peptide. The base peak in the mass spectrum is the protonated molecule at $m/z = 1141$, but there are also sodium $[MNa]^+$ and potassium $[MK]^+$ cation adduct peaks. Similar to the spectra of atenolol no fragment ions are observed in the mass spectrum of gramicidine S and reserpine. SALDI ion signals were measured for different amounts of analytes over a range of two orders of magnitude by changing the concentration of the deposited solutions. A typical dependence of the signal on the analyte concentration is illustrated in Fig. 16.8 for reserpine. Very similar calibration curves were obtained for atenolol and gramicidin S. It was found that the linearity was better than 0.98 for all three compounds studied. The reproducibility was monitored by measuring the analytical signal using the same conditions but different ZnO samples. Twenty replicate analyses were carried out over a 1-week period for

Fig. 16.8 Calibration curve for reserpine



each of the studied compounds. The relative standard deviation was less than 15% for all three compounds. This result clearly indicates the capability of ZnO films for the quantitative analysis of low molecular weight drugs. These observations prove that nc-ZnO based SALDI is a soft ionization technique. However, as it was shown earlier [24] SALDI mechanism involves the thermally induced desorption of ions. This can result in at least partial decomposition of thermally unstable compounds.

This study demonstrates that ZnO films are very stable and show good sensitivity in the examined range of the analyte concentrations. The obtained mass spectra are “clean” with almost no chemical background and with no or very specific fragmentation of the analyte ions. The detection limits are in the 2–20 femtomol range. Good reproducibility under the same experimental conditions was found for all analytes. The high purity, the ease reproducible fabrication, good analytical parameters, and the ability to analyze samples rapidly make thin ZnO films a potentially powerful tool for the detection of small bioorganic and organic molecules especially in the field of drug analysis with the SALDI method.

Acknowledgements This research was carried out as part of the activities of the Contract No. DO02-207/2008 funded by the Bulgarian NSF and project NANOPV of the 7FP of the EC program.

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Chapter 17

A Study of the Kinetics of the Electrochemical Deposition of $\text{Ce}^{3+}/\text{Ce}^{4+}$ Oxides

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Abstract The kinetics of cathodic electrodeposition of Ce^{3+} and/or Ce^{4+} oxides from alcoholic electrolytes on gold substrates has been studied. It was found that, depending on the oxygen content in the CeCl_3 -based electrolyte, Ce_2O_3 (in oxygen atmosphere) or CeO_2 (in an inert atmosphere), respectively, were obtained. XPS studies clearly separated the two valence states of Ce ions in the oxide layers. The microstructure of the coatings was analyzed by atomic force microscopy (AFM).

Keywords Electrodeposition · Cerium oxides · Cathodic processes

Introduction

A number of publications can be found in the literature on the properties of CeO_2 as a effective corrosion inhibitor in aqueous environments and as a protector of alloys from high temperature corrosion [1,2]. Additionally there is a growing interest in the semiconducting properties of this material and its application as a base of oxygen conducting ceramics in low temperature solid oxide fuel cells (SOFC) [3,4]. Finally ceria is widely used in catalytic reactions as a reducible oxide support material in emission control catalysis [5,6]. Optimization of these applications requires a complex understanding of its electrochemical behaviour. In our previous works [7,8] we have demonstrated the possibility of cathodic electrodeposition of metal oxides including CeO_2 and Ce_2O_3 . The layers obtained are homogenous and show perfect adhesion to the substrate.

The purpose of this work is to investigate the kinetics of electrodeposition of CeO_2 and Ce_2O_3 from non-aqueous electrolytes.

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Experimental

The solution used consisted of a saturated univalent alcohol containing 0.1–0.3 M LiCl (Merck) as an electroconducting additive to which 0.1–0.3 M $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (Merck) was added.

A reference electrode [Ag/AgCl] in an aqueous solution of 3 M KCl (Merck) with a constant potential of 0.20 V with respect to a saturated hydrogen electrode was used. All results are expressed with respect to this electrode. The working electrode was an Au wire with a purity of more than 99.99%, mounted in Teflon holders. The potential range of +1 to –3 V with respect to the Ag/AgCl electrode was investigated. As counter electrode a platinum ring was used. The experiments were carried out in a solution aerated under natural conditions. When an inert atmosphere was needed, Ar of high purity was blown through the electrolyte for 1 h.

The measurements were performed with a 68 TS 1 Wenking potentiostat, a VSG 72 Wenking scan generator and a PM 8041 Philips X Y recorder. The layer structure was studied with an atomic force microscope (AFM Q-Scope 250 from Quesant Instrument Corporation (USA)).

Results and Discussion

As demonstrated in our previous work [7,8] oxygen plays an important role in the reduction of metal ions in alcoholic electrolytes. It was also found that the electro-deposition process in aerated solutions results in the formation of Ce_2O_3 , but in deaerated electrolytes in the deposition of CeO_2 . Therefore it is important to study the processes leading to the formation of either CeO_2 or Ce_2O_3 in both aerated and deaerated (argon purged) solutions.

The cyclic voltammetry curves (Fig. 17.1) clearly show the differences in the current/potential dependence caused by the existence of dissolved oxygen in the electrolyte. The large plateau in the range –0.25 V to –1.4 V consists of poorly resolved reduction peaks. A clear polarization effect was observed for potentials higher than –1.4 V. In argon the process supposed to take place is the reduction of hydrogen, followed by decharging of Ce ions. Anyway it was not possible to separate these peaks by changing the electrolyte composition or the sweep rate.

The galvanostatic and potentiostatic experiments provided much more information about this complicated reduction process.

Oxygen Reduction

First we investigated the oxygen reduction process (Fig. 17.2) in electrolytes containing only LiCl as supporting electrolyte, keeping the ionic strength equal to the electrolytes containing Ce. Two limited currents can be seen in Fig. 17.2a at

Fig. 17.1 Cyclic voltammograms on an Au electrode in an electrolyte containing 64 g/l $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ before and after purging with Ar for 1 h

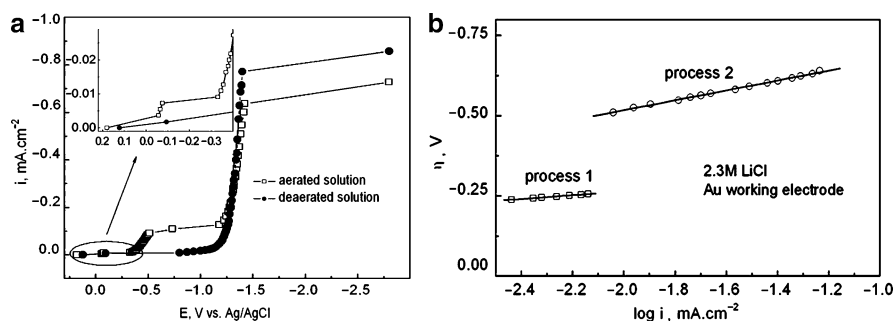
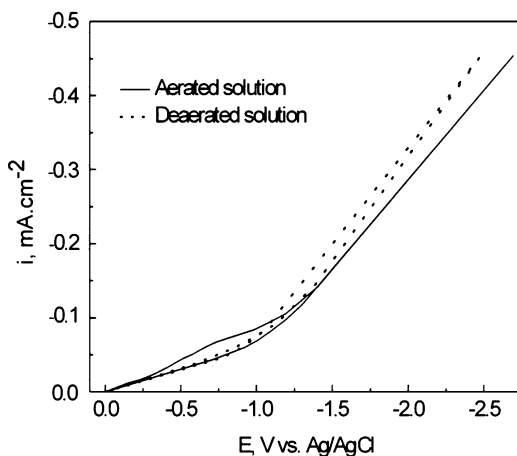
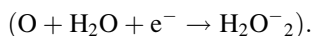


Fig. 17.2 Potentiostatic current-potential of a gold electrode in 2.3 M LiCl (a) and Tafel plots of the current/voltage characteristics of a gold electrode in the same solution (b)

potentials of $E_1 = -0.07$ V and $E_2 = -0.52$ V, respectively, representing two different stages of oxygen reduction. The first limited current was associated with a reduction of atomic oxygen. According to literature [9] the potentials of complete oxygen reduction are more positive than that of an incomplete reduction, i.e.- peroxide formation:



The Tafel constant b (Fig. 17.2b) has a classical value of 0.05885 V with an exchange current $i_{01} = 3.49 \times 10^{-7}$ mAcm^{-2} . Supposing a transfer coefficient value around $\alpha \sim 0.5$, the number of exchanged electrons should be two, which corresponds to the reduction of one O atom. The second limited current is much higher than the first one. The b value is 0.148 V, which we believe is due to a one electron transfer process with a transfer coefficient between 0.4 and 0.5. Additionally, the exchange current density is tenfold higher: $i_{02} = 3.36 \times 10^{-6}$ mAcm^{-2} .

The results obtained on the reduction of oxygen in an electrolyte containing only electrochemically inactive species (LiCl) lead to the conclusion that a more preferable reaction is the incomplete reduction of oxygen, leading to peroxide formation. Both reactions are irreversible and obey the Tafel law. This conclusion is very important in understanding the mechanisms of depositing oxides on the negative electrode (at reduction process).

Ce₂O₃ Deposition in Aerated Solutions

The addition of a Ce salt to the electrolyte changes the shape of the E/i curves (Fig. 17.3a). The oxygen plateaus remain, but a new one, associated with a hydrogen-limited current, followed by a Ce complex ion reduction, is obtained at a potential of $E = -1.5$ V vs. Ag/AgCl. So the oxygen reaction precedes the Ce ion reduction.

It is well known that the presence of metal cations (Me^{n+}) enhances the stability of metal peroxides [7].

In our opinion the peroxide ion formed on the surface first creates a complex with Ce^{3+} which is then electrochemically reduced to Ce_2O_3 . For this reason it is possible to deposit directly Ce_2O_3 on the cathode substrate and not metallic Ce, despite the higher negative potential of the Ce^{3+}/Ce redox couple ($E = -2.43$ V vs. a standard hydrogen electrode). However, the end product is not metallic Ce but directly an oxide [7,8]. Fig. 17.4a presents an AFM image with the typical oxide surface structure of the electrodeposited Ce_2O_3 film.

According to a method proposed by Frumkin [10], the dependence

$$\left[\frac{\partial \ln i}{\partial \ln c} \right]_{E - ((RT)/(n_2 F)) \ln c} = - \frac{n_1}{n_2} \quad (17.1)$$

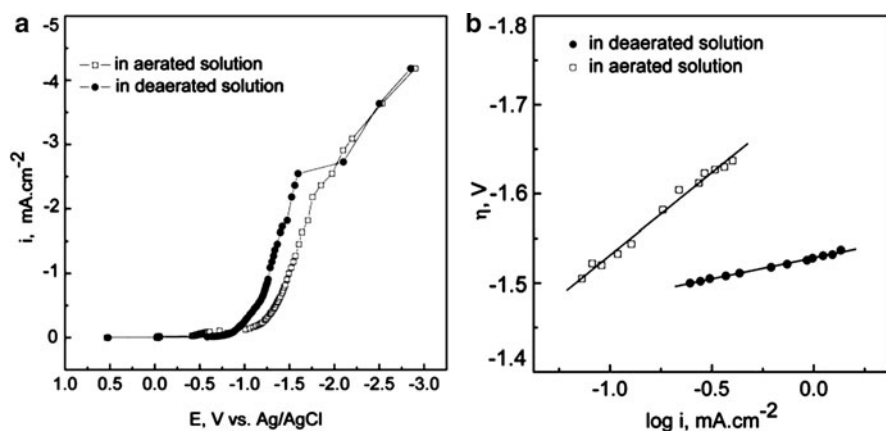


Fig. 17.3 Potentiostatic current/potential curves of a gold electrode in 0.3 M $CeCl_3 \cdot 7H_2O$ (a) and Tafel plots of the current/voltage characteristics of a gold electrode in the same solution (b)

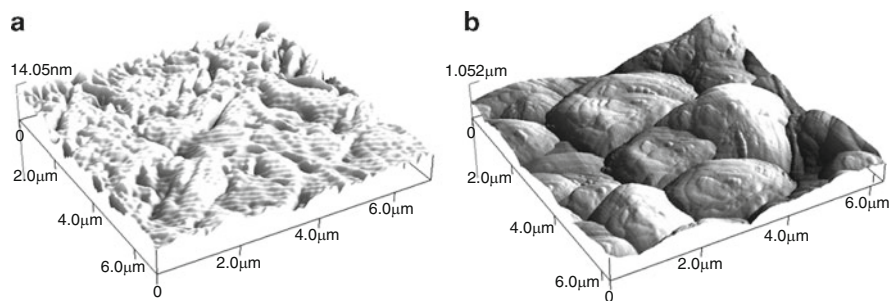


Fig. 17.4 AFM images of Ce_2O_3 (a) and CeO_2 (b) on gold substrates

permits the determination of the charge of an ion participating in an electrochemical reaction. In the above equation n_1 is the charge of the ion being investigated, and n_2 is the charge of the lithium cation in electrolyte. Determining the dependence of the current on the concentration of LiCl $\ln c$ at constant $E - (RT/n_2F)$, one can obtain the ion charge from the slope of the straight line. The charge of the cerium complex as determined on the basis of this equation is $n = +1$.

The partial current of the reaction of Ce_2O_3 formation and the corresponding Tafel parameters were determined (Fig. 17.3b) by the weight method (weighing the samples after 30 min deposition time at constant voltages).

According to these results we calculated from the Tafel slope and $n = 1$ a value of 0.3 for the transfer coefficient α . Thus we concluded that the Ce_2O_3 deposition process is under strong charge transfer control with a relatively low transfer coefficient. Because of the poor electronic conductivity of the oxide film the maximal thickness we obtained was up to 10 μm .

Ce Electrodeposition from Inert Solutions

It can be seen Fig. 17.3 that in the curve recorded in an electrolyte purged for 1 h with Ar the oxygen limited current misses. A Faraday process can be observed only for a potential of $E = -0.7$ V. On the other hand by XPS we detected Ce as a metal deposited at a potential of $E \geq -1.4$ V [7]. So the first process is obviously hydrogen reduction, followed by Ce deposition. As can be seen from Fig. 17.4b the film structure in this case differs considerably from that of Ce_2O_3 . A classical spiral crystal growth, typical for metals, can be seen. This is one of the reasons why we could obtain much thicker films up to 23 μm , compared to about 10 μm thickness of Ce_2O_3 layers [2,3]. Since Ce is unstable in air it can be easily oxidized, forming preferably CeO_2 . Nevertheless our attempts to detect cerium in the metallic state in XPS spectra (by depth profiling with Ar^+ bombardment) [7,8] were without success. In our opinion, according to the surface structure, our films are not dense enough to prevent oxygen permeation and subsequent oxidation.

Conclusions

The kinetics of Ce_2O_3 and CeO_2 film deposition/formation were studied. The parameters of oxygen and Ce ion reactions were determined by potentiostatic and galvanostatic measurements. It was demonstrated that the electrochemical reduction of oxygen plays an important role in the electrode processes.

On the basis of the results obtained the charge of the reacting Ce ions was determined both in aerated and inert solutions. A different structure of the layers in the presence/absence of oxygen was observed. A direct electrochemical reduction of positively charged Ce-oxygen complexes to Ce_2O_3 was suggested. We suppose that in inert solutions the formation of metallic cerium is the main reaction followed by oxidation of the layer formed to CeO_2 .

Acknowledgment This work has been realized with the support of the Bulgarian National Fund for Scientific Investigations under Contract DO 02-242/TK-01-185.

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Part IV.3

Chalcogenide Glasses

Chapter 18

Multicomponent Chalcogenide Glasses: Advanced Membrane Materials for Chemical Sensors and Nanosensors

Sylvia Boycheva and Venceslav Vassilev

Abstract The present report describes the development of chemical sensors selective to heavy metal ions with membranes based on multicomponent chalcogenide glasses (ChGs). ChGs containing a GeSe_2 -glass-former, a $\text{Sb}_2\text{Se}_3(\text{Sb}_2\text{Te}_3)$ -network-modifier and heavy metal chalcogenides MeCh (Me = Zn, Cd, Sn, Pb; Ch = Se, Te) were synthesized and applied as active membrane components in chemical sensors. The main aspects of material synthesis, sensor design and analytical test results as well as concepts for the potential-generating mechanisms are discussed.

Keywords Chemical sensors · Chalcogenide glasses · Heavy metals · Water control

Introduction

Recently, the increased necessity for ecological and health risk assessment and for pollution prevention requires novel solutions for extremely fast, reliable and low-cost control. Potentiometric chemical sensors bear possibilities for rapid detection, but the main restrictions for their wide practical application originate from the insufficient chemical durability and selectivity, which requires the development of novel membrane materials.

Chalcogenide glasses (ChGs) are advanced materials for chemical sensors due to their better resistance in acidic and redox media, better selectivity and reproducibility

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of the analytical characteristics, and longer life time as compared to liquid and polycrystalline membranes [1]. As a rule, ChG membranes are reversible to metal ions included in the glassy alloys, and thus their selectivity could be managed [2–4]. Suitable for potentiometric applications are materials with low conductivities where the ionic part of the conductance exceeds that of the electronic transport. Chalcogenide glass-formers dissolve comparatively high percentages of metal chalcogenides; in this way the membrane selectivity towards special ions could be managed. In addition, multicomponent ChGs possess excellent glass-forming abilities and allow properties control by varying the chemical composition in wide ranges. According to the trends of device miniaturization, ChGs can be easily obtained in form of amorphous thin film by conventional deposition techniques due to their disordered structure; thin film chemical sensors allow the detection of trace level concentrations with extremely fast response [4, 5].

Experimental

Synthesis of Multicomponent ChGs

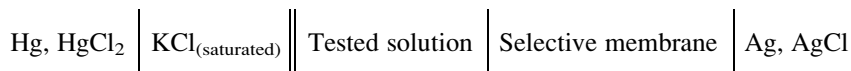
Multicomponent ChGs were obtained from preliminary synthesized compounds starting from pure elements (5 N) by direct monotemperature synthesis in evacuated (0.01–0.10 Pa) quartz ampoules. The thermal regimes were selected according to the physicochemical peculiarities of the initial and intermediate compounds and the final products to ensure completed interaction between the starting components. During the heating process several thermal holdings were performed at about 40–50°C above the melting points of each initial, intermediate and final component. The maximal synthesis temperature, depending on the ChG alloy composition, reached values between 600°C and 1100°C. Finally, vibration stirring was applied to homogenize the melt, which was rapidly quenched to room temperature in air, ice water or in liquid nitrogen.

Chemical Sensor Design

Several constructional types of ChG membranes are known [1]. The most common are “homogeneous”, i.e. disks either cut from bulk ChG specimens and polished or prepared from ChG powders by pressing. The disks are hermetically attached to the end of glass, polyethylene or quartz tubes, and an electrolytic or ohmic contact can be realized between the inner reference electrode and the membrane. These homogeneous membranes allow long time of exploitation and, after continuous work, can be easily restored by surface polishing and conditioning.

Composite membranes have been developed in order to overcome the problems originating from the insufficient hardness of the ChGs. They consist of ChG powders homogeneously dispersed in an inert matrix. A better analytical performance is insured by the design of all-solid-state sensors of the so-called “coated wire” type, for which a homogenous mixture of a polymer and a small amount of ChG powder (1–5%) is coated on to reference Ag/AgCl electrodes.

Our measurements were performed in the following standard electrochemical cell:



A calomel electrode was used as a comparative semielement. The electrochemical cell potential was measured with an accuracy of ± 0.2 mV in sequence of progressively increasing concentrations of standard solutions and under constant magnetic stirring (200 min^{-1}). Before each series of measurements, membrane conditioning was carried out in a $10^{-3} \text{ mol l}^{-1}$ solution of the potential-determining ion for stabilization of the calibration functions.

Results and Discussions

The glass-forming regions in the multicomponent $\text{GeSe}_2\text{-Sb}_2\text{Se}_3(\text{Sb}_2\text{Te}_3)\text{-SnSe}$ (CdSe) systems are presented in Fig. 18.1.

Obviously, the $\text{GeSe}_2\text{-Sb}_2\text{Se}_3(\text{Sb}_2\text{Te}_3)$ couples give broad glass-forming regions where significant amounts of the MeChs (up to 57 mol% SnSe and 27 mol% CdSe in the $\text{GeSe}_2\text{-Sb}_2\text{Se}_3$ and $\text{GeSe}_2\text{-Sb}_2\text{Te}_3$ systems, respectively) can be dissolved.

The designed sensors were tested with respect to their basic analytical characteristics: stability, linearity L (mol l^{-1}) and slope S (mV dec^{-1}) of the calibration function, working pH-range, limits of detection LD (mol l^{-1}), response time τ_{95} (s) and selectivity coefficients (K_{ij}) in the presence of different ions. Typical calibration functions of ChG chemical sensors selective to Cd^{2+} - and Sn^{2+} -ions are plotted in Fig. 18.2. The ChG compositions applied as membrane active components, the

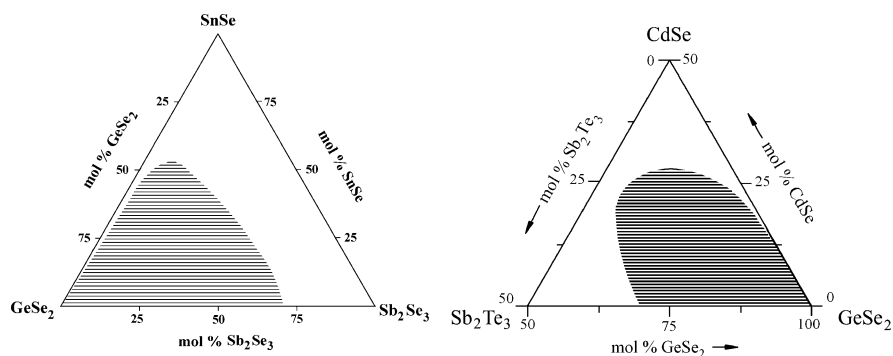


Fig. 18.1 Glass-formation in the $\text{GeSe}_2\text{-Sb}_2\text{Se}_3(\text{Sb}_2\text{Te}_3)\text{-SnSe}(\text{CdSe})$ systems

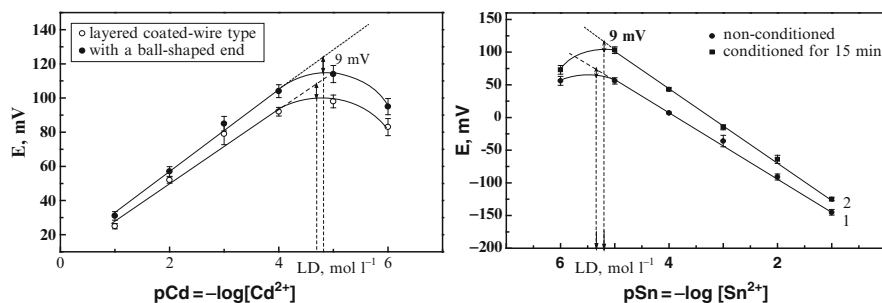


Fig. 18.2 Calibrations curves of ChG chemical sensors selective to Cd^{2+} - and Sn^{2+} -ions

Table 18.1 Analytical characteristics of chemical sensors with ChG membranes

Detected ion	Membrane composition, mol. %	Constructional type	L , mol l^{-1}	S , mV dec^{-1}	LD , mol l^{-1}
Pb^{2+}	$(\text{GeSe}_2)_{56}(\text{PbSe})_{24}(\text{PbTe})_{20}$	Coated-wire	10^{-5} to 10^{-1}	25.8	5.20×10^{-6}
	$(\text{GeSe}_2)_{54}(\text{PbSe})_6(\text{PbTe})_{40}$	Coated-wire	10^{-5} to 10^{-1}	19.0	3.50×10^{-6}
Sn^{2+}	$(\text{GeSe}_2)_{54}(\text{Sb}_2\text{Se}_3)_{36}(\text{SnSe})_{10}$	Coated-wire	10^{-5} to 10^{-1}	56.5	6.34×10^{-6}
	$(\text{GeSe}_2)_{36}(\text{Sb}_2\text{Se}_3)_{24}(\text{SnSe})_{40}$	Coated-wire	10^{-5} to 10^{-1}	56.0	6.47×10^{-6}
Cd^{2+}	$(\text{GeSe}_2)_{60}(\text{Sb}_2\text{Se}_3)_{15}(\text{SnSe})_{25}$	Layered coated-wire	10^{-4} to 10^{-1}	24.0	2.20×10^{-5}
Zn^{2+}	$(\text{GeSe}_2)_{64}(\text{Sb}_2\text{Se}_3)_{16}(\text{ZnSe})_{20}$	Coated-wire	10^{-4} to 10^{-1}	29.0	7.90×10^{-5}
	$(\text{GeSe}_2)_{54}(\text{ZnSe})_6(\text{ZnTe})_{40}$	Homogeneous	10^{-5} to 10^{-1}	17.0	5.0×10^{-7}

membrane type and the main analytical characteristics of chemical ChG sensors selective to Pb^{2+} -, Sn^{2+} -, Cd^{2+} -, Zn^{2+} -ions are summarized in Table 18.1.

The proposed chemical sensors based on multicomponent ChGs with GeSe_2 -glass-former show a reliable analytical performance with linear calibration functions in the concentration range of $10^{-5}(10^{-4}) - 10^{-1} \text{ mol l}^{-1}$ of the detected ions. The slopes for Sn^{2+} -selective sensors correspond to the Nernstian value for one-valence ions, while those selective to Pb^{2+} -ions to that for two-valence ions. The minimal detection levels are of the order of $10^{-6} \text{ mol l}^{-1}$ (Table 18.1). The limits of the working pH-range $\text{pH}_{\min} \leq \text{pH} \leq \text{pH}_{\max}$ depend on the concentration of the detected ions; for most of the devices tested $\text{pH}_{\min} = 1$, while $\text{pH}_{\max}$ is limited by the precipitation of metal hydroxide into the solution; it is lower in concentrated solutions. In strong acidic media ($\text{pH} < 1$), the sensor membranes are preserved without damages, but their analytical parameters are worsened. No irreversible changes in the membrane materials were observed as a result of chemical attacks or aging processes.

The response time τ_{95} , which is the time for the establishment of the equilibrium potential, was on the order of several seconds, even less for the Cd^{2+} -selective sensors. The establishment of the dynamic equilibrium $\text{Me(II)}_{\text{solid} \rightarrow \text{solution}} \leftrightarrow \text{Me(II)}_{\text{solution} \rightarrow \text{solid}}$ depends on the membrane type, the composition of the active component and the ionic strength of the solution.

The cross-sensitivity of the ChG sensors was investigated in the presence of a number of different ions, which commonly accompany the corresponding detected ions in the analytical media. In most cases, comparatively low values were obtained for K_{ij} , which means that these ions do not interfere the determination of the main ions at concentration levels of 10^{-3} to $10^{-2} \text{ mol l}^{-1}$ and lower [6].

A model to explain the sensitivity mechanism of ChG membrane sensors has been proposed by Vlasov [7] assuming the existence of a modified surface layer (MSL), which is formed on the membrane surface after the contact with the analyzed electrolyte. The MSL results from the interaction taking place between the solution and the partially destroyed glassy network, which is accompanied by the creation of active exchange centers. The generation process is a direct ionic exchange between the electrolyte and the induced centers on the ChG membrane surface.

During the investigation of GeSe_2 -based membranes, some peculiarities in their analytical behavior were observed: (1) in the initial measurements the time necessary for the establishment of a stable potential was much longer than that after continuous measurements; (2) for some membranes, the slope of the calibration function decreases from a value typical for univalent ions ($\sim 59 \text{ mV dec}^{-1}$) in the beginning of the test and stabilizes at the slope for two-valence ions ($\sim 29 \text{ mV dec}^{-1}$) during the next measurements [8]; (3) the calibration functions have slopes typical for anions. Additional assumptions are required to explain these analytical features observed.

In ChG systems containing atoms with unshared electron pairs, e.g. S, Se and Te, a heterolytic break of the chemical bonds leads to the creation of positively and negatively charged defect centers. This formation of charged defect centers in GeSe_2 -based glasses is schematically presented in Fig. 18.3a.

In the initial measurements, the exchange process is stipulated by Me^{2+} -ions in negatively charged $[\text{Se}(\text{GeSe}_{3/2}\text{R}_1\text{R}_2)]^-$ defect centers, resulting in slopes for

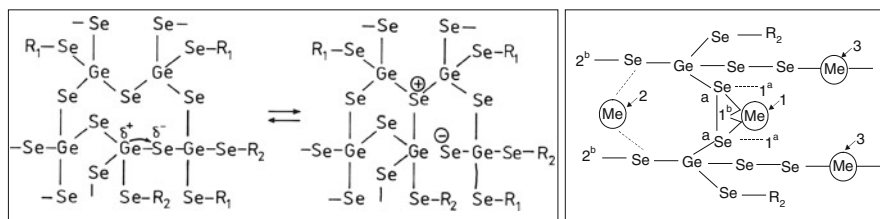


Fig. 18.3 Defect centers in GeSe_2 -based ChGs: (a) formation of positively and negatively charged one-valence defect centers; (b) structure of negatively two-valence charged defects after membrane conditioning

univalent anions. After conditioning, the negatively charged $[\text{Se}(\text{GeSe}_{3/2}\text{R}_1\text{R}_2)]^-$ defects possessing a higher mobility than the positive $[\text{Se}(\text{GeSe}_{3/2}(\text{R}_1)_2\text{R}_2)]^+$ can interact with each other or with other structural fragments resulting in negative two-valence defects (Fig. 18.3b).

During ChG synthesis, Me atoms occupy position 3 and participate in the initial working stage of the sensors. After continuous measurements, Me^{2+} -ions from the solution occupy position 2 in the defect centers (Fig. 18.3b). Simultaneously, the bond between the two bridged Se atoms breaks, resulting in the formation of two novel bonds (position 1^a, Fig. 18.3b). Further, the Me^{2+} -ions coming from the solution occupy position 1 connecting the two free bonds 1^a, as meanwhile Me^{2+} -ions from position 2 pass into the solution. Again two free bonds 2^b are formed. The consecutive occupation of the active positions 1 and 2 in the defect center is repeated ensuring permanent sensor work. This potential-generating mechanism explains the membrane reversibility and why in the beginning the time necessary for stable potential establishment is much longer than after continuous work.

Conclusion

Multicomponent ChGs based on GeSe_2 -glass-formers containing MeCh (Me = Zn, Cd, Sn, Pb; Ch = Se, Te) are advanced membrane materials for chemical sensors reversible to heavy metal ions. The proposed devices guarantee a reliable determination in acidic media, a good selectivity and detection limits of $\sim 10^{-6} \text{ mol l}^{-1}$. Thin film membranes based on the proposed compositions will have advantages for trace concentration level detection and faster response.

Acknowledgements The authors thanks to the NSF (Ministry of Education, Science and Technology of the Republic of Bulgaria) for grant DO 02-123/2008.

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Chapter 19

Optical Properties of Thin Ge-Se-In Chalcogenide Films for Sensor Applications

Plamen Petkov and Emil Petkov

Abstract (GeSe₅)_{1-x}In_x chalcogenide glasses with 5,10,15,20 mol% In have been investigated. Some physico-chemical characteristics have been obtained: the density ρ , compactness δ , and molar volume V_m . The free volume percentage FVP has been attained; correlations with the mean coordination number Z are discussed. The number of constraints per atom N_{co} as a function of the average coordination number has been calculated. The correlations between composition and properties of the glasses are discussed in terms of structural transformations in the glassy matrix. The processes of vacuum evaporation and condensation in the Ge-Se-In system were investigated. The films deposited under the conditions used are amorphous and without 3D defects as proven by TEM analysis. The optical spectra of the thin films have been studied with a view to understand the role of indium on the film behavior. An optical characterization method based on transmission and reflection spectra at normal incidence of uniform thin films has been used to obtain the thicknesses and optical constants of as-deposited and annealed samples. The dispersion of the refractive index is discussed in terms of the single-oscillator Wemple-DiDomenico model. The absorption edges are described using both the Urbach rule and the ‘nondirect transition’ model proposed by Tauc. The variations in the refractive index, the band-gap, and the oscillation energy of the films after annealing are discussed in terms of rearrangements of the main structure units.

Keywords Chalcogenide glasses · Thin films · Optical properties · Sensors

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Introduction

A rising interest in the possible use of optical sensors for miniaturized devices has lead to an extensive study of chalcogenide glasses (ChGIs) in recent years due to their flexible structure, enormous variation in properties, and almost unlimited ability of doping and alloying making them promising materials for sensors for monitoring pollutant gases in the environment [1]. Moreover, ChGIs are conducive for use in fiber optics and integrated optics since they have many unique optical properties [2–4]. Due to their IR transparency, photosensitivity, high optical non-linearity, and rare-earth doping potential, these glasses have been utilized to fabricate photonic devices such as fibers [5], planar waveguides [6], gratings [7], all-optical switches [8], and fiber amplifiers [9]. Germanium chalcogenides have traditionally been used for mid-IR fibers with transmission windows up to 12 μm . In addition, germanium-doped chalcogenides exhibit photoconductivity and band gap shrinkage with increasing doping, suggesting their potential application in low-cost mid-IR detection, which necessitates the investigation of their optical properties and their ability to appropriately modify the band structure [10–17].

For many of above mentioned applications, thin films are necessary. The wide practical application of thin amorphous chalcogenide films, especially of vitreous Ge-containing condensates, is closely connected with their transparency in the visible and near IR spectral regions and with the possibility to create optical media with defined values of the refractive index, dispersion, and extinction coefficient [18–21]. The relatively low energy of the chemical bonds in Ge-based chalcogenide glasses offers the opportunity for photostructural transformations and a number of other light-induced effects, all of which are typically accompanied by considerable changes in the optical constants of the chalcogenides.

Many methods for thin film preparation have been studied. Some include spin-coating, evaporation of one or more materials at low pressures and high temperature in vacuum, ionic and magnetron sputtering, pulsed laser deposition, and chemical vapor deposition. The preparation of chalcogenide thin films of complex compositions can be a difficult task and classical deposition methods can often not be used to form films with a strict stoichiometry match to the target.

We present the preparation of films from Ge–Se–In glasses by thermal evaporation. We further establish a correlation between the film composition and the optical properties of the glasses as determined from chemical and physical property measurements.

Experiment

Sample Preparation

1. Bulk Glass Synthesis

Glassy alloys of $(\text{GeSe}_5)_{1-x}\text{In}_x$ ($x = 0, 5, 10, 15, 20$) were prepared by the quenching technique. The respective amounts of Ge, Se and In elements with

5 N purity were mixed and sealed in quartz ampoules evacuated down to 1.33×10^{-3} Pa. The ampoules were heated with a rate of 2 K/min up to 1,200 K. During heating they were constantly rocked to obtain homogeneous glassy alloys. After holding and rocking for about 12 h, the melt was rapidly quenched in ice-cooled water.

2. Thin Film Deposition

Thin films were deposited from the relevant bulk glasses by thermal vacuum evaporation in a Leybold LB 370 vacuum system. The process conditions were: a residual pressure in the chamber of 1.33×10^{-3} Pa, a distance between the evaporation source and the substrates of 0.12 m, an evaporation area of $1.2 \times 10^{-6} \text{ m}^2$ of an inductively heated tantalum evaporator; they were carefully monitored and examined. The substrates were rotated during the deposition to prevent the preparation of inhomogeneous and non-uniform films. The evaporation temperature ranged from 600 to 800 K; it was controlled by a Ni-Ni/Cr thermocouple. The films were annealed in vacuum for 1 h in a furnace at a temperature of 390 below the glass transition temperature of the glasses.

Properties Examination

1. Bulk glasses behavior

The glassy nature of the alloys was verified by X-ray diffraction. The Philips diffractometer used worked in θ - 2θ Bragg-Brentano geometry with Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$) and a graphite monochromator for the diffracted beam. The diffraction data were collected for 60 s at each 0.2° step over a 2θ range from 5 to 150° corresponding to scattering vectors Q between 0.4 and $8 \text{ \AA}^{-1}$ ($Q = 4\pi\sin\theta/\lambda$). All X-ray investigations were performed at ambient temperature. The diffraction intensities were corrected for the background, incoherent (polarization and absorption) and multiple scattering.

Essential physical-chemical characteristics of the glasses were derived from experimental results and theoretical considerations:

- The density was measured by a pycnometric method and calculated by the formula given elsewhere [22] with an average accuracy of 0.5%.
- The compactness of the materials was calculated using the relation

$$\delta = [(\sum c_i A_i)/\rho_i - (\sum c_i A_i)/\rho]/(\sum c_i A_i)/\rho \quad (19.1)$$

where c_i , A_i and ρ_i are the atomic fraction, atomic weight and density of the components, and ρ is the theoretical value of the density.

- The molar volume was obtained by the equation:

$$V_m = (\sum c_i A_i)/\rho \quad (19.2)$$

where A_i is the atomic weight of the i^{th} component, c_i is the molar content of this element in the sample, and ρ is the measured density. The experimental V_m data were correlated to the theoretical molar volume V_T determined as a sum of the molar volumes of the components multiplied by the atomic fraction of each of them: $V_T = \sum c_i V_i$.

- The free volume percentage FVP in the glass was obtained according to:

$$\text{FVP} = (V_m - V_T)/V_m \times 100\% \quad (19.3)$$

- The average coordination number Z that expresses the number of the nearest neighbor atoms of Ge, Se and In was estimated as theoretical value according to Ref. 5 as $Z = 4x + 2y + 3z$, where x , y and z are the atomic fractions of Ge, Se and In, respectively.
- The number of constrains per atom can be calculated according to the Phillips [23] assessment $N_{co} = N_d$, i.e. the number of topological constraints N_{co} of an atom is equal to the number of degrees of freedom N_d . N_{co} is defined by:

$$N_{co} = N_a + N_b = Z/2 + (2Z - 3) \quad (19.4)$$

where N_a and N_b are the radial and the axial bond strengths, respectively.

2. Thin Films Properties

The film composition was investigated by Auger electron spectroscopy, the film structure was studied by means of scanning electron microscopy (SEM, JEOL 2,000) and transmission electron microscopy (Philips TEM 400).

Optical transmission and reflection spectra of as-prepared and annealed films were investigated in the spectral region from 400 to 2,500 nm. The spectra were obtained using a computer controlled double beam UV/VIS/NIR spectrophotometer (JASCO V-670) with a wavelength accuracy of ± 0.3 nm in the UV/VIS region and ± 1.5 nm in the NIR region. The basic optical parameters were calculated using the Wemple-DiDomeniko model of single optical oscillator [24]. The film thickness was estimated from the optical transmission spectra by the Swanepoel method and compared with the SEM results.

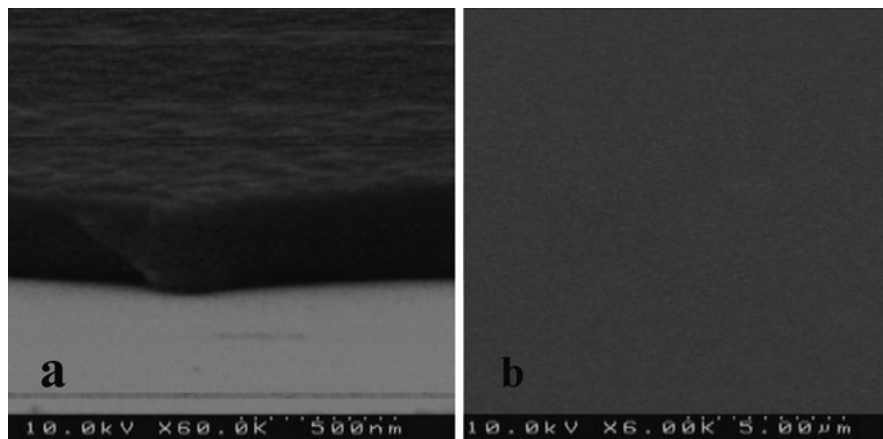
Results

Bulk Glasses Behavior

Table 19.1 summarizes the parameters derived from the density study, the molar volume and the compactness, and the values obtained from correlations between the experimental data and theoretical approaches. In an ideal glass the value of mechanical constraints N_{co} is equal to 3 which defines the maximum of the mechanical

Table 19.1 Physico-chemical properties of the Ge-Se-In compounds

Composition	Density [kg m^{-3}]	Z	$V_m 10^{-5} [\text{m}^3 \text{mol}^{-1}]$	δ	N_a	N_b	N_{co}
$\text{Ge}_{17}\text{Se}_{83}$	4338	2.34	1.8	0.04	1.17	1.68	2.85
$\text{Ge}_{16}\text{Se}_{79}\text{In}_5$	4545	2.37	1.75	0.09	1.18	1.72	2.9
$\text{Ge}_{15}\text{Se}_{75}\text{In}_{10}$	4669	2.4	1.75	0.30	1.2	1.8	3
$\text{Ge}_{14}\text{Se}_{71}\text{In}_{15}$	4666	2.43	1.79	0.11	1.215	1.86	3.075
$\text{Ge}_{13}\text{Se}_{67}\text{In}_{20}$	4767	2.46	1.79	0.11	1.23	1.92	3.15

**Fig. 19.1** SEM cross section (*left*) and top view picture (*right*) of thin $(\text{GeSe}_5)_{80}\text{In}_{20}$ film

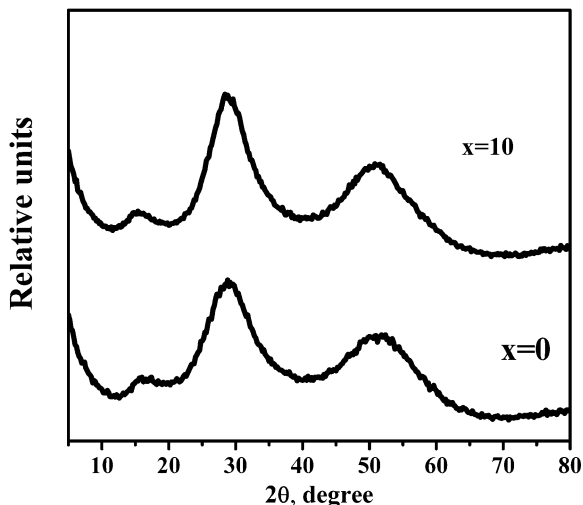
strength of the network [8]. For $(\text{GeSe}_5)_{1-x}\text{In}_x$ the value $N_{co} = 3$ is reached in samples with 10 mol.% indium, indicating a structural transition at this composition. The development of density and molar volume shows an almost linear increase with the In content with small deviations for samples with 10 mol.% In where the threshold is expected as predicted by the mechanical constrain values.

Characterisation of the Condensates

As-prepared films are dark red coloured, homogeneous on the surface and in the depth as established from profile measurements (Fig. 19.1a). The top-view SEM-picture reveals the uniform and smooth surfaces of the films of this study (Fig. 19.1b). Neither defects (liquation) nor traces of initial nucleation are visible.

The chemical composition of the thin films was found to be close to the composition of the targets used. The conditions of evaporation and condensation were studied to optimize the preparation of films uniform in thickness and composition.

Fig. 19.2 X-ray diffraction patterns of $(\text{GeSe}_5)_{1-x}\text{In}_x$ films



The amorphous nature of the films was proven by TEM and XRD studies. The diffraction patterns of all films are very similar with broad halos and without sharp peaks of crystalline phases. The electron diffractograms also prove the amorphous character of the layers by the absence of sharp rings in the patterns (Fig. 19.2).

Kinetics of Evaporation and Condensation

Basic equations of the gas theory have been applied to study the evaporation and condensation processes. The free evaporation in vacuum from a small area evaporator is defined by the specific evaporation rate v_e from the equation:

$$v_e = 0.584 \alpha_e p_0 \sqrt{\frac{M}{T_e}} \exp\left(-\frac{Q_e}{RT_e}\right) \quad (19.5)$$

where α_e is the evaporation coefficient, p_0 the residual pressure, M the molar mass, T_e the evaporation temperature, Q_e the evaporation energy and R the universal gas constant. The experimental results obtained for $(\text{GeSe}_5)_{1-x}\text{In}_x$ layers are presented in Fig. 19.3 (left).

Since the process of condensation is similar to the evaporation the specific condensation rate v_c can be determined by a similar equation:

$$v_c = k \alpha_c \sqrt{\frac{1}{T_s}} \exp\left(-\frac{Q_c}{RT_s}\right) \quad (19.6)$$

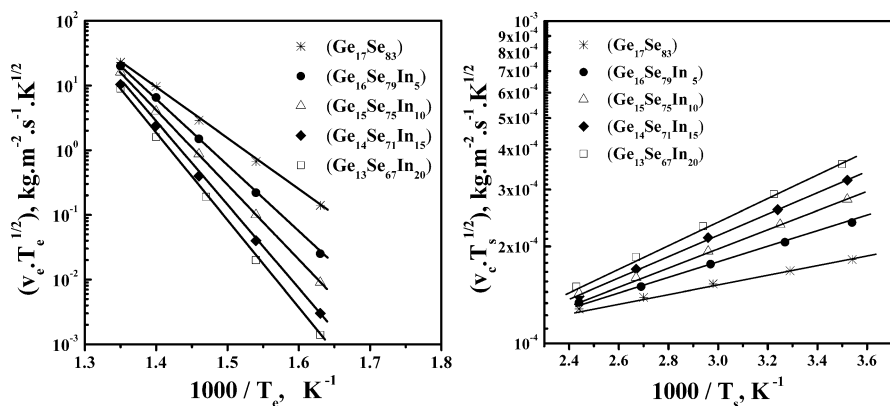


Fig. 19.3 Evaporation (*left*) and condensation (*right*) rates vs temperature

Table 19.2 Evaporation and condensation energy values of the deposited thin films

No	Composition, mol%	Evaporation energy, kJ/mol	Condensation energy, kJ/mol
1	$\text{Ge}_{17}\text{Se}_{83}$	126	5.99
2	$\text{Ge}_{16}\text{Se}_{79}\text{In}_5$	130	6.21
3	$\text{Ge}_{15}\text{Se}_{75}\text{In}_{10}$	137	6.50
4	$\text{Ge}_{14}\text{Se}_{71}\text{In}_{15}$	148	6.84
5	$\text{Ge}_{13}\text{Se}_{67}\text{In}_{20}$	155	7.03

where α_c is the condensation coefficient, T_s the substrate temperature, and Q_c the condensation energy.

The specific evaporation rate of the layers rises with temperature and the selenium amount in the film in the entire temperature range studied as seen in Fig. 19.3 (left). Higher evaporation temperatures favor the process and increase the rate of evaporation by several orders of magnitude, with very similar values in the region of the highest evaporation temperature.

The values of the specific condensation rate v_c , calculated by Equ. (19.6), are plotted in Fig. 19.3 (right). The results show a regular increase of the condensation rate with the indium addition in the films.

The evaporation energies determined from the slope of the graphical dependence $\ln(v_e T_e^{1/2}) = f(1/T_e)$ with an accuracy of ± 0.5 kJ/mol are given in Table 19.2.

The variations in the evaporation and condensation energy values can be viewed in terms of the compositional and structural changes in the films. During the evaporation process of binary Ge-Se glasses the vapor phase most probably consists of GeSe and Se_n units as already reported in Ref. [25,26]. The evaporation enthalpy of GeSe (151 kJ/mol) and the sublimation enthalpy of Se_n (120 kJ/mol) possess relatively similar values and therefore co-evaporation of GeSe fragments and Se_n molecules is very reasonable. Another point of view which supports

this suggestion is the reduction of the absolute number of “free” selenium atoms during the evaporation process since a selenium deficiency strongly supports the idea of co-evaporation of GeSe and Se_n and In_2Se_3 molecules.

The energy needed to break the bonds grows with the indium content; this leads to an increase of the energy required for evaporation. In additives in GeSe_5 glasses bring about changes in the glass packing and alloying effects in the host Ge-Se network. Since the energy of Se-In bonds (201,8 kJ/mol) is higher compared to that of Se-Se single bonds of 184.2 kJ/mol, the average bond energy of the system increases and the stability of the material grows [27]. The increase in the number of structural fragments containing indium in the vapor phase results in a reduction of the evaporation rate as presented in Fig. 19.3. In films with a Ge/Se ratio 5 the increased amount of selenium results in a decreased fraction of high energetic Ge-Se bonds (205.6 kJ/mol) and a corresponding decrease of the network cross-linking.

The higher the temperature of evaporation the easier is the process of evaporation is due to the easier migration of the units in the vapor phase. The logical result is the higher specific rate of evaporation obtained for all samples studied.

Apparently, a decrease of the Se content facilitates the condensation process while indium addition plays the opposite role (Table 19.1). Such a behavior is probably related to the so-called “migration” condensation mechanism which is typical for chalcogenide materials [28]. The condensation energy includes the diffusion energy of the particles on the surface, their kinetic energy and the desorption energy. The GeSe and Se_n molecules adsorbed on the surface possess a kinetic energy much higher than the energy for surface diffusion. The molecules freely move and change their position until they become finally “entrapped” somewhere on the surface (in spots with a low surface energy). In the next step, entrapped molecules become agglomerates which include a large number of molecular fragments. These condensates are more stable and resistant against re-evaporation.

Finally, an increase of the indium content in the glassy matrix constituted by selenium and germanium atoms probably leads to gradual structural changes: the degree of cross-linking and packing increases due to an increased average bond energy in the system. The latter is explained by the replacement of low energy Se-Se bonds with high energy In-Se ones with a negligible change of the fraction of Ge-Se bonds. Probably the higher average bond energy is the crucial factor that defines the higher evaporation and condensation energies of Ge-Se-In layers.

Optical Parameters of the Films

The transmission spectra recorded within the spectral range of 400–2,500 nm show interference maxima and minima at higher wavelengths approaching the transmission of substrate. A red shift of the interference-free region is visible in Fig. 19.4 with increasing indium content. This red shift of the film transmission

Fig. 19.4 Spectral dependence of the films transmission

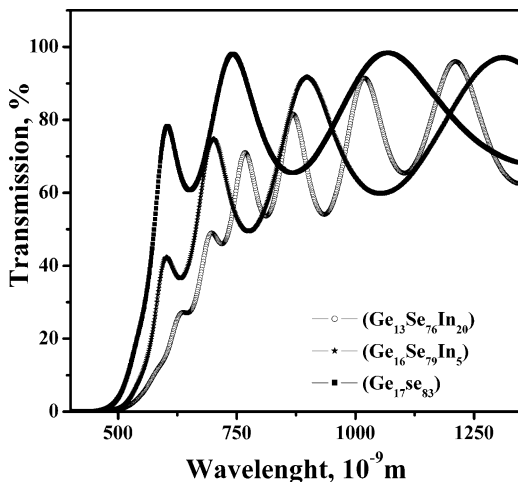
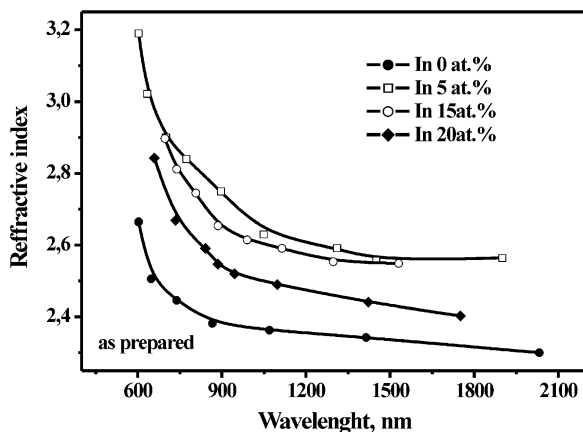


Fig. 19.5 Spectral dependence of the refractive index



proves that in the Urbach tail, i.e. below the optical absorption edge, the light can generate mobile carriers (holes) in the films.

The presence of maxima and minima with almost equal intensities confirms the optical homogeneity of the deposited film, i.e. no scattering or absorption occurs at longer wavelengths. The transmission spectra recorded after annealing exhibit a red shift of the optical absorption edge, most probably due to structural transformations and an increase in the optical density of the film.

The spectral dependencies of the refractive index were calculated from the optical transmission spectra of as-deposited and annealed thin films using a modified Swanepoel method [29]. The error in the determination of the refractive index was evaluated to ± 0.0015 . The addition of 5 at.% indium causes an increase of the refractive index values (Fig. 19.5).

Further addition of indium shifts the values back and reduces the refractive index. The unusual increase of the index can be viewed as result of the mechanism of the preparation process. The indium atoms are most probably situated at the film/substrate interface due to so-called migration mechanism which is typical for chalcogenide deposition. The films become optically denser in the interface area resulting in higher values of the refractive index. The increase of the number of migrated indium atoms allows a better optical homogenization and the appearance of new structural units, namely In_2Se_3 randomly distributed in the chalcogenide matrix which leads to an optical homogenization of the film. After annealing the refractive index shifts to higher value which suggest a re-organization in the films. The changes are more expressed in films without indium whereas in films with higher indium concentrations the changes are negligible.

The optical transmission T is a very complex function and strongly depends on the absorption coefficient α . α was determined from the envelope of the interference maxima and minima of the transmission spectra using an equation based on the modified Swanepoel method. In the strong absorption region ($\alpha \geq 10^4 \text{ cm}^{-1}$), which involves optical transitions between the valence and conduction bands, the absorption coefficient is, according to the 'non-direct transition' model proposed by Tauc [30], given by the following equation

$$(\alpha h\nu) = B(h\nu - E_g)^m \quad (19.7)$$

Here $h\nu$ is the effective photon energy, E_g the optical band gap, B a constant proportional to the square of the joint density of states, and m an index with values of $1/2$, $3/2$, 2 and 3 , depending on the nature of the electronic transitions and on the relation between the localized state density and the energy.

Figure 19.6 illustrates the experimentally obtained relation of $(\alpha h\nu)^{1/2}$ versus the photon energy $h\nu$. The absorption of the films gets stronger with increasing indium content as confirmed by the red shift of α as a function of the wavelength in the region of the optical energy investigated (Fig. 19.6, inset). The shift is probably due to the influence of the heavier indium atoms and the metallic bonds formed by the indium introduction. The good linear relation of the $(\alpha h\nu)^{1/2}$ vs $h\nu$ plot indicates that the absorption mechanism in the Ge-Se-In films are non-direct transition [31]. The optical gap E_g for non-direct transition can be obtained from the interception $(\alpha h\nu)^{1/2}$ vs $h\nu$ with the energy axis at $(\alpha h\nu)^{1/2} = 0$; it can be also derived also from the spectral distribution of the absorption coefficient α , calculated as the energy for which $\alpha = 2 \times 10^4 \text{ cm}^{-1}$ (also known as E_g^{04} method).

The values of optical band gap calculated by both approaches, E_g and E_g^{04} , reveal a decrease with the indium content as seen in Fig. 19.7. The error in the determination of the E_g values was evaluated to $\pm 0.01 \text{ eV}$.

According to the single-effective oscillator model proposed by Wemple and DiDomenico, [24] the optical data could be described to an excellent approximation by the following relation

$$n^2 - 1 = E_d E_0 / (E_0^2 - (h\nu)^2) \quad (19.8)$$

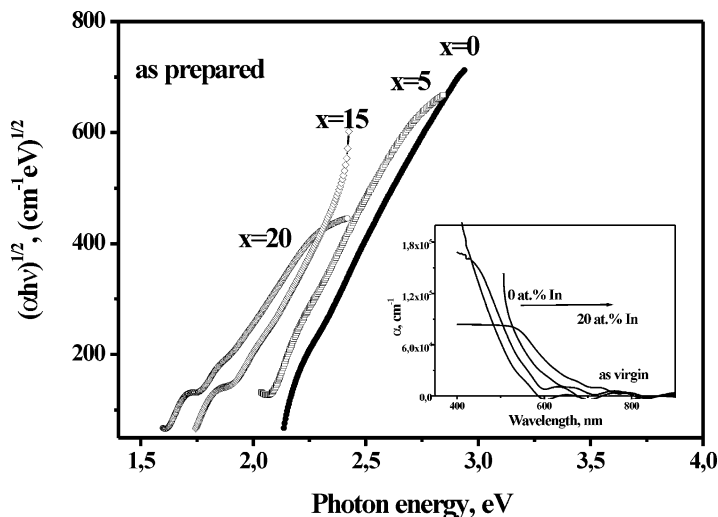
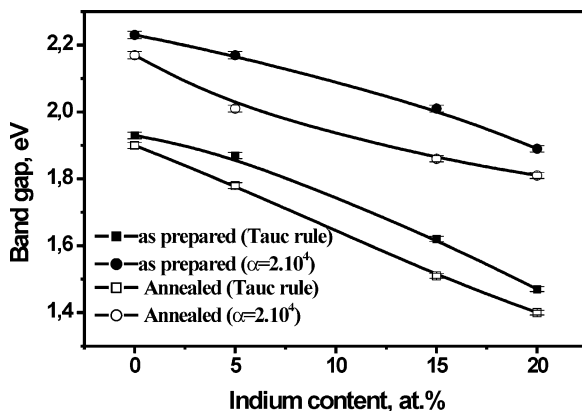


Fig. 19.6 Experimentally obtained relation of $\alpha hv^{1/2}$ versus the photon energy ($h\nu$)

Fig. 19.7 Thermal dependence of the optical band gap in the Ge-Se-In system as a function of the indium content



where n is the refractive index, E_0 is the energy of the effective dispersion oscillator (also called average energy gap) and E_d is the oscillator strength or the dispersion energy which measures the average strength of the optical interband transitions. Plotting $(n^2 - 1)^{-1}$ against $(h\nu)^2$ allows us to determine the oscillator parameters by fitting a straight line to the points. The value of E_0 determined from the slope, E_d , defined as intercept on the vertical axis as well as the values of basic optical constants (n and k) at wavelength 800 nm and the refractive index n_o at wavelength infinity are given in Table 19.3.

Table 19.3 Optical parameters of as prepared and annealed films

In content	As-deposited films				Annealed films			
	0	5	15	20	0	5	15	20
n_{800}	2.401	2.807	2.748	2.662	2.543	2.866	2.688	2.686
k_{800}	0.0203	0.0211	0.0247	0.0199	0.0113	0.0181	0.0194	0.0179
E_g , eV	1.93	1.87	1.62	1.47	1.90	1.78	1.51	1.40
E_g^{04} , eV	2.23	2.17	2.01	1.89	2.14	2.01	1.85	1.80
E_d , eV	18.1	18.4	20.37	16.25	20.85	26.8	22.5	21.8
E_o , eV	3.83	2.73	3.18	2.24	3.83	3.71	3.65	3.62
n_o	2.392	2.775	2.721	2.633	2.538	2.872	2.679	2.652

Discussion

To understand the nature of electronic processes in non-crystalline semiconductors due to optical interactions, it is first of all necessary to investigate their energy spectrum and the phenomena of charge carrier transfer in the materials. The energy spectrum of electronic states in the range $h\nu > E_g$ can be studied from the reflectivity spectrum of light in the fundamental absorption band where $h\nu$ is the photon energy and E_g is the optical gap. Of special interest is the study of the optical features of non-crystalline semiconductors near the absorption edge. It is known that the absorption edge is sensitive to the composition and to the material structure as well as to external factors such as electric and magnetic fields, and optical, heat, electrons and other radiations. Under the influence of these factors optical parameters of non-crystalline semiconductors suffer reversible and irreversible changes. The study of such phenomena allows not only to clarify the mechanisms of light absorption in matter with a significant degree of disorder of its structure, but also to suggest possible practical applications.

The reduction of E_g with the indium content can be accounted for in terms of differences in the structure of the films prepared by vacuum thermal evaporation. The decrease is most probably caused by the formation of new “broken” bonds due to the indium atoms. These defective bonds can act as carrier traps resulting in the band gap narrowing. The optical band gap values of the annealed films show lower values which suggest an increase in the number of defective bonds after temperature treatment.

The decrease of n_o , E_d and E_o may be also attributed to the formation of more numbers of defect centres and the increase in disorder with the increase of the In content. This is in accordance with the Mott and Davis model [31] which states that the width of localized states near the mobility edges depends on the degree of disorder and the defects present in the amorphous structure. In particular, it is known that unsaturated bonds along with some saturated bonds (such as dative bonds) are produced due to an insufficient number of atoms in the amorphous films. These unsaturated bonds are responsible for the formation of some defects in the films. Such defects produce localized states in the amorphous solids. The deflection in the properties above the threshold of $N = 2.4$ is due to changes

in the local structure arrangement. The threshold does not affect the optical band gap but changes the trend of the refractive index values. The decrease of E_o could be attributed to the dissolving of In atoms with an atomic radius larger than that Se atoms forming Se–In bonds with the longest bonding distance and increasing the number of scattering center. The oscillator strength or the dispersion energy which measures the average strength of the interband optical transitions follows the trend of the refractive index values.

After temperature treatment the dispersion in the average energy gap values becomes smaller which indicates higher optical densities of the films.

The variation in optical parameters with In incorporation is mainly attributed to the change in stoichiometry. The In additives in the GeSe_5 host matrix must bring about a compositional change in the host network of Ge–Se, i.e. an alloying effect at higher indium concentrations. According to Philips [23], the molecular structure of melt-quenched $\text{Ge}_x\text{Se}_{100-x}$ alloys may be described by chemically ordered clusters embedded in a continuous network. Some of these clusters are Se_n chains, corner-sharing tetrahedral $\text{Ge}(\text{Se}_{1/2})_4$ and ethane-like $\text{Ge}_2(\text{Se}_{1/2})_6$ structural units. In the $(\text{GeSe}_5)_{100-x}\text{In}_x$ system of this study, the first two structures are possible, since the Ge content is close to 20 at.%,

Acknowledgments The authors would like to express their gratitude to the Bulgarian National Science Fund for the financial support under the contract BG051PO001/07/3/3-02/58.

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Chapter 20

Atomic Structure of $(\text{Ge}_{0.2}\text{Se}_{0.8})_{85}\text{B}_{15}$ and $(\text{Ge}_{0.2}\text{Se}_{0.8})_{85}\text{In}_{15}$ Glasses

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B. Beuneu, W. Hoyer, N. Mattern, and J. Eckert

Abstract The atomic structure of $(\text{Ge}_{0.2}\text{Se}_{0.8})_{85}\text{B}_{15}$ and $(\text{Ge}_{0.2}\text{Se}_{0.8})_{85}\text{In}_{15}$ chalcogenide glasses has been studied with X-ray diffraction, neutron diffraction and extended X-ray absorption fine structure measurements. The reverse Monte Carlo simulation technique has been used for the generation of atomic configurations satisfying the experimental data sets and some constraints. The models obtained are analyzed in terms of partial pair distribution functions, most probable interatomic distances and coordination numbers.

Keywords Boron · Chalcogenide glasses · Germanium selenide · Indium

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Introduction

Chalcogenide glasses have attracted high interest of the basic and applied science due to their applications as information storage media, chemical sensors, optical transmitters and amplifiers. It is important that the physical properties such as electroconductivity, photoconductivity, thermal diffusivity, optical band gap and absorption of amorphous chalcogenides can widely vary with composition [1, 2]. This enables a proper choice of alloys for a specified application.

Ge-Se alloys exhibit a good glass forming ability up to about 45 at.% Ge [1, 2]. The structure of Ge-Se glasses has been extensively investigated so far (see for example Refs. [3, 4] and the citations therein). A model based on $\text{GeSe}_{4/2}$ tetrahedra as structural units in the binary Ge-Se glasses has been widely accepted. The excess Ge or Se atoms form homonuclear bonds (either Ge-Ge or Se-Se) aside the stoichiometric GeSe_2 structure. Introduction of a third element into the tetrahedral structure of Ge-Se alloys causes changes of the glass properties and structure [5–7]. For example, the optical band gap increases upon addition of boron to GeSe_4 or GeSe_5 [5], while the optical band gap notably decreases if indium is added [6]. Addition of B significantly reduces the absorption coefficient and transmission losses in Ge-Se-B glasses in the middle infrared region [5].

It has been shown recently [7] that in ternary $\text{GeSe}_4\text{-In}$ and $\text{GeSe}_5\text{-In}$ glasses the indium bonds to the Se atoms which are in excess in respect to the stoichiometric GeSe_2 composition. However, the mean coordination number of In is somewhat larger than three, which suggests that while the majority of In atoms is threefold coordinated, some In atoms may have four nearest Se neighbours. Taking into account that boron is also a trivalent element, but the size of boron atoms is much smaller as compared to indium [8], it is interesting to investigate the behaviour of boron upon addition to Se rich Ge-Se alloys.

Experimental Details

Chalcogenide glasses of the nominal compositions $\text{Ge}_{20}\text{Se}_{80}$, $(\text{Ge}_{0.2}\text{Se}_{0.8})_{85}\text{B}_{15} = \text{Ge}_{17}\text{Se}_{68}\text{B}_{15}$ and $(\text{Ge}_{0.2}\text{Se}_{0.8})_{85}\text{In}_{15} = \text{Ge}_{17}\text{Se}_{68}\text{In}_{15}$ were prepared from elemental Ge, Se, B and In of 99.999% purity. For convenience, we will further denote these alloys as GeSe_4 , $\text{GeSe}_4\text{B}_{15}$ and $\text{GeSe}_4\text{In}_{15}$, respectively. The samples were prepared in evacuated ($\sim 10^{-3}$ Pa) and sealed quartz ampoules by conventional synthesis in a rotary furnace. The molten alloys were kept at 1,200 K for 48 h to ensure their homogenization and then quenched in ice water.

X-ray diffraction experiments were carried out at the BW5 experimental station at HASYLAB (DESY, Hamburg, Germany). The samples were filled into thin walled (0.02 mm) quartz capillaries of 2.0 mm inner diameter. The energy of the incident beam was 100 keV. The size of the incident beam was $1 \times 2 \text{ mm}^2$. The scattered intensity was recorded by a Ge solid-state detector. The raw data

were corrected for background, absorption, polarization, detector dead-time and variations in the detector solid angle.

Extended X-ray absorption fine structure (EXAFS) measurements were carried out at the Ge, Se and In K-absorption edges at the beamline X of HASYLAB in transmission mode using fixed-exit Si(111) and Si(311) double-crystals. The samples were finely ground, mixed with cellulose and pressed into tablets. The sample quantities in the tablets were adjusted to the compositions and the selected edges. The intensities before and after the sample as well as after a reference sample were recorded by gas ionisation chambers. The first and the second chamber were filled with the mixtures of Ar/Kr, having 10% and 50% absorption, respectively. The third chamber was filled with Kr (100% absorption). The EXAFS spectra were obtained with 0.5 eV steps in the vicinity of the absorption edge. The measuring time was weighted with the photoelectron wave number k during the collection of the signal.

The neutron diffraction measurements were carried out at the 7 C2 diffractometer (LLB, CEA-Saclay, France). The samples were filled into thin walled (0.1 mm) vanadium containers with 7 mm diameter. The raw data were corrected for detector efficiency, empty instrument background, scattering from the sample holder, multiple scattering and absorption.

Results and Discussion

The X-ray and neutron diffraction total pair distribution functions (PDF) of the binary GeSe_4 and ternary $\text{GeSe}_4\text{In}_{15}$ and $\text{GeSe}_4\text{B}_{15}$ are plotted in Figs. 20.1 and 20.2.

In the case of $\text{GeSe}_4\text{In}_{15}$ alloy (Fig. 20.1), there is a remarkable decrease of the first maximum of the XRD and ND pair distribution functions as compared to the GeSe_4 binary composition. This peak (~ 2.36 Å) reflects Ge-Se (2.36 ± 0.02 Å [4]) and Se-Se (2.32 ± 0.02 Å [4]) pairs which make the main contribution to the total PDF (see Tables 20.1–20.3 for the XRD and ND weighting coefficients). The peak at about 2.6 Å on the XRD pair distribution function is related to

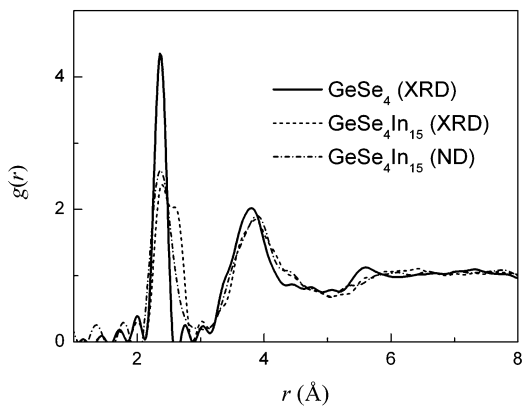


Fig. 20.1 Total pair distribution functions for binary $\text{Ge}_{20}\text{Se}_{80}$ and ternary $(\text{Ge}_{0.2}\text{Se}_{0.8})_{85}\text{In}_{15}$ glasses obtained from XRD and ND measurements

Fig. 20.2 Total pair distribution functions for binary $\text{Ge}_{20}\text{Se}_{80}$ and ternary $(\text{Ge}_{0.2}\text{Se}_{0.8})_{85}\text{B}_{15}$ glasses obtained from XRD and ND measurements

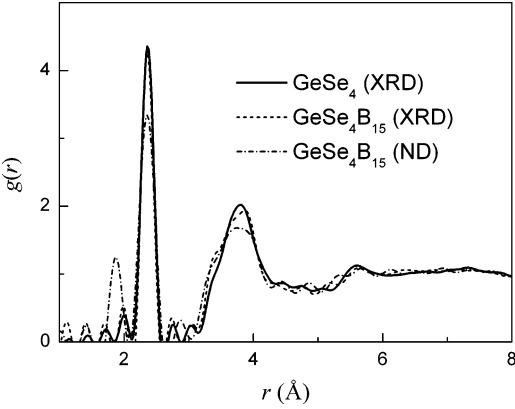


Table 20.1 XRD and ND weighting coefficients w_{ij} (%) for the $\text{Ge}_{20}\text{Se}_{80}$ composition. The XRD values are calculated for the scattering vector $Q = 4\pi \sin\theta/\lambda = 0$ (λ is the X-ray wavelength, θ is half the scattering angle)

Pairs, ij	Ge-Ge	Ge-Se	Se-Se
XRD	3.63	30.84	65.53
ND	4.17	32.51	63.32

Table 20.2 XRD and ND weighting coefficients w_{ij} (%) for the $(\text{Ge}_{0.2}\text{Se}_{0.8})_{85}\text{In}_{15}$ composition (the XRD values are calculated for the scattering vector $Q = 0$). Bond enthalpy values for the i - j pairs (in kJ/mol) taken from [8]

Pairs, ij	Ge-Ge	Ge-Se	Ge-In	Se-Se	Se-In	In-In
XRD	2.29	19.51	6.20	41.45	26.36	4.19
ND	3.52	27.39	3.08	53.34	12.00	0.67
Bond enthalpy	264	489	—	332	247	100

Table 20.3 XRD and ND weighting coefficients w_{ij} (%) for the $(\text{Ge}_{0.2}\text{Se}_{0.8})_{85}\text{B}_{15}$ composition (the XRD values are calculated for the scattering vector $Q = 0$). Bond enthalpy values for the i - j pairs (in kJ/mol) taken from [8]

Pairs, ij	Ge-Ge	Ge-Se	Ge-B	Se-Se	Se-B	B-B
XRD	3.44	29.28	0.95	62.22	4.04	0.07
ND	3.35	26.07	3.82	50.77	14.90	1.09
Bond enthalpy	264	489	—	332	462	297

In-Se pairs as this value (2.6 Å) agrees with the sum of the covalent radii of In and Se [8]. Besides, only the contribution of these pairs is significantly high in the X-ray scattering experiment (Tables 20.1 and 20.2).

Due to the negligibly small contribution of B-containing pairs to the total X-ray scattering intensity (Tables 20.1 and 20.3), the XRD pair distribution functions of the binary GeSe_4 and ternary $\text{GeSe}_4\text{B}_{15}$ alloys are virtually the same (Fig. 20.2). The situation changes if neutron diffraction is applied. A peak at about 1.87 Å appears in the ND pair distribution function of the $\text{GeSe}_4\text{B}_{15}$ glass, which might be related to either Ge-B or Se-B pairs as the size of Ge and Se atoms is very

similar [8]. However, taking into account that all Ge atoms already have four nearest Se neighbours, and that Ge and B are practically immiscible [9], it is improbable that boron bonds to germanium in the $\text{GeSe}_4\text{B}_{15}$ glass.

The formation of B-Se pairs is supported by the fact that the enthalpy of these bonds is relatively high (Table 20.3). The relatively high value of the B-B bond enthalpy suggests that B-B pairs can also be formed. To prove these suppositions and to determine the number of nearest neighbours in the $\text{GeSe}_4\text{B}_{15}$ glass we modelled the structure of the $\text{GeSe}_4\text{B}_{15}$ glass with the reverse Monte Carlo (RMC) simulation technique [10, 11] by fitting simultaneously the four experimental data sets (XRD, ND and EXAFS at the Ge and Se absorption edges).

The structure modelling has been performed with the RMC++ program [12, 13]. The backscattering amplitudes and phases needed to obtain the model EXAFS curves from the pair distribution functions were calculated by the FEFF8.4 program [14]. The simulation box contained 20,000 atoms. A number density of $0.0365 \text{ \AA}^{-3}$ was calculated with the densities of amorphous GeSe_4 [1] and amorphous boron [15]. The simulations were performed under the assumption that neither Ge-Ge nor Ge-B bonds are formed in the ternary $\text{GeSe}_4\text{B}_{15}$ glass. It was supposed in all simulation runs that similarly to GeSe_4 and GeSe_4In_x glasses [7], Ge is fourfold coordinated in the ternary $\text{GeSe}_4\text{B}_{15}$ glass as well. We have performed simulations where the coordination numbers of Se and B were also constrained ($N_{\text{Se}} = 2, N_{\text{B}} = 3$). Almost no differences in the quality of the fits have been observed between these runs. Fits obtained by the simultaneous modelling of XRD, ND and EXAFS measurements for the $\text{GeSe}_4\text{B}_{15}$ glass with a fixed Ge coordination number and ‘free’ Se and B environments are compared with the experimental data in Fig. 20.3. The partial pair distribution

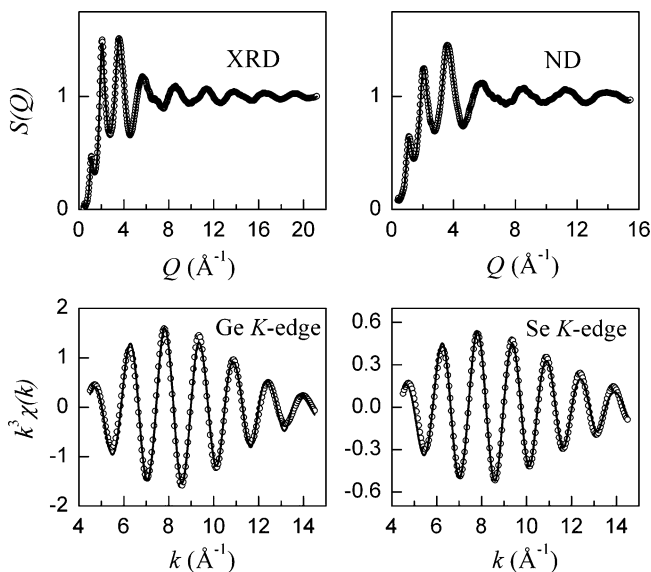


Fig. 20.3 XRD and ND structure factors, and EXAFS spectra for $(\text{Ge}_{0.17}\text{Se}_{0.83})_{85}\text{B}_{15}$ glass. Circles: measurement; lines: data obtained by simultaneous RMC simulation of the experimental XRD, ND and EXAFS data

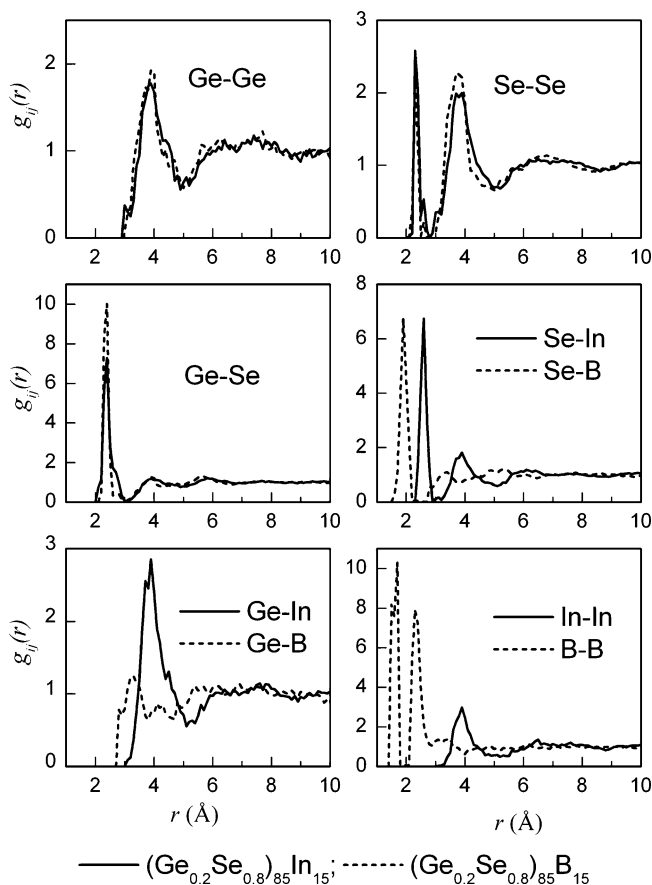


Fig. 20.4 Partial pair distribution functions for glassy $(\text{Ge}_{0.2}\text{Se}_{0.8})_{85}\text{In}_{15}$ [7] and $(\text{Ge}_{0.2}\text{Se}_{0.8})_{85}\text{B}_{15}$ obtained with RMC

functions $g_{ij}(r)$ corresponding to this model configuration of the $\text{GeSe}_4\text{B}_{15}$ glass are presented together with the respective curves for $\text{GeSe}_4\text{In}_{15}$ glass [7] in Fig. 20.4. The mean nearest neighbour distances r_{ij} and coordination numbers N_{ij} obtained are listed in Table 20.4.

Se-Se and Se-B coordination numbers for the $\text{GeSe}_4\text{B}_{15}$ glass obtained with and without Se and B constraints are practically the same ($N_{\text{SeSe}} \approx 0.7$, $N_{\text{SeB}} \approx 0.4\text{--}0.5$). The decrease of the mean Se-Se coordination number from 1.1 in the binary GeSe_4 down to 0.7 in the $\text{GeSe}_4\text{B}_{15}$ glass can be related, similarly to the ternary $\text{GeSe}_4\text{In}_{15}$ glass, to the break of some Se-Se pairs. It is reasonable that boron intrudes between the Se atoms and bonds them. However, in opposite to the Ge-Se-In glasses where In-In bonding is not significant, B-B bonds can be formed along with B-Se bonds in the ternary $\text{GeSe}_4\text{B}_{15}$ glass. The difference of the B-B coordination numbers (1.12 and 0.47, Table 20.4) can be explained by the relatively

Table 20.4 Mean interatomic distances r_{ij} and coordination numbers N_{ij} for $\text{Ge}_{20}\text{Se}_{80}$, $(\text{Ge}_{0.2}\text{Se}_{0.8})_{85}\text{B}_{15}$ and $(\text{Ge}_{0.2}\text{Se}_{0.8})_{85}\text{In}_{15}$ glasses obtained with RMC modelling. Ge-Ge, Ge-In, Ge-B and In-In pairs were not allowed in the models. The data for $\text{Ge}_{20}\text{Se}_{80}$ and $(\text{Ge}_{0.2}\text{Se}_{0.8})_{85}\text{In}_{15}$ glasses are taken from Ref. [7]

Alloy Pairs	$\text{Ge}_{20}\text{Se}_{80}$		$(\text{Ge}_{0.2}\text{Se}_{0.8})_{85}\text{B}_{15}$			$(\text{Ge}_{0.2}\text{Se}_{0.8})_{85}\text{In}_{15}$	
	r_{ij} (Å)	N_{ij}	N_{ij}			r_{ij} (Å)	N_{ij}
			constrained: $N_{\text{Ge}} = 4$; $N_{\text{Se}} = 2$; $N_{\text{B}} = 3$		constrained: $N_{\text{Ge}} = 4$		
Ge-Se	2.37	3.87	2.36	3.95	3.96	2.36	3.89
Se-Ge	2.37	0.97	2.36	0.99	0.99	2.36	0.97
Se-Se	2.35	1.12	2.33	0.71	0.70	2.36	0.95
Se-B(In)	—	—	1.92	0.41	0.47	2.58	0.73
B(In)-Se	—	—	1.92	1.85	2.12	2.58	3.33
B-B (In-In)	—	—	1.60	1.12	0.47	—	—
N_{Ge}	—	3.87	—	3.94	3.96	—	3.89
N_{Se}	—	2.09	—	2.07	2.16	—	2.65
$N_{\text{B(In)}}$	—	—	—	2.99	2.59	—	3.33

large uncertainty due to the small contribution of these pairs to the total pair distribution functions. The B-B partial pair distribution function has two sharp peaks. The first can be interpreted as the distance of two covalently bonded boron atoms, while the second is due to boron atoms bound to the same selenium atom.

Summary

The atomic structure of $\text{Ge}_{20}\text{Se}_{80}$, $(\text{Ge}_{0.2}\text{Se}_{0.8})_{85}\text{B}_{15}$ and $(\text{Ge}_{0.2}\text{Se}_{0.8})_{85}\text{In}_{15}$ chalcogenide glasses has been modeled by means of the reverse Monte Carlo simulation technique using experimental XRD, ND and EXAFS data. In our models, $\text{GeSe}_{4/2}$ tetrahedra are the main structural units of all glasses studied. The excess Se atoms build homonuclear Se-Se bonds. Addition of either In or B atoms results in a decrease of the Se-Se coordination number, and the formation of Se-In (respectively Se-B) bonds. It is suggested that homonuclear B-B bonds are formed along with B-Se bonds in the ternary $\text{Ge}_{17}\text{Se}_{68}\text{B}_{15}$ glass.

Acknowledgments This study has been supported by the German Academic Exchange Service (DAAD) and the Bulgarian Ministry of Education and Science. P. Jónvári was supported by a Bolyai Research Fellowship of the Hungarian Academy of Sciences. I. Kaban thanks DESY for the support of the XRD and EXAFS measurements at HASYLAB (Hamburg, Germany). The experiment at LLB was supported by the European Commission through the Access Activities of the Integrated Infrastructure Initiative for Neutron Scattering and Muon Spectroscopy (NMI3), supported by the European Commission under the 7th Framework Programme through the Key Action: Strengthening the European Research Area, Research Infrastructures, Contract NMI3/FP7 no: 226507.

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Chapter 21

Surface Development of $(\text{As}_2\text{S}_3)_{1-x}(\text{AgI})_x$ Thin Films for Gas Sensor Applications

Kolyo Kolev, T. Petkova, Cyril Popov, Plamen Petkov,
and F. Muktepavela

Abstract Thin $(\text{As}_2\text{S}_3)_{100-x}(\text{AgI})_x$ ($x = 0-40$) films were deposited by thermal vacuum evaporation from the respective bulk glasses; their structure and morphology before and after illumination with light have been studied by scanning electron microscopy (SEM). As-deposited films show fractional evaporation and surface inhomogeneities but after illumination they become uniform on the surface and in the depth as revealed by SEM top-view and cross-section images. Mechanical parameters like stress and microhardness of as-prepared and illuminated films were also investigated. The results from the stress measurements show variation in both the sign and the magnitude of the values with increasing AgI content and with time. Pure As_2S_3 layers possess a low tensile stress. The addition of AgI initially reduces the tensile stress and turns it to compressive for higher AgI concentrations. The exposure to light does not affect significantly the magnitude of the stress. The microhardness of the thin films decreases when the content of AgI increases. Furthermore, the microhardness in the surface region of the films is higher than in depth; it increases after the exposure to light.

Keywords Chalcogenide glasses · Mechanical properties · Stress · Microhardness

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Introduction

Chalcogenide glasses and thin films have become attractive materials for applied research because of their structure, properties, and easy preparation. They have many current and potential applications in optics, optoelectronics, chemistry, and biology (optical elements, gratings, microlenses, waveguides, bio- and chemical sensors, solid electrolytes, batteries, etc.) [1–8].

However, despite the attractiveness and great application potential of these glasses, very often dissociation and fractional evaporation of individual components of the glasses can be observed during the preparation process. On the other hand, we know from the work of Kostyshin et al. [9], reported as early as the mid-1960s that illumination of chalcogenide/metal film structures with light with photon energies comparable to that of the band gap of the material leads to rapid penetration of the metal into the semiconductor. This process was named photodiffusion or “photodoping” [10–12]. Based on the above observations, we study this effect aiming to improve our films quality. For this purpose, the films were exposed to a polychromatic lamp equipped with a collimator and an IR-cut filter.

Experimental Details

The bulk $(\text{As}_2\text{S}_3)_{100-x}(\text{AgI})_x$ ($x = 0-40$) samples were prepared by the standard melt-quenching technique from As_2S_3 , previously synthesized by us, and commercial AgI (Alfa Aesar, Johnson Matthey). The initial substances with a total weight of 5 g were sealed in evacuated quartz ampoules (10^{-3} Pa). They were slowly heated in a furnace with a rate of 10 K/min. The temperature was kept constant at the melting point of each component (AgI and As_2S_3) for around 2 h while the melt was continuously stirred for better homogenization. After melting the ampoules were quenched rapidly in a mixture of water and ice.

Thin films were deposited from the corresponding bulk glasses by thermal vacuum evaporation in a standard high-vacuum set-up (Hochvakuum B 30.2). The process conditions were as follows: a residual pressure in the chamber of 1.33×10^{-3} Pa, a distance between the evaporation source and the substrates of 0.12 m, and evaporation temperatures ranging between 1,200 and 1,300 K, depending on the glass composition. A covered inductively heated tantalum ribbon evaporator was used. The substrates were rotated during the deposition which allowed to obtain a uniform thickness of the films. The evaporation time was determined by the desired thickness of the films. The latter was controlled by cross-section scanning electron microscopy (SEM, Hitachi S-4000).

The microhardness of the films, as-deposited and illuminated, was investigated as a function of the composition using a self-adjusting tester. The diagonal length of the imprints was measured with a Neophot-30 microscope (Carl Zeiss).

Load and loading time were $0.14 \div 20$ g and 15 s, respectively, for all samples. For each sample the measurements were repeated at least ten times, the deviation in the calculated values did not exceed 5%. After the first measurement the films were illuminated for 60 min with a xenon lamp with polychromatic light and an intensity of 150 mWcm^{-2} equipped with a collimator and an IR-cut filter to avoid sample heating. The error of the microhardness values was about $\pm 5\%$ also in this case.

The film stress was evaluated by the bending method using silicon micro-machined cantilevers, onto which the chalcogenide films under investigation were deposited. These cantilever substrates consist of seven beams with a thickness of 35 μm , widths between 0.7 and 2.0 mm and lengths between 2.0 and 8.0 mm; this configuration allows accurate stress measurements in a wide range. The deflection of the cantilever beams, from which the curvature of the substrate was determined, was measured by the depth of the focus of an optical microscope.

Results

Surface Morphology and Microhardness

As-deposited $(\text{As}_2\text{S}_3)_{100-x}(\text{AgI})_x$ films show slight fractional evaporation and a high roughness (Fig. 21.1, top). After illumination, they become smoother and more uniform (Fig. 21.1, bottom) both on the surface and in the depth as revealed by the SEM top view and cross section images.

The microhardness (HV) study showed a tendency of a slight decrease with the AgI concentration (Fig. 21.2). The compositional dependence of the microhardness

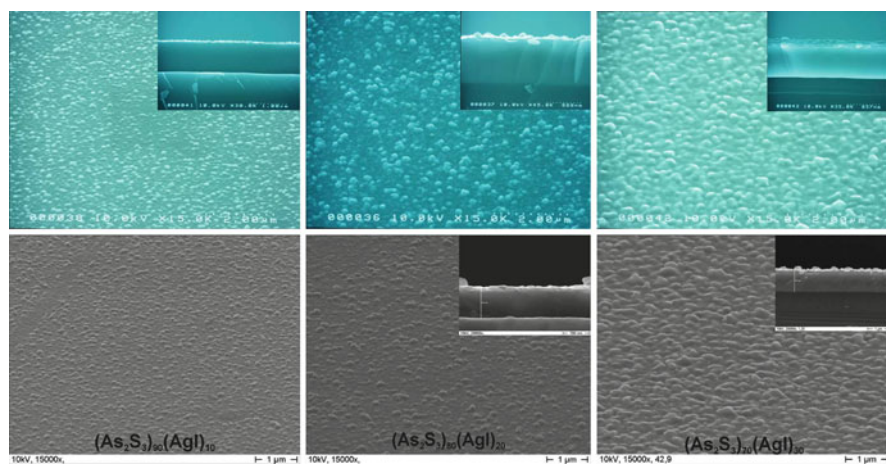


Fig. 21.1 SEM micrographs of $(\text{As}_2\text{S}_3)_{100-x}(\text{AgI})_x$ amorphous layers with magnification of 15,000 $\times$: (top) as-deposited films; (bottom) illuminated layers

Fig. 21.2 Microhardness of $(\text{As}_2\text{S}_3)_{100-x}(\text{AgI})_x$ thin films

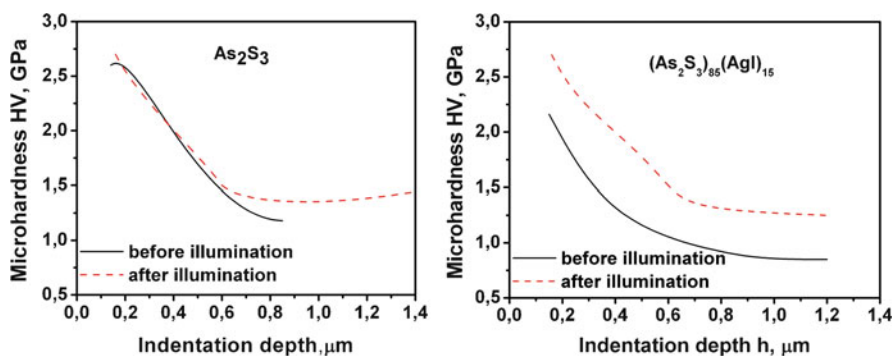
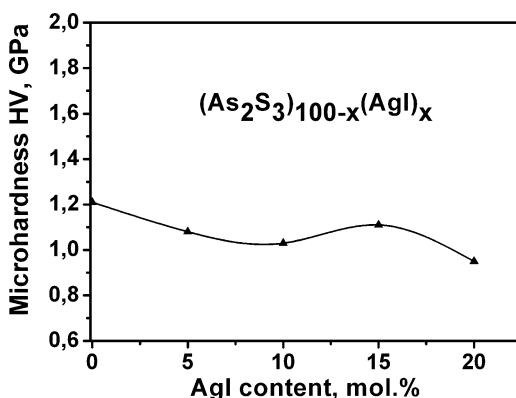


Fig. 21.3 Microhardness of thin As_2S_3 (left) and $(\text{As}_2\text{S}_3)_{100-x}(\text{AgI})_x$ (right) films before and after illumination

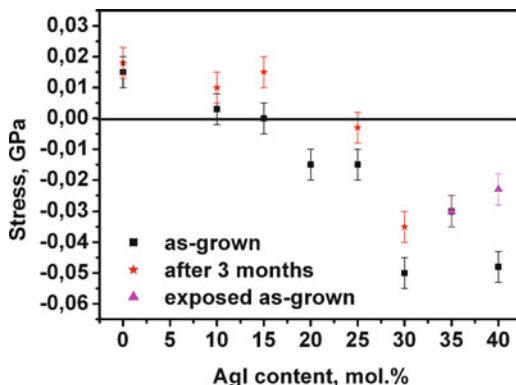
viewed at the atomic scale is related to the energies of the bonds that must be broken when the microindenter penetrates into the glass sample. The results are logical and similar to those for other AgI-containing glasses [13].

The microhardness at the film surface is higher than in the bulk; in addition after exposure to light it increases both in the surface region and in the depth of films with AgI, as shown in Fig. 21.3.

Stress

The film stress σ measured by the cantilever bending method was calculated by Stoney's equation:

$$\sigma = \frac{E}{6(1-\nu)} \frac{D^2}{Rd},$$

Fig. 21.4 Intrinsic stress of $(\text{As}_2\text{S}_3)_{100-x}(\text{AgI})_x$ thin films

where d is the film thickness, R the radius of the curvature of the substrate, E and ν the Young's modulus and Poisson ratio of the substrate, respectively, and D the substrate thickness. The results from the stress measurements show a change in its sign and magnitude with the AgI content and with time. Pure As_2S_3 samples show low tensile stresses. The addition of AgI initially reduces the tensile stress and turns it to compressive for higher concentrations (Fig. 21.4). In the region of compressive stress a slight relaxation is observed after 3 months. As expected, exposure to light does not affect significantly the magnitude of the stress.

Discussion

Before starting an investigation of the mechanical properties, it would be instructive to check the homogeneity and overall structural arrangement of the layers. For this purpose, we have used SEM imaging with high magnifications. As seen from the images in Fig. 21.1 (top), the layers are obviously rough and fractional. Most probably the silver iodide is decomposed during the preparation; silver is the component evaporated latest since it is the element with the highest melting temperature. This fact could compromise the following measurements and analysis. In order to overcome this shortcoming of the layers, we have used the ability of chalcogenide materials to undergo photoinduced changes. It is well-known that photoillumination of a bi-layer metal/chalcogenide structure leads to an enhanced dissolution rate of certain metals, especially Ag, into the chalcogenide [14]. On the base of this assumption, we have illuminated the layers with polychromatic light. The results clearly show that after 1 h of illumination the layer surfaces become smoother and less fractional (Fig. 21.1, bottom). This effect is valid also for the core of the films as seen from the cross-section images of the samples (insets in Fig. 21.1).

The variation of the microhardness with the AgI content can be discussed in terms of the chemical bond theory. The microhardness is a non-electronic property depending on the average bond energy between the atoms composing the glass. The initial binary As_2S_3 glass is a typical covalent material; therefore the action of light does not affect the glass bonding (Fig. 21.3, left). The quasi-binary glasses under study can be considered as mixed, covalent–ion glasses. The introduction of AgI in the glassy matrix initiates the formation of non-covalent bonds. The average bond enthalpy of the new complex glass becomes smaller as the content of AgI increases as the bond enthalpy of silver iodide is lower (234 kJmol^{-1}) as compared to that of As_2S_3 (379.5 kJmol^{-1}). The decrease of the bond strength results in lowering of the hardness and facilitates bond break after light illumination (Fig. 21.3, right).

Furthermore, the bond lengths and angles are quite likely to change in mixed glasses, which would also affect their microstructure. Most probably the AgI molecules occupy microvoids in the glass; as a result the density increases and the structure stabilizes, as reported in Ref. [15]. The packing and stabilization of the structure leads to a reduction of the tensile stress; films with 10–15 mol% AgI are free of stress (Fig. 21.4). These stress-free films show slightly higher microhardness as seen in Fig. 21.2. Further increase of the AgI content turns the stress to compressive. Summarizing the data presented above it is very reasonable to assume that the structure is changing due to the creation of mixed bonds leading to variations of the microhardness and intrinsic stress of the films with composition.

The microheterogeneity of the films is the reason for higher values of the microhardness at the surface than in the depth. With the increase of the indentation depth up to 600–700 nm HV decreases and is two times lower close to the film/substrate interface. The effect of light illumination on the microhardness presented in Fig. 21.3 clearly reveals that the As_2S_3 matrix does not show any change in the microhardness. In contrast, AgI doping leads a rise of the microhardness both on the surface and in the depth by almost 50%. The hardness of the glasses is a function of the strength of the individual bonds and the atomic packing density. The bond strength of a certain compound determines the ratio between elastic and plastic deformation. The light causes plastic deformation due to photoinduced structure transformations in the films resulting in a higher microhardness.

Conclusions

The structure and the morphology of $(\text{As}_2\text{S}_3)_{100-x}(\text{AgI})_x$ amorphous layers before and after illumination with polychromatic light have been studied by SEM. As-deposited films show fractional evaporation and surface inhomogeneity. The films become uniform on the surface and in depth after the illumination. The results from the stress measurements show alteration in both the sign and the

magnitude with increasing AgI content and with the time. The addition of AgI initially reduces the tensile stress and turns it to compressive for higher concentrations. Exposure to light does not affect significantly the magnitude of the stress. The microhardness of the films decreases with increasing amount of AgI. After illumination the layers possess a larger microhardness on the surface region as well as in the bulk in films with AgI while the microhardness of binary As_2S_3 films remains constant.

Acknowledgments The authors would like to express their gratitude to the Bulgarian National Science Fund for the financial support under the contract BG051PO001/07/3/3-02/58.

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Chapter 22

Thin As-Se-Sb Films as Potential Medium for Optics and Sensor Application

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G. Socol, and I.N. Mihailescu

Abstract Thin films have been deposited onto quartz substrates by the pulsed laser deposition (PLD) method from the corresponding glassy bulk As-Se-Sb chalcogenide materials. Photoinduced changes have been observed after illumination of the films with a Xe lamp. The transmission spectra of the thin films have been measured before and after irradiation and the optical constants have been derived by the Swanepoel method. The results suggest feasible applications of these materials for waveguide-sensors.

Keywords Chalcogenide glasses · Thin films · Optical waveguides

Introduction

Most amorphous chalcogenide materials demonstrate attractive optical properties, like high refractive index, large nonlinearity and excellent transmission in the infra-red region of the spectrum [1, 2]. The high IR transparency makes them suitable for optical waveguides for mid-IR fiber-optic sensors. The waveguides

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allow the detection of the vibrations of organic molecules present in the IR spectral range.

Under action of light the chalcogenides exhibit many photoinduced and also electron beam induced phenomena [3, 4] like photoexpansion [5, 6], reversible photodarkening [7] etc. The illumination by band gap light changes the internal and/or surface structure of the chalcogenide materials and leads to red or blue shifts of the optical absorption edge [7]. This shift causes changes of the optical constants (Δn , Δk) and variations of physical-chemical properties (microhardness, density, solubility). The photo-induced structural changes caused by laser light in chalcogenide layers selectively enhance the refractive index in the exposed regions, and thus provide a convenient method to form channel waveguides proper for biosensor application [6]. In this paper photoinduced changes in the three-component glassy $(\text{AsSe})_{100-x}\text{Sb}_x$ system have been studied as a function of the composition. The variation of the refractive index after exposure of the films to Xe lamp illumination is discussed.

Experimental Details

Glassy $(\text{AsSe})_x\text{Sb}_x$ alloys with antimony amounts of $x = 0, 5, 10, 15$ mol% were prepared in bulk form using the melt-quenching technique. Step-wise regime of the synthesis includes:

The first stage is the preparation of binary AsSe glass from respective amounts of arsenic and selenium with 5 N purity (Alfa Aesar); the mixture was placed in quartz ampoules, evacuated down to $\sim 10^{-3}$ Pa and heated in a rotary furnace. The melt was continuously stirred to ensure better homogenization while the temperature was maintained constant at the glass melting point for several hours and subsequently quenched in a mixture of ice and water. The second steep, the synthesis of $(\text{AsSe})_{100-x}\text{Sb}_x$ glasses, was accomplished by the same preparation procedure as described above using a mixture of the required amounts of AsSe and Sb.

PLD was performed in a high vacuum deposition chamber ($p = 10^{-4}$ Pa) at room temperature using an UV KrF*excimer pulsed laser source ($\lambda = 248$ nm, $\tau = 25$ ns). The quartz substrates were carefully cleaned with deionized water in a TRANSONIC T 310 ultrasonic bath. They were placed parallel to the target at a separation distance of 6 cm. For the deposition of each film we applied 4,000 subsequent laser pulses at a repetition rate of 5 Hz. The laser beam was adjusted at 45° to the target surface and focused through an anti-reflection coated MgF_2 lens placed outside the chamber to get an incident fluence of 1.6 J/cm^2 .

The optical properties of the films were studied before and after exposition to the monochromatic light of a Xe lamp. The optical transmission spectra of $(\text{AsSe})_{100-x}\text{Sb}_x$ films were recorded in the wavelength range from 400 to 2,500 nm at room temperature using a double-beam computer-controlled JASCO spectrophotometer with an accuracy of ± 0.5 nm.

Results and Discussion

The transmission spectra of as-deposited and illuminated As-Se-Sb thin films are shown in Fig. 22.1.

The absorption edge gradually shifts to longer wavelengths when Sb is added into the As-Se amorphous matrix. Figure 22.2 presents the dependence of the absorption edge shift (defined as transmission $T = 10\%$) on the Sb content in $(\text{AsSe})_{100-x}\text{Sb}_x$. The observed shift of the absorption edge is probably caused by the formation of additional defect states, localized just above the valence band.

Transmission spectra of the samples recorded after their irradiation show a move of the spectra toward shorter wavelength, i.e. a photobleaching effect is observed after exposure of the films (dashed lines in Fig. 22.1). The occurrence of photobleaching is strongly related to the source of the light exposure, the intensity of the illumination light and the illumination time [8]. The effect is very sensitive to the film composition and deposition technique. When the Sb content in $(\text{AsSe})_{100-x}\text{Sb}_x$ films is increased, a suppression of the photoinduced effects is observed. The decrease of the photobleaching effect is in agreement with our previous investigation [9], where the photodarkening effect in the As-Se-Ag

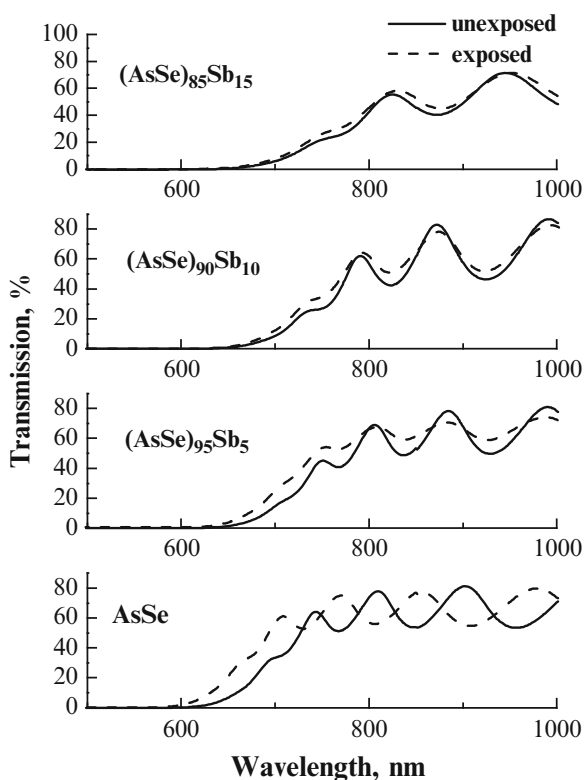


Fig. 22.1 Transmission spectra of $(\text{AsSe})_{100-x}\text{Sb}_x$ thin films before and after illumination

Fig. 22.2 Shift of the absorption edge in the high absorption region ($\alpha > 10^4$) as a function of Sb concentration

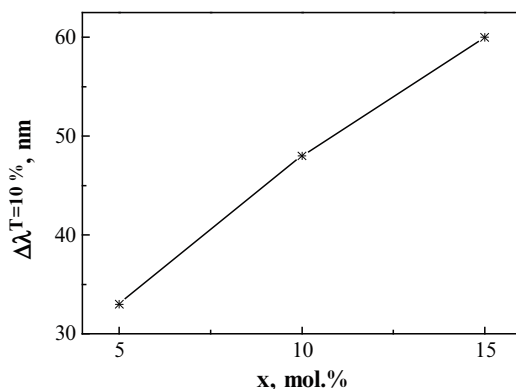
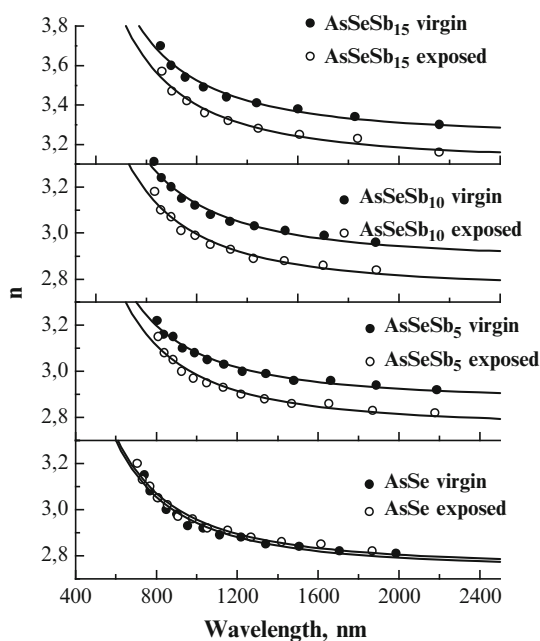


Fig. 22.3 Spectral dispersion of the refractive index n of as-deposited and illuminated films



system is masked due to the production of metal-chalcogen electronic bonding states on top of the valence band [10].

The refractive index and the thickness of $(\text{AsSe})_{100-x}\text{Sb}_x$ films, as-deposited and after Xe lamp illumination, were estimated from their transmission spectra using an equation based on the modified Swanepoel method [11, 12]. Figure 22.3 shows the spectral dependence of the refractive index $n(\lambda)$ of PLD films. The spectral dispersion of the refractive index shows that the refractive index of the As-Se-Sb films varies in the range 2.8–3.7 and increases with the addition of

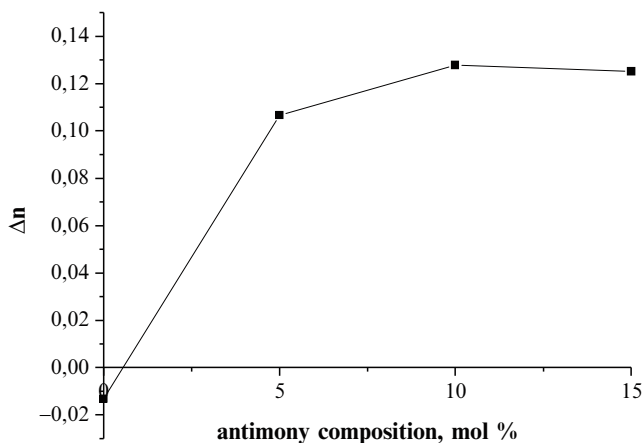


Fig. 22.4 Change of the refractive index n at 1,560 nm as a function of Sb composition

antimony in the films. This tendency is probably related to the structure and to the higher polarizability of the larger Sb atoms with an atomic radius of 138 pm, compared to Se atoms with an atomic radius of 116 pm.

After film illumination the refractive index values diminish. The reduction is the larger, the higher the amount of antimony. Figure 22.4 illustrates the compositional dependence of the refractive index changes (n is measured at 1,560 nm). The photoinduced change of the refractive index is defined as the difference between the refractive index of virgin films and that after radiation: $\Delta n = n(\text{virgin}) - n(\text{exposed})$. The variations in the values show a sharp increase after the first addition of antimony, and almost saturation when the Sb amount reaches 10 mol%.

The suppression in the photoinduced effects and the constant values of Δn suggests stable packing formation in the studied films due to the key role of antimony.

Conclusions

Thin amorphous $(\text{AsSe})_{100-x}\text{Sb}_x$ films were obtained by pulsed laser deposition from the corresponding bulk glass materials and their optical properties were investigated. The introduction of antimony into the chalcogenide matrix leads to a red shift of the absorption edge. As a result of light exposure of the films, realized by Xe lamp illumination, photobleaching effect is observed. The addition of antimony decreases the photobleaching effect and contributes to the stabilization of the glassy matrix. The refractive index of the As-Se-Sb films varies in the range 2.8–3.7 and increases with the addition of antimony in the films. It changes after illumination. The results obtained demonstrate that amorphous thin As-Se-Sb films have a wide transmission window and undergo photoinduced changes after

illumination, which results in changes of the optical constants. These features make the investigated materials suitable for the creation of planar optical waveguides with different geometries, applicable in mid-IR fiber-optic sensing.

Acknowledgments The authors are grateful for the financial support of the European Social Fund, Human Resources Development Program, under contract BG 051PO001/07/3.3-02/58/17.06.2008 and of the German Academic Exchange Service under DAAD-PPP Project.

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Chapter 23

Structure of AgI-AsSe Glasses by Raman Scattering and *Ab Initio* Calculations

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Plamen Petkov, and S.N. Yannopoulos

Abstract We report a structure investigation of $(\text{AsSe})_{100-x}(\text{AgI})_x$ bulk glasses using Raman spectroscopy and ab initio calculations. Raman spectra recorded at off-resonance conditions indicate appreciable structural changes caused by the incorporation of AgI into the base glass structure. Ab-initio and density functional theory calculations were employed to study the geometric and vibrational properties of molecular units that are parts of the glass structure.

Keywords Chalcogenides · Sensors · Raman scattering · *Ab-initio* calculations

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Introduction

Chalcogenide glasses have proved a very fertile field of experimental and theoretical research over the last 30 years due to several applications of these materials which are the outcome of a dazzling variety of athermal photoinduced phenomena [1]. Among the most promising applications of chalcogenide glasses doped with mobile metals and metal halogens is their potential use as chemical sensors and microsensors [2]. The fact that these amorphous inorganic materials can be easily prepared in bulk or thin film form is a major advantage. They also possess a high chemical stability and can easily change properties with small variations in the glass composition. All these features are common requirements for materials applied in gas sensors [3, 4 and references therein] and for the detection of heavy metals in aqueous solutions [5, 6].

Despite some progress in the field, no systematic studies exist up to now that provide a rationale for the role of the structure of the glass matrix and the doping extent on the sensing properties of the material. To understand such relations one has to study materials that can form glasses over a wide range of compositions and various doping levels. The binary system As_xSe_{100-x} offers this possibility because it can be prepared in glassy form for a wide range of compositions exceeding the stoichiometric threshold for $x_{As} = 40$, reaching eventually up to $x_{As} = 70$.

Methods

Experimental Details

$(AsSe)_{100-x}AgI_x$ ($x = 10, 20, 30$) glasses have been prepared as described elsewhere [7]. Off-resonance Raman spectra were recorded with the aid of a Fourier Transform (FT) Raman spectrometer (model FRA 106/S, Bruker, 1,064 nm) in order to avoid undesired photoinduced effects. The signal was detected by a liquid-nitrogen-cooled CCD Ge-detector. The laser power was set at 150 mW to avoid heat-induced effects. The number of scans was 100, the resolution 2 cm^{-1} .

First Principles Calculation Details

The Hartree-Fock (HF) molecular orbital theory as implemented in the GAUSSIAN 03 program package was utilized in the present study in order to calculate the structural details of two cage-like molecular units As_4Se_n ($n = 3, 4$). The accuracy of the computational method and the basis sets, which have been chosen for the investigated systems, has been tested by comparing the calculated

properties with other theoretical and experimental structural data that are available in the literature. The electronic structure of the atoms participating in the investigated structures are described by the Ahlrichs TZV basis sets [8].

Results and Discussion

In order to quantitatively analyze the Raman spectra of glasses one must make use of the so-called *reduced representation*. The reduction considers the distortion of the experimental Raman spectra that has taken place in view of the finite sample temperature and the wavelength dependence of the scattered light. The Stokes-side reduced Raman intensity (I^{red}) is related to the experimentally measured one (I^{exp}) via the equation:

$$I^{red}(\tilde{\nu}) = (\tilde{\nu}_0 - \tilde{\nu})^{-4} \tilde{\nu} [n(\tilde{\nu}, T) + 1]^{-1} I^{exp}(\tilde{\nu}) \quad (23.1)$$

where $n(\tilde{\nu}, T) = [\exp(\hbar\tilde{\nu}/k_B T) - 1]^{-1}$ is the Bose occupation number; $\hbar$ and k_B are the Planck and Boltzmann constants, respectively; the term in the fourth power is the correction for the wavelength dependence of the scattered intensity; $\tilde{\nu}$ is the Raman shift in cm^{-1} , and $\tilde{\nu}_0$ denotes the wavenumber of the incident radiation.

Figure 23.1 illustrates the reduced Raman spectra of $(\text{AgI})_x(\text{As}_{50}\text{Se}_{50})_{100-x}$ glasses. The spectra have been normalized (arbitrarily) in order to highlight the changes in the relative peak intensities. They reveal that appreciable structural changes take place upon alloying the base glass with AgI. The spectrum of the $\text{As}_{50}\text{Se}_{50}$ glass exhibits a few sharp peaks superimposed on a broad background at high energies [180–300 cm^{-1}] which are assigned to vibrational stretching modes and a number of sharper ones at low frequencies [110–175 cm^{-1}] originating from bending or deformation modes of the various structural units. The addition

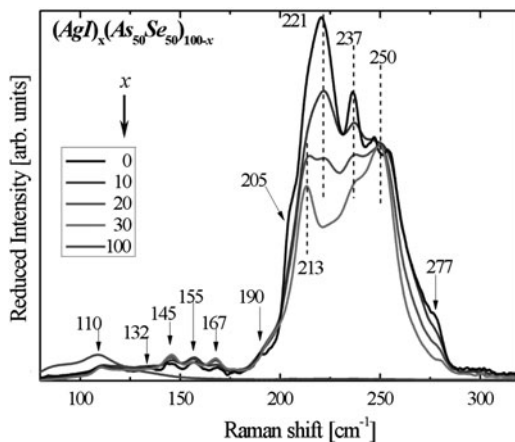


Fig. 23.1 Reduced Raman spectra of $(\text{AgI})_x(\text{As}_{50}\text{Se}_{50})_{100-x}$ glasses and crystalline AgI

of AgI causes severe reduction in the intensity of the sharp high energy peaks at 221, 237, and 247 cm^{-1} , which become severely suppressed for AgI 30%, while a new sharp mode appears at 213 cm^{-1} . In the bending mode regime, relative intensity changes are mainly observed, while the number of these sharp modes does not depend on the AgI content. The overall spectral envelope from 200 to 300 cm^{-1} narrows progressively with AgI addition.

Using the methods described in Section 2.2 we have undertaken a full optimization of the structures of two cage-like molecules. In As_4Se_4 (D_{2d} symmetry, realgar-type molecule) there are three homonuclear As-As bonds; all As atoms are equivalent. On the other hand, in As_4Se_3 (C_{3v} symmetry) there are three equivalent As atoms forming the basal triangle of the unit and an apex As atom which is only bonded to S atoms. Table 23.1 contains the structural parameters of the cage-like units as estimated by the HF method. As_b and As_a stand for the basal and apical As atoms in As_4Se_3 .

Vibrational analysis was performed at the HF level theory for both molecules in order to obtain the harmonic frequencies of the vibrational modes. The calculated spectra are constructed from the harmonic vibrational frequencies and Raman activities obtained using Gaussian type distributions. A common full-width of 5 cm^{-1} was chosen for all vibrational lines to achieve a satisfactory agreement in the spectral shape of experimental and calculated curves. Figure 23.2 shows experimental and theoretical Raman spectra for the As_4Se_4 and As_4Se_3 cage molecules. The experimental spectra are taken from [11] and [12], respectively.

The calculated frequencies of isolated molecules differ from the true experimental values if these units are embedded in a condensed phase due to the neglect of the effect of intermolecular interactions. Therefore, in order to compare experimental and calculated spectra, scaling factors are frequently employed. Thus, the spectra were scaled by a common factor for all lines. The scaling factor is 0.85 for As_4Se_4 . We observe that with a single scaling factor we achieve a very good agreement between experimental and calculated spectra for the stretching modes. The corresponding scaling factor for As_4Se_3 is 0.87, which also results in a satisfactory agreement between experiment and calculations.

In order to understand the nature of the structural changes caused by AgI addition we have first to clarify the structure of the $\text{As}_{50}\text{Se}_{50}$ glass. Based on the

Table 23.1 Calculated and experimentally determined bond distances (Å) and angles ($^\circ$) at various level of theory, of the As_4Se_4 and As_4Se_3 cage-like models with D_{2d} and C_{3v} symmetry ([i] Ref. [9]; [ii] Ref. [10])

Bond length/angle	As_4Se_4 (D_{2d})		As_4Se_3 (C_{3v})
	HF/TZV	Exp. [i, ii]	HF/TZV
As-As	2.555	2.568	2.461
As-Se	2.377	2.389	($\text{As}_a\text{-Se}$) 2.371 ($\text{As}_b\text{-Se}$) 2.367
$\angle(\text{As-Se-As})$	97.6	99.6	101.9
$\angle(\text{Se-As-Se})$	94.6	–	99.4
$\angle(\text{As-As-Se})$	101.4	101.3	104.1

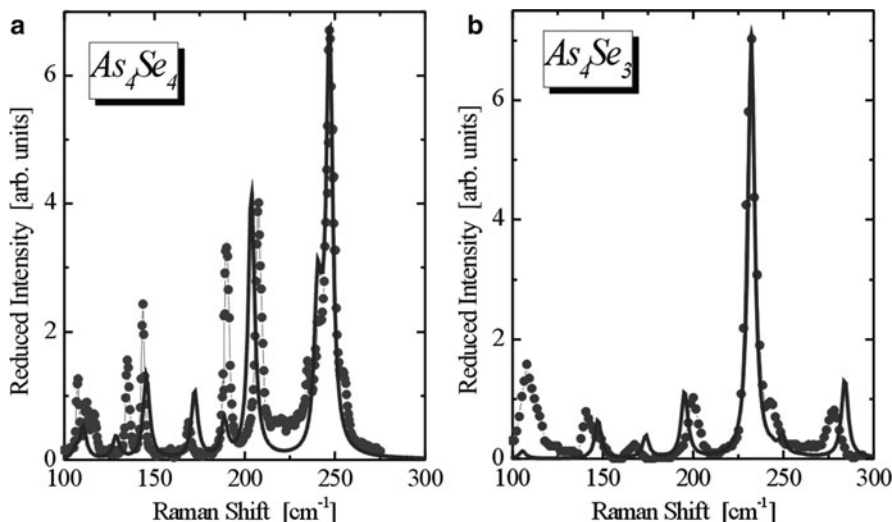


Fig. 23.2 Experimental (solid circles) and theoretically calculated (solid lines) Raman spectra of crystalline (a) As_4Se_4 and (b) As_4Se_3

Raman spectra we consider the structure of this glass as a combination of three components: (1) a stoichiometric-like network structure, resembling the structure of As_2Se_3 . This network structure is characteristically reflected by the very broad spectral envelope of the $\text{As}_{50}\text{Se}_{50}$ glass on top of which sharp lines are situated; (2) another network-like contribution from mixed $\text{AsAs}_{3-n}\text{Se}_n$ pyramids which are practically in the same spectral range as the stoichiometric pyramids; (3) cage-like molecules (As_4Se_4 , As_4Se_3) decoupled from the network structure, demonstrated by the appearance of sharp peaks in the $\text{As}_{50}\text{Se}_{50}$ spectrum (Fig. 23.1).

As shown in Fig. 23.1, the addition of AgI causes severe changes in the structure of the $\text{As}_{50}\text{Se}_{50}$ glass. This finding has to be compared with the structural changes in other similar $(\text{AgI})_x(\text{As}_2\text{Se}_3)_{100-x}$ glasses [13] where it was reported that the Raman spectra of the mixtures for AgI contents up to 60 mol% are almost identical with that of the base glass. To account for this observation, it was suggested [13] that the network matrix in the mixed glasses consist of $\text{AsSe}_{3/2}$ pyramidal units, whilst a significant number of Ag atoms are tetrahedrally bonded to I, in a similar way as in crystalline α -AgI. Comparing the Raman spectra of the AgI-doped stoichiometric glass [13] and the AgI-doped symmetric glass in our case we conclude that the existence of homonuclear As-As bonds ($E_{\text{bond}} = 46$ kcal/mol) act as weak centers which are more easily disrupted by iodine ions than As-Se bonds ($E_{\text{bond}} = 52$ kcal/mol). Inspecting Fig. 23.1, it becomes evident that iodine ions attack As-As bonds in both types of As-rich environments (2) and (3) described above. Indeed, we observe a decrease in the intensity of the sharp lines at 221, 237, and 247 cm^{-1} , which eventually disappear for 30% AgI. The first arises from As-rich environments in mixed pyramids, while the other two originate from vibrations of the decoupled cage-like As_4Se_4 ,

As₄Se₃ molecules. Further, a decrease in the width of the spectral envelope from 200 to 280 cm⁻¹ is evident which reflects the modes of the network of mixed AsAs_{3-n}Se_n pyramids. The systematic decrease of the band at 277 cm⁻¹ and of the low-frequency background below 100 cm⁻¹ caused by increasing AgI further, point to the degradation of the mixed pyramidal network.

The distinctive role of Ag and I ions in the AsSe glass structure has been studied by X-ray and neutron diffraction studies [14]. It was found that Ag tends to form bonds with Se atoms increasing the connectivity of the glass structure. In contrast, I bonds preferentially to As atoms causing a reduction in the mean coordination number of the glass. Therefore, in our case, the addition of AgI is also expected to lead to the formation of Ag-Se and As-I (terminal) bonds in mixed chalcogenide pyramids AsSe_mI_{3-m}. The small cross section of Ag-Se vibrations renders the corresponding mode not visible in the Raman spectra. In order to identify the As-I Raman bands of these new species we have to recall that the AsI₃ pyramidal unit (C_{3v} symmetry) exhibits its symmetric $\nu_1(A)$ and antisymmetric $\nu_3(E)$ stretching vibrational modes at 212 and 201 cm⁻¹, respectively [15]. Therefore the 213 cm⁻¹ which is the dominant band in the AgI 30% reflects As-I bond stretching modes in AsSe_mI_{3-m} pyramids.

Conclusions

Raman scattering and first principles calculations have been employed to study structural details of AgI-doped As₅₀Se₅₀ glasses. Calculations were applied to cage-like molecular As₄Se_n (n = 3, 4) units, providing geometrical data (bond lengths and bond angles) and harmonic vibrational frequencies. Calculated Raman spectra exhibit satisfactory agreement with the experimental ones for the corresponding molecular crystals. Analysis of reduced Raman spectra revealed that three structural motifs dominate the As₅₀Se₅₀ glass structure, i.e. a network of As₂Se₃ pyramids, another network of mixed AsAs_{3-n}Se_n pyramids, and molecules (As₄Se₄, As₄Se₃) decoupled from the network structure. The addition of AgI causes appreciable structural changes and in particular the reduction of the As-rich environments, i.e. mixed pyramids and cage-like molecules. Mixed chalcogenide pyramids AsSe_mI_{3-m} appear progressively with increasing AgI.

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Chapter 24

Optical Properties of As-Based Chalcogenide Glasses

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Abstract Photostructural transformations in amorphous films of chalcogenide glasses (ChG) under light irradiation are presently of scientific and practical interests. As the composition of the ChGs determines the kind of structural units and the mean coordination number, in the present work amorphous films of the chalcogenide systems $\text{As}_{100-x}\text{Se}_x$ ($x = 40\text{--}98$) and $\text{As}_{40}\text{Se}_{60}\text{:Sn}_y$ ($y = 0\text{--}10.0$ at.% Sn) were studied. Experimental investigations of the transmission spectra and the photodarkening relaxation characteristics of the amorphous films under study, including the thickness dependence, are presented.

Keywords Amorphous chalcogenide films · Optical absorption · Refractive index · Photoinduced phenomena

Introduction

The optical properties of, and the photoinduced phenomena in chalcogenide glasses are very attractive for many applications in photonics and optoelectronics [1]. Amorphous arsenic selenide films usually became darkened under irradiation with light from the region of fundamental optical absorption $h\nu \geq E_g$, and the so-called photodarkening effect takes place. The increase of the optical absorption is accompanied by a red shift of the absorption edge and an increase of the refractive index. The kinetics of the photodarkening process in $\alpha\text{-As}_{100-x}\text{Se}_x$ thin films also were investigated. It was shown that non-stoichiometric amorphous $\text{As}_{50}\text{Se}_{50}$ and $\text{As}_{60}\text{Se}_{40}$ films are more sensitive to photostructural transformations under light exposure; the sensitivity decreases with increasing content Se in $\text{As}_{100-x}\text{Se}_x$ glasses.

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Experimental

$\text{As}_{100-x}\text{Se}_x$ ($x = 40\text{--}98$) and $\text{As}_{40}\text{Se}_{60}\text{:Sn}_y$ ($y = 0\text{--}10.0$ at.% Sn) glasses were synthesized from the elements (As, Se, Sn) of 6 N purity by the conventional melting technique. The amorphous $\text{As}_{100-x}\text{Se}_x$ and $\text{As}_{40}\text{Se}_{60}\text{:Sn}_y$ thin films ($L = 0.2\text{--}5.0$ μm) were prepared by thermal “flash” evaporation in vacuum onto glass substrates kept at $T_{\text{subs}} = 100^\circ\text{C}$. To initiate photostructural transformations in the film samples continuous He-Ne lasers ($\lambda = 630$ nm, $P = 0.6$ mW and $\lambda = 540$ nm, $P = 0.75$ mW) were used as sources of light exposure.

Results and Discussion

The optical transmission of amorphous $\text{As}_{100-x}\text{Se}_x$ ($L \sim 1.3$ μm) was investigated at room temperature (as-deposited, heat treated in vacuum at $T_{\text{treat}} = 120^\circ\text{C}$ for 1 h, and exposed to light with an illuminance of 50,000 Lx for 1 h). An increasing of the As content in the $\text{As}_{100-x}\text{Se}_x$ system shifts the absorption edge to the red region of the spectra. The band gap of amorphous $\text{As}_{40}\text{Se}_{60}$ thin films, determined from the absorption spectra, is $E_g = 1.82$ eV. This is in good agreement with the experimental data presented in Ref. [2], according to which the optical band gap decreases from $E_g = 1.95$ eV for $\text{As}_8\text{Se}_{92}$ down to $E_g = 1.83$ eV for $\text{As}_{36}\text{Se}_{64}$.

The shift of the absorption edge after light exposure and heat treatment is for all amorphous $\text{As}_{100-x}\text{Se}_x$ films accompanied by a corresponding change of the refractive index n . For the calculation of the optical constants the program PARAV-V1.0 was used [3]. The degree of the absorption edge shift to the red region depends on the composition of the amorphous film, the intensity and time of the exposure, and the heat treatment. The influence of the light exposure at a transmission level of $T = 20\%$ is manifested by shift of the absorption edge $\Delta\lambda = 920$ nm observed for amorphous $\text{As}_{60}\text{Se}_{40}$; it decreases with increasing Se content down to $\Delta\lambda = 2\text{--}5$ nm for $\text{As}_5\text{Se}_{95}$ and $\text{As}_{10}\text{Se}_{90}$.

Increasing the Sn concentration in amorphous $\text{As}_{40}\text{Se}_{60}$ thin films shifts the absorption edge to the red region of the spectra. Simultaneously, the refractive index n increases (Fig. 24.1). For $x = 2.0$ at.% Sn the refractive index is $n = 3.5$ at $\lambda = 800$ nm. Figure 24.2 shows the influences of light exposure and heat treatment on the degree of modification of the refractive index for amorphous $\text{As}_{40}\text{Se}_{60}\text{:Sn}_{1.0}$ thin films. In these cases, the light exposure as well as heat treatment increases the refractive index n .

Photodarkening relaxation was measured during illumination for as-deposited amorphous $\text{As}_{100-x}\text{Se}_x$ ($x = 40\text{--}98$). The relaxation of the relative optical transmission $T(t)/T(0)$ of the $\text{As}_{100-x}\text{Se}_x$ films is shown in Fig. 24.3. It is described by the stretched exponential function $T(t)/T(0) = A_0 + A\exp[-(t - t_0)/\tau]^{(1-\alpha)}$. Here t is the exposure time, τ the apparent time constant, A the amplitude while t_0 and A_0 are the initial values, and α is the dispersion parameter ($0 < \alpha < 1$). The relaxation

Fig. 24.1 Dispersion curves of the refractive index n for amorphous $\text{As}_{40}\text{Se}_{60}$ (1), $\text{As}_{40}\text{Se}_{60}:\text{Sn}_{0.5}$ (2), $\text{As}_{40}\text{Se}_{60}:\text{Sn}_{1.0}$ (3), and $\text{As}_{40}\text{Se}_{60}:\text{Sn}_{2.0}$ (4) thin films

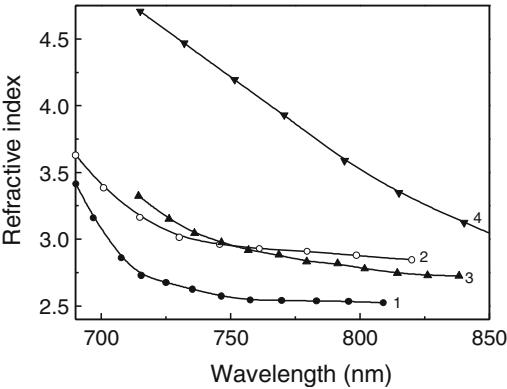


Fig. 24.2 Dispersion curves of the refractive index n for amorphous $\text{As}_{40}\text{Se}_{60}:\text{Sn}_{1.0}$ thin films: as-deposited (1), as-deposited and light exposed (2), heat treated (3), heat treated and exposed (4)

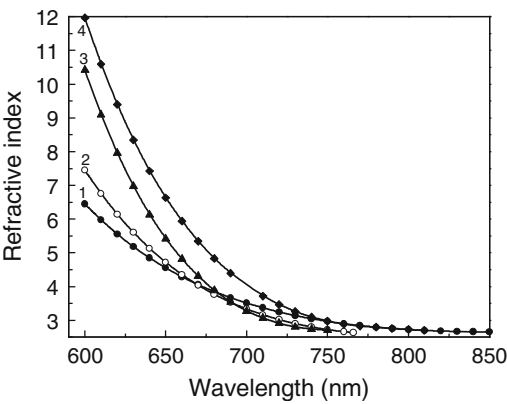


Fig. 24.3 Photodarkening kinetics (T/T_0) of as-deposited amorphous $\text{As}_{28}\text{Se}_{72}$ (1), $\text{As}_{40}\text{Se}_{60}$ (2), and $\text{As}_{50}\text{Se}_{50}$ (3) films vs. exposure time t . The excitation wavelength was $\lambda_{\text{exc}} = 0.63 \mu\text{m}$

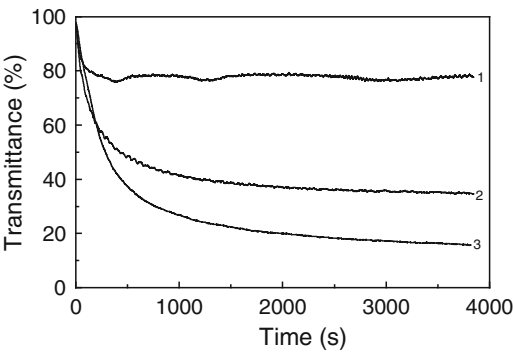


Fig. 24.4 The dependence of transmission versus exposure time for amorphous $\text{As}_{60}\text{Se}_{40}$ films of different thickness L : 0.27 μm (1), 0.69 μm (2), 2.04 μm (3), 4.07 μm (4)

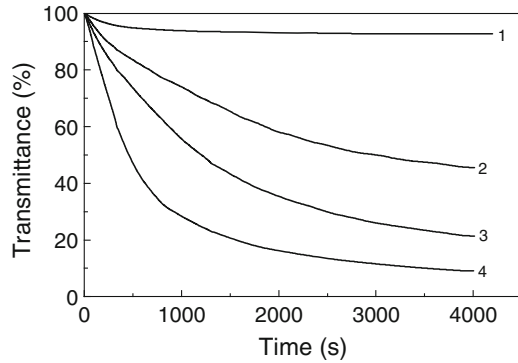
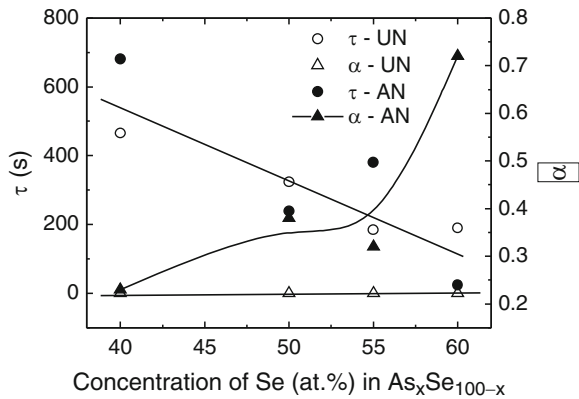


Fig. 24.5 The dependence of the parameters τ and α of the stretched exponential law for as-deposited (UN) and annealed (AN) amorphous $\text{As}_{100-x}\text{Se}_x$ thin films



of the relative optical transmission $T(t)/T(0)$ of amorphous $\text{As}_{60}\text{Se}_{40}$ films of different thickness is shown in Fig. 24.4.

The experimental data show that for thicker films the photodarkening is stronger; it is almost absent for films with thicknesses about $L \leq 0.2\text{--}0.3 \mu\text{m}$. The dependence of the relaxation time τ and the dispersion parameter α for as-deposited (UN) and annealed (AN) films is shown in Fig. 24.5. The dispersion parameter α is close 0.3 for almost all UN $\text{As}_{100-x}\text{Se}_x$ films and non-monotonously changes with composition.

Under our experimental conditions, for the AN films a low value of the dispersion parameter of $\alpha \approx 0.3$ was observed for $\text{As}_{45}\text{Se}_{55}$; it increases up to $\alpha \approx 0.6\text{--}0.65$ for $\text{As}_{40}\text{Se}_{60}$ and $\text{As}_{60}\text{Se}_{40}$. Such a behaviour of the dispersion parameter α with composition may be associated with the structure of the investigated glasses.

The fact that α is increasing for Se-rich compositions indicates an increased ordering of the structure of the amorphous films. The composition dependence of the photodarkening may be caused by different ratios of homopolar (As-As, Se-Se) and heteropolar chemical bonds (As-Se) in the investigated amorphous films, which are responsible for the photodarkening [4].

Summary

Photostructural transformations in amorphous $\text{As}_{100-x}\text{Se}_x$ ($x = 40\text{--}98$) and $\text{As}_{40}\text{Se}_{60}:\text{Sn}_y$ ($y = 0\text{--}10.0$ at.% Sn) films were investigated. Amorphous $\text{As}_{60}\text{Se}_{40}$ and $\text{As}_{50}\text{Se}_{50}$ films are more sensitive to light irradiation; they exhibit a large modifications of the refractive index ($\Delta n/n = 0.394$). Changes of the optical transmission of the films under illumination may be described by a stretched exponential law with the dispersive parameter in the range $0.4 \leq \alpha \leq 1.0$.

The composition dependence of the transmission spectra, the photodarkening characteristics, and the kinetics of recording holographic information of films of the glassy system $\text{As}_{100-x}\text{Se}_x$ was investigated. It was established that non-stoichiometric $\text{As}_{50}\text{Se}_{50}$, $\text{As}_{55}\text{Se}_{45}$, and $\text{As}_{60}\text{Se}_{40}$ exhibit a higher sensitivity to light exposure, the sensitivity decreases with increasing Se content in $\text{As}_{100-x}\text{Se}_x$ glasses.

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Chapter 25

IR Impurity Absorption in $\text{GeS}_2\text{-In}_2\text{S}_3\text{-AgI}$ Chalcohalide Glasses

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Abstract IR absorption spectra of $(80-x)\text{GeS}_2\text{-}20\text{In}_2\text{S}_3\text{-}x\text{AgI}$ (GIS-AgI) chalcohalide glasses with $x = 15$ and 20 mol% are studied in the $4,000\text{--}400\text{ cm}^{-1}$ region. The effect of the AgI content on the measured IR bands connected with O-, H- and C-based absorbed impurities is analysed.

Keywords Chalcohalide glasses · $\text{GeS}_2\text{-In}_2\text{S}_3\text{-AgI}$ system · Optical properties · IR impurity absorption

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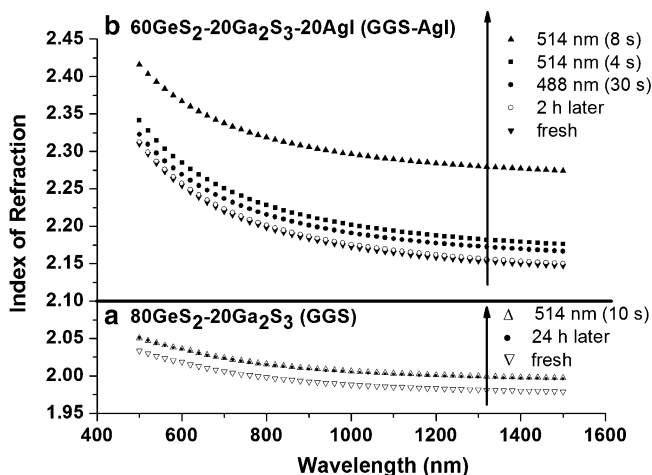


Fig. 25.1 Changes of the refractive indices of GGS (a) and GGS-AgI (b) obtained before and after laser exposing [1]

Introduction

Recently, a new kind of photoinduced effect, i.e. total recovery of the photorefraction (“self-healing”) at room temperature has been found for AgI-doped chalcocalide glass with a high glass transition temperature ($T_g = 636$ K), as shown in Fig. 25.1 for $60\text{GeS}_2\text{-}20\text{Ga}_2\text{S}_3\text{-}20\text{AgI}$ (GGS-AgI) [1]. Further in-situ measurements of the reversible photodarkening in this material (GGS-AgI) in comparison with an AgI-free sample (GGS) have proven the enhanced photosensitivity (Fig. 25.2) and the “self-healing” effect with the addition of AgI [2]. It has been expected by the present authors that such a fast auto-recovery property in AgI-doped chalcocalide glasses can be utilized for optical signal processing. Thus, it is of interest to investigate the structure and properties of such AgI-doped chalcocalide glasses.

In the present work we study IR impurity absorption processes in the chalcocalide glass $\text{GeS}_2\text{-In}_2\text{S}_3\text{-AgI}$ (GIS-AgI) which is similar to GGS-AgI.

Experimental

Bulk glass samples of the $(80-x)\text{GeS}_2\text{-}20\text{In}_2\text{S}_3\text{-}x\text{AgI}$ (GIS-AgI) system with $x = 15$ and 20 mol% were synthesized from high purity elements (5 N Ge, In, and S) and 5 N AgI powder at $1,000^\circ\text{C}$ in evacuated (10^{-3} Pa) fused silica ampoules for 24 h, then quenched in air from 900°C to room temperature. To remove mechanical strains formed after synthesis the glass samples obtained were annealed at 300°C for 6 h. Samples with a size of $10 \times 10 \times 1 \text{ mm}^3$ were

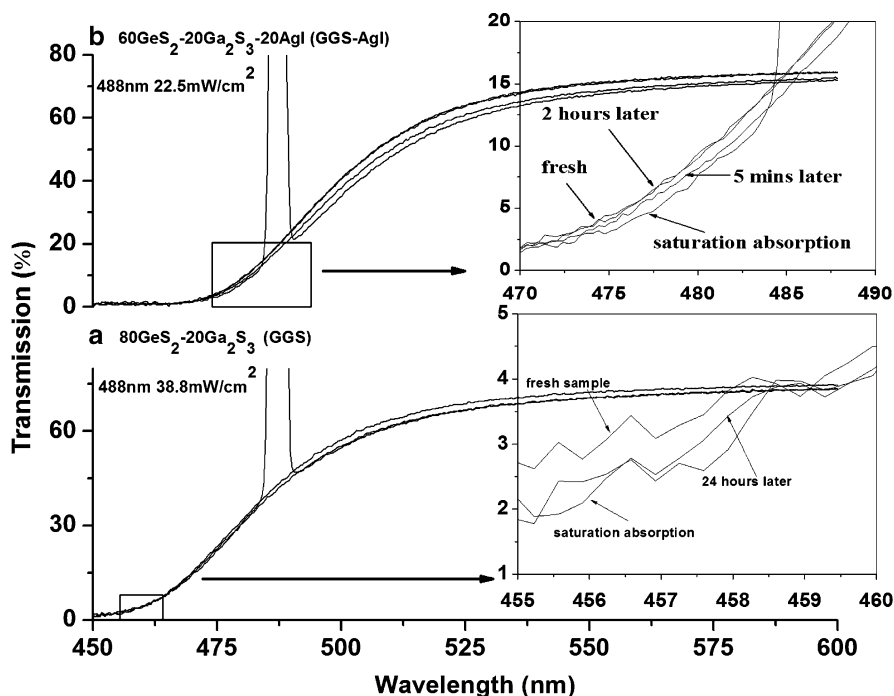


Fig. 25.2 Transmission spectra of GGS (a) and GGS-AgI (b) obtained before (as indicated by “fresh” in the insets) and after 5 min, 2 h and 24 h laser exposure [2]

polished to good optical quality. The amorphous state of the samples was verified by XRD measurements.

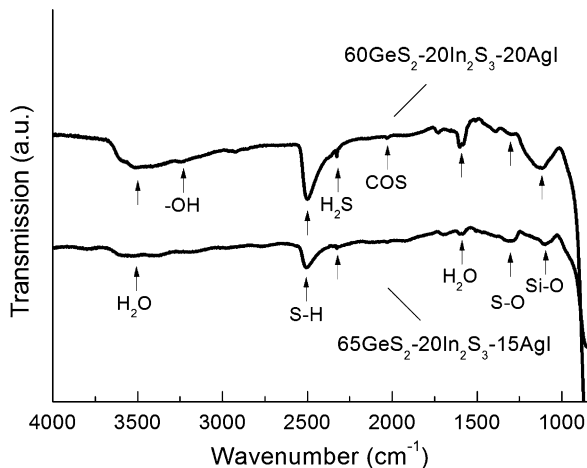
The IR absorption spectra were measured in the $4,000\text{--}400\text{ cm}^{-1}$ wavenumber range at ambient temperature using a Bruker IFS 66 (Germany) Fourier transform infrared spectrometer.

Results

Figure 25.3 shows IR absorption spectra measured for $65\text{GeS}_2\text{-}20\text{In}_2\text{S}_3\text{-}15\text{AgI}$ and $60\text{GeS}_2\text{-}20\text{In}_2\text{S}_3\text{-}20\text{AgI}$. The spectra of the investigated glasses are characterized by a large number of impurity absorption bands [3,4], namely: molecular water (H_2O) at $3,520\text{ cm}^{-1}$; hydroxyl ($-\text{OH}$) groups at $3,240\text{ cm}^{-1}$; sulphur-hydrogen ($-\text{S}-\text{H}$) complexes at $2,500\text{ cm}^{-1}$; molecular H_2S at $2,325\text{ cm}^{-1}$; carbon-containing groups ($\equiv\text{C}-\text{O}-\text{S}-$) at $2,030\text{ cm}^{-1}$; molecular adsorbed water (H_2O) at $1,590\text{ cm}^{-1}$; sulphur-oxygen ($-\text{S}-\text{O}-$) complexes at $1,305\text{ cm}^{-1}$; and silicon impurities in the form of $\text{Si}-\text{O}$ bonds at $1,100\text{ cm}^{-1}$.

It was found that a decrease of the GeS_2 amount and the corresponding increase of the AgI content in the GIS-AgI glass composition results in an increase of the

Fig. 25.3 IR absorption spectra for $65\text{GeS}_2\text{-}20\text{In}_2\text{S}_3\text{-}15\text{AgI}$ and $60\text{GeS}_2\text{-}20\text{In}_2\text{S}_3\text{-}20\text{AgI}$ glasses



intensity of practically impurity absorption bands all detected, especially of the H_2O bands at $3,520$ and $1,590\text{ cm}^{-1}$ and the band of $-\text{S}-\text{H}$ complexes, while the intensity of the $-\text{S}-\text{O}-$ band decreases with decreasing GeS_2 content.

Conclusion

The effect of the AgI content on the IR impurity absorption in $65\text{GeS}_2\text{-}20\text{In}_2\text{S}_3\text{-}15\text{AgI}$ and $60\text{GeS}_2\text{-}20\text{In}_2\text{S}_3\text{-}20\text{AgI}$ glasses was analysed, showing an enhancement of the intensity of practically all O-, H- and C-based impurity absorption bands detected. The only exception observed were $-\text{S}-\text{O}-$ complexes the concentration of which decrease with addition of AgI . The results obtained must be taken into account in the process of fabrication of the chalcogenide glasses investigated in IR optical devices and sensors.

Acknowledgments This work was partly supported by the Ministry of Education and Science of Ukraine and the Ministry of Science and Technology of the People's Republic of China in the framework of Bilateral Ukrainian-Chinese Cooperation on Science and Technology (2009–2010).

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Chapter 26

New Chalcogenide Glasses from the $\text{GeSe}_2\text{--Ag}_2\text{Se--AgI}$ System for Nanostructured Sensors

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Abstract New chalcogenide glasses from the $\text{GeSe}_2\text{--Ag}_2\text{Se--AgI}$ system with potential application as active materials for sensor elements have been synthesized. The glass forming region was determined by means of XRD and electron microscopic analyses. The main physicochemical properties, the density d , Vickers microhardness H_V and the temperatures of glass-transition T_g , crystallization T_{cr} and melting T_m were determined. A correlation between these properties and the composition of the investigated glasses is established and discussed.

Keywords Glass formation · Chalcogenide glasses · Physicochemical properties

Introduction

The chalcogenide glasses attract increasing practical and theoretical interest due to the possibility of their application in sensorics. Monchev et al. [1] have developed thin Ge--S--AgI sensors for acetone and ammonia detection placed on cantilevers and have determined the change of the resonance frequency caused by the chemisorption of these gases. Kozicki and Mitkova [2] have described the change of the

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resonance frequency and the Q-factor caused by an electrically forced Ag-ion transport.

There are many data in the literature on silver diffusion in similar systems [2,3]. The mobile silver can move to the surface where it will form stable or unstable compounds with NH_3 , SO_2 [4], halogen-hydrogen compounds, etc.

In this context the aim of the present work is to synthesize new chalcogenide materials from the $\text{GeSe}_2\text{--Ag}_2\text{Se--AgI}$ system, to determine its region of glass formation and the main physicochemical properties of the glasses obtained as a first approach towards their investigation as an active material for gas sensors.

Experimental

For the synthesis of samples from the $(\text{GeSe}_2)_x(\text{Ag}_2\text{Se})_y(\text{AgI})_z$ system ($x+y+z = 100$ mol%) preliminary prepared GeSe_2 and Ag_2Se (Ge and Se with 5 N, Ag with 4 N purity) were used, as well as AgI (99.99%, Merck). The synthesis was performed by the melt-quenching technique. The melts were quenched in ice cold water with a cooling rate of $10\text{--}15\text{ K s}^{-1}$.

The obtained bulk materials were investigated by X-ray diffraction (XRD, TUR-M16 diffractometer with CuK_α -irradiation and a Ni-filter) and SEM (scanning electron microscope Philips 515) analyses.

The thermal characteristics (temperatures of glass-transition T_g , crystallization T_{cr} and melting T_m) of some samples were determined by differential thermal analysis using a set-up from the F. Paulik-J. Paulik-L. Erdey system produced by the MOM-Hungary company with a heating rate of 10 K min^{-1} and $\gamma\text{-Al}_2\text{O}_3$ as reference substance. The density d of the samples was determined by the hydrostatic method with toluene as immersion fluid. The Vickers microhardness HV was measured with a PMT-3 microhardness meter with a loading of 10 g. The final HV value was obtained as an average of 20 measurements.

Results and Discussions

The XRD measurements show that some samples are amorphous without diffraction maximums but with the amorphous X-ray plateau characteristic for this state. An other group of compositions is characterized by a weaker plateau and low-intensity reflexes; these are the compositions on the glass forming border. The XRD patterns of the crystalline samples, lying outside the glass forming region, possess well-expressed peaks. SEM investigations confirmed the results of the XRD analysis.

Based on the syntheses and investigations performed the glass forming region within the $\text{GeSe}_2\text{--Ag}_2\text{Se--AgI}$ system was outlined (Fig. 26.1). It lies partially on the $\text{GeSe}_2\text{--AgI}$ line and extends towards the center of the Gibbs' concentration triangle. On the $\text{GeSe}_2\text{--Ag}_2\text{Se}$ line only one glassy-crystalline sample was obtained

Fig. 26.1 Region of glass formation in the GeSe_2 – Ag_2Se – AgI system

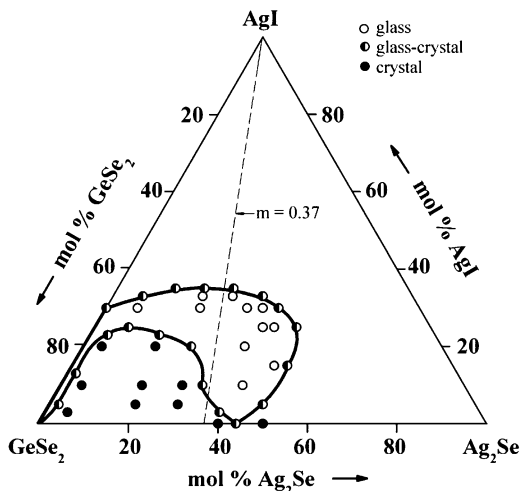


Table 26.1 Properties of glassy samples with the composition $(\text{GeSe}_2)_x(\text{Sb}_2\text{Se}_3)_y(\text{AgI})_z$, $m = y/(x + y)$

Composition			m	T_g , K	T_{cr} , K	T_m , K	HV, kgf mm ⁻²	d, g cm ⁻³
GeSe ₂	Ag ₂ Se	AgI						
49.5	40.5	10	0.45	514	572	826	82	5.43
44	36	20	0.45	490	562	799	72	5.40
38.5	31.5	30	0.45	457	591	831	61	5.37
49	21	30	0.30	500	615	884	66	4.79
63	7	30	0.10	567	610	912	75	4.32

which corresponds to the eutectic point of the state diagram [5]. The maximum solubility of AgI in the glasses is ~ 35%.

The results of the determination of the physicochemical properties of some glassy samples are presented in Table 26.1.

The glass-transition temperature T_g of the investigated glasses changes from 457 to 567 K (Table 26.1). The dependencies $T_g(z)_{m=\text{const}}$ and $T_g(m)_{z=\text{const}}$ are considered to examine the influence of each of the compounds on T_g . The linear form of these dependencies shows that the addition of Ag_2Se and/or AgI does not lead to structural changes in the glass. The initial components Ag_2Se and AgI are typically crystalline compounds, thus the decrease of T_g with z for $m = \text{const}$ is logical.

The values of the crystallization temperature T_{cr} weakly depend on the glass composition; as for $(\text{GeSe}_2)_{55}(\text{Ag}_2\text{Se})_{45}$ –AgI glasses they vary between 562 and 591 K ($\bar{T}_{cr} = 575$ K), and for the glasses with $z = 30$ mol% AgI from 591 to 615 K ($\bar{T}_{cr} = 606$ K) (Table 26.1), i.e. one can say that one glassy “phase” exist but with changeable composition crystallizes.

The T_m values of the first group are between 799 and 831 K ($\bar{T}_m = 819$ K), those of the second between 831 and 912 K ($\bar{T}_m = 876$ K), i.e. one can suppose that these are the melting temperatures of the above mentioned glassy “phase”.

The density d of the investigated glassy samples is between 4.32 and 5.43 g cm⁻³. At constant values of the ratio $[\text{Ag}_2\text{Se}]/[\text{GeSe}_2]$, i.e. $m = y/(x + y) = \text{const}$ (Table 26.1) the density of the glasses decreases insignificantly with the increase of the AgI content, since these samples are situated on the right side of the point with the composition $(\text{GeSe}_2)_{63}(\text{Ag}_2\text{Se})_{37}$ (Fig. 26.1). This point corresponds to a crystalline sample with a density $d = d_{\text{AgI}} = 5.68 \text{ g cm}^{-3}$. For the glasses lying on any line connecting points with compositions $m > 0.37$ ($z = 0$) and the apex of the Gibbs' triangle ($z = 100 \text{ mol\% AgI}$), d will decrease with increasing AgI. Vice versa, for the sections going through points with $m < 0.37$ d increases with the increase of the AgI content. With the addition of Ag_2Se at a constant AgI concentration (Table 26.1), the density logically increases since $d(\text{Ag}_2\text{Se}) \gg d(\text{GeSe}_2)$.

The microhardness (HV) changes from 61 to 104 kgf mm⁻². With addition of Ag_2Se and/or AgI to GeSe_2 , HV decreases (Table 26.1). The influence of the composition on this parameter is expected since $\text{HV}(\text{Ag}_2\text{Se}, \text{AgI}) < \text{HV}(\text{GeSe}_2)$.

Conclusion

New chalcogenide glasses from the GeSe_2 – Ag_2Se –AgI system were synthesized and its glass forming region was outlined. The main physicochemical properties (temperatures of glass-transition, crystallization and melting; density and microhardness) of some glassy phases were determined. A correlation between the properties and the glass composition was established and discussed.

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Part IV.4

Further Glasses

Chapter 27

Thermally Induced Nanostructures in Samarium-Doped Glass Ceramics for X-Ray Sensor Applications

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Abstract There is much interest in various glass-ceramics doped with rare-earth (RE) metals for x-ray storage phosphor and/or x-ray scintillator applications for potential use in high resolution x-ray imaging. The phosphor and scintillator properties of these glass ceramics depend on the formation of RE embedded nanocrystals in their structure. The heat treatment and annealing of the starting RE-doped glasses is critically important to the formation and control of the glass ceramic nanocrystals. We have studied the thermal and photoluminescence properties of Sm-doped fluorochlorozirconate glass ceramics. We selected useful host compositions and appropriate heat treatment and annealing procedures needed to grow the required RE-doped nanocrystals in a glass matrix for sensor applications.

Keywords Glass ceramics · Nanostructuring · Rare-earth doping · Thermal properties · DSC · TMDSC, photoluminescence · Storage phosphors and scintillators

Introduction

A number of alkaline, alkaline earth and various other metal based materials composed as borate, phosphate, oxide and/or fluorite glasses and glass-ceramics (GS), when suitably doped with lanthanides or rare-earths (RE) such as Sm- or Eu-ions, have been shown to behave as storage phosphors and/or x-ray scintillators; e.g. [1–4]. The use of RE doped crystals for digital X-ray imaging was commercialized years ago; however, a new and different approach has shown that RE-doped glasses and

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GC have greater potential for high resolution x-ray imaging [3,4]. Further, some rare-earth ions have their valency converted, e.g. Sm^{3+} becomes converted to Sm^{2+} upon irradiation in certain glass hosts, which has the potential for measuring high dose radiation, e.g. radiation emitted from a synchrotron light source [5]. In one class of fluoro-chlorozirconate (FCZ) GCs based on the well-known ZBLAN, the active RE ions are embedded in BaCl_2 nanocrystals, which are dispersed in the glass matrix. The formation of nanocrystals, their structure and size, play an important role in the photoluminescence of rare-earth ions in FCZ GCs. Heat treatment and annealing of the starting RE-doped FCZ glasses in various gaseous atmospheres are important for the formation and control of the nanocrystals [6].

We have studied the thermal and photoluminescence properties of Sm- and Eu-ions embedded in fluoro-chlorozirconate (FCZ) glasses and glass ceramics. We have focused on FCZ GCs because of their low-phonon energies, which restrict non-radiative transitions, and good transparency of the emitted photoluminescent light. We present results on the thermal properties of FCZ glasses and GCs obtained by DSC (differential scanning calorimetry) and TMDSC (temperature-modulated DSC) measurements, X-ray luminescence and photoluminescence measurements in which we examine the X-ray luminescence yield under different gaseous annealing conditions. As a result of these experiments, it has been possible to select useful host compositions and to establish various heat treatment and annealing procedures needed to grow the required nanocrystals in the glass matrix.

Experimental Procedure

We have already described the preparation of FCZ glasses with a base composition of 53.5% ZrF_4 + 3% LaF_3 + 3% AlF_3 + 20% NaF + 0.3% InF_3 + 20% BaF_2 and BaCl_2 [6]; we have also pointed out the importance of substituting BaCl_2 for BaF_2 in the formation of nanocrystals in FCZ glass-ceramics. We used 99.99% purity SmCl_3 as a dopant. The amounts of rare earth (RE) doping were varied in the range 0.05–2 mol.%.

Differential Scanning Calorimetric (DSC) and Temperature Modulated DSC (TMDSC) experiments were performed using a TA Instruments DSC Q100 and a DSC 2910 with attached Fast Air Cooling System (FACS) and Refrigerating Cooling System (RCS). Details regarding the thermal measurements and the advantages of TMDSC compared to DSC have been described elsewhere (e.g. [7]). The evaluation of DSC and TMDSC results was performed with the TA Instruments Universal Analysis (UA) software.

Photoluminescence (PL) was excited by the emission of an ORIEL high pressure mercury lamp filtered by a set of optical filters forming a narrow spectral band in the UV range with the maximum centered around 360 nm. An ORIEL cornerstone 1/8 m monochromator and an ORIEL cooled InGaAs photodiode were used to measure the steady state PL spectrum. The X-ray luminescence (XL) was excited using a Gendex GX-1,000 x-ray set-up with a tungsten anode tube operating up to

100 kV. The x-ray beam was filtered by 2.7 mm Al. The XL spectra were recorded using a Stellar Net EPP2000 spectrophotometer. The XL yield of the samples under investigation was measured with a 2 in. PTFE integrating sphere (IS200, Thorlabs) as described previously [6].

Results and Discussion

Figure 27.1 shows the photoluminescence (PL) and x-ray luminescence spectra obtained for optical and x-ray excitation respectively. The emissions have been attributed to Sm^{3+} ions. The spectra are almost identical in the range of 550–750 nm. While the spectra are identical, there are differences in the dependence of the integrated intensity of PL and XL on the partial Cl-content as shown in Figs. 27.2 and 27.3.

In our previous work [6] we presented experimental evidence based on thermal analysis (DSC and TMDSC) that point to the formation of two phases (Cl-rich and F-rich regions) in FCZ glasses when the partial chlorine content was 10% or higher. The partial amount of Cl is defined as the ratio of the Cl-concentration C_{Cl} to the

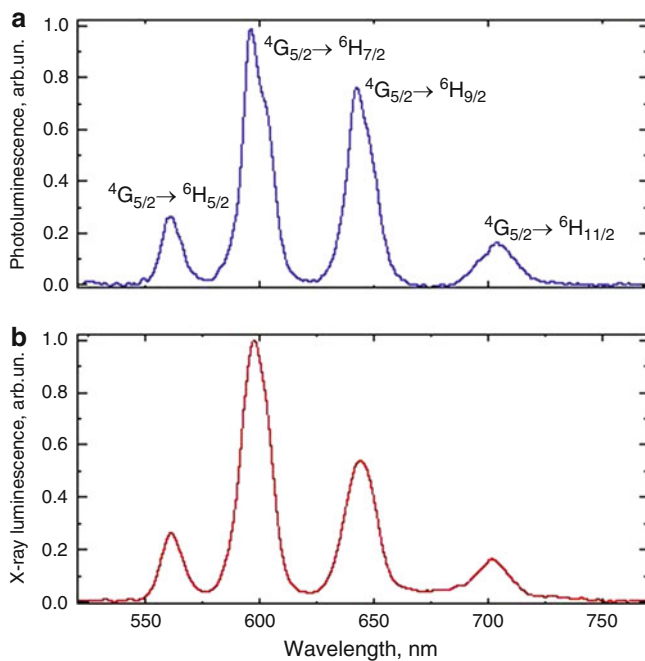


Fig. 27.1 Comparison of (a) photoluminescence and (b) x-ray luminescence spectra of Sm^{3+} ions embedded in FCZ glasses and glass ceramics

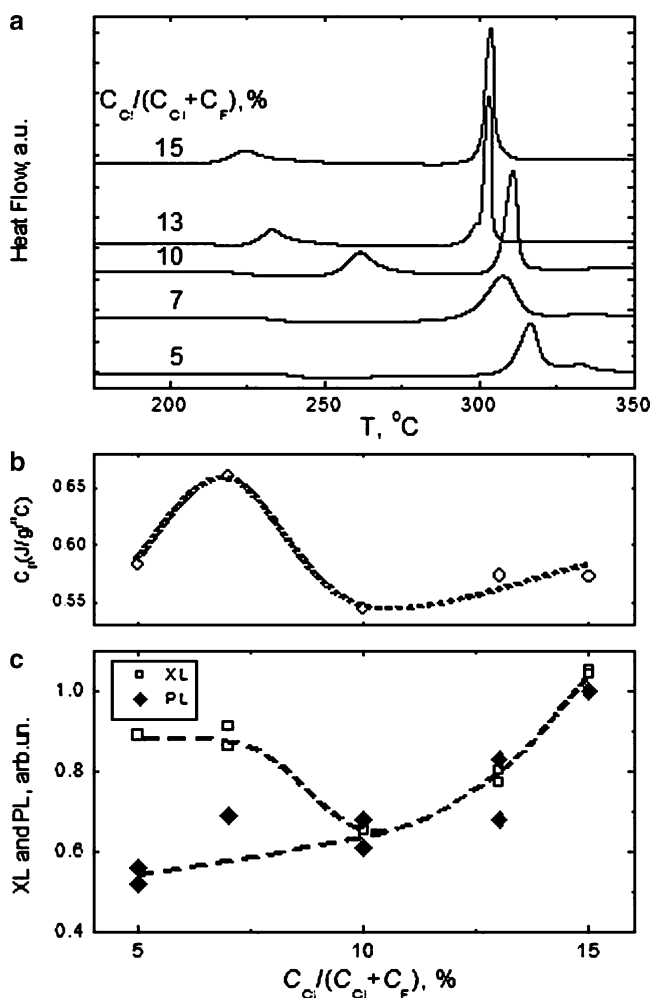


Fig. 27.2 (a) DSC thermograms with varying amounts of the partial content of Cl, doped with 1% SmF_3 at a heating rate of 10 K/min; (b) heat capacity C_p (at 160°C) versus the partial content of Cl in FCZs with 1% SmF_3 . C_p was measured by TMDSC; (c) XL and PL intensity integrated over the range 500–800 nm versus the partial Cl content in 1% Sm FCZs (the curves are guides to the eye)

overall concentration of halogens, i.e. $R_{Cl} = C_{Cl}/(C_{Cl} + C_F)$ when BaF_2 in ZBLAN glasses is substituted by BaCl_2 to form FCZs from ZBLAN, and after appropriate treatments get the corresponding glass ceramic. Figure 27.2 shows that the separation process of chlorine-rich phases from the main fluorite glass matrix affects not only the thermal properties as observed in DSC (heat flow) and TMDSC (heat capacity) results but also the XL and PL properties which exhibit a similar dependence on the relative amount of Cl in the FCZ materials studied.

Fig. 27.3 XL and PL intensity versus the concentration of Sm. The PL linearly depends on C_{Sm} , while the XL clearly demonstrates a sublinear dependence. The lines are guides to eye

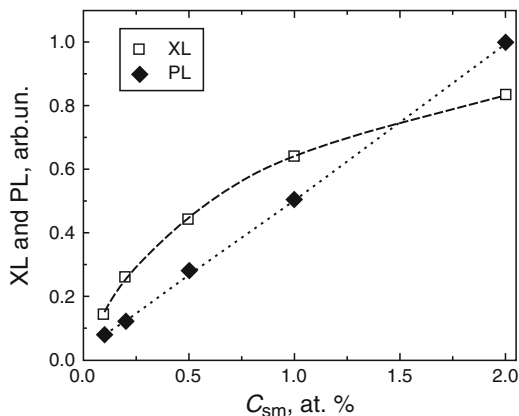


Figure 27.2a shows the transformation of the host glass with the addition of Cl. The glass becomes non-uniform with regions oversaturated with Cl. BaCl_2 nanocrystals are formed in the latter regions under annealing. The dependence of the heat capacity (C_p) on the partial Cl-content in Fig. 27.2b provides additional support to the view that there is a change in the structure of FCZ glasses above a partial Cl-content of 10%. Figure 27.2c shows that there is a good correlation between the XL and C_p dependencies on the Cl concentration while the PL monotonously increases with C_{Cl} . The excitation of the PL process involves a direct excitation of the RE ions, that is, excitation and emission are resonant transitions between ionic levels. On the other hand, XL excitation first involves the generation of an energetic primary electron through the photoelectric effect. The energetic primary electron then generates many electron-hole pairs by ionization of the host glass which then has to diffuse in the glass matrix to the RE-centers where they can recombine through Sm^{3+} levels. Thus, the XL excitation depends strongly on the structure of the host glass. Consequently, we should not be surprised to observe a correlation between the XL and C_p since both depend on the glass structure. The observed difference between PL and XL is therefore due to the different nature of the excitation process involved in the two luminescence processes.

Based on the results presented in Fig. 27.2, we have used only the FCZ glass with a partial Cl content of 13% in further experiments. Figure 27.3 shows the dependence of integrated XL and PL (UV excitation) of Sm-doped FCZ with 13% Cl on the Sm-concentration. It can be seen that while the PL increases linearly with the Sm-concentration, the XL possesses a sublinear dependence, which is not unusual for some phosphors. The difference between the two results is likely to be due to the different nature of the excitation process involved in PL and XL.

The annealing temperature and time are important parameters in controlling the formation and growth of nanocrystals. Figure 27.4 shows DSC thermograms of an unannealed FCZ:Sm glass sample and that for a glass ceramic sample that was obtained by annealing the glass sample at 270°C for 30 min (in a 5% H_2 -95% Ar gas mixture).

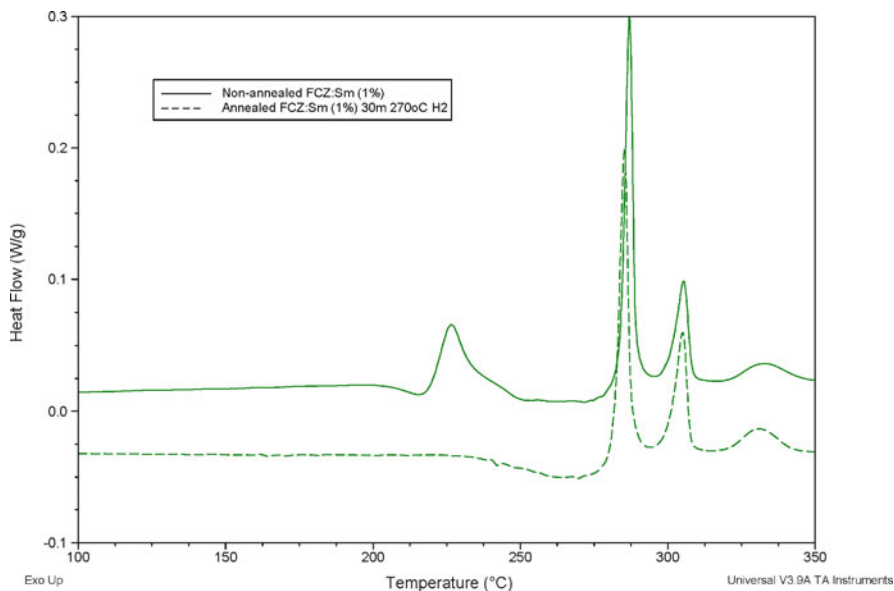


Fig. 27.4 DSC heat flow vs temperature curves of non-annealed and annealed at appropriate conditions (temperature, time, ambient gas) FCZ:Sm (1%) glass samples to form a transparent nanocrystalline Sm-doped FCZ glass ceramic material

The first scan has an exothermic crystallization peak at roughly 225°C that corresponds to the nucleation and growth of BaCl₂ nanocrystals in the glass host. The exothermic peaks at about 280°C correspond to the crystallization of the glass host. Although the latter two in some sense define the annealing temperature window that is needed to form a glass ceramic, annealing at high temperatures can easily lead to the crystallization of the whole glass. For example, samples annealed at temperatures higher than 275°C for 30 min are opaque (white) polycrystalline materials while samples annealed at 250°C below 275°C are transparent, and similar to the non-annealed glasses. The annealing in this temperature interval (250–275°C) allows the Cl-rich phase to crystallize and form luminescence-active nanocrystals in the glass matrix. It is important to maintain the material transparency for practical applications, which means that annealing temperatures and times must be chosen carefully.

In the present case we have used annealing temperatures in the range 250–270°C, which are above the lowest crystallization (BaCl₂) peak and sufficiently below the main crystallization peak of the FCZ material.

We have measured the XL as a function of exposure as shown in Fig. 27.5 for various FCZ:Sm samples annealed under different conditions as described in the legend. The XL yield, as expected, increases linearly with exposure but the overall x-ray sensitivity (or the slope of the XL yield vs exposure plot) depends strongly on the annealing conditions. The exposure was changed by changing the exposure time (from 50 ms to 5 s). The lowest sensitivity was for a sample that was not annealed,

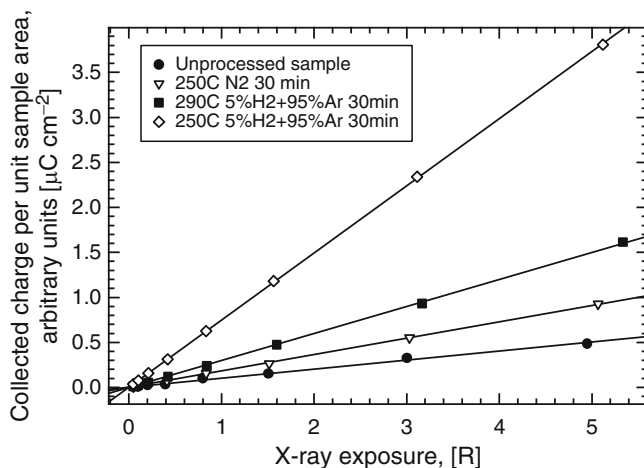


Fig. 27.5 Dose–response curves of differently treated FCZ:0.2%Sm samples. All samples have equal thickness and the signal was normalized to the sample area

i.e. Sm^{3+} doped FCZ glass. Annealing at 250°C for 30 min in an inert N_2 atmosphere, improves the sensitivity somewhat. On the other hand, the same annealing temperature and time in a reducing atmosphere ($\text{H}_2 + \text{Ar}$) leads to a large increase, almost by an order of magnitude, with respect to the FCZ:Sm glass, and about a factor 4 with respect to the sample annealed in N_2 atmosphere. Notice, however, that when we anneal the glass at a higher temperature, 290°C for 30 min, again in a reducing atmosphere, we actually get a lower sensitivity than the previous case (250°C annealing in H_2 gas). The reason is that the sample becomes opaque due to the crystallization of the whole glass. Our observations are in agreement with those reported by others stating that the scintillation efficiency depends on the annealing conditions and sequence [2,8].

Note that, although there are significant changes in the XL with annealing as apparent in Fig. 27.5, the PL remains relatively unaffected.

Summary and Conclusion

We have examined samarium-doped fluorochlorocirconate glass ceramics with potential applications for x-ray detection and sensing.

As the partial Cl-content (with respect to the total halogens in the structure) increases, there is a drop in the heat capacity at a partial Cl content of about 10%, which corresponds to the appearance of two structurally different regions (Cl-rich and F-rich phases) in the glass which were reported previously. The X-ray luminescence yield also drops at this composition whereas the photoluminescence yield increases monotonically with the partial Cl-content. We have shown the importance

of establishing appropriate annealing conditions (temperature, time and ambient atmosphere) to crystallize selectively the Cl-rich phase in order to form BaCl₂ nanocrystals in the glass matrix and, at the same time, maintain a transparent glass ceramic material. We found that annealing at 250–270°C for 30 min in a mixture of H₂ (5%) and Ar (95%) atmosphere produces Sm-doped glass ceramics that have x-ray luminescence yield (sensitivity) up to an order of magnitude higher than as-prepared FCZ:Sm glasses and at least a factor of four more than those samples annealed under an inert atmosphere (N₂).

While the PL yield increases linearly with the Sm-concentration, the XL yield increases sublinearly with the Sm-concentration. We have confirmed that the FCZ:Sm XL sensitivity is strongly influenced by the sample annealing sequence, while the PL remains relatively unaffected.

Acknowledgments The authors are grateful to the New Zealand Foundation for Research, Science and Technology, and the Natural Sciences and Engineering, Research Council (NSERC) for financial support.

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Chapter 28

Synthesis and Phase Composition of Fe/Mn Containing Nanocrystals in Glasses from the System $\text{Na}_2\text{O}/\text{MnO}/\text{SiO}_2/\text{Fe}_2\text{O}_3$

Ruzha Harizanova, Vikram S. Ranghuwanshi, Dragomir Tatchev, Ivailo Gugov, Armin Hoell, and Christian Rüssel

Abstract Oxide glass-ceramics containing ferrimagnetic nanocrystals are of fundamental and practical interest due to their electrical and magnetic properties. Depending on phase composition, size and volume fraction of the crystalline phase formed, the precipitated crystals are applied as parts of ferrofluids, in magnetic resonance imaging and as parts of biomagnetic sensors for the detection of different chemical and biochemical substances. In the present investigation, glasses from the system $\text{Na}_2\text{O}/\text{MnO}/\text{SiO}_2/\text{Fe}_2\text{O}_3$ are produced by the conventional melting technique; after applying appropriate time-temperature programs, the nanocrystalline magnetic phase is precipitated in a glass matrix. The phase composition and microstructure of the formed glass-ceramics is studied by x-ray diffraction, and scanning and transmission electron microscopy. Anomalous small angle x-ray scattering experiments are used to gather information about the phase composition and structure of the nano-sized crystals formed, as well as about their size distribution.

Keywords Oxide glasses · Nanocrystallisation · magnetic nanoparticles

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Introduction

The preparation of oxide glasses containing polyvalent ions of 3d-metals with fairly high concentrations has been intensively investigated for a long time due to their electrical and magnetic properties [1–3]. It is possible to obtain glassy materials and to precipitate nano-sized transition metal-based crystals with narrow size-distribution and different volume fractions during thermal annealing. This is both of practical and theoretical interest [1]. The prepared nanocrystals find a wide range of applications as parts of ferrofluids and contrast agents in magnetic resonance devices [2,4], as well as parts of biomagnetic and biochemical sensors for the diagnosis of different chemical species [5] and diseases [6].

Subject of the present investigation is the synthesis of glasses in the system $(1-x)(16\text{Na}_2\text{O}/10\text{MnO}/74\text{SiO}_2)/x\text{Fe}_2\text{O}_3$ with high iron and manganese concentrations and the precipitation of transition metal-containing magnetic nanocrystals in the glasses obtained.

Experimental

Preparation of the Glasses

Reagent grade raw materials (Na_2CO_3 , MnCO_3 , SiO_2 , Fe_2O_3 or $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) were used for the preparation of the glasses. The batches (100 g) were homogenized and melted in SiO_2 -crucibles using a MoSi_2 -furnace and melting temperatures in the range from 1,400 to 1,450°C (kept for 1.5 h in air). Some of the melts were quenched on a Cu-block and some were cast into a pre-heated graphite mould. The glasses cast into the graphite mould were transferred to a muffle furnace and kept at 480°C for 10 min. Then, the furnace was switched off and the samples were allowed to cool. All glassy samples were annealed at temperatures in the range from 520 to 700°C, according to the values determined for the glass-transition temperature T_g , for times from 10 min to 100 h.

Characterization Methods

The phase compositions were analyzed by X-ray diffraction (XRD, Siemens, D 5000), using $\text{CuK}\alpha$ -radiation at 2θ -values in the range from 10 to 60°. The glass-transition temperature and the softening point were determined by dilatometry (Netzsch DIL 402 PC). The microstructure was investigated by scanning electron microscopy (SEM, JEOL 6510LV), using a backscattered electron (BSE) detector, and transmission electron microscopy (TEM, Hitachi H-8100). Additional information about the phase composition and the size of the precipitated nanocrystals was gathered by means of anomalous small-angle x-ray scattering ASAXS: 7 T-MPW-SAXS beamline at the Helmholtz Zentrum Berlin (BESSY II) [7].

Results and Discussion

Glasses were formed for both the oxidized and the reduced samples, i.e. those prepared from Fe_2O_3 and those prepared using FeC_2O_4 , with iron oxide concentrations ≤ 15 mol% and a MnO concentration of about 8.5 mol%. The crystallization temperatures were chosen according to the T_g values obtained by dilatometry. The crystallization attempts for both reduced and oxidized compositions show that the formation of a ferrimagnetic nano-sized crystalline phase is possible for the reduced composition $13.6\text{Na}_2\text{O}/8.5\text{MnO}/62.9\text{SiO}_2/15.0\text{Fe}_2\text{O}_{3-y}$, i.e. for a ratio $\text{Mn}/\text{Fe} \sim 1/2$. The latter is in accordance with literature data [8]. After annealing at temperatures up to 600°C , the formation of solid solutions of MnFe_2O_4 (JCPDS 88–1965) and Fe_3O_4 (JCPDS 87–2334) was observed (see Fig. 28.1). This phase is a mixed spinel of the type $(\text{Mn}, \text{Fe})^{\text{II}}(\text{Mn}, \text{Fe})_2^{\text{III}}\text{O}_4$. However, with respect to the relatively broad peaks and the proximity of the main reflexes of the two phases, an exact determination of the chemical composition of the crystalline phase formed only by means of XRD is impossible.

The data from electron microscopy reveal the formation of only one crystalline phase for all annealing times and temperatures, as shown in Figs. 28.2 and 28.3. The scanning and transmission electron microscopy images support the hypothesis that in the investigated samples the desired nano-sized crystalline phase, the ferrimagnetic spinel $(\text{Mn}, \text{Fe})^{\text{II}}(\text{Fe}, \text{Mn})_2^{\text{III}}\text{O}_4$, is precipitated for all annealing times and in the whole temperature range studied. The estimation of the crystallite sizes applying Scherrer's equation to the XRD-patterns showed that for annealing times ≥ 2 h ferrimagnetic nanocrystals with sizes from 10 to 60 nm are formed and no further growth is observed.

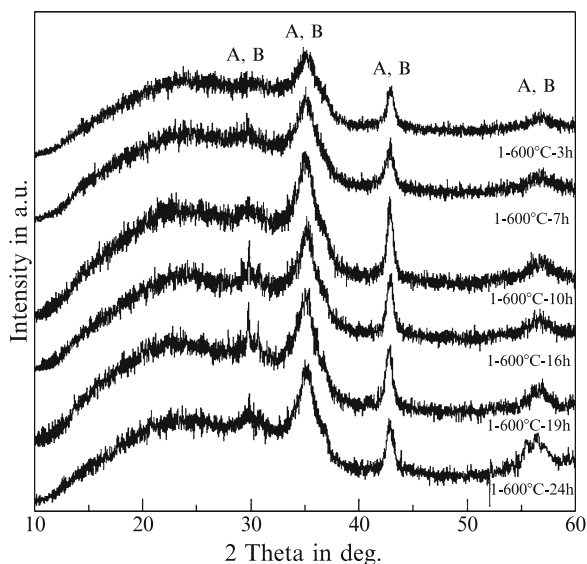


Fig. 28.1 XRD patterns of reduced samples with the composition $13.6\text{Na}_2\text{O}/8.5\text{MnO}/62.9\text{SiO}_2/15.0\text{Fe}_2\text{O}_{3-y}$, heat-treated at 600°C for different times: formation of mixed crystals MnFe_2O_4 (A) and Fe_3O_4 (B)

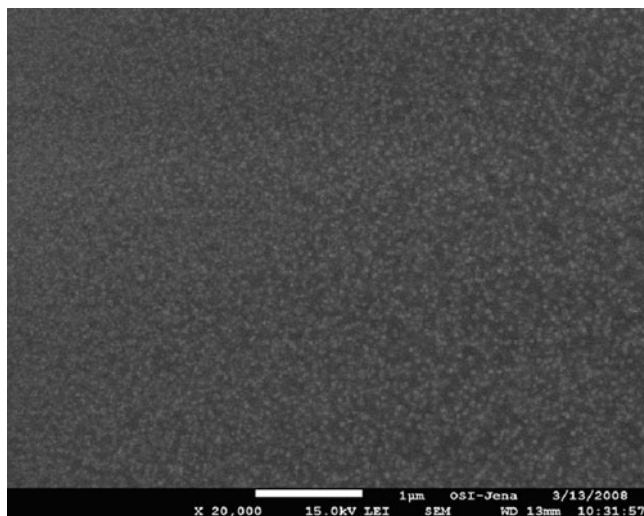


Fig. 28.2 SEM (BSE) image of a C-covered sample with 15 mol% $\text{Fe}_2\text{O}_{3-y}$ and 8.5 mol% MnO , crystallized for 24 h at 550°C : formation only of one morphological type of crystals

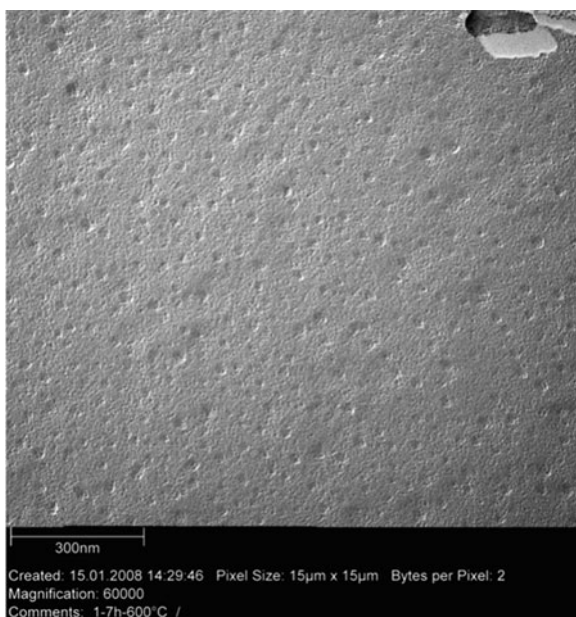


Fig. 28.3 TEM-replica of a sample with 15 mol% $\text{Fe}_2\text{O}_{3-y}$ and 8.5 mol% MnO kept 7 h at 600°C

In order to gather complementary information on the size-distribution and to clarify the phase composition of the precipitated nanocrystals, we utilized the anomalous small angle x-ray scattering (ASAXS) technique. While conventional XRD simply reveals the formation of Fe and Mn based phases during the heat treatment of the glasses, ASAXS curves at the Fe and Mn absorption edges of these glasses depend on the variation of the scattering factors at different energies and thus provide information about the composition, size and size-distribution of the particles in the glass matrix. We performed the ASAXS experiment on several thermally treated glass samples at the Fe and Mn edges at the 7 T-MPW-SAXS beamline at the Helmholtz Zentrum Berlin, Germany (BESSY II). In normal SAXS the scattering factor is independent of the energy of the photons and equal to the atomic number Z , however, for ASAXS, energy dependent terms play an important part. This dependence renders ASAXS sensitive to different chemical elements, in our case Fe and Mn. Figure 28.4 shows the ASAXS effect at the Fe-edge. When approaching the absorption edge, the scattering intensity decreases because here the atomic scattering factor belonging to Fe atoms decreases. The same experiment was performed at the Mn-edge which also shows the ASAXS effect. The curves presented provide us information on the particle size and the content of the resonant element in the particle, as already observed for other multicomponent systems [9]. The experimental data were further processed by applying the spherical core-shell model. Variation of the scattering contrast of shell and core shows the formation of two types of Fe-Mn-O containing phases. The exact phase composition was not identified up to now, but the scattering data suggests that the phase building the core contains more Fe than the phase forming the shell. Fitting the spherical core-shell model revealed that the radius of the core is around 17 nm and the shell is approximately 2 nm thick.

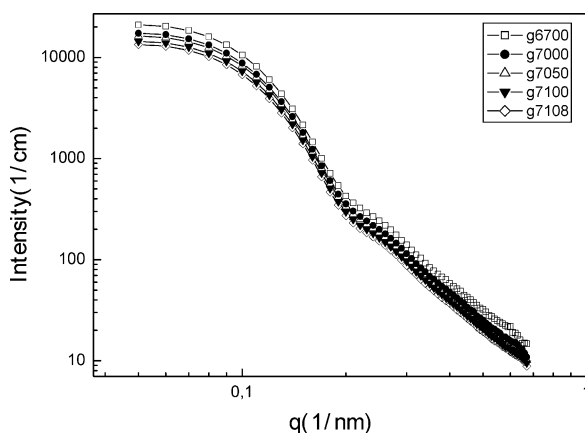


Fig. 28.4 ASAXS effect observed while recording spectra for energies from 6.700 to 6.7108 keV (i.e. around the Fe absorption edge) for a sample annealed at 550°C for 20 min

Conclusions

The ferrimagnetic spinel phase of the type $(\text{Mn, Fe})^{\text{II}}(\text{Fe, Mn})_2^{\text{III}}\text{O}_4$ was precipitated in glasses of the investigated composition at annealing temperatures up to 600°C. For crystallization times $t \geq 2$ h, at all annealing temperatures, the size of the nanocrystals formed varied from 10 to 60 nm and hardly changed with prolonged heat-treatment. The phase composition of the ferrimagnetic nanoparticles was studied by SAXS and showed the formation of Fe-Mn-O-based core-shell structures in which the core is enriched in Fe.

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Part IV.5
Nanoparticles and
Other Nanostructures

Chapter 29

Nanostructured Materials in Different Dimensions for Sensing Applications

Per Morgen, J. Drews, Rajnish Dhiman, and Peter Nielsen

Abstract Future sensing elements should be more specific, more sensitive, more reversible, and faster than today's elements. These future sensing devices will either be integrated with suitable signal detection circuitry, typically based on Si microelectronics, or with optical signal detection, and finally interfaced to relevant state-of-the-art signal recognition hard- and software. Some of the more critical uses of sensors are in the dynamic surveillance of system parameters in complex machinery or in biological systems, such as our own bodies. Most of these demands are likely to be met by the continued rapid development of functional nanomaterials including bio-nanomaterials and biocompatible nanomaterials. A strong and increasing trend, also clear at this NATO-ASI, is the focus on using Au-dots deposited on various substrates for optical field enhancements and for other synergistic effects on electronic properties such as sheet conductivity, when deposited on polymer films or on metal oxide surfaces. Gas sensing with metal oxide surfaces is another very active area of development, where the high surface to volume ratio of thin films or nano-crystalline objects are in focus. In this report we demonstrate examples of the processing of silicon surfaces, aluminum surfaces and wooden saw dust powders to create nanostructured materials with interesting functional properties in novel types of self-limiting and self-organizing growths of one-, two- and three dimensional nano-template (i.e. nano-building block) systems, with a range of functionalities, as-formed, or after further integration. However, the focus in this report is on the growth processes and further treatments, as these are relatively new, and thus not widely known, but

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highly relevant for the functional properties of the resulting nanostructures, and for integration of the structures with silicon or in more complex systems.

Keywords Growth of nanostructured materials · Film growth on silicon surfaces · 1-, 2-, 3-Dimensional nano-template systems · $\text{Si}_3\text{N}_4/\text{SiO}_2/\text{Si}$ · $\text{Al}_2\text{O}_3/\text{Si}$ · Porous alumina · SiC/Si · SiC nano-whiskers

Introduction

The era of nano-science – and with it: nanotechnology – is relatively young but extremely fertile. Despite of this the entry of nanotechnology in our everyday lives the transfer of the exciting developments in the research laboratories into shelved products is still largely waited for. This process is nowadays imminent in certain sectors such as food technology, based on the reports at this NATO-ASI, or is happening on a large scale as seen in the widespread examples of self-cleaning and antiseptic surfaces resulting from deployment of TiO_2 nano-particles. However, at the 2010 NATO-ASI in Sozopol the focus is on nanomaterials for sensors, as a worthy embodiment of the current research in nanomaterials. The change to nanomaterials for use in sensors has often been a “linear” process, merely attempting to scale down dimensions from corresponding micro-devices to *gain speed and costs* and merely scaling-up *specific* functionalities and sensitivities due to an enhanced surface to volume ratio of nanostructures. As an example, the medieval use of Au nano-particles or clusters to stain glass in different colors is now copied and varied intelligently in a range of critical applications, using and enhancing optical signals for implementing new optical detection methods [1].

A number of carbon based nano-materials have been discussed at this NATO-ASI and in the scientific literature, where they are attracting a high interest and high expectations for new applications as components of new types of sensors: carbon nanotubes and fullerenes [2], graphene [3], diamondlike thin films [4], nanoparticulate diamonds [5], and even thin epitaxial diamond films [6]. These carbon nanostructures show a very directly exploitable connection between their structural perfection and their electronic and optical (and mechanical) properties. This has already made them very interesting prototype systems for sensors and active electronic devices, based on the critical and significant changes in properties due to occurrence of defects, dopants and attached molecules or atoms. They are also highly biocompatible, which helps in targeting them for developments of bio-sensing components and as implant coating elements.

Still a large class of gas and ionic sensors rely on Si-based systems in configurations known from the MOS (metal-oxide-semiconductor) systems based on thin film configurations. In our work we are exploring the – similar to carbon nanostructures – intimate connection between surface structures and electronic properties of silicon surfaces to tailor the chemical reactivity (and electronic

properties) of silicon surfaces to the adsorption of gas molecules or metal atoms. We have discovered new growth scenarios to produce nanometer thin oxides and nitrides in direct self-limiting reactions on heated silicon surfaces, and we have also devised new growth scenarios simulating two-pulse atomic layer deposition techniques [7], but using only the pure elements themselves, in processes to grow aluminum oxide and aluminum nitride layers on silicon at room temperature. In similar processes we grow silicon oxide and silicon nitride layers on other surfaces, or on top of each other. These methods are self-limiting, and thus offer a good reproducibility and high latitude to processing parameters. Finally we demonstrate the growth and processing of SiC layers on Si, using a methane microwave plasma. The same plasma source is used to activate nitrogen for nitridation purposes. As a result of these processes we obtain graphene islands on a Si (111) surface.

In addition to silicon surfaces, we use and study thin aluminum films deposited on top of silicon, in amorphous, microcrystalline or epitaxial crystalline phases. Parallel to this we are studying the oxidation and nitridation of single crystal aluminum surfaces for comparison with the properties and reactivity of the films on silicon surfaces, or for comparison of the surface properties and reactivity between silicon and aluminum.

The anodization of aluminum foils in acid electrolytes is known to produce ordered porous oxide/hydroxide structures with a bottom layer of very compact aluminum oxide (barrier oxide layer) with a scallop-shaped structure “imprinted” by the overlying pore structure [8]. By varying the process parameters the pore sizes and ordering of the structures may be controlled. In another contribution [P. Nielsen et al., this NATO-ASI] we demonstrate the use of the scallop formed barrier oxide layer to form self-organizing Au-nano-dot structures by sputter deposition of Au on these structures in different quantities. The resulting structures are optically active, enhancing optical fields in proper wavelength ranges. The use of such structures for optical sensing such as surface enhanced Raman spectroscopy (SERS) of adsorbed molecules was demonstrated, with superb results [9].

Finally, in [R. Dhiman and P. Morgen, this NATO-ASI], we report work with nanostructured SiC forms (nanoporous, nanonodular, and nanowhiskers) to study their applications as hydrogen sensors and hydrogen storage materials. Wooden saw dust powder particles are used as “cheap and natural” starting materials in one part of this project, in parallel with wooden samples with porous structures, which are preserved in impregnation reactions with Si-containing agents at high temperatures. During this project we have come across some interesting reactions creating a densely woven fibrous material consisting of crystalline whiskers or fibers of various allotropes of SiC.

The experimental techniques cover a wide range of specialized tools, from synchrotron radiation to hardness measurements. The projects have included numerous coworkers over the years, involved mostly in the experimental work, but also in theoretical modeling of the reactivity of Al-based nanostructures on Si surfaces.

Experimental Procedures and Tools

Traditional Surface Studies

A large part of our activity till today has been based on traditional surface science procedures and tools. This means that the cleaning of surfaces and subsequent depositions and reactions are done under ultrahigh vacuum conditions (base pressures around 10^{-8} Pa), assuring cleanliness, repeatability and maximum control of reaction steps. The qualitative and quantitative analyses of the surfaces and reactants are carried out with surface sensitive techniques based on electrons or ions, i.e. X-ray induced photoemission (XPS) of core level electrons, synchrotron radiation induced photoemission of core-level and valence band electrons, with optimum sensitivities to the surface atoms and surface structural properties; electron induced Auger electron spectroscopy (AES), with imaging capabilities, and in combination with ion-beam etching for depth profiling. Gas dosing and metallic depositions are done in-situ, or in adjacent preparation systems, with monitoring by various specific techniques and tools. The surface temperatures of Si are measured with an optical pyrometer [10], calibrated for Si emissivity, during heating of the Si samples, which is performed with a direct current through the $25 \times 10 \text{ mm}^2$ size sample. The samples are *n*-type with a resistivity of $5 \text{ } \Omega \text{ cm}$. Gas dosing is monitored with a quadrupole rest-gas mass spectrometer, and metal evaporation rates are calculated from the flux received by a 6 MHz quartz crystal oscillator, with proper geometrical corrections and further checked with X-ray photoemission intensities. Activation of nitrogen and methane gases is done by passing the gas through a pressure differential glass capillary encased by a microwave cavity. The character of the constituents in the plasma resulting from the microwave interaction with the gas is monitored with an optical spectrometer, and the plasma is focused through the capillary in the direction of the surface to be affected. The pressure difference between the cavity region and the inside of the ultrahigh vacuum chamber is around 100 times.

After completion of analyses and processing in ultrahigh vacuum some samples were transferred to a scanning electron microscope (SEM) for further checks of structural or topographic effects, including energy dispersive X-ray emission spectroscopy (EDS) of the bulk – or average surface – concentrations, or for non-uniformity effects. Samples of nanowhiskers of SiC were kindly analyzed by a colleague in Copenhagen with a transmission electron microscope (TEM).

Electrochemical Processing

The second type of surface processing reported here is electrochemical anodization of aluminum in various (weak) acids, typically oxalic acid. A double-walled glass container with circulating cooling water allows the processes to be run at 0°C ,

which is required to produce the best order. Both the anode and the cathode are made of Al-foils. They are of equal active areas; the positive Al-electrode is annealed at 500°C in an Ar atmosphere and electro-polished prior to anodization. On this electrode the anodization creates an oxide layer, which is porous and very regularly ordered, when the process is well controlled with respect to temperature and the voltage/current programming applied [11]. It is the aim of an ongoing project to explore the use of these nanoporous aluminum oxide structures as sensor elements, as well as to gain a more fundamental understanding of the self-organizing nature of this – and similar – anodization processes with other materials. In the contribution by P. Nielsen et al. the sensor structures consist of self-organizing nanoparticles of Au, which are formed on the oxidized aluminum structure remaining at the bottom of the pores after etching them totally away. The top layer of this structure consists of a specially bonded oxide of aluminum, which during the growth of the pores has an important role in the transport of oxygen and aluminum ions between the substrate and the acid solution. This bottom oxide layer is not etched away with chromic phosphorous acid, contrary to the hydrous oxide forming the pores. Impedance spectroscopy was employed during the studies of various factors involved in the growth of the porous films, to see if the most important mechanisms could be determined from such studies, involving both transport and structural changes during growth. This technique is also strongly recommended for sensing purposes [12].

Impregnation Reactions to Form SiC

In the third type of process, nanoscale SiC structural elements with pores, nodules, and whiskers/fibers are created in reactions at high temperatures (around 1,500°C) between Si, SiO₂, SiO, TEOS (tetra-ethyl-orto-silicate), and C-containing materials such as wood from trees with preserved pore structures or saw dust at high temperatures inside a furnace with a flow of Ar gas. Actually several steps in such reactions are envisioned to explain the outcomes under the prevailing reaction conditions briefly discussed in the contribution by R. Dhiman and P. Morgen. Thus in one case direct reactions in the gas phase, but with a surface nucleation center, between CO and SiO, are invoked to explain the experimental findings of whisker growth away from the original C-structured substrate.

This project is aimed at creating SiC nanostructure conglomerates with extremely high specific surface areas for hydrogen storage purposes. The techniques central to this project are X-ray diffraction (XRD), XPS and AES, and SEM/EDS, but micro-Raman spectroscopy is also extremely useful for the studies of the structural modifications of SiC and the complex samples after processing. Actually the combination of these techniques is necessary to distinguish the relative quantities of various structural elements, which may be present due to incomplete reactions or processing steps. Relevant (larger) SiC structures have been tested for hardness values with a nano-indenter system, and surface area measurements are done with a BET-instrument [13], measuring the surface area through

adsorption of nitrogen. Weight and density changes of the C-forms during the reactions/impregnations are also monitored.

Experimental Procedures and Results

Ultra Thin Film Studies with Si Substrates

The easiest method to form an oxide layer on a Si surface with is by direct oxidation at elevated temperatures [14]. The computer hardware industry has perfected this process till the “65 nm” generation of complementary metal-oxide-semiconductor (CMOS) circuitry for microprocessors, which have a 1.2 nm nitrogen doped oxide insulator in the field effect transistors (FETs). In the current and next generations of CMOS FETs for high performance processors several new higher-permittivity dielectric compounds are replacing SiO_2 due to tunneling problems at this and lower thicknesses of SiO_2 . The thickness of these dielectric materials is scaling (upwards) with respect to the required lower effective SiO_2 thickness by the ratios of their permittivity to that of SiO_2 to alleviate tunneling leakage problems. The use of such materials is opening up a mixed bag of other problems related to material processing issues and long term stability [15]. One of the possible candidate dielectric materials is Al_2O_3 , which we have studied and report on in the next section.

Another important compound material in this industry is Si_3N_4 . However, reactions between nitrogen gas and a Si surface to form Si_3N_4 directly are not possible without some kind of activation, due to the strong bond of the nitrogen molecule. Similarly for methane (CH_4) the reactivity with a Si surface is very low without activation.

To activate these gases we use an external microwave source which is interacting with the gas inside a suitably sized resonance cavity encasing a glass tubulation including a capillary tube, which acts as a pressure differential between the discharge region and the inside of the vacuum chamber. The plasma produced in the discharge is focused through the capillary on the Si surface, which may be kept at a constant temperature during the exposure (“remote plasma”). The actual temperature range is from room (or below) temperature to $1,300^\circ\text{C}$. For nitrogen the discharge produces a 50%/50% mixture of atomic and molecular species. We assume that only the atomic species are reactive at these low pressures [16], and measure exposures by the half of the total nitrogen exposures. Exposures are normally given in Langmuir: 1 L exposure is equal to the number of molecular collisions per sec per cm^2 at a partial pressure of 10^{-6} Torr (1.33×10^{-4} Pa) of the gas during its reaction with the surface.

We have recently studied oxidation of Si_3N_4 , and nitridation of SiO_2 at elevated temperatures. The first process is possible but the second not. Thus to produce a suitably mixed system of oxide and nitride, starting with oxide near the Si surface/interface, in order to try to preserve the good interface properties of the oxide/Si

interface, we developed an atomic layer deposition procedure for the growth of thin layers of oxide and nitride of Si at low temperatures on any substrate.

This process involves the initial deposition of slightly less than a monolayer of dispersed Si atoms on the surface in question. This system is then exposed to oxygen or activated nitrogen, which creates instant binding with the Si atoms, in a self-limiting process (unless the underlying substrate may take up the reacting gas as well, but this is not so likely at low temperatures). The cycle may then be repeated to grow thicker layers.

The same procedure is applied to grow Al-oxide or Al-nitride films on different substrates, and eventually to grow sandwiched structures of these compounds. A similar method was used to grow Ti-oxide films on SiO₂, while it is also envisaged that Ti-nitride films may be grown at low temperatures in this way. All these films grown at low temperature are amorphous. Of course the use of these film structures is limited, if their properties under further processing, such as involving heating steps, are not investigated. This is therefore a very important part of this kind of research, which will be demonstrated in the following paragraph.

Layered Oxide/Nitride Structures on Si

We have grown a thin layer of SiO₂ on a Si(111) *n*-type surface in a reaction between molecular oxygen and the Si sample heated to 500°C, which we earlier have reported as self-limiting, i.e. the reaction stops by itself after having grown around 0.8 nm of oxide on the Si surface [17]. On top of that we deposit a thin film of 4 layers of Si-nitride grown in the way described above at room temperature. This structure is then studied during thermal processing, with the use of synchrotron radiation induced photoemission.

Figure 29.1 shows how the Si 2p core level photoelectron spectrum changes during deposition and processing of the layered structure at gradually increasing temperatures. The sample was held at each of the temperatures indicated for 15 min, then cooled down to room temperature before the spectra were recorded.

These spectra show structures due to Si atoms in the bulk, at the interface and in the oxide/nitride. The bulk peaks are found at the lowest binding energies, while the electrons emitted from Si atoms bonded with oxygen or nitrogen atoms with different coordination geometries are found with the highest binding energies. Structures at intermediate binding energies are due to interface coordination. The binding energies are deduced from the kinetic energies of the photoelectrons. These are detected with an electrostatic spectrometer, and the formula used to convert measured kinetic energies ($E_{kinetic}$) to binding energies ($E_{binding}$) is:

$$E_{binding} = E_{photon} - E_{kinetic} - \text{work function correction} \quad (29.1)$$

where E_{photon} is the photon energy (of the synchrotron radiation) and the *work function correction* takes care of any difference in the work functions of sample and

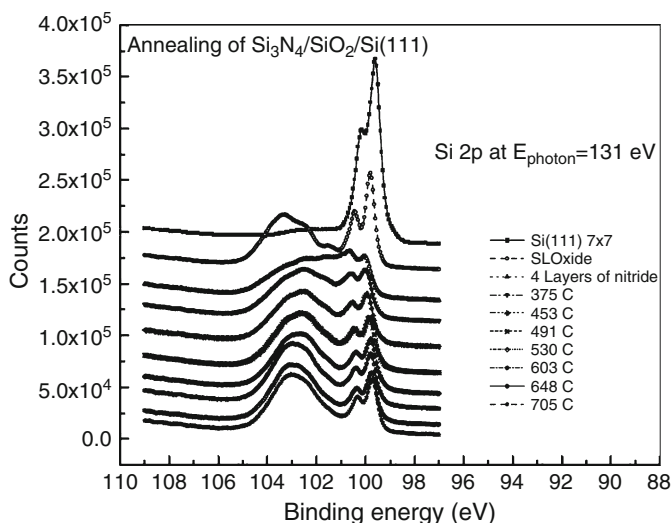


Fig. 29.1 Si 2p core level spectra obtained with a photon energy of 131 eV at ASTRID, University of Aarhus, Denmark

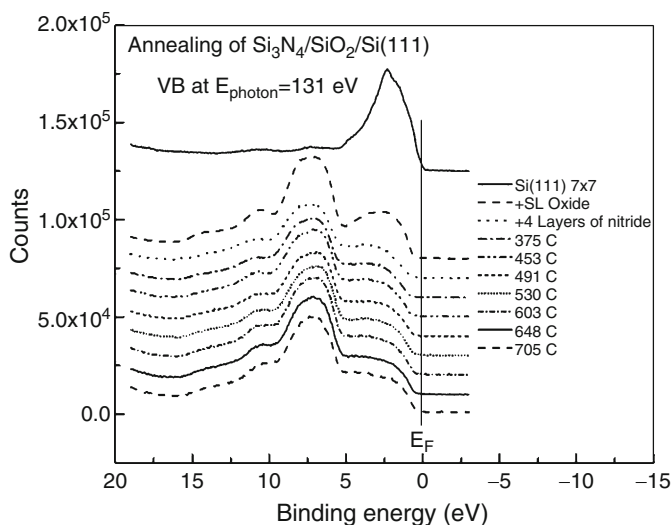


Fig. 29.2 Photoemission from the valence band, recorded at 131 eV photon energy at ASTRID, the University of Aarhus, Denmark. The position of the Fermi level is at zero binding energy

analyzer. The Fermi level position is indicated in the spectra of the valence band (Fig. 29.2), defined with an effective binding energy of zero, *i.e.* the Fermi level is used as the reference for the binding energy scale, when all samples are grounded at the same point as the spectrometer.

The structure of the valence band changes significantly between the clean Si surface and after deposition of the overlayer. This experiment measures essentially the density of states of the valence electrons. Normally the analysis of these results would include a spectrum fitting procedure to extract and track the relative intensity and position changes of the various components involved in the two types of spectra [18]. In this case, however, a simpler procedure allows us to estimate the structural changes during the processing steps. We plot the shift of the major peak in most of the Si 2p spectra (the Si 2p_{3/2}), or – alternatively – the upper edge of the valence band, which are both seen to vary systematically during the processing. By doing this, we track the band bending in the Si surface due to charges outside this surface, i.e. in the overlayer.

We interpret the results shown in Fig. 29.3 and the details of the spectra of Figs. 29.1 and 29.2 as pointing to a region between 500°C and 600°C where the mixing of the nitride and oxide layers produces a stable composition of nearly 1:1 of nitride and oxide and, consequently, a stable level of near-interface defects. At higher temperatures oxygen leaves the sample, which turns into a nitride layer on Si, and the higher temperatures also anneal the defects out. We can see that the oxidation tends to produce a downwards band bending (towards higher binding energies) due to positive charges accumulating near the interface, and an enhanced effect when the nitride layer is deposited above it. The heating steps, which are causing the nitride to penetrate the oxide, produce an upward band bending (towards lower binding energies), due to an increasing amount of negative charges produced near the interface to Si in the process.

These results are interesting for the understanding of the properties of semiconductor-oxide-nitride-oxide-semiconductor (SONOS) programmable memory

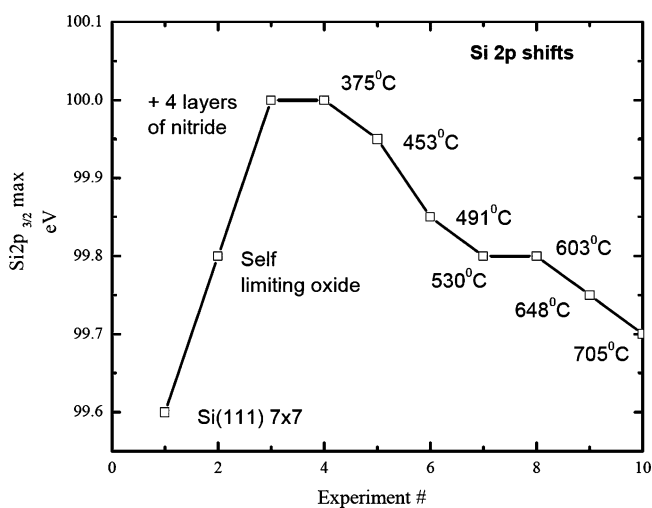


Fig. 29.3 Changes in the binding energy of the bulk Si 2p_{3/2} peak (the major peak in the spectra). These shifts indicate the varying band bending in the Si surface below the overlayer

devices [19]. These devices make use of a sandwich structure of Si_3N_4 between a thick insulating and a thin tunneling SiO_2 layer, where the nitride layer is programmed by a voltage stress pulse across the entire structure, inducing charged defects in this layer. Our results indicate that such structures, in the thickness regime investigated here, should not be allowed to reach the temperature regime above 400°C during operation where inter-diffusion clearly starts to occur.

The use of this kind of mixed oxide/nitride structures (1:1) as a gate dielectric alternative to either pure SiO_2 or to N-doped SiO_2 at the 1.0–1.5 nm scale produced here could be an interesting alternative to the currently favored recipes. The 1:1 composition would offer diffusion limitations for B (dopant in the polysilicon gate material) and zero effective stress. (We were actually suggested to investigate this system by someone closely connected with industrial research, as this way of producing these sandwich structures was seen as a novel route to get the desired 1:1 mixture of oxide and nitride). A remaining issue, however, is the uniformity of the mixture.

Reaction Between Al and a Thin SiO_2 Layer to Form Al-Oxide on Si

The growth of ultra-thin films of Al-oxide and Al-nitride on Si or other substrates at room temperature by the atomic layer deposition method described above offers the same possibilities for studies of the properties and processing of interesting sandwich structures made with these compounds. We have also studied, but not yet reported, direct oxidation and nitridation of single crystalline Al surfaces at elevated temperatures, for comparison with studies of oxidation and nitridation of various types of Al-layers deposited on Si (111) and Si (100) surfaces, including epitaxially grown crystalline films [20] on Si (111).

The oxide films grown at room temperature react with the Si substrate during heating to produce a mixed silicate-like interlayer. This would compromise the use of such oxides for current Si-based MOS devices, but similar problems exist for most of the other new gate dielectric compound systems, which are also prone to undergo a transition from an amorphous to a crystalline (microcrystalline) structure, typically at $500\text{--}700^\circ\text{C}$, with resulting adverse changes of the insulating and diffusive properties.

To circumvent the silicate formation reaction, we devised a scheme using the self-limiting growth of a 0.8 nm layer of Si-oxide on Si (100) as a starting point for a reaction with Al metal, deposited in the right quantity on the surface of this oxide to consume all the Si-oxide and convert it into Al-oxide. Thus we intended to use the Si-oxide as a sacrificial starting system. The results are illustrated in Figs. 29.4 and 29.5. In Fig. 29.4 the features in the Si 2p spectra reveal among others how the bonding of oxygen to Si atoms, giving rise to the feature at 103.8 eV binding energy, is diminished to almost non-existence during the reaction at progressively higher temperatures. At the final thermal steps the structure of the Si 2p spectrum closely resembles that of a clean Si (100) surface, but strongly shifted due to band bending at the Si surface, induced by the negative charging of un-reacted Al atoms

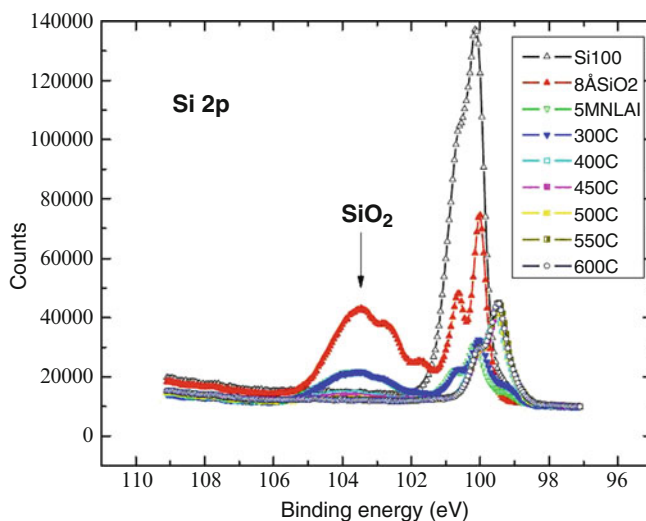


Fig. 29.4 The reaction of 5 monolayers of Al deposited on 0.8 nm SiO₂ on a Si (100) crystal surface. The Si 2p spectra were recorded with 130 eV photons at ASTRID, University of Aarhus, Denmark

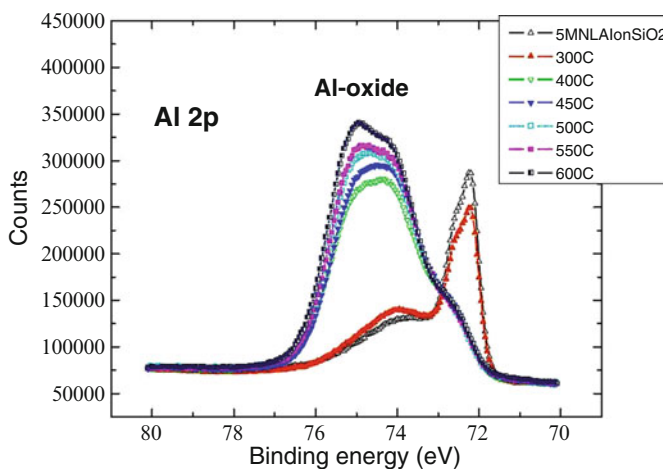


Fig. 29.5 The reaction of 5 monolayers of Al deposited on 0.8 nm SiO₂ on a Si (100) crystal surface. The Al 2p spectra were recorded with 130 eV photons at ASTRID, University of Aarhus, Denmark

on the top surface. Further experiments have been done to demonstrate that the Al-oxide layer is uniformly covering the Si (100) surface.

Similar spectra for the Al 2p electrons, recorded at nearly the same depth as the Si 2p electrons, namely at a sample depth of about 1 nm for 95% of the signals for a

uniform phase, clearly show that the metallic Al 2p doublet peak at 72 eV is converted to an oxide spectrum with structures around 76 eV binding energy (Fig. 29.5). The structure in the Al-oxide peak at 600°C is indicative of crystalline order in the oxide. Not the entire coverage of Al was converted in this experiment, but excess Al (negatively charged atoms at the surface) can easily be removed by further heating cycles at 600°C.

The exciting conclusions, which can be drawn from this experiment are that it is possible to grow a uniform, approximately 1 nm thick layer of Al-oxide on top of a Si surface, which does not show any signs of silicate formation. The Si surface next to the Al-oxide is almost as perfect as a pristine Si (100) surface, but its potential is shifted due to charges of the top Al atoms and photon induced charging of the Al-oxide layer. These findings indicate that the electronic properties of this system are highly suitable for a MOS-FET component. Other parameters of this system favoring such an application are the higher dielectric constant, compared to SiO₂ and some of the “best” band-offsets with Si compared to all other compounds, both for n-type MOS and for p-type MOS applications. Finally the dielectric breakdown strength of Al-oxide is significantly higher than for SiO₂.

Growth of SiC on Si and Structural Changes by Oxidation and Heating Treatments

In many applications of SiC films and SiC surfaces the use of a SiC film grown on a Si surface would clearly be advantageous. In a recent paper heteroepitaxial 3 C-SiC (111)/Si (111) was used to produce graphene [21].

The growth of SiC on Si may be realized with our “remote” microwave plasma source with methane gas, which is decomposed with the simultaneous production of a significant fraction of atomic hydrogen radicals. Our results with this procedure are illustrated in Fig. 29.6, showing the Si 2p and C 1s spectra during and after the reaction of a Si (111) surface with the methane plasma, at 900°C.

The largest exposure has created a more than 2 nm thick reacted layer of SiC, evidenced by the 2 eV shifted Si 2p spectrum and the C 1s peak near 283 eV [21]. However, the C 1s peak at 285.5 eV indicates a high amount of *sp*² C–C bonding.

In an attempt to reduce the non Si–C bonded C, the sample was first oxidized at 500°C in several steps, and the oxide later removed gradually by heating in steps up to 1,200°C. The results of this are seen in Fig. 29.7. After these steps the final spectra show one dominating C 1s peak at 283 eV and a small *sp*² peak at 285 eV, and a Si 2p spectrum at the position of clean Si (111), but differently broadened. These spectra were stable after several heating cycles at 1,200°C. We interpret these results as showing the formation of islands of graphene on SiC/Si (111) through these procedures, like in [21], but probably as islands formed on the Si (111) surface. Thus the formation of a thin crystalline SiC layer on Si surfaces by the plasma process holds great promise for various applications.

Besides nanometer thick film structures and graphene layers, there is high interest in nanostructured SiC elements for catalyst support systems, for diesel

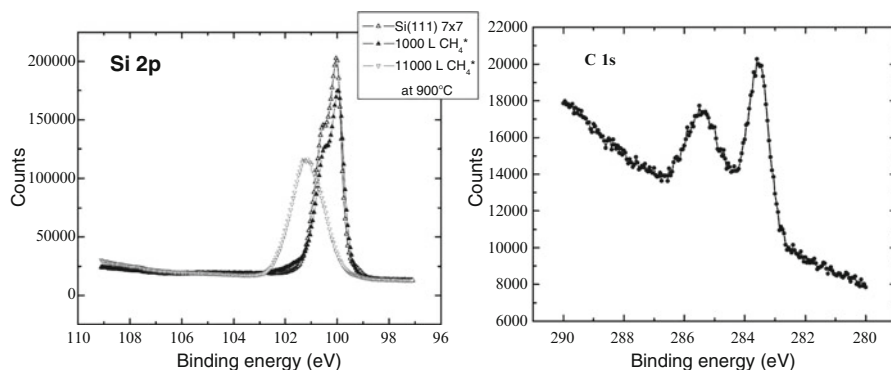


Fig. 29.6 A Si (111) surface exposed to a methane microwave plasma at 900°C substrate temperature. The *left panel* shows the Si sp spectra, the *right panel* the C 1s spectrum after 11,000 L effective total exposure with methane plasma (the active fraction is not known)

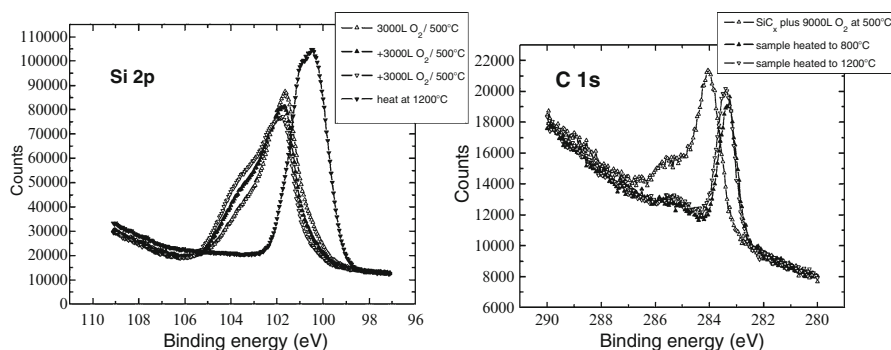


Fig. 29.7 The final system in Fig. 29.6 (11,000 L CH₄*/900°C) is shown after oxidation and heating treatments. The *left panel* shows the effects on the Si 2p spectra, while the *right panel* shows the effects on the C 1s spectra

exhaust particle filters, for hydrogen storage, and for refractory ceramics, like in incineration plant linings. We currently study mesoporous and microporous systems formed from wood preforms, by impregnating these with Si in a furnace at high temperatures. A particularly interesting system is formed looking like “nano-Rockwool™” whiskers of SiC.

Nanostructured SiC Structures, Whiskers

Whiskers of SiC are formed from (wooden) saw dust particles, impregnated with TEOS at room temperature, dried, and then heated in a furnace at 1,400°C. The TEM

Fig. 29.8 TEM picture of SiC whiskers

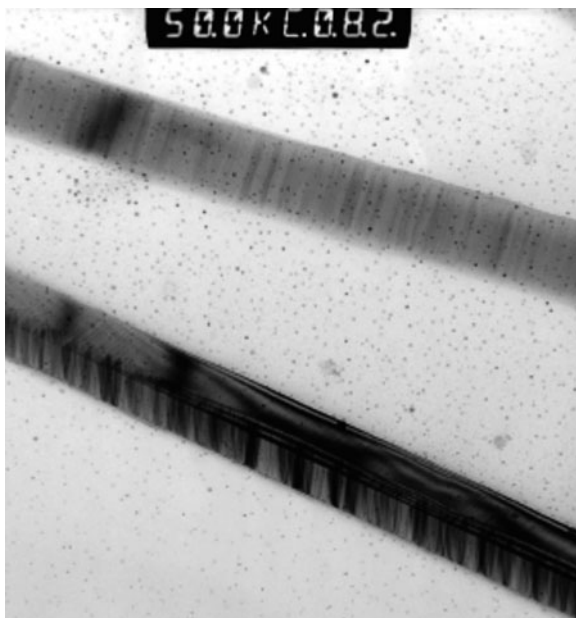


Fig. 29.9 SEM picture of SiC whiskers

and SEM pictures in Figs. 29.8 and 29.9 show some of the aspects of these structures. Further details are given in [R. Dhiman, P. Morgen, this NATO-ASI].

Porous Alumina Films as Templates for Self-Organizing Au Nanoparticle Patterns

Several methods have been studied to optimize the growth of highly ordered, porous alumina films by anodic processes with acid electrolytes [22]. For sensing applications self-organizing Au nanostructures are formed on the scallop-shaped barrier oxide layer remaining on top of the aluminum after etching away the porous oxide structure (Figs. 29.10 and 29.11, see [P. Nielsen et al., this NATO-ASI]). These structures have very high optical field enhancement effects for use in surface enhanced Raman spectroscopy [9].

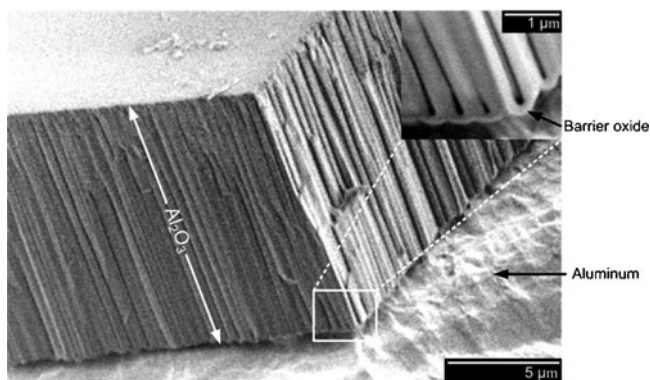


Fig. 29.10 Porous alumina structures

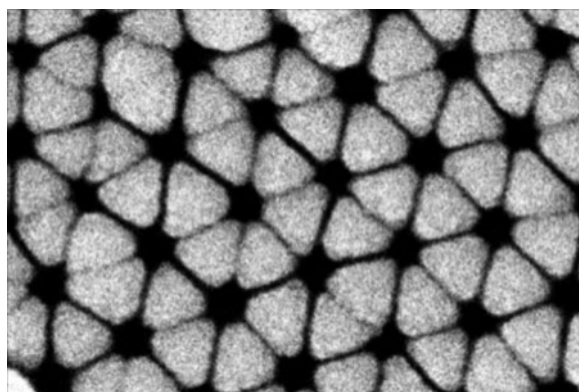


Fig. 29.11 Self-organized Au nanoparticles (edge of particles: 100 nm)

Summary and Outlook

The future of nanostructured sensors is bright, further developments are only waiting for our imagination. However, the deployment of nanoparticles is still a

controversial issue, with its potential hazards. The difficulties in handling of individual nanoelements, such as carbon nanotubes, have been seen as a potential showstopper, unless their growth locations and growth directions could be controlled. Such efforts are now starting to become successful with fibrous woven alumina substrates [23].

The continued downscaling of thin film-based structures on – or integrated with Si-based electronic elements – is leading the way for various types of sensing elements, including mechanical types, and functional biosensors. New materials, such as crystalline epitaxial diamond films, graphene on various substrates, or complex 3-D woven nano-systems such as SiC whiskers studied here, will open up further applications as sensors and in high specific surface area applications.

Au nanoparticle-based systems are currently the most actively explored sensors, in a wide range of disciplines, due to the ease of fabrication and very manageable optical properties, as demonstrated in this and several other contributions.

Acknowledgements We thank the organizers of the 2010 NATO-ASI at Sozopol for the arrangement and their enthusiasm to create such a lively atmosphere for the exchange of ideas and experiences. Many former students and colleagues have participated in the projects reported here: Kjeld Pedersen (Aalborg University), Zheshen S. Li (ASTRID, Aarhus University), Ali Bahari (Iran), Jeanette Hvam, Erik Folven, Uffe Møller, Søren Foeghmoes, and the technicians Danny Kyrping and Torben Sørensen. The funding from the Danish Research Councils for the FINST Consortium and the granting of a PhD stipend from the Danish Program Committee for Sustainable Energy and Environment are gratefully acknowledged.

This work was done partly in collaboration with the FINST consortium (Denmark) and is also supported by the Danish Research Council Development Agency for Sustainable Energy and Environment.

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Chapter 30

Field Enhancement in Plasmonic Gold Nanostructures on Templates of Anodized Aluminum for Sensor Applications

Peter Nielsen, Ole Albrechtsen, Jonas Beermann, and Per Morgen

Abstract We produced and characterized randomly distributed as well as ordered, highly enhancing, large-area Au nanoparticles (NPs) formed on porous templates of anodized Al. Characterization was done with reflection spectroscopy, far-field two-photon luminescence (TPL) scanning optical microscopy (SOM), and surface enhanced Raman spectroscopy (SERS) measurements. Our fabricated structures are evidently versatile for practical molecular sensing.

Keywords Self-organizing gold nanostructures · Nanoporous alumina templates · Electric field enhancement effects · Sensor applications

Introduction

Self-organizing metallic nanostructures attract increasing attention due to immense active surface areas and numerous proposed applications within sensor technology, opening up new avenues to meet the demand for high molecular sensitivity. Self-organizing hexagonally ordered porous Al_2O_3 templates have been intensively studied due to their ability of hosting ordered or randomly distributed metallic NPs incorporated in e.g. sensors and solar cells. By carefully tailoring the temperature, anodization time, and voltage for a given electrolyte, the dimensions of the pores can be controlled over a wide range [1]. Recently, we demonstrated how to

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use templates grown under mild (MA) and hard anodization (HA) [2] conditions for large-area self-organizing Au nanostructures [3,4]. Here we investigate the enormous electromagnetic field enhancement (FE) in the vicinity of ordered and randomly distributed Au NPs on anodized Al templates [5].

Fabrication of Al/Al₂O₃ Templates

Fabrication details [2–5] of the Al/Al₂O₃ templates by MA in phosphoric acid and HA in oxalic acid (Fig. 30.1b, c) are illustrated in Fig. 30.1a. In brief, the

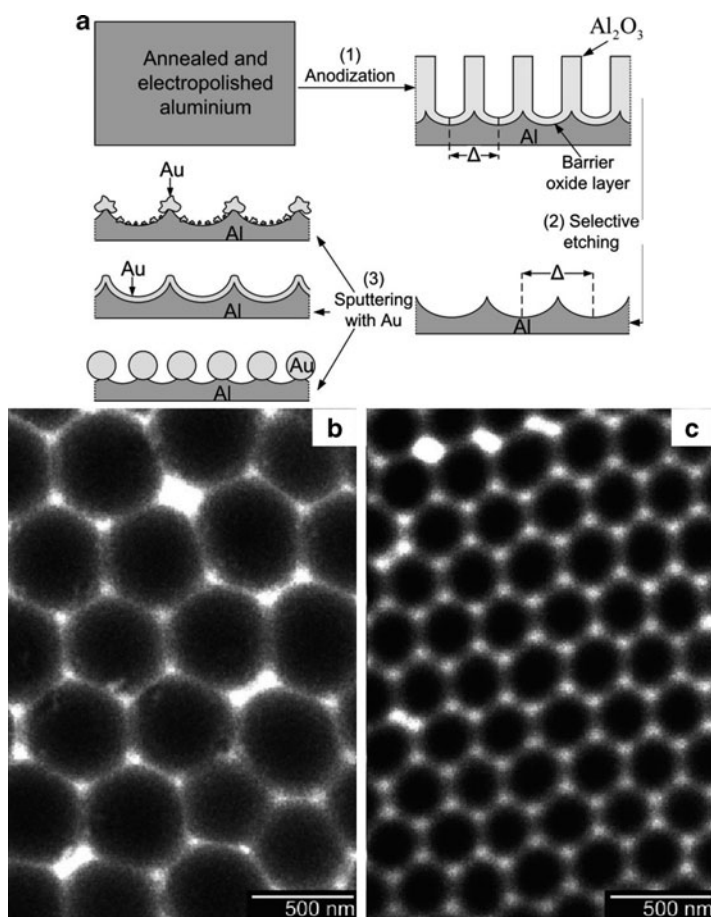


Fig. 30.1 (a) Schematic of the fabrication process; (b–c): scallop-shaped templates embossed by the pores made by (b) MA in phosphoric acid and (c) HA in oxalic acid

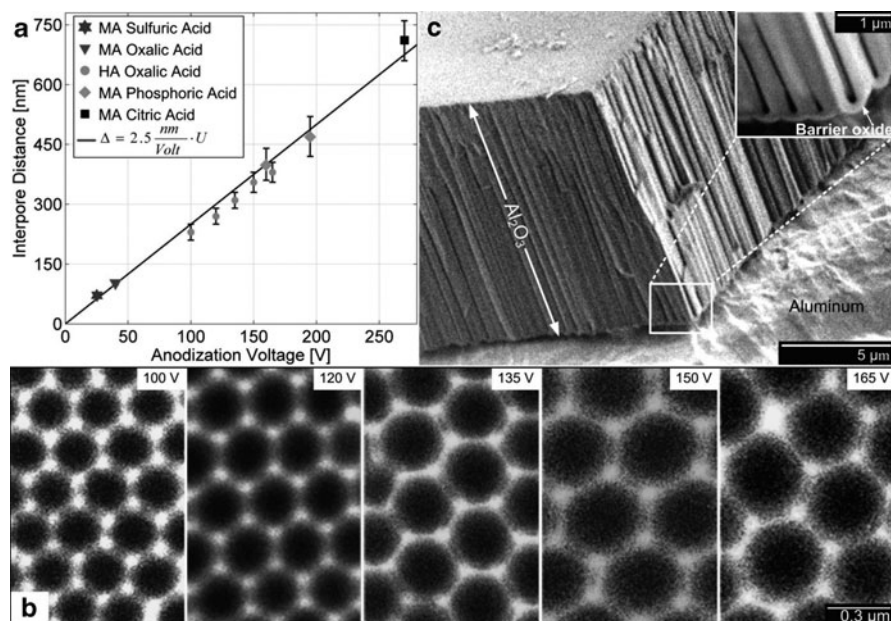


Fig. 30.2 (a) Relation between anodization voltage and IPD for a number of anodization techniques as obtained by our group. (b) SEM micrographs demonstrating the continuous tunability of the IPD in the case of HA with oxalic acid. (c) SEM micrograph of an oxide layer grown under MA conditions in phosphoric acid, with the barrier oxide shown by the inset

anodization of annealed and electropolished 1 mm thick Al sheets forms an Al_2O_3 pore layer with inter-pore distances (IPD) Δ controlled by the applied anodization voltage (Fig. 30.2a, b). With HA in oxalic acid the IPD can be tuned continuously in the range from ~ 230 to ~ 380 nm by applying voltages of 100–165 V. Structures made by MA in phosphoric acid at 190 V and by HA in oxalic acid at 120 V have IPDs of ~ 500 nm and ~ 270 nm, respectively, with pores running vertically into the Al_2O_3 (Fig. 30.2c) terminating with a scallop-shaped barrier oxide. The barrier oxide embosses the remaining Al/ Al_2O_3 ; the longer the pores are grown, the better is the hexagonal pore ordering at the bottom. The porous Al_2O_3 is removed by selective etching, and the embossed barrier oxide (Fig. 30.1b, c) is utilized as template for sputtering of Au, resulting in ordered (to different degrees) or randomly distributed NPs (Fig. 30.3, left).

Characterization of Various Gold Nanostructured Samples

The density of randomly distributed Au NPs covering the bottom of the Al/ Al_2O_3 templates can be controlled by adjusting the sputtering conditions such as the target-sample angle and the amount of Au. The NP density and the IPD of the

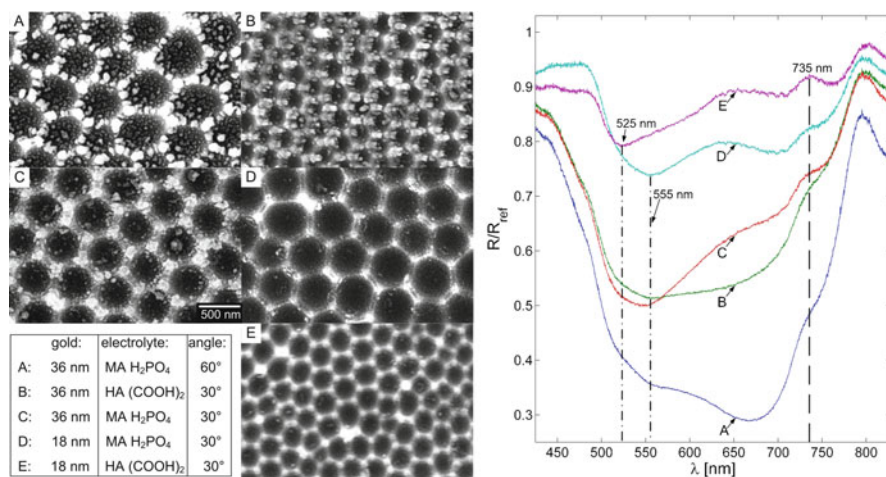


Fig. 30.3 *Left:* SEM micrographs of templates covered with differing amounts of Au NPs [5]. *Right:* corresponding reflection spectra from the substrates A to E

underlying template affect the spectral position of surface plasmon resonances which is manifested in the reflection spectra from substrates A to E (Fig. 30.3, right). The laser excitation at 735 nm (dashed line) applied in the TPL measurements and the spectral position of the resonances attributed to the difference in IPD (dashed-dotted lines at ~525 nm and ~555 nm for sample E and D, respectively) are indicated. By applying a TPL-SOM setup (Fig. 30.4a) with a fs laser as excitation we obtained the first harmonic (FH) image (Fig. 30.4b) on B along with corresponding TPL image (Fig. 30.4c). Sample D is less densely covered with NPs and, accordingly, fewer very bright spots are seen in the TPL image (Fig. 30.4d). The maximum and average FE reaches as much as 1,400 and 270, respectively, on substrate B, which showed the highest FE of substrates A to E as well as a very dense coverage of hot-spots. High FEs are essential, when functionalized plasmonic nanostructures are prepared for sensors and are here related to the small NPs densely covering the pore bottom. Raman spectra (Fig. 30.5) were collected from a flat Au reference and from the ordered NPs (shown in the SEM micrographs) formed by Au sputtering on the templates made by HA in oxalic acid. The Au has self-aggregated into ordered hemispheres only separated by small gaps that could form EM hot-spots with high FE. The SERS enhancement is proportional to the FE squared.

Templates with tunable dimensions were fabricated by various anodization techniques and were sputter-coated with Au to form randomly distributed or hexagonally ordered Au nanostructures. TPL-SOM and SERS indicate a very high FE. Reflection spectroscopy revealed a broad localized surface plasmon resonance, which could be advantageous for broadband optical molecular sensors with special view to single molecule detection.

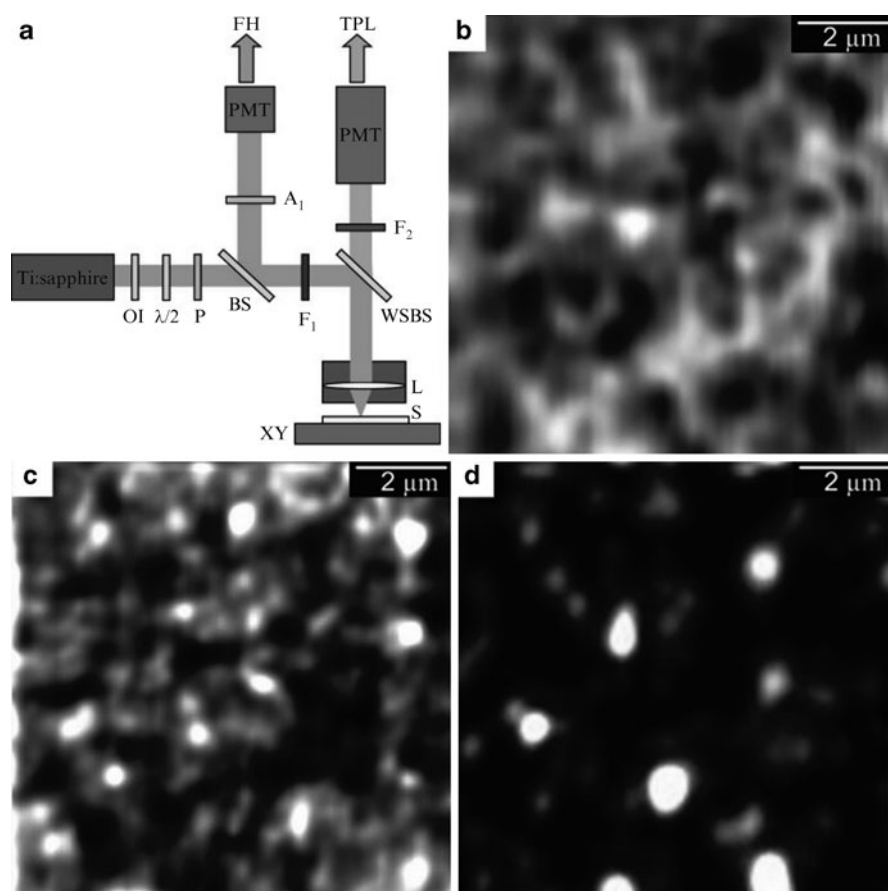


Fig. 30.4 (a) The experimental set-up for TPL-SOM working in reflection with a pulsed fs laser as excitation. (b) FH image obtained at 735 nm excitation on substrate B along with (c) corresponding TPL image. (d) The less dense spots in the TPL image recorded on substrate E [5]

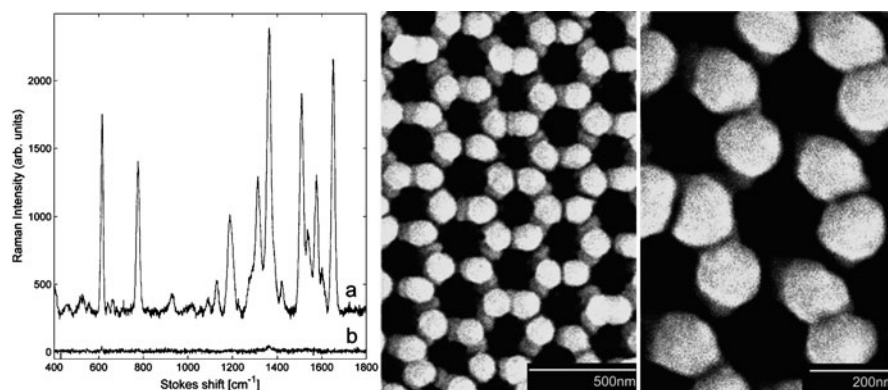


Fig. 30.5 Left: Raman spectra collected from a flat Au reference (b) and from the nanostructured substrate (a) shown on the SEM micrographs at the right

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Chapter 31

Growth of SiC Nano-Whiskers on Powdered SiC

Rajnish Dhiman and Per Morgen

Abstract SiC nano-whiskers may become important functional elements of future micro-electro-mechanical-systems (MEMS) components and gas sensors. We have developed some relatively easy procedures to form such SiC nanostructures from saw dust. The whiskers have been characterized by Raman microscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

Keywords SiC · Nano-whiskers · Tetraethyl orthosilicate (TEOS) · Saw dust · Gas phase reaction

Introduction

Silicon carbide nano-whiskers are important nano-materials due to their physical and chemical properties like high strength, high hardness, high thermal conductivity, low coefficient of thermal expansion, corrosion resistance, wide band-gap, etc. Due to their mechanical properties SiC whiskers can be very effective materials for the reinforcement of composite materials [1,2]. Silicon carbide whiskers could find applications in catalysis of gas reforming reactions, gas sensors, biosensors, bio-compatible components, in fuel cells and Li-ion batteries. Silicon carbide nano-whiskers can also be very interesting elements for the semiconductor industry, with electronic and optical applications due to properties like a wide band gap (2.39–3.33 eV) [3], high electron mobility, high breakdown electric field strength (3–5 MV/cm) and as they can sustain harsh conditions like high temperatures, high pressures, high frequencies and high powers [4,5].

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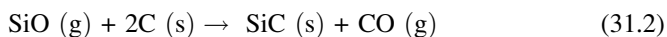
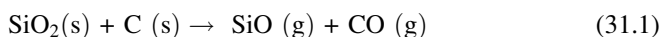
Experimental

In this work we have synthesized crystalline SiC nano-whiskers by infiltrating wooden powders (saw dust) with a viscous silicon precursor solution. Nano-whiskers are then being formed along with SiC clusters in this process.

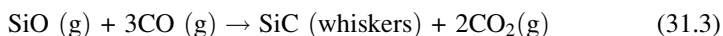
Grinding of beech wood produced the wooden powder (saw dust). Then this powder was infiltrated with an acidic silica precursor solution made by mixing TEOS (tetraethyl orthosilicate), HCl (hydrochloric acid) and ethanol in the molar ratio of 1:1.5:17. The wood powder was fully soaked in this solution for 24 h. Then the powder-solution mixture was dried for 12 h in air. Now this solid was heated to 1,400°C for 6 h in a tubular furnace using an Ar flow to create a non-reactive environment. Upon completion of these steps the samples were analyzed using SEM, XRD and TEM. The confirmation of the presence of SiC whiskers and the determination of their nature was most convincingly done with a Raman microscope. In this technique a laser beam of 514 nm wavelength was focused on the whiskers with the help of an optical microscope.

Results and Discussion

The TEOS solution gets uniformly distributed in the wood powder. Stored in air, the volatile organic components of the solution evaporate leaving silica inside the pores of the wood powder. Heating the impregnated wood powder to 900°C transforms it to a pure carbon structure in the non-reactive argon environment. Silicon carbide powder clusters are then being formed in the presence of SiO₂ by the following two-step reaction [6,8] at 1,400°C:



The SiC nano-whiskers are formed everywhere on these SiC clusters and on unreacted carbon powder, growing uniformly everywhere on the initial powder grains. This leads to the assumption that they have grown by a reaction different from that form the SiC clusters. The proof is the growth of SiC nano-whiskers on the silica deposited on the solidified SiO at the cold ends of the alumina tube inside the furnace, where a mixture of silicon and silica is heated along with the carburized wood to form SiC as in our other work based on “shape memory synthesis” [8], which in fact involved the same two reactions (31.1) and (31.2). This indicates that these nano-whiskers must have grown by a pure gas phase reaction at 1,400°C:



These reactants for the gas phase reaction are uniformly present inside the powder as by-products of reactions (31.1) and (31.2) of the SiC powder. The SiC nano-structures are observable with an optical microscope showing the Rock-woolTM-like nature of the fibers growing over the SiC and carbon clusters.

Figure 31.1 shows SEM pictures of such SiC nano-structures where the fibers are found to have lengths in the range of 10–15 μm and diameters varying from 50 to 150 nm. A few have larger diameters of around 250 nm and some a small diameter of around 25 nm. The nano-whiskers found over the bulk of the powder are generally very straight while those on the top are sometimes somewhat curved.

Figure 31.2 shows TEM pictures and electron diffraction patterns from a spot positioned on one of these nano-whiskers which suggests that the whiskers are crystalline with a high occurrence of stacking faults. Figure 31.2b suggests that the whiskers in the picture are square in shape. Figure 31.2c shows electron diffraction

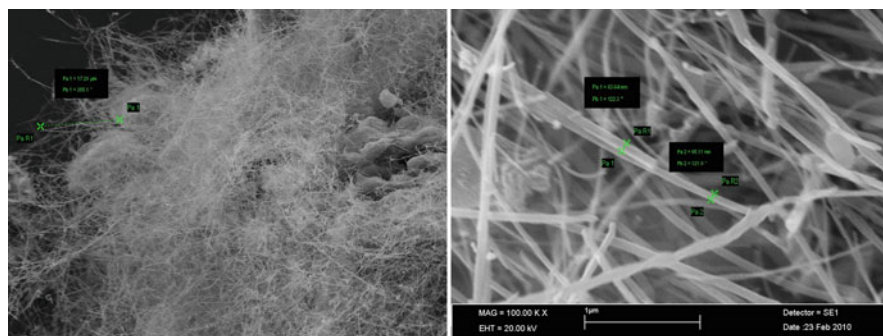


Fig. 31.1 SEM pictures of SiC fibers at different magnifications

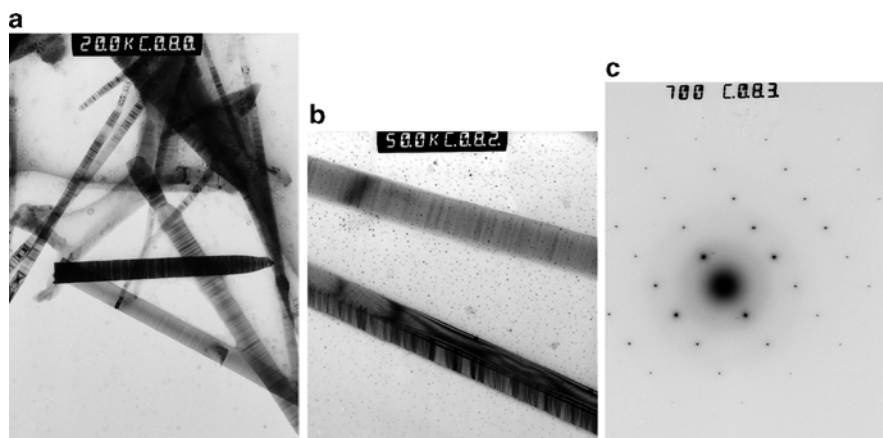


Fig. 31.2 (a) and (b) TEM pictures of some SiC nano-whiskers; (c) electron diffraction patterns from a spot on one of the whiskers suggesting a (112) orientation

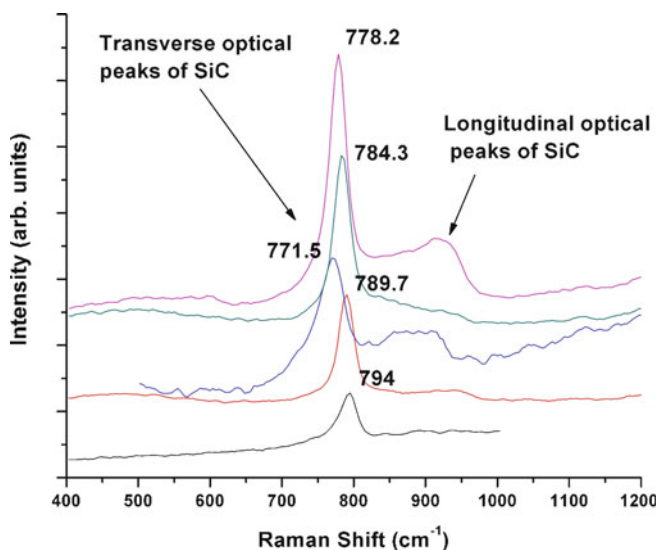
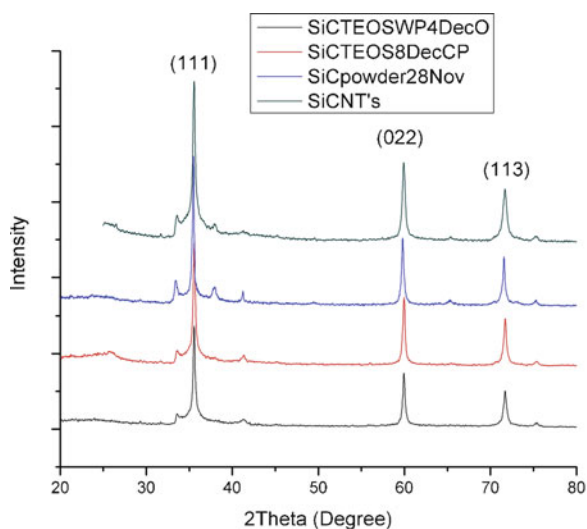


Fig. 31.3 Raman spectra of some different nano-whiskers

Fig. 31.4 XRD pattern of the samples showing crystallinity



pattern of one of the whiskers, having a (112) orientation. Figure 31.3 shows Raman spectra of the whiskers with 514 nm laser excitation focused individually over the whiskers. From Fig. 31.3, changing peak positions for different whiskers can be seen indicating that they may have different crystal structures like 2H, 4H, 6H, 15R (α -SiC); 3C (β -SiC) whiskers are also found [7].

Figure 31.4 shows X-Ray pattern of different samples proving the formation of crystalline SiC. Our samples also contain unreacted amorphous carbon as evident in

the XRD pattern of the sample named SiCTEOS8DecCP as a hump near 25.5° . This amorphous unreacted carbon can be removed by oxidizing the sample in air at 700°C for 3 h. Thereafter this hump had disappeared in the pattern of sample SiCTEOSWP4DecO. Although we cannot figure out exactly the nature of the nano-whiskers from the XRD patterns as they also contains the contribution from SiC clusters, the Raman microscopy spectra confirm the nano-whiskers as SiC.

Conclusion

Silicon carbide nano-whiskers have been grown by gas phase reaction of silicon monoxide and carbon monoxide at a temperature of $1,400^\circ\text{C}$. They are found to be crystalline with many stacking faults and different phases of SiC.

Acknowledgements The authors acknowledge the PhD scholarship funded by The Danish Program Committee for Sustainable Energy and Environment (2104-05-0073).

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Chapter 32

Tin Oxide Whiskers: Antimony Effect on Structure, Electrophysical, Optical and Sensor Properties

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L. Calvo-Barrio, and Aleksandre M. Gaskov

Abstract Tin dioxide whiskers have been grown from SnO vapor in a tube furnace in a flowing mixture of argon and oxygen at a constant source temperature, and the effect of the oxygen concentration in the carrier gas on the morphology, structure, and phase composition of the whiskers was studied. Single-crystal SnO₂ whiskers can only be obtained in a narrow range of oxygen concentrations. Tin dioxide whiskers doped with different concentration of antimony (0–0.25 at.%) have been grown from SnO and Sb₂O₃ mixtures in a tube furnace in a flowing mixture of argon and oxygen at a constant source temperature. The whiskers are about 100 μm in length and well crystallized. They possess a high structural perfection. The influence of Sb on crystal structure, morphology, optical properties of the SnO₂ whiskers is discussed. The electrophysical properties and sensitivity of individual whisker towards NO₂ and CO have been investigated.

Keywords Whiskers · ATO · Semiconducting materials · Conductivity · Optical band gap · Growth from vapor · Gas sensor

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Introduction

Quasi-one-dimensional (1D) crystals are of interest for both basic research and practical applications because they possess all key features of nanocrystalline materials (quantum size effects) and markedly surpass nanoparticles in stability, carrier mobility, and quantum yield of photochemical processes, which is of particular importance in creating optoelectronic transducers, field effect transistors, and chemical sensors [1]. The results reported to date provide conclusive evidence that the functional properties of 1D crystals of oxide semiconductors are very sensitive to their morphology, structural perfection of the material, deviations from stoichiometry, and impurities. All of these characteristics are governed by the conditions under which the crystals were grown and heat-treated. It has been shown that almost all processes for solution or vapor growth of 1D crystals of oxide semiconductors on gold seeds yield doped material. The best possibilities for the growth of undoped, structurally perfect 1D crystals of oxide semiconductors are offered by vapor growth in a horizontal flow reactor at high temperatures in vacuum [2]. This approach has been successfully used to grow 1D crystals of different oxides, but there are only empirical relationships between the growth conditions and structure, morphology, and dimensions of the crystals. Parameters playing a key role in determining the morphology and properties of vapor-grown quasi-one-dimensional nanocrystals are the temperature, carrier-gas flow rate, and oxygen partial pressure during growth. There is a great amount of works concerning the properties of 1D structures of undoped SnO_2 , where the free charge carrier concentration is determined by the deviation of the composition from stoichiometry. Such materials possess high structural perfection and thus high resistivity, which makes them unsuitable for application as materials for gas sensors and transparent semiconductive oxides (TCOs). One way to improve the conductivity of such crystals is to modify them by donor additives, which allow the increase of free carrier concentration. Doping with Sb can modify the optical and electrical properties of SnO_2 , but the mechanisms of the influence of Sb is not clear [3–6].

Experimental

SnO_2 whiskers were grown in a controlled gaseous environment in a flow reactor which could be heated up to $1,200^\circ\text{C}$ by an automatic tube furnace (Fig. 32.1). The starting material used was tin monoxide, SnO (Fluka). All growth runs were performed at a constant temperature of $1,030^\circ\text{C}$ in flowing argon. The flow rate of the carrier gas was varied from 10 to 750 ml/min and was maintained by an automatic flow controller with an accuracy of ± 1 ml/min.

Sb doped tin dioxide whiskers have been grown from $\text{SnO} + \text{Sb}_2\text{O}_3$ mixture (Fluka) in a controlled gaseous environment. All growth experiments were

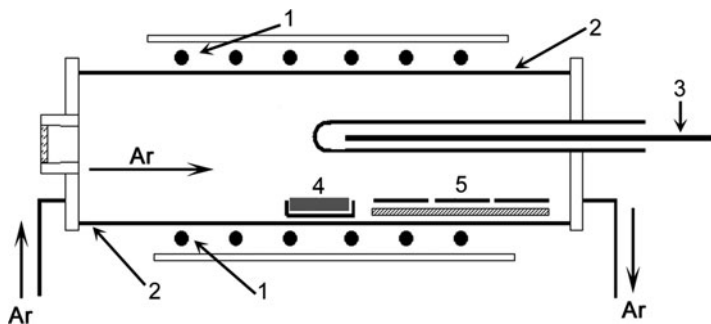


Fig. 32.1 Schematic of the reactor for whisker growth: (1) heater, (2) ceramic tube, (3) thermocouple, (4) SnO charge in a crucible, (5) substrates

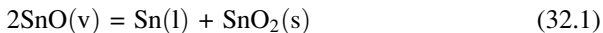
performed at a constant temperature of 1,030°C in an argon/oxygen gas mixture. The flow rate of the carrier gas was maintained constant by an automatic flow controller with an accuracy of ± 1 ml/min. The average growth time was 5 h. The ratio $[Sb/(Sb + Sn)] \times 100\%$ in the source mixture was varied from 0 to 33.3 at. %.

Results and Discussion

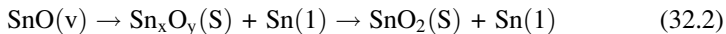
Properties of Whiskers Grown in Ar Atmosphere

If no oxygen was added to the argon used as the carrier gas [7], crystals grew on the tube walls in the 700°C zone.

The SEM micrographs in Fig. 32.2 illustrate the morphology of the grown whiskers. They are more than 0.5 mm in length and show no preferential orientation. The presence of droplets on the whisker tips (Fig. 32.2 inset) indicates that the growth process follows the vapor–liquid–solid mechanism, in which the liquid phase is the metallic tin resulting from SnO disproportionation:



XRD data indicate that samples are mixed-phase (Fig. 32.3) and contain Sn_3O_4 and Sn in addition to SnO_2 (cassiterite). No SnO was detected in the samples. Sn_3O_4 is not a thermodynamically stable phase but is an intermediate product of SnO disproportionation according to the scheme [8].



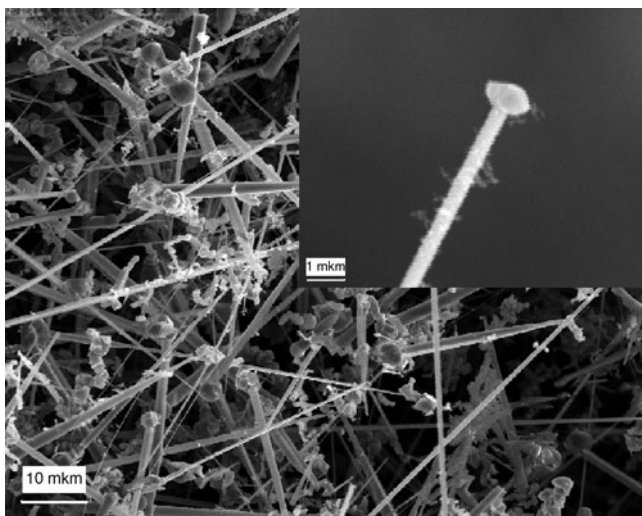


Fig. 32.2 SEM micrographs of whiskers grown in flowing Ar. Inset: individual whisker

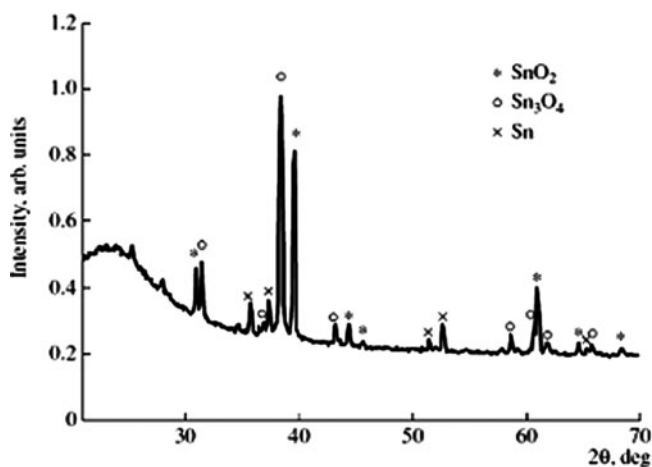


Fig. 32.3 XRD patterns of whiskers grown in flowing Ar

Properties of Whiskers Grown in a Mixture of Ar and O₂

In the presence of oxygen, crystals grew at the edge of the crucible, in the 1,030°C zone. Under such conditions, we obtained only whiskers, without dendrites or three-dimensional crystals (Fig. 32.4). The whiskers ranged from 1 to 3 μm in diameter and up to 100 μm in length. Raising the oxygen concentration in the carrier gas to above 0.2 vol% leads to the oxidation of SnO to SnO₂ directly in the crucible,

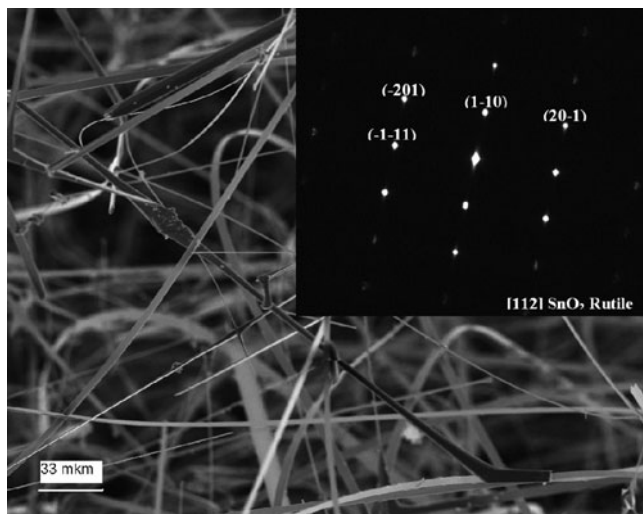


Fig. 32.4 Morphology of whiskers grown in a flowing mixture of Ar and O₂. Inset: SAED pattern of SnO₂ whiskers

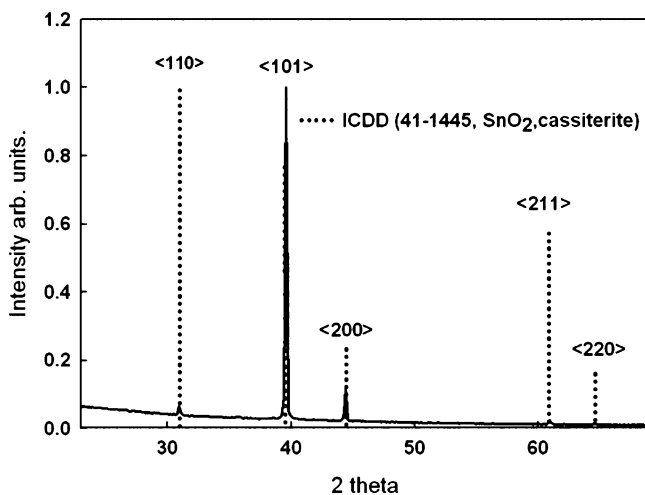


Fig. 32.5 XRD pattern of whiskers grown in a flowing mixture of Ar and O₂



which reduces the SnO vapor pressure, thereby preventing whisker growth.

Figure 32.5 shows the XRD pattern of whiskers grown in the presence of oxygen. The only phase in the samples is cassiterite. Comparison of the XRD intensities from 1D crystals and crystalline SnO₂ powder (ICDDPDF, 41-1445) indicates that the crystals grow in the [101] direction. According to electron

diffraction results, the whiskers consisted of cassiterite, in accordance with the XRD data, and were single-crystal throughout (Fig. 32.4 inset).

The growth of tin dioxide whiskers is shown to be extremely sensitive to the oxygen concentration in the carrier gas. At low O_2 concentrations during growth, the resulting whiskers contain tin in lower oxidation states, and dendritic crystals appear. Raising the oxygen concentration in the carrier gas to above 0.2 vol% leads to the oxidation of SnO to SnO_2 , thereby preventing whisker growth. Only in a narrow range of O_2 concentrations (0.03–0.2 vol%) we obtained single-crystal SnO_2 (cassiterite) whiskers with no additional phases or dendrites.

Properties of Whiskers Doped with Antimony

Morphology

Pure and antimony doped tin dioxide whiskers have been grown from SnO or $SnO + Sb_2O_3$ mixture in a controlled gaseous environment in a flow reactor. Figure 32.6 shows the morphology of the obtained $SnO_2(Sb)$ whiskers. They range from 10 to 100 μm in diameter and from 0.01 to 1 mm in length and are well crystallized. With increasing Sb concentration in the source mixture the crystals change from white cotton-like to straight whiskers with a grey metallic shine, become longer and dendrites-free. In whiskers synthesized from $SnO + Sb_2O_3$ mixtures one can observe not only wires, but also belt-structures. The color change may be due to a charge transfer between Sb^{3+} and Sb^{5+} within a random array of disordered SnO_6 and SbO_6 octahedra.

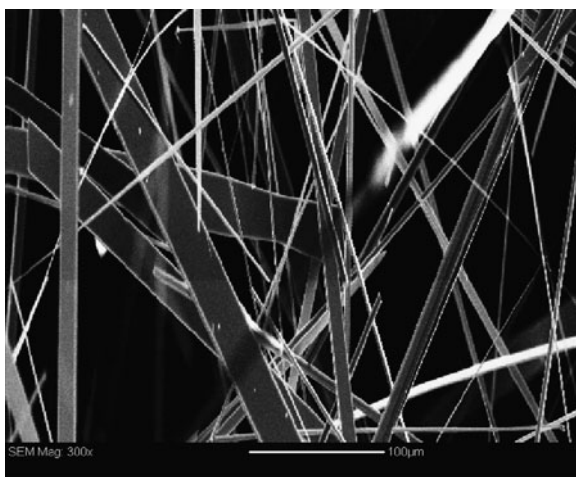


Fig. 32.6 Morphology of $SnO_2(Sb)$ whiskers

Composition

Investigations by laser ionization mass spectrometry (LIMS) show that the total concentration of antimony in the whiskers changes from 0 to 0.25 at.%. The concentration of Sb in the whiskers is much lower than in source mixture but the dependence of Sb concentration in $\text{SnO}_2(\text{Sb})$ whiskers vs. Sb concentration in the initial source mixture possesses monotonous character (Fig. 32.7).

Auger measurements could evaluate the antimony concentration at the surface and in the volume of SnO_2 whiskers. All measurements have been done on $10 \times 10 \mu\text{m}$ areas inside individual whiskers. The analysis of pure SnO_2 whiskers (without Sb) shows a small peak at an energy of 440–460 eV, where the Sb signal should appear. So Sb can be clearly detected in these materials. The Auger spectra of $\text{SnO}_2(\text{Sb})$ whiskers show Sb peaks (452 eV, $M_5N_{4.5}N_{4.5}$; 460 eV $M_4N_{4.5}N_{4.5}$) [9] together with Sn peaks (427 eV, $M_5N_{4.5}N_{4.5}$; 435 eV, $M_4N_{4.5}N_{4.5}$) [10] in all samples. After argon sputtering to remove about 100 nm material from the surface of the crystals no Sb signal appears in any sample (Fig. 32.8). So the antimony is predominantly distributed on the surface of the whiskers but from the Auger-spectra it is difficult to distinguish antimony (III) (usually at 458.7 eV) from antimony (V) at 457.8 eV.

Figure 32.9 shows IR absorption spectra of our whiskers with different antimony concentration. The spectra contain features attributable to surface hydroxyls ($3,500\text{--}3,700 \text{ cm}^{-1}$), adsorbed water molecules ($1,540 \text{ cm}^{-1}$), adsorbed CO_2 ($2,200\text{--}2,400 \text{ cm}^{-1}$), carbonate groups ($1,300\text{--}1,400 \text{ cm}^{-1}$), and atomic groups in the crystal lattice of SnO_2 ($1,450, 770, 757, 705, 630, 618, 605, 564, 477, 465, 366\text{--}368, 290, 273, 243, \text{ and } 226 \text{ cm}^{-1}$) [8,11]. In the wavenumber range $800\text{--}1,200 \text{ cm}^{-1}$ a feature is observed, which can be assigned to the vibrations of

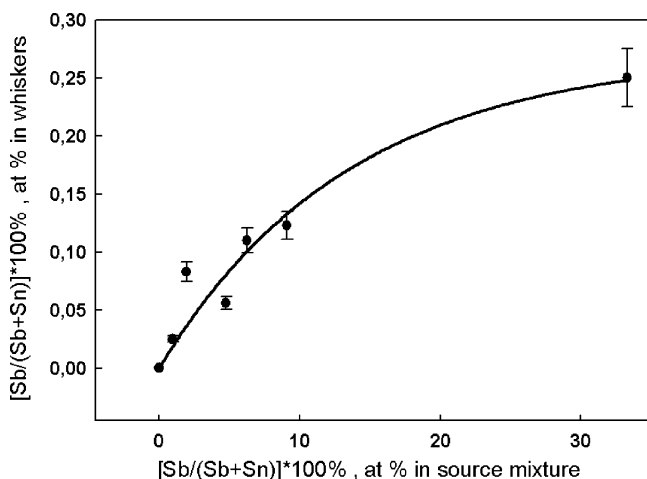


Fig. 32.7 Sb concentration in $\text{SnO}_2(\text{Sb})$ whiskers vs. Sb concentration in the source mixture

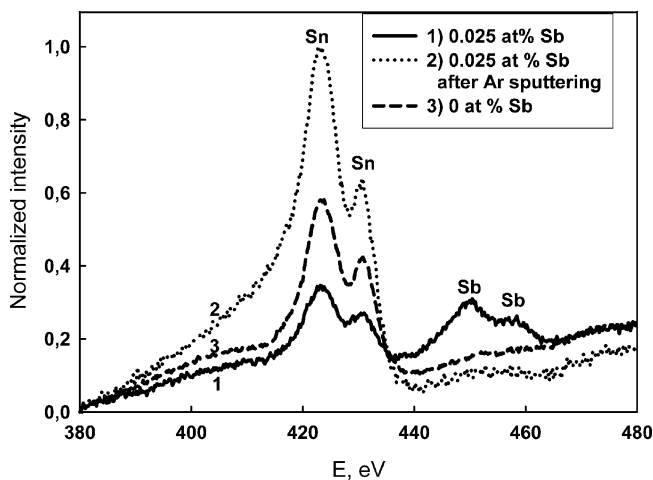


Fig. 32.8 Auger spectra of the SnO_2 and $\text{SnO}_2(\text{Sb})$ whiskers

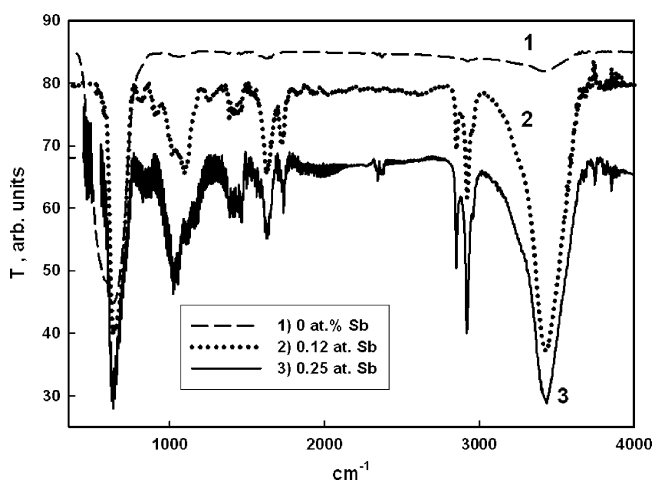


Fig. 32.9 IR spectra of whiskers doped with 0, 0.12 and 0.25 at.% Sb

‘surface cation–oxygen’ bonds of Sb_6O_{13} ($\text{Sb}_2\text{O}_3 \cdot 2\text{Sb}_2\text{O}_5$) [12]. The intensity of this peak grows with increasing antimony concentration, which demonstrates that the content of antimony on the surface of the whiskers increases, too. This fact is in agreement with the Auger results.

Structure

It was found by electron diffraction that the whiskers consist of one phase: cassiterite SnO_2 . The XRD pattern of SnO_2 whiskers is shown in Fig. 32.10. All diffraction peaks can be perfectly indexed to the tetragonal cassiterite structure of SnO_2 .

A comparison of the intensities in the XRD pattern from 1D crystals and SnO_2 powder diffraction (ICDD PDF, 41-1445) indicates that the whiskers grow preferential in [101] direction. This is in agreement with literature data [3,13]. The increase of the total Sb concentration (LIMS) results in changes of the XRD spectra. One can observe the augmentation of [200] line intensity (Fig. 32.10). It may be caused by the appearance of belt-structures (Fig. 32.6), which have a second geometrical dimension (the width of the belts), and by an increase of the fraction of these two-dimensional crystals.

The increase of the SnO_2 cell parameters (Table 32.1) and lattice volume has been found only for $\text{SnO}_2(\text{Sb})$ whiskers containing 0.25 at.% antimony (total Sb concentration determined by LIMS).

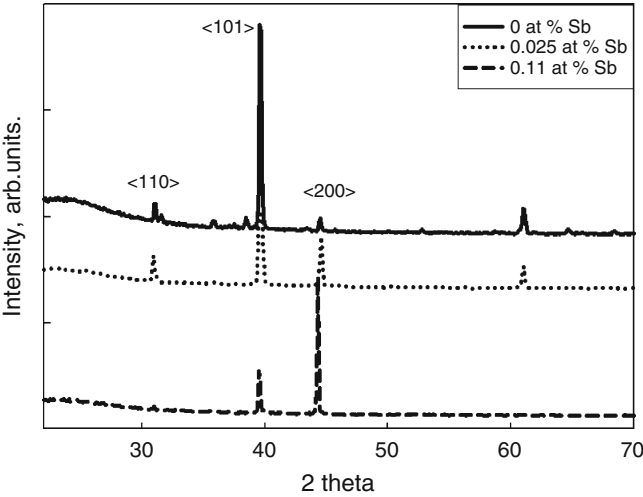


Fig. 32.10 XRD patterns of SnO_2 and $\text{SnO}_2(\text{Sb})$ whiskers

Table 32.1 SnO_2 cell parameters and lattice volume of $\text{SnO}_2(\text{Sb})$ whiskers (XRD)

[Sb]/([Sb] + [Sn]) × 100% (LIMS)	SnO ₂ cell parameters		
	a, Å	c, Å	V, Å ³
0	4.7375 (3)	3.1867 (3)	71.522 (8)
0.06	4.73743 (16)	3.18664 (17)	71.518 (4)
0.12	4.73764 (22)	3.18678 (23)	71.528 (6)
0.25	4.7380 (3)	3.1878 (3)	71.564 (8)

It was demonstrated [14] that in $\text{SnO}_2(\text{Sb})$ nanoparticles with Sb concentrations lower than 6 at.% the impurity (antimony) does not form a separate oxide phase. The antimony incorporated into the SnO_2 lattice exists in two oxidation states, Sb^{3+} and Sb^{5+} , forming a solid solution. The $\text{Sb}^{3+}/\text{Sb}^{5+}$ content ratio determines the SnO_2 cell parameters. To explain the changes of the cell parameters observed in our work it is necessary to compare the ionic radii for the 6-coordinated Sn^{4+} (0.69 Å), Sb^{5+} (0.61 Å) and Sb^{3+} (0.76 Å) [15]. The ionic radius of Sb^{3+} is larger than that of Sn^{4+} , so the behavior of the cell parameters may be due to the substitution of Sn^{4+} by Sb^{3+} in the SnO_2 crystal structure. Another possible explanation of the increase of the lattice parameter is the incorporation of Sb^{5+} ions on interstitial positions of the cassiterite structure of SnO_2 .

Electrical Properties

The electrophysical measurements demonstrate that the increase of the total Sb concentration results in a decrease of the electrical resistivity of the individual whiskers (Fig. 32.11) as well as in a change of the conduction mechanism. $\text{SnO}_2(\text{Sb})$ whiskers with total Sb concentrations of 0.11–0.25 at.% show metallic conduction: their resistivity becomes lower with decreasing temperature. Other samples (with total Sb concentrations less than 0.11 at.%) demonstrate a non-monotonous resistivity dependence with temperature. Lowering the temperature first leads to a decrease of the whisker resistivity but then to an increase. One can

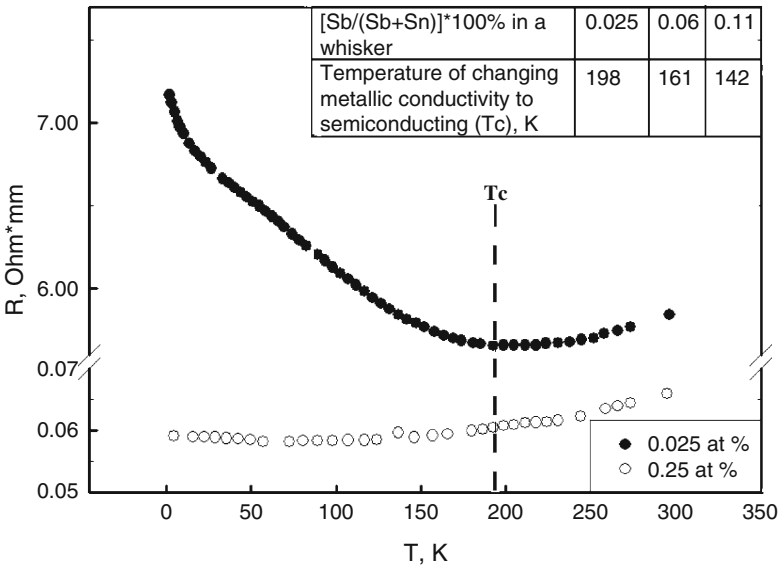
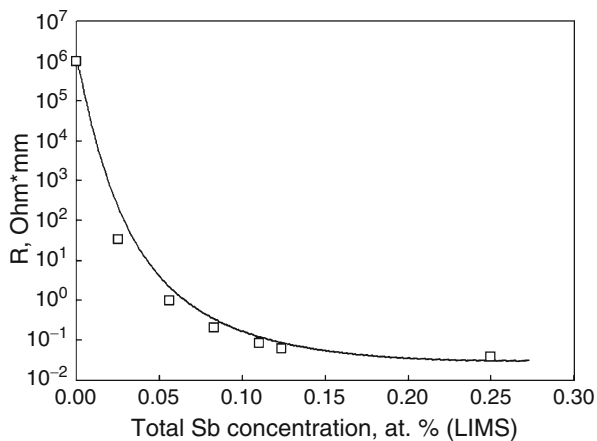


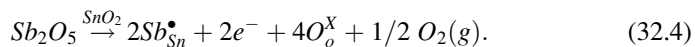
Fig. 32.11 Temperature dependence of the resistance measured on individual whiskers $\text{SnO}_2(\text{Sb})$ with two different contents of Sb atoms

Fig. 32.12 Dependence of the resistance ($T = 300\text{K}$) of individual $\text{SnO}_2(\text{Sb})$ whiskers vs. total Sb concentration

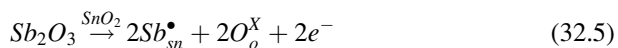


see two regions in the plot: at temperatures higher than a certain threshold T_c the whiskers behave as a metal (the material at these temperatures is a degenerately doped semiconductor), while at temperatures lower than T_c the whiskers become semiconducting. The resistance of an individual whisker at $T = \text{const}$ decreases with increasing antimony concentration and then becomes constant for whiskers with a total antimony concentration above 0.11 at. % Sb (Fig. 32.12). This correlates with the changes in the temperature behavior of the whiskers resistance.

Antimony (Sb^{5+}) is a common n-type dopant, which occupies tin (Sn^{4+}) sites in the cassiterite structure and improves its electrical properties according to the following mechanism [16]:



The surface enrichment of antimony (Sb^{3+}) increases the free charge carriers near the surface due to the substitution of Sn^{2+} , thereby significantly increasing the conductivity [15]:



Optical Measurements

We have also studied the light absorbance by whiskers. A part of the typical absorbance spectrum of SnO_2 whiskers is shown in Fig. 32.13. The threshold in the spectrum at λ_b corresponds to the beginning of the interband absorption and provides information on the band gap energy ΔE [17,18], which can be easily estimated from the value of λ_b found from the graphs [17–19] by:

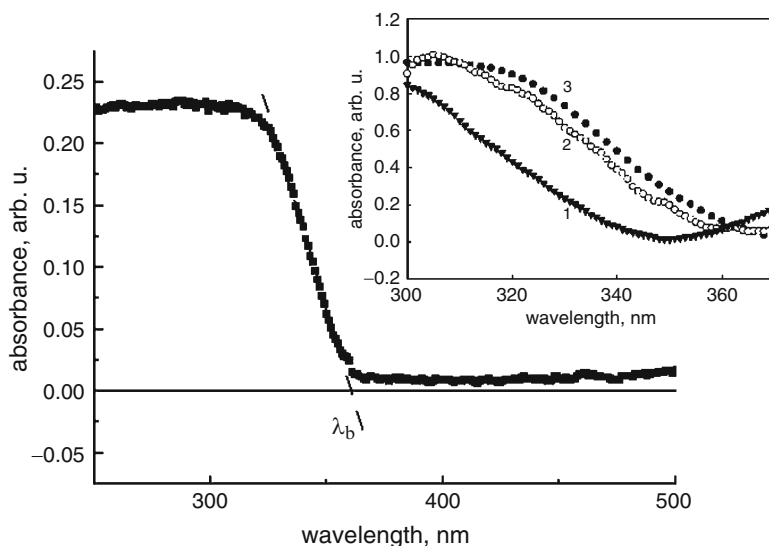


Fig. 32.13 Light absorbance spectrum of SnO_2 whiskers with a Sb concentration of 0.12 at.%. The inset shows the absorbance threshold positions in the spectra of whiskers with different average Sb concentration: (1) pure SnO_2 , (2) 0.06 at.% Sb, (3) 0.12 at.% Sb

$$\Delta E = h \cdot c / \lambda_b, \quad (32.6)$$

where h is Plank's constant and c is the light speed. The position of this threshold in the spectra was found to shift towards larger wavelength (lower energies) with increasing antimony concentration in the whiskers (see the inset in Fig. 32.13).

The resulting dependence of the band gap energy on the antimony concentration is presented in Fig. 32.14. The dependence is not linear; it turns into a plateau at Sb concentrations higher than about 0.11 at.%. Such a behavior of the band gap found in optical measurements is completely consistent with the behavior of the resistance of the whiskers (Fig. 32.12) and with the change in the temperature dependence of the whiskers resistance (Fig. 32.11).

All these facts can be explained by the solubility limit of Sb^{5+} in SnO_2 and by the fact that Sb^{5+} ions in the crystal volume contribute more to the conductance and the band gap width than Sb^{3+} ions on the surface. This can be due to the large volume to surface ratio of the whiskers. So reaching the solubility limit of Sb^{5+} ($[\text{Sb}] > 0.11$ at.%) results in invariability of the specific resistance value and the band gap of the whiskers.

This concept was proven by Auger measurements, which revealed that Sb is mainly distributed on the surface of the whiskers (Fig. 32.8). At high dopant levels (Sb concentration 0.25 at.%) a metallic conductivity of the whiskers is observed, while the semiconductor band gap in the optical absorbance spectrum is still present. This fact can also be explained by the distribution of the excess Sb ions

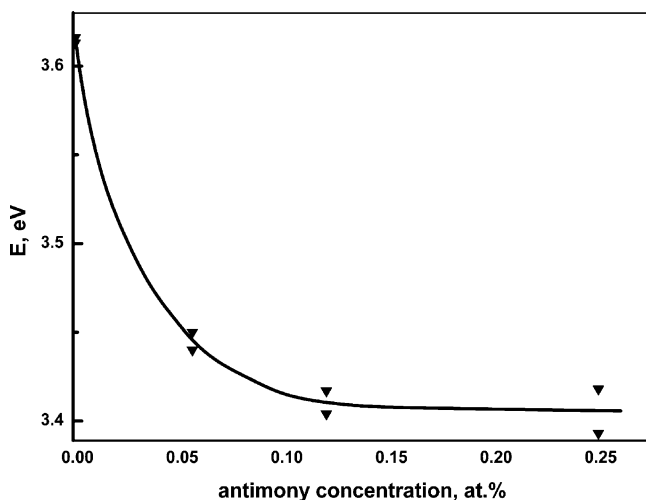


Fig. 32.14 The band gap energy E of $\text{SnO}_2(\text{Sb})$ whiskers vs total Sb concentration

mainly at the surface layer of the whiskers. Under these conditions a thin SnO_2 layer on the surface is first reaching the level of Sb doping necessary for the metal-like conductivity which starts lowering the resistance of the semiconductor. However the light can still penetrate to the inner semiconductor layers of the whisker; thus one can observe the semiconductor band gap light absorption.

Gas Sensor Measurements

The sensor measurements were performed on an individual $\text{SnO}_2(\text{Sb})$ whiskers towards oxidizing (NO_2) and reducing (CO) gases. The whiskers were selectively sensitive towards NO_2 .

The whisker was fixed on a microelectronic chip with the help of Ag-contacts (Fig. 32.15). Figure 32.16 demonstrates the change of the sensor resistance (0.12 at. % Sb) during NO_2 explosion at 150°C . The gas sensitivity S is defined as R/R_0 where R is the electrical resistance in NO_2 and R_0 is the resistance in air. Such materials are sensitive to changes of the concentration of the gases to be detected. The dependence of the sensor signal on temperature in Fig. 32.17 demonstrates that the maximum of the sensor sensitivity can be observed at 150°C .

For CO sensor measurements the operating temperature was varied from 100°C to 350°C . The DC conductance G was monitored during exposure to a gas mixture containing 100 ppm CO in air and pure air.

Whiskers are not sensitive towards CO ; no change in conductivity has been detected. Such a behavior can be explained in the following way: at constant temperature the conductance of whisker is

Fig. 32.15 Image of an individual whisker on the microelectronic chip

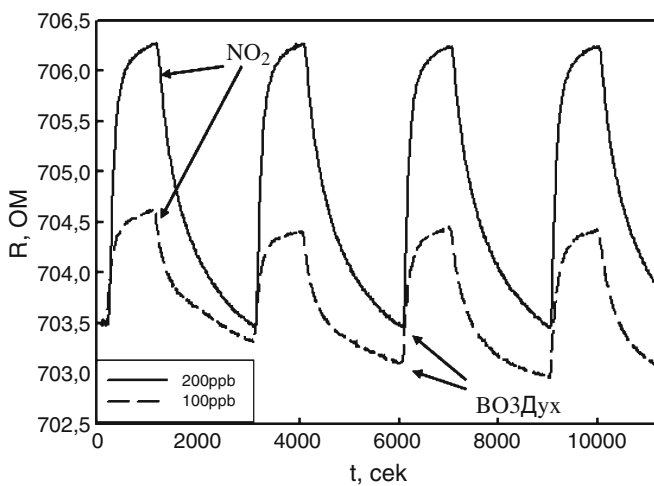
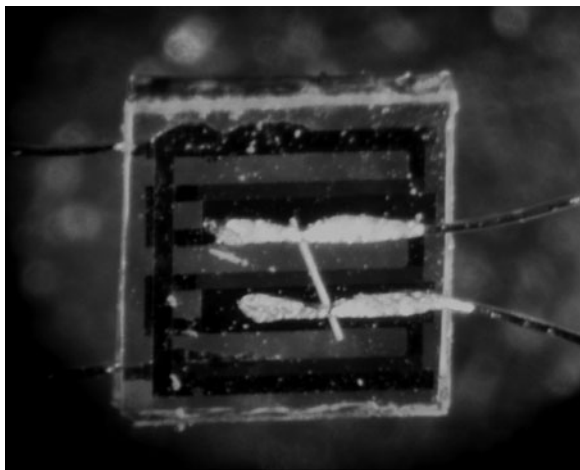


Fig. 32.16 Response of a whisker doped with 0.12 at.% Sb at 150°C in the presence of 100 and 200 ppb NO₂

$$G = \frac{\pi D^2 e \mu n}{4L} \quad (32.7)$$

where D is the diameter, L the length of the whisker, μ the carrier mobility, e the elementary charge and n the carrier concentration.

On the surface of SnO₂ ionosorbed oxygen creates a 10–100 nm thick electron-deficient layer:

$$W = L_D \left(\frac{eV_S}{KT} \right)^{1/2} \quad (32.8)$$

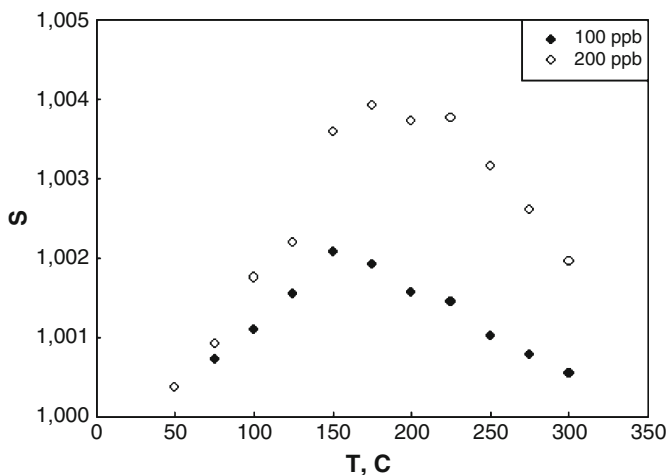


Fig. 32.17 Dependence of the sensor signal towards 100 and 200 ppb NO_2 on temperature

with the Debye length $L_D = (\epsilon\epsilon_0 kT/e^2 n)^{1/2}$ and the adsorbate-induced band-bending $V_s = Q_s/2\epsilon\epsilon_0 en$. The conductance of the whisker in an oxidizing environment is:

$$Go = ne\mu \frac{\pi(D - 2W)^2}{4L} \quad (32.9)$$

Assuming W to be significantly smaller than D , the sensor signal for reducing gases ($(S = G - Go)/Go$) can be estimated as [20]:

$$S \approx \frac{4W}{D} \quad (32.10)$$

The carrier concentration n_0 in tin oxide is $5 \times 10^{-17} \text{ cm}^{-3}$ [20]. If we suppose that one Sb^{5+} ion releases one electron into the SnO_2 conduction band and that in 1 cm^3 of SnO_2 there are $\sim 4.7 \times 10^{23} \text{ Sn}^{4+}$ ions (here we suppose a volume of 4.7 Å^3 of the SnO_2 cell) then whiskers doped with 0.12 at.% Sb contain 5.6×10^{20} electrons in 1 cm^3 . This assumption is confirmed by the resistance of individual whiskers (Fig. 32.12). So 0.12 at.% Sb increases the carrier concentration from 5×10^{-17} to $5.6 \times 10^{-20} \text{ cm}^{-3}$. As the width of the deficient layer is $W \sim L_D \times V_s^{1/2} \sim n^{-1/4}$ and the diameter of the whiskers more than $1 \mu\text{m}$, S becomes too low; this explains why such.

Gas-oxidizing NO_2 , increasing W , decreases G of the whiskers. However this change in conductivity not exceed 0.5% (Fig. 32.17), but it is possible to use such materials for the detection of oxidizing gases in presence of reducing gases.

Conclusion

The growth of tin dioxide whiskers is shown to be extremely sensitive to the oxygen concentration in the carrier gas. We established that only in a narrow range of O₂ concentrations (0.03–0.2 vol%) whiskers were single-crystal SnO₂ (cassiterite) with no additional phases or dendrites. We obtained single-crystalline antimony-doped SnO₂ whiskers by an *in situ* doping process based on the vapor-liquid–solid growth mechanism. Auger measurements revealed that Sb is mainly distributed on the surface of the whiskers but at the same time antimony is also incorporated into the SnO₂ lattice and increases the lattice parameters of SnO₂. Antimony allows to control the resistance and band gap of SnO₂ whiskers but causes insignificant changes in the structure of the crystals. The whiskers possess a high transmittance in the visible region being suitable for several applications where good transparency and conductivity is needed. Whiskers as opposed to nanopowders and thin films of SnO₂(Sb) are selective towards oxidizing gases in the presence of reducing gases. Sensor measurements demonstrate that Sb-doped SnO₂ will find promising applications for gas sensors with low resistance.

Acknowledgments This work has been supported by FP7-NMP-2009 EU-RU project 247768 S3 and Russian Agency “Rosnauka” project 02.527.11.0008.

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Chapter 33

Excimer Laser Preparation of SnO₂ and SnO₂/TiO₂ Nanoparticles

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Abstract A single pulse of an ArF excimer laser induces efficient oxidation of Sn (CH₃)₄ and Sn(CH₃)₄/Ti(Oi-C₃H₇)₄ in the gas phase. The direct deposition of stoichiometric tin dioxide, tin monoxide and mixed tin/titanium dioxide is demonstrated. Structural changes at 300°C and 500°C in both vacuum and air are studied by means of XRD and Raman spectroscopy. Transmission electron microscopy shows that the nanoparticles possess a mean diameter about 40 nm.

Keywords Tin oxides · Titanium dioxide · Excimer laser · Nanostructures

Introduction

Tin dioxide has recently received great scientific interest due to its wide range of applications. The reported applications reach from overcoating of magnetic recording media through electrodes for electrochromic and optoelectronic devices [1], as ITO electrodes in photoelectrochemistry or important part of Li-ion batteries [2,3]. Tin dioxide is one of the most sensitive materials for semiconductor gas sensors [3,4]. The reasons are the convenient physicochemical properties of tin dioxide: a high reactivity to reducing gases and a low working temperature due to adsorption of oxygen on the naturally non-stoichiometric surface. The sensitivity of SnO₂ sensors is increased by doping. Doped SnO₂ was demonstrated to possess a better or tuned selectivity and lower working temperature. Transition metals or metal oxides are the most promising dopants studied [5].

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SnO₂-based layers or nanoparticles were prepared by numerous techniques, e.g. sol-gel [6], chemical vapour deposition (CVD) [7], spray pyrolysis [8], pulsed laser ablation [9] or high energy ball milling [10]. Because the properties of the gas sensors depend on surface parameters, polycrystalline or nanocrystalline structures are preferred. For this reason new techniques to produce tin dioxide with modified surfaces are investigated.

In this work we present a new technique for the preparation of SnO₂-based nanoparticles. The suitability of this technique for efficient preparation of SnO₂ and SnO₂/TiO₂ materials is demonstrated.

Experimental Part

SnO₂-based nanoparticles were prepared in a 1 l glass reactor equipped with a PTFE stopcock and a quartz window. The nanoparticles were deposited on tantalum, quartz or glass substrates and then used for analysis. Tetramethyltin (99%, Aldrich), titanium tetraisopropoxide (Strem Chemicals) and oxygen (Linde) were used as precursors without any purification. The reaction mixture was prepared using a standard vacuum line, pumped by a rotation pump to a pressure of 3 Pa and equipped with a membrane pressure gauge (Barocel, Edwards). Mixtures of 450 Pa Sn(CH₃)₄, 15 or 30 Pa Ti(Oi-C₃H₇)₄ and 3.00–10.0 kPa O₂ were prepared; an ArF laser (193 nm, 60 mJ/pulse, Semento Estonia) was used to initiate the oxidation.

Analyses of the gaseous products, the depletion of the reactants, and of the deposit were conducted by FTIR spectroscopy (Impact 400, Thermo Nicolet). FTIR spectra of the deposit were collected on Ta substrates with resolution 2 cm⁻¹ using an specular reflection accessory. Raman spectra were collected using a Nicolet Almega XR spectrometer (Thermo Electron) with 473 nm excitation, equipped with an Olympus scientific microscope BX-51. The samples were accommodated and measured on a polished tungsten substrate.

Thermal treatments were performed in a tube furnace (Thermolyne 21100). The temperature ramp was set at 10°C/min; the samples were maintained at the desired temperatures (300°C, 500°C) for 2 h and then cooled to room temperature. Deposits on different substrates were annealed in air or in a vacuum. The quartz tube with the deposit was evacuated by a turbostation (Pfeiffer Vacuum TCP 380).

X-ray diffraction data were collected at ambient pressure and temperature using a Philips X'Pert MPD system with the Co K_α1 line ($\lambda = 0.17889$ nm) in the angular range from $2\theta = 5$ –85°. Energy-dispersive X-ray spectroscopy (EDX) and scanning electron microscopy (SEM) measurements were performed on a XL 30 CP (Philips) equipped with an EDX detector PV 9760; the accelerating voltage was selected in range from 5 to 25 kV. The chemical composition was measured on a beryllium substrate and taken from several μm^2 . Transmission electron microscopy (TEM) and electron diffraction (ED) analyses were performed on a Philips EM 201 microscope operated at 80 kV.

Results and Discussion

Tetramethyltin, titanium tetraisopropoxide and oxygen were used as precursors. Gaseous mixtures of $\text{Sn}(\text{CH}_3)_4/\text{O}_2$ were prepared in the reactor at room temperature, $\text{Sn}(\text{CH}_3)_4/\text{Ti}(\text{Oi}-\text{C}_3\text{H}_7)_4/\text{O}_2$ mixtures in the same reactor heated to 100°C .

A single pulse of an ArF laser (193 nm) explosively decomposed the reaction mixture and results in efficient formation of solid deposits along with gaseous products. The explosive decomposition was accompanied by a blue light flash. The conversion of the organometallic compounds was calculated from FTIR spectra measured before and after the reaction using the stretching and bending vibrations of $\text{Sn}(\text{CH}_3)_4$ (2,984, 770 and 529 cm^{-1}) and $\text{Ti}(\text{Oi}-\text{C}_3\text{H}_7)_4$ (1,130, 1,007, 815 and 615 cm^{-1}). The organometallic precursors were depleted completely from the gas phase (conversions observed were higher than 99% for both precursors); nanostructured oxides as solids together with gaseous oxidation products were formed.

Characterization of the Tin Dioxide Nanoparticles

A white solid material deposited on the reactor walls and the substrates accommodated in the reactor was formed when a tetramethyltin/oxygen mixture with excess of O_2 was reacted. The gaseous products found in the reactor were CO_2 and water. Characterization of the deposit was performed after removing the gaseous products adsorbed on the large sample surface by vacuum. The sample adhesion to the glass reactor walls and substrates was loose.

The chemical composition of the as-prepared sample was studied by the EDX technique. The bulk composition found was $\text{Sn}_{1.00}\text{O}_{1.89}$ and shows that the oxidation of $\text{Sn}(\text{CH}_3)_4$ in excess oxygen affords pure tin dioxide. A low content of carbon (probably adsorbed CO_2) and silicon traces (from the glass reactor) were also observed.

X-ray diffraction reveals that only one crystalline modification of SnO_2 is present in the sample (Fig. 33.1a). The crystal form recognized by this technique is cassiterite which possesses a tetragonal unit cell with a space-group symmetry of P42/mnm .

Heating to 300°C and 500°C in air and vacuum at a pressure 10^{-3} Pa has no influence on the sample stoichiometry. The samples were identified as cassiterite SnO_2 in the whole temperature range.

Raman and FTIR spectra also confirm the formation of SnO_2 and its stability at elevated temperatures in both vacuum and air. Figure 33.2 shows the Raman spectra of SnO_2 samples. Characteristic vibrations 637, 698 and 780 cm^{-1} are typical for SnO_2 ; similar values were reported in the literature [11].

FTIR spectra (Fig. 33.3) measured on tantalum substrates by the specular reflection technique show the major broad bands of SnO_2 centered at 615 and 675 cm^{-1} [11].

Transmission electron microscopy reveals that particles are ball shaped with a broad diameter distribution (Fig. 33.4a). The typical diameter is about 40 nm, but

Fig. 33.1 X-ray diffraction pattern of (a) cassiterite SnO_2 , (b) *syn*-romarchite SnO , and (c) a SnO sample annealed to $500^\circ\text{C}/2\text{ h}$ in vacuum

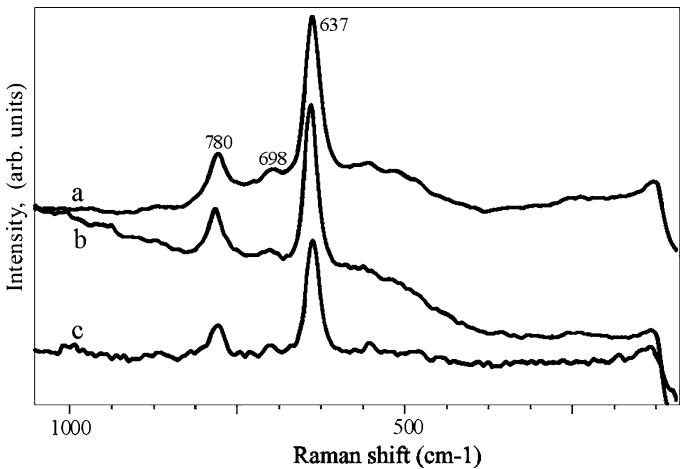
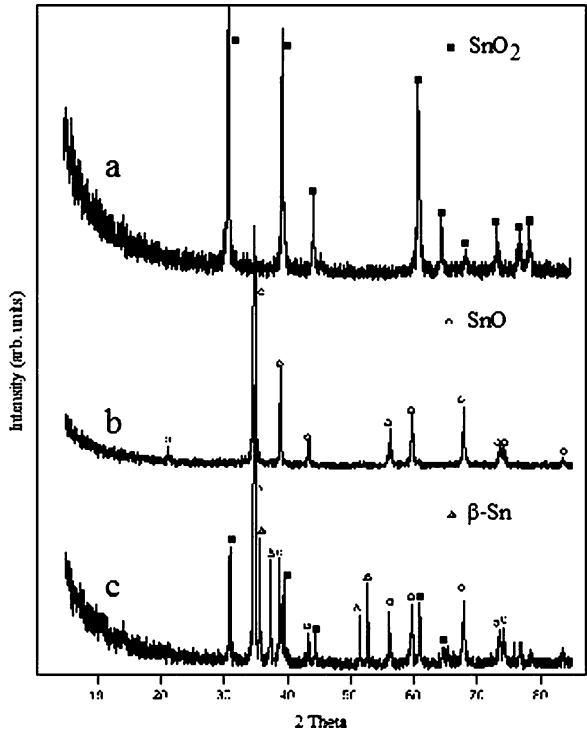


Fig. 33.2 Raman spectra of (a) as-prepared and (b, c) vacuum annealed deposits (b): 300°C , (c): 500°C for 2 h

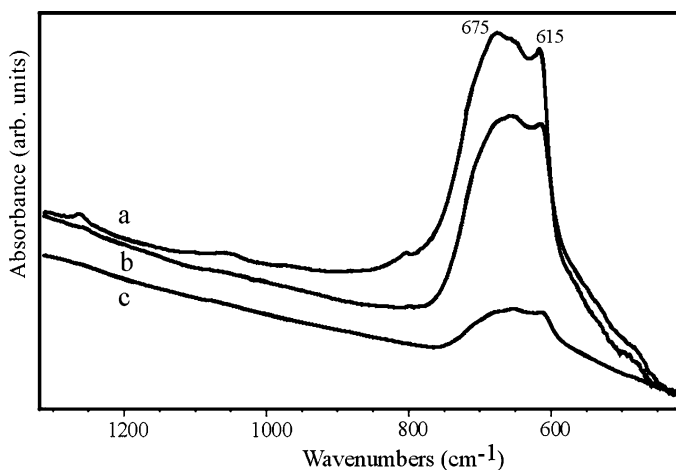


Fig. 33.3 FTIR spectra of the same samples

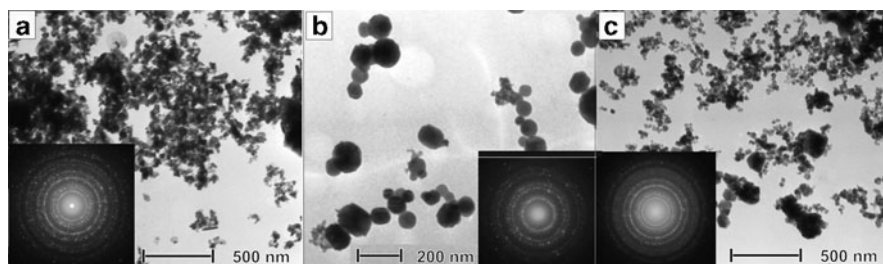


Fig. 33.4 TEM images of (a) SnO_2 , (b) SnO and (c) $\text{SnO}_2/\text{TiO}_2$ nanoparticles. ED patterns are shown as insets

larger particles up to $1\ \mu\text{m}$ are also present. Electron diffraction confirms the nanocrystalline character of the particles prepared. The fitting procedure also confirms the presence of cassiterite in agreement with the XRD results.

Characterization of the Non-Stoichiometric Tin Oxides

The reaction conducted in a mixture of $\text{Sn}(\text{CH}_3)_4/\text{O}_2$ with an understoichiometric amount of oxygen has also an explosive course accompanied by a bright blue flash, but the deposit possesses a dark brown colour. With a 20% deficiency of oxygen the reaction affords mainly carbon monoxide, CO_2 and water. Traces of methane and higher hydrocarbons are detected in the FTIR spectrum. The EDX analysis shows a bulk stoichiometry of $\text{Sn}_{1.00}\text{O}_{1.16}$. Some carbon is also detected; its presence is a consequence of the partial oxidation of the precursor. The X-ray diffractogram is

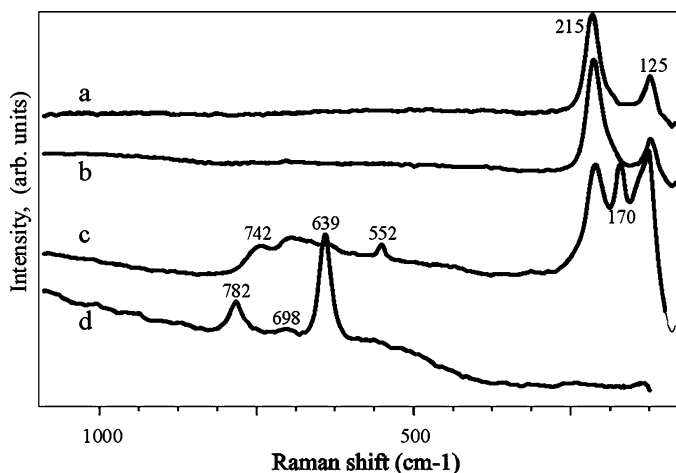


Fig. 33.5 Raman spectra of the (a) as-prepared, (b, c) vacuum annealed and (d) air annealed deposits (b) 300°C, (c) 500°C, (d) 300°C

depicted in Fig. 33.1b; a comparison with the spectral database revealed the formation of crystalline syn-romarchite SnO (PDF 06-0395) as the only crystalline phase present in the solid deposit. This crystalline phase is tetragonal with the symmetry space group P4/mnm.

Both Raman and FTIR spectra of the as-prepared deposit show peaks different from those of the SnO₂ phase presented in the previous part. The Raman spectrum (Fig. 33.5a) shows intense peaks centered at 125 and 215 cm⁻¹. The corresponding FTIR spectrum (Fig. 33.6a) shows two broad bands at 407 and 507 cm⁻¹ that could be ascribed to the tin monoxide [12,13].

Samples heated to 300°C and 500°C in vacuum or in the presence of air show a different behaviour. Heating in air to 300°C leads to the formation of SnO₂ by oxidation, and the bands characteristic for SnO₂ are observed in both Raman (Fig. 33.5d) and FTIR spectra. The colour changes to white due to a complete oxidation.

On the other hand heating in vacuum leads to new bands, recognized by XRD (Fig. 33.1c) as a mixture of the cassiterite SnO₂, romarchite SnO and tetragonal β-Sn.

Raman and FTIR spectroscopies were used to follow the temperature changes. The as-prepared sample heated to 300°C in vacuum is almost stable, only one new and broad band centered at 679 cm⁻¹ is visible in the FTIR spectrum (Fig. 33.6b). This minor structural change has no influence to the Raman spectrum (Fig. 33.5b). Increased temperature leads to an almost complete structural change, accompanied by a decrease of the former bands and the appearance of new ones. In the Raman spectrum new bands at 170, 552 and 742 cm⁻¹ have appeared (Fig 33.5c). The former bands of SnO almost disappeared, and broad bands between 600 and 750 cm⁻¹ are observed in the FTIR spectrum. In this broad band we can expect contributions of the bands recognized in the SnO₂ sample (see Fig. 33.3). The inset

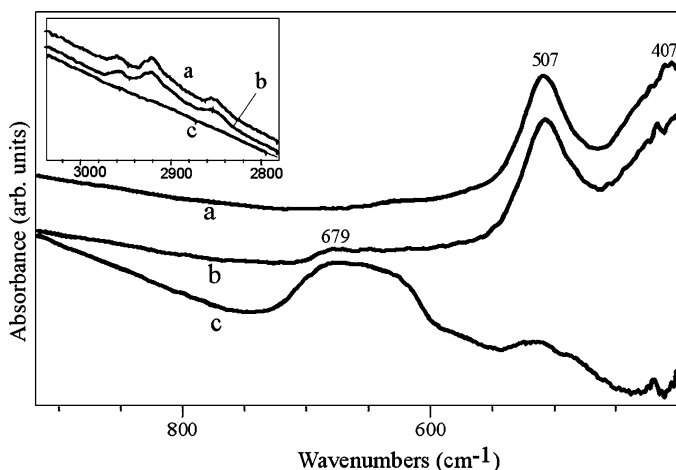


Fig. 33.6 FTIR spectra of (a) as-prepared and (b,c) vacuum annealed deposits (b): 300°C, (c): 500°C for 2 h)

of Fig. 33.6 shows the C-H stretching region of the FTIR spectrum. The bands represent C-H vibrations in $-\text{CH}_3$ groups which means that under incomplete oxidation conditions methyl groups are preserved. Even at 300°C they are stable; at higher temperatures (500°C) the methyl groups are released (probably as methane) or decomposed to graphite (higher intensity of the $1,600\text{ cm}^{-1}$ band in the Raman spectra). The brown colour of the as-prepared deposit has changed by annealing in vacuum to black as a consequence of the observed graphitization. The formation of graphitic carbon is confirmed by intense Raman bands centered at $1,375$ and $1,588\text{ cm}^{-1}$.

The results observed could be explained by disproportionation of tin monoxide. It disproportionates under heating to Sn and SnO_2 , but a Sn_3O_4 phase is sometimes also observed. Raman peaks 145 and 171 cm^{-1} are reported for this Sn_3O_4 phase [14]; similar bands are visible in our spectrum (170 cm^{-1} and a shoulder at about 140 cm^{-1} , Fig. 33.5b). The bands at 552 and 742 cm^{-1} thus should be regarded as further Raman vibrations of the Sn_3O_4 phase. Based on the comparison of the Raman and FTIR spectra of the vacuum heated SnO we can conclude that the band at 679 cm^{-1} in the infrared spectrum belongs to this intermediate Sn_3O_4 phase.

TEM analysis shows the formation of nanoparticles with diameters of about 100 nm which are of nanocrystalline nature as seen from the ED pattern (Fig. 33.4b).

Characterization of TiO_2 -Doped SnO_2

The reaction of $\text{Sn}(\text{CH}_3)_4$ and $\text{Ti}(\text{Oi-C}_3\text{H}_7)_4$, performed in a reaction cell heated to 100°C in excess of oxygen affords a white solid deposit and a gaseous mixture of CO_2 and water as oxidation products. Two different ratios of the tin and titanium

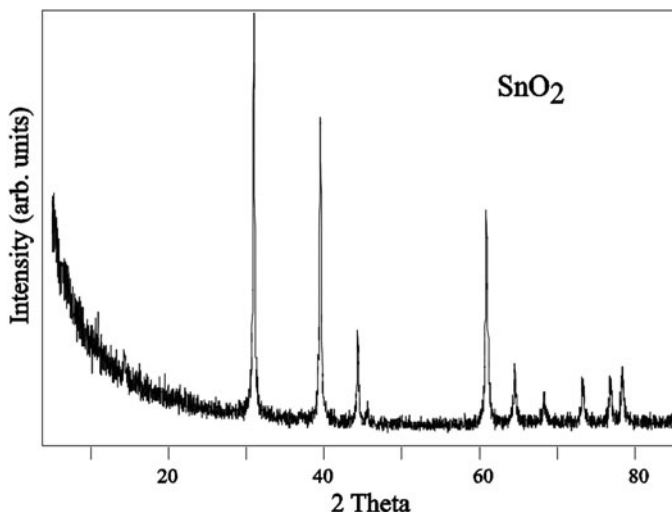


Fig. 33.7 X ray diffraction pattern of $\text{SnO}_2/\text{TiO}_2$ nanoparticles

precursors were studied. The deposits had a loose adhesion to the substrates. The corresponding bulk compositions as revealed by EDX are $\text{Sn}_{1.00}\text{Ti}_{0.03}\text{O}_{1.92}$ and $\text{Sn}_{1.00}\text{Ti}_{0.05}\text{O}_{1.89}$. X-ray diffraction shows formation of cassiterite SnO_2 as the only crystalline phase (Fig. 33.7). Raman spectroscopy is a more powerful technique for the identification of TiO_2 phases due to its higher sensitivity. The Raman spectra of the as-prepared and annealed samples (300°C and 500°C in air) also show evidence for the presence of crystalline SnO_2 . With increasing annealing temperature the bands of tetragonal SnO_2 are stronger (252 , 639 , 700 and 781 cm^{-1}), and a new band centered at 481 cm^{-1} appears (Fig. 33.8). But it seems that this band is not a result of titanium dioxide crystallization, but only of a better organization of the SnO_2 . A similar weak band with a Raman shift of 473 cm^{-1} was observed after ball milling of SnO_2 [11].

Much work was done on SnO_2 -doped titania. It seems that tin dioxide stabilizes the anatase phase; the transformation of anatase to rutile appears at higher temperatures [15,16]. On the other hand, some authors show that tin dioxide promotes the anatase to rutile transformation through a solid solution of $\text{TiO}_2/\text{SnO}_2$ [17]. Pure amorphous TiO_2 is known to crystallize as anatase at temperatures between 250°C and 450°C . At higher temperatures anatase transforms to rutile. In our sample no rutile is observed at 500°C , although some authors state that the presence of tetragonal SnO_2 may promote the rutile TiO_2 crystallization. Based on XRD and Raman results we may conclude that our sample contains tetragonal SnO_2 along with amorphous TiO_2 (or an amorphous solid solution of $\text{SnO}_2/\text{TiO}_2$). Transmission electron microscopy shows nanoparticles with diameters of about 40 nm . The electron diffraction pattern also confirms the presence of cassiterite SnO_2 as the only crystalline phase; diffuse rings give evidence for the presence of amorphous material.

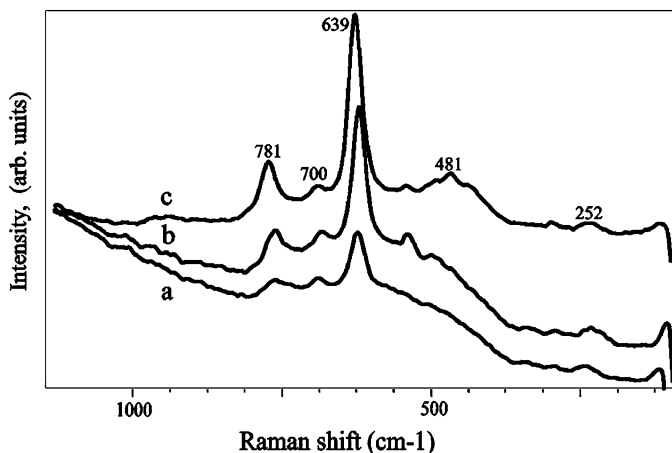


Fig. 33.8 Raman spectra of $\text{SnO}_2/\text{TiO}_2$: (a) as-prepared and annealed to (b) 300°C and (c) 500°C in air

Conclusions

The technique presented in this work seems to be very efficient for the preparation of metal oxides and mixed oxides from organometallic precursors. Direct preparation of stoichiometric tin dioxide, tin monoxide and mixed tin/titanium dioxide was presented. Structural changes caused by annealing at 300 and 500°C in both vacuum and air were studied by means of XRD and Raman spectroscopy. Transmission electron microscopy shows that nanoparticles possess a mean diameter about 40 nm.

Acknowledgements The support of the Grant agency of the Czech Republic No. 203/09/1117 is gratefully acknowledged.

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Chapter 34

Polymer Cholesteric Liquid Crystal Flakes as New Candidates for Display and Sensor Applications

Anka Trajkovska Petkoska

Abstract In this paper polymer cholesteric liquid crystal (PCLC) flakes will be introduced as a novel form of particles for active applications, like electronic paper displays, as well as for sensors. The concept of electro-optic applications based on PCLC flakes is very attractive, because it offers a possibility for *thin, reflective, lightweight, flexible devices that use little power*. The uniqueness of PCLC flakes lies in their bright, saturated and full color capability, as well as their circular polarization effects, without the need of additional color filters and polarizers.

Keywords Polymer cholesteric liquid crystals (PCLC) · PCLC flakes · Dopants · Display applications · PCLC flake-based sensors

Introduction

Polymer cholesteric liquid crystal (PCLC) flakes have unique electro-optical properties, such as *selective reflection and circular polarization* due to their intrinsic cholesteric nature, which are useful for numerous passive and active electro-optic applications like electronic paper displays, sensors or security applications.

In the text below, a brief overview of liquid crystal materials will be given. *Liquid crystals* (LCs) represent a special type of condensed matter, which falls between disordered isotropic liquids and 3-D-ordered solid crystals. They possess the fluidity of a liquid phase, and have at the same time a certain degree of the orientational and/or positional order as the crystal lattice. In general, LC materials consist of highly-anisotropic rod-like or discotic molecules. The anisotropic

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molecular shape and the presence of a certain degree of order are responsible for the significant anisotropic optical, electrical, magnetic, and mechanical properties. According to the microscopic order and the interaction between the molecules, there are different classes of LCs phases, such as nematic, cholesteric, smectic and discotic LCs [1,2]. The LC materials presented in this work are *thermotropic cholesteric* LCs [3,4]. *Cholesteric LC (CLCs)* consist of uniaxially-oriented LC molecules within the nematic sublayers with an orientation described by the so-called *director*. The director rotates in a helical fashion around an axis perpendicular to the sublayers with the period p (*pitch length*) [1]. The rotational direction defines the *handedness* of the cholesteric phase, which can be *left-* or *right-handed* [4,5]. The pitch length and the helical twist sense together with the refractive index of the cholesteric material determine the optical properties of this mesophase, among which is the selective reflection. “*Bragg-like*” *selective reflection* from a CLC film occurs at wavelengths that satisfy the following relationship [6]:

$$\lambda_0 = \bar{n}p \left[\cos \frac{1}{2} \left\{ \sin^{-1} \left(\frac{1}{\bar{n}} \sin \phi_i \right) + \sin^{-1} \left(\frac{1}{\bar{n}} \sin \phi_s \right) \right\} \right]$$

for $\phi_i = \phi_s = 0$ and $\lambda_0 = \bar{n}p \cos \phi$.

Here, λ_0 is the wavelength at which the reflection occurs [7], $\bar{n}$ is the average refractive index given as

$$\bar{n} = \sqrt{(n_e^2 + 2n_o^2)/3}$$

n_e and n_o are the extraordinary and ordinary indices of refraction of the nematic sublayers, respectively, and ϕ_i and ϕ_s are the angles of incidence and observation, respectively.

The bandwidth of selective reflection, $\Delta\lambda$ is determined by the birefringence of the material Δn , expressed as

$$\Delta l = p\Delta n \text{ and } \Delta n = n_e - n_o$$

When *circularly polarized light* having the same handedness as that of the cholesteric film incides on the cholesteric stack, it will be totally reflected and maintain the handedness of the incident beam, while circularly polarized light of the opposite sense will be transmitted undisturbed. Outside the selective reflection band, light incident on a cholesteric film will be unaffected regardless of its polarization state [8]. The reflected color of a CLC film (which can be from the deep UV to the far IR region) depends on the chemical structures of the LC molecules, their orientations, the nature and concentration of chiral dopants, the thickness of the CLC layer and other factors, such as temperature, pressure, magnetic and/or electric fields [5]. The helical molecular order can be fixed if the degree of freedom of molecular motion is limited; e.g. by high molecular weight CLC materials or by cross-linking. This means that the

selective reflection color can be fixed in a class of CLCs known as *polymer cholesteric liquid crystals (PCLCs)*. The long-chain nature of PCLCs may result in glass-formation, ease of processing into large-area, monodomain, defect-free films, and good mechanical and thermal stability [9,10]. PCLC materials can be, also, used in form of particles, so-called flakes. Most of the techniques for the preparation of films and irregularly shaped flakes are covered in previous reports [10–12]. Due to the disadvantages of irregularly shaped flakes (random shapes, no control over their dimensions, great thickness variations, sharp edges that causes light scattering), it was of crucial importance to find a way to shape the PCLC material or film into shaped particles (flakes) of predetermined dimensions [13–16]. The method of producing tailored PCLC flakes will be given in the next section.

PCLC flakes have the potential to be used in numerous passive and active optoelectronic applications. *Passive applications* of flakes include the use in the military as decals in decorative/cosmetic inks and paints, in document security, in stereoscopic printing, and as retarders, waveplates, filters and polarizers. In *active applications*, PCLC flakes can be used for camouflage of military vehicles, smart windows, color filters, multi-color flexible displays like “electronic papers”, smart cards, electronic labels and billboard signs. The concept of electronic paper and sensors based on PCLC flakes will be given in the text below. It offers possibility for thin, reflective, lightweight, flexible devices that use little power [2,10,17–20].

Materials and Experimental

Shaped PCLC Flakes

To overcome the flake size variations, and consequently, to be able to control and model the flake behaviour in an electric field, a method for manufacturing shaped flakes based on the *soft lithography* technique was invented by the present author (Fig. 34.1) [13–16]. Shaped flakes are produced in a flexible polydimethylsiloxane (PDMS) mold with a pattern on it. Namely, a patterned silicon wafer is used as a rigid master on which PDMS elastomeric material is casted (Fig. 34.1a). After hardening, the PDMS replica is peeled off from the silicon wafer to give an inverse replica of the structured wafer. Such a replica constitutes a flexible mold for forming shaped flakes (Fig. 34.1d). Depending on the design on the patterned silicon wafer (Fig. 34.1b, c), different shapes of flakes (Fig. 34.2) can be manufactured in the PDMS molds. Different techniques were used for the characterization of the shaped PCLC flakes [13,14]. They were characterized in terms of their shape, surface structure and uniformity using polarized optical microscopy (POM, Fig. 34.2), scanning electron microscopy (SEM, Fig. 34.3), white light interferometry, and other techniques.

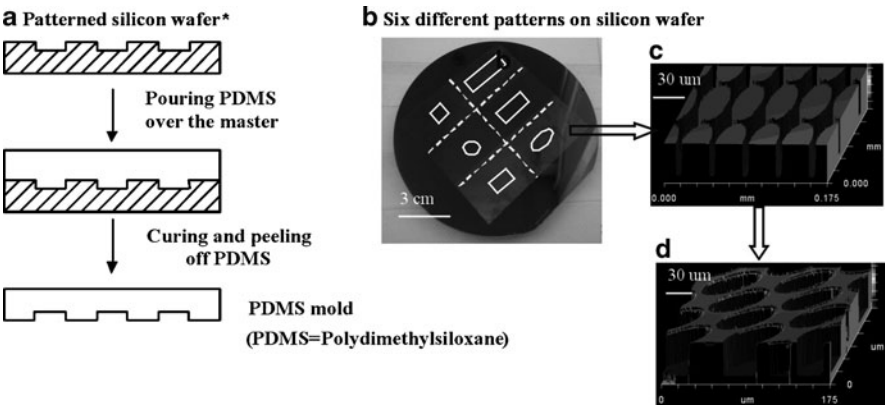


Fig. 34.1 (a) Scheme of the process to produce a PDMS mold on a rigid patterned silicon wafer, (b) patterned silicon wafer, (c) example of ellipsoidal shaped pattern on the silicon wafer scanned with a white light profilometer, (d) white light profilometer image of a PDMS mold as an inverse replica of the patterned silicon wafer shown in (c)

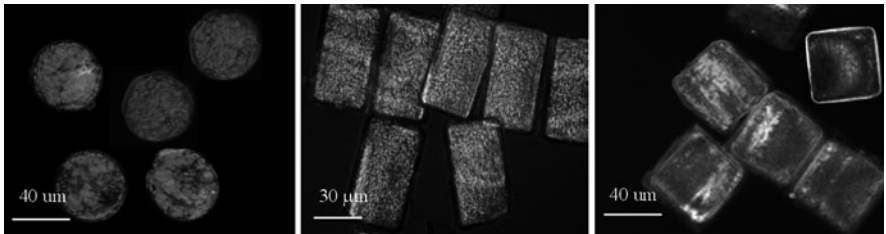


Fig. 34.2 Shaped flakes characterized by POM in the reflective mode with crossed polarizers (Under illumination at near normal incidence, the flakes appear red, green and blue (from left to right))

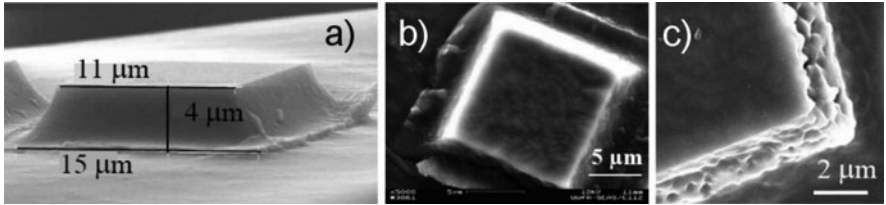


Fig. 34.3 Shaped flakes characterized by SEM: (a) dimensions of a square shaped flake made of single PCLC material, (b) top view of the square flake, (c) shaped flake made of multiple layers of different PCLC materials

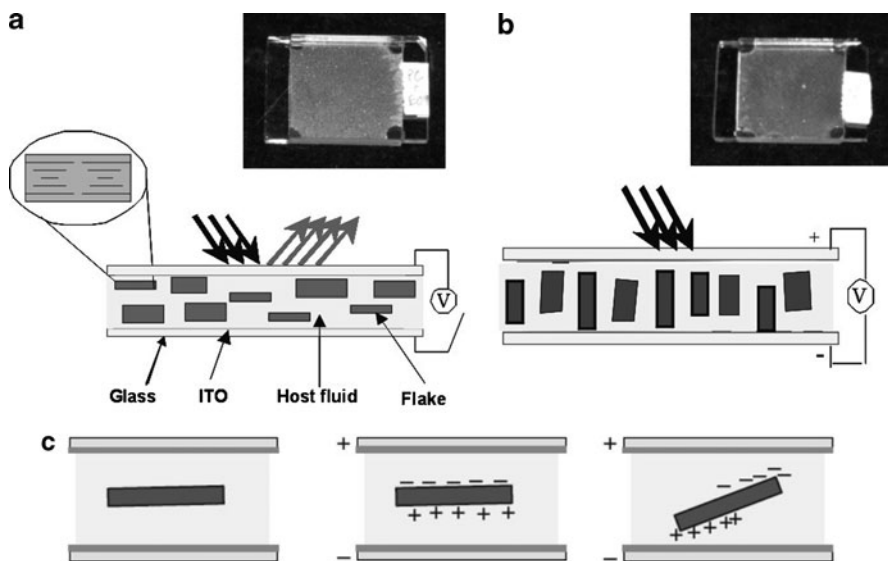


Fig. 34.4 Typical cell device filled with a suspension of flakes and host fluid: (a) before, and (b) after application of an electric field. Insets: photos of actual cell devices: before (reflective-bright state) and after application of the field (dark-nonreflective state); (c) Generation of a dipole moment on a flake particle when an electric field is applied (Maxwell-Wagner polarization)

Electro-Optical PCLC Devices

An electro-optic device consists of a cell assembled of two indium tin oxide (ITO) covered glass substrates, which is filled with a suspension of PCLC flakes in a suitable host fluid (e.g. propylene carbonate, gamma butyrolactone, ethylene glycol) [13,14]. When an alternating current (a.c.) field is applied to the test device (shown in Fig. 34.4a), flakes that initially lie nearly parallel to the cell substrates rotate for 90° around their longest axis. For example, an electric field of $\geq 10 \text{ mV}_{\text{rms}}/\mu\text{m}$ (*rms*: root mean square) between 10 and 1,000 Hz initiates flake reorientation with a temporal response on the order of ten to hundreds of milliseconds. The selective reflection colors start to shift and then diminish as the flakes rotate (Fig. 34.4b) [13–15].

Results and Discussions

The results accomplished in this work are summarized into three parts:

1. The mechanism leading to the flake reorientation in a host fluid (a fluid with a relatively high dielectric constant and a low/moderate conductivity) under the applied a.c. field is due to *Maxwell-Wagner polarization*. Charges accumulate

on the boundaries between the flake and the host fluid, inducing an interfacial surface polarization and a dipole moment (Fig. 34.4c) [13,14,21]. The interfacial polarization of PCLC flakes allows the required driving voltage for their 90° reorientation to be lower than for other competitive technologies (e.g. E-Ink and Gyricon, where electrophoresis of charged particles with a permanent dipole moment is the main operation mechanism [18,19]). Due to their intrinsic cholesteric nature, *PCLC flakes provide bright, saturated, full color capabilities and circular polarization effects without the need of additional color filters and polarizers placed on rigid or flexible substrates* (Fig. 34.5a, b). They can reach more than 50% reflectivity (e.g. by multilayers of various PCLC materials as it was shown in Fig. 34.3c) with switching times from tens to hundreds ms and fields of tens of $\text{mV}/\mu\text{m}$ of the cell thickness. Devices based on PCLC flake/host systems envisioned for sensor applications can work with visible light switching (bright-dark states) by using voltage-coded flakes, e.g. flakes with different shapes/sizes or flakes made up of different materials, and/or changing the pitch length by exposing to vapours from certain organic chemicals (Fig. 34.5c) [13,14]. Such sensors can be made of PCLC flake materials that are sensitive to particular vapors. For instance, the vapors may cause “swelling” of the material, and thus, changes in the helical twist of the nematic sublayers.

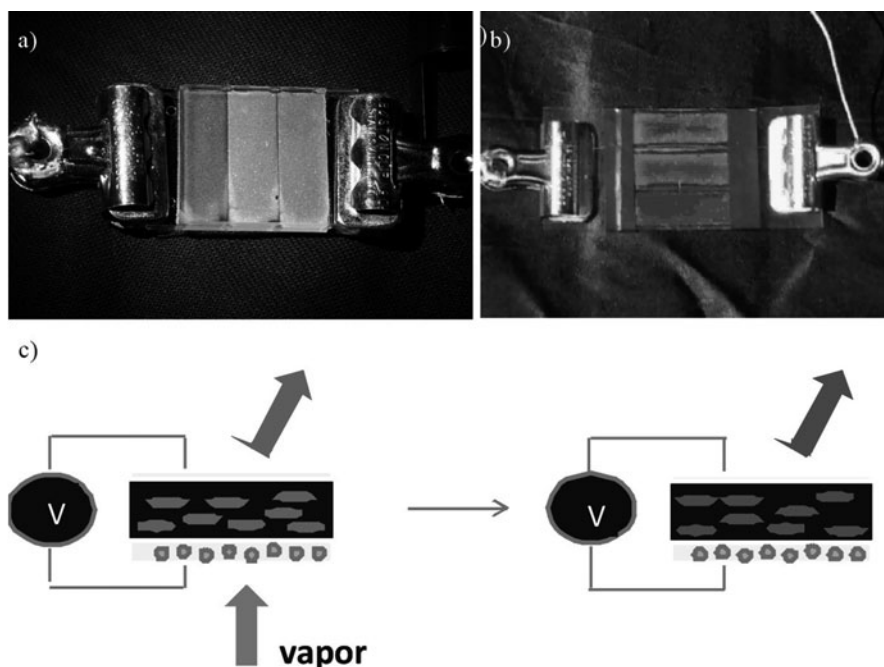


Fig. 34.5 Three-color PCLC flake devices: (a) on rigid, (b) on flexible substrates (cell thickness $\sim 100\ \mu\text{m}$, ITO-coated Mylar substrates); (c) vapour-sensitive device based on PCLC flakes (Note: the substrates of the cell are vapour porous)

Changes in the helical twist, i.e. changes in the pitch length, causes a change of the flakes' reflected color.

2. The electro-optical behavior of PCLC flake reorientation in a suitable host fluid under an applied electric field was mathematically modeled with the software package MATLAB Simulink [13,22]. The model was based on the assumption that the driving force for the flake reorientation is a combination of three torques in the system: *electrostatic, hydrodynamic and gravitational torques*, when an electric field is applied. (Note: the moment of inertia was calculated to be several orders of magnitude smaller than the other torques and was therefore neglected, as well as no translational motion of the flakes in the system was observed). The predicted model data agrees very well with the experimental observations without using any adjustable parameters. The reorientation time of the flake was found to be a function of: (a) shape and size of the flakes, (b) PCLC material (doped vs. undoped, crosslinked vs. non-crosslinked PCLC), (c) the host fluid properties, and (d) the parameters of the applied electric field [13,14].
3. The flake work was extended to the d.c. (direct-current) regime by *doping the PCLC material* used for flake manufacturing. The goal for PCLC doping was mainly to enhance the dielectric properties of the materials which are hosted in fluids like insulating silicone oils (non-expensive, long-lasting, stable properties over a long period of time, etc.). Dopants used in this work were: (a) carbon-based dopants (carbon blacks, single-walled and multi-walled nanotubes); (b) metal-based dopants (Al flakes, ITO, carbonyl iron); and (c) inorganic dopants (BaTiO_3 , TiO_2), which varied from nano- to micrometer dimensions [13,14,22–24].

Acknowledgements This work was done at the University of Rochester, Laboratory for Laser Energetics in Rochester, NY, USA. The author thanks her supervisor Professor Stephen D. Jacobs, PhD, and his team: Mr. Kenneth Marshall and Dr. Tanya Kosci for their supervision and guidance. The author also acknowledges the Laboratory for Laser Energetics (University of Rochester, Rochester, NY) for a Horton Fellowship support.

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Chapter 35

Properties of Vanadium Bronzes Synthesized by Different Methods

Albena Aleksandrova, B. Banov, and A. Momchilov

Abstract Vanadium bronzes are extensively studied mainly due to the reversible Li^+ insertion into its structure but also to their interesting redox, catalytic, conductive or magnetic properties. They can be synthesized via different methods such as melting, solid-state reaction (SSR), “wet” chemistry (sol–gel) or self-combustion reactions (SCR). Small-size particles of the vanadium bronze $\text{K}_2\text{V}_8\text{O}_{21-y}$ were obtained by the “wet” chemistry synthesis method. An additional treatment method has been developed that improve some of the main electrochemical characteristics of these materials such as the active cathode mass. The changes of the physico-chemical property after this treatment were studied. We consider that vanadium bronzes treated by this method could be applied as sensor materials with enhanced properties.

Keywords Vanadium bronzes · Physicochemical properties · Hydrothermal activation

Introduction

Vanadium based compounds are extensively studied because of their interesting redox, electrochemical [1,2], electrochromic, thermochromic [3], catalytic [4] and magnetic properties [5–7]. The oxides exhibit an anisotropy of both electronic [5] and ionic properties and appear to be good candidates for many applications. For example, among the oxides, alkaline vanadium bronzes (MV_3O_8 , $\text{M} = \text{Li}, \text{Na}, \text{K}$) are used as active electrode material in rechargeable batteries, especially Li-ion batteries [1,8]. Some other vanadates show catalytic activities in the oxidative dehydrogenation of hydrocarbons. Most of these materials are examined as

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promising materials for chemical sensors due to the growing risks of dangerous gas escape, water pollution etc. Polycrystalline V_2O_5 , $V_2O_5 \cdot nH_2O$ xerogels and vanadium bronzes are considered as promising sensor materials for the quantitative detection of atmospheric humidity [5], ethanol vapour [9], nitrogen dioxide, amines [10] etc. The properties of these materials to be used for sensors are determined by their physicochemical characteristics as a consequence of the preparation methods and techniques. The aim of this work was to obtain vanadium bronzes by a “wet” chemistry synthesis method.

Experimental

Vanadium bronzes $K_2V_8O_{21-y}$ were obtained via the “wet” chemistry method developed by our group. The method consist of the following steps: Preparation of the precursor (solid product) by drying $NH_4V_3O_8$ and KOH solutions mixed in the proper ratio (ratio K:V = 1:4). To this end the precursor was heated to 500°C for 72 h. This temperature is consistent with the equilibrium phase diagram between V_2O_5 and KVO_3 [11]. After the heating process the product obtained was ball milled for 1 h.

Additionally, the synthesized samples were treated by a special method developed by our group. The sample was placed in a porcelain crucible and hydrothermally treated at 200°C for 24 h in a hermetically sealed steel-device (autoclave). The bottom of the autoclave was filled up with distilled water so that the product was prevented from direct contact with the water. During the hydrothermal activation process the water vapor pressure corresponds to 16 atm. This pressure is high enough to allow the insertion of water molecules into the structure of the vanadium bronze. The amount of the incorporated water depends of the type of the bronze and varies from 0.5 up to 3 water molecules per vanadium bronze unit formula. The water vapor was adsorbed on the material powder during cooling down the autoclave in the furnace. Thereafter, the sample obtained was dried at 100°C to remove the moisture. Heating at 200°C to extract most of the incorporated water molecules from the compound structure was applied when it was to be used as an active material for Li-ion batteries.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed in a porcelain crucible in air with a heating rate of $10K\ min^{-1}$ with a Stanton Redcroft STA 1500 analyzer in order to optimize the synthesis conditions of the precursor. The chemical composition and the state of the compounds with a K:V = 1:4 ratio were studied using X-ray photoelectron spectroscopy (XPS). The XPS studies were performed with an Escalab MkII system (England) with Al K_{α} radiation ($h\nu = 1486.6\ eV$); the total instrumental resolution was $\sim 1\ eV$. X-ray diffraction (XRD) analysis was carried out with a Philips APD 15 diffractometer with Cu K_{α} radiation. The morphology of the sample was investigated with scanning electron microscopy (JEOL Superprobe 733).

Results and Discussion

With the aim to evaluate the exact experimental heating conditions for the production of $K_2V_8O_{21-y}$ compounds we conducted a thermal analysis. A solid product prepared by drying $NH_4V_3O_8$ and KOH solutions mixed in the proper ratio was heated with a constant rate 10 K min^{-1} to 500°C . In Fig. 35.1 the results obtained from thermal-gravimetric analysis and differential thermal analysis are plotted. Both curves demonstrate that the chemical interaction between $NH_4V_3O_8$ and KOH proceeds at temperatures in the range from 350°C to 500°C . On the base of these results we selected the temperature of 500°C as adequate to obtain $K_2V_8O_{20.8}$ compounds, which is in agreement with the phase diagram given by Volkow [11].

XPS analysis was used to investigate the chemical composition and bonding state of the compound with a ratio $K:V = 1:4$. The spectra of K, V and O are presented in Fig. 35.2. The K 2p peaks indicate that the potassium exists in the state of K^+ (Fig. 35.2a). High-resolution XPS spectra further confirm that vanadium only shows an oxidation state of V^{5+} . Peaks representing other valence states are absent (Fig. 35.2b).

The XRD phase analysis of the sample synthesized with a ratio of $K:V = 1:4$ is based on JCPDS card 24-0906 and Poushard's data. Poushard gives two different phases in the " $V_2O_5 - KVO_3$ " phase diagram: $K_2V_8O_{20.8}$ and $K_2V_8O_{21}$ [12]. The data from card 24-0906 are for the non-stoichiometric compound $K_2V_8O_{21-y}$. Figure 35.3a shows the pattern of the sample compared with the data mentioned above. Most of the sample pattern peaks coincide with those from card 24-0906 and Poushard's data for the compound $K_2V_8O_{20.8}$; so it can be concluded that the synthesized compound is $K_2V_8O_{21-y}$ where y is between 0 and 0.2. Then the sample was hydrothermally treated in two subsequent steps up to 200°C . Comparing the diffractogram of the untreated compound with that of the hydrothermally treated one, it was observed that the two main peaks shift to lower angles (at about $2\theta = 8.17^\circ$) (see the insets in the diagrams); this is valid for other peaks as well. This is most probably due to the insertion of water molecules into the structure of the sample. The lower peaks intensity is an indication of crystalline degradation and

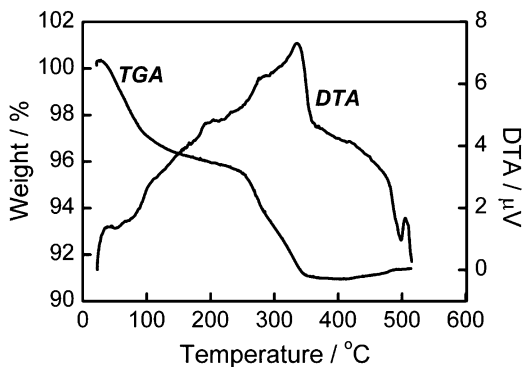


Fig. 35.1 TGA/DTA curves of the precursor used

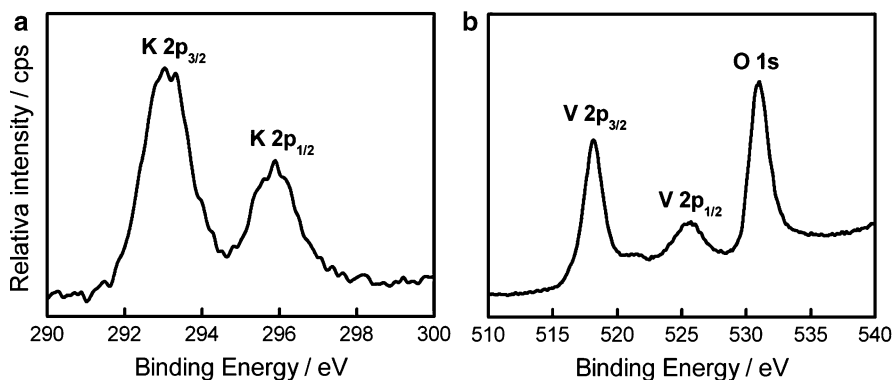


Fig. 35.2 High-resolution XPS spectra of the synthesized compound: (a) K2p; (b) V2p and O1s

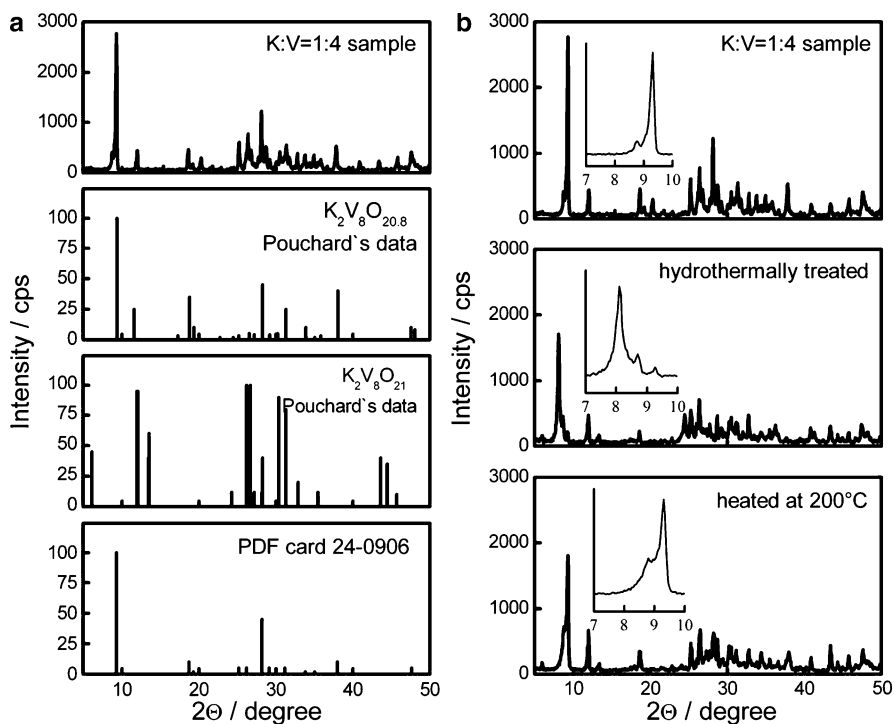


Fig. 35.3 XRD pattern of (a) a K:V = 1:4 ratio sample comparison with Pouchard's data for $K_2V_8O_{20.8}$, $K_2V_8O_{21}$ and JCPDS card Number 24-0906; (b) before treatment, after hydrothermal activation and heating at 200°C

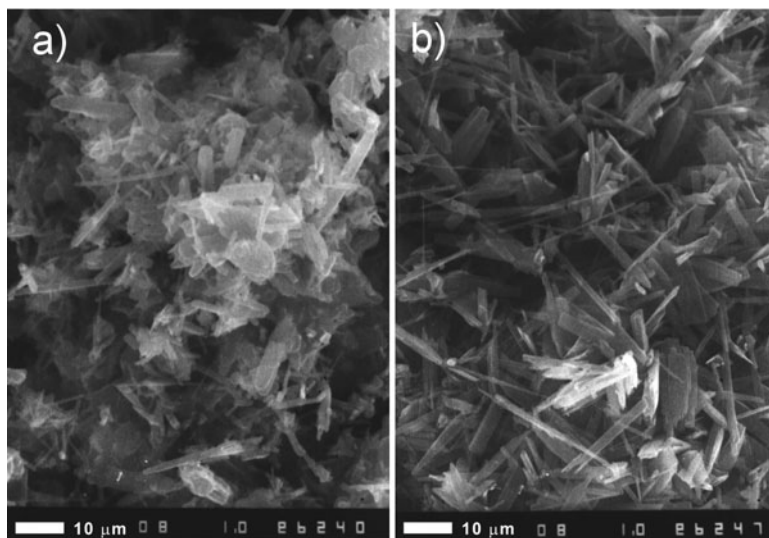


Fig. 35.4 SEM images of an untreated (a) and a treated (b) sample with a ratio K:V = 1:4

decreasing of the particles size. After heating to 200°C the larger part of the inserted water is removed, and the two main peaks restore their positions to the previous angles (Fig. 35.3b). Such changes of the peak positions have been previously described for LiV_3O_8 subjected to an identical treatment procedure [1]. This similarity is an indirect indication that the potassium vanadate structure is layered like that of lithium vanadate. Such a layered structure causes an anisotropy of the conductivity along and across the layers; thus such compounds could substitute vanadium oxides [5]. Both water-inserted vanadium bronzes (potassium and lithium) can be applied in moisture sensors like vanadium xerogels [5].

The microstructure of both hydro-thermally treated and untreated materials was examined by means of scanning electron microscopy. The SEM images obtained are presented in Fig. 35.4. It is clearly evident that the hydro-thermal treatment results in a more uniform distribution of detached dendrite-shaped crystals. The manner of particle splitting and the shape of the particles, compared to that of lithium bronze [1], are also an indirect indication for a layered structure of the compound.

Conclusions

The potassium bronze $\text{K}_2\text{V}_8\text{O}_{20.8}$ most probably possesses a layered structure, which causes anisotropy of some physical properties. This compound could be applied in different sensors as a replacement for vanadium oxides. The hydro-thermal activation process developed by our group can insert water molecules into the structure of the vanadium bronzes. The water content of such compound

starts from 0.5 and reaches up to 3 mol water per vanadium bronze unit formula depending on the treatment temperature and the type of the bronze. The hydrothermally treated bronzes could replace vanadium oxide xerogel that is used in moisture and other sensors.

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Part V
Sensors and Biosensors

Part V.1

Optical Sensors

Chapter 36

Semiconductor Lasers for Sensor Applications

Christian Gilfert and Johann Peter P. Reithmaier

Abstract Starting with a short historical synopsis this paper gives a brief introduction into semiconductor lasers. The working principles and the necessary fabrication technology are examined. Semiconductor laser systems offer unique characteristics, rendering them superior to other types of lasers. By combining different compound semiconductors a huge range of wavelengths spanning from ultra-violet (UV) to the far-infrared (FIR) can be covered. Hence, by applying sophisticated bandgap and photonic engineering, tailored far-infrared lasers are able to address a vast amount of applications. The existing semiconductor laser technology is suitable to meet the requirements of highly sensitive optical sensing for various applications.

Keywords Compound semiconductors · Diode · p-n junction · p-i-n junction · MBE · MOVPE · Laser · Sensors · Quantum well · Quantum dot · Quantum cascade laser

Introduction and Brief Historical Synopsis

Since the development of the first semiconductor laser many applications became reality, such as optical storage devices (CD, DVD, Blu-Ray) or optical high speed network connections established by fiber cables and driven by semiconductor lasers. Introducing the laser to other well-known applications improved their performance by exploiting the very special properties of laser light. This makes laser systems interesting for material processing techniques as welding and drilling allowing for higher accuracy, throughput and quality of the fabricated elements.

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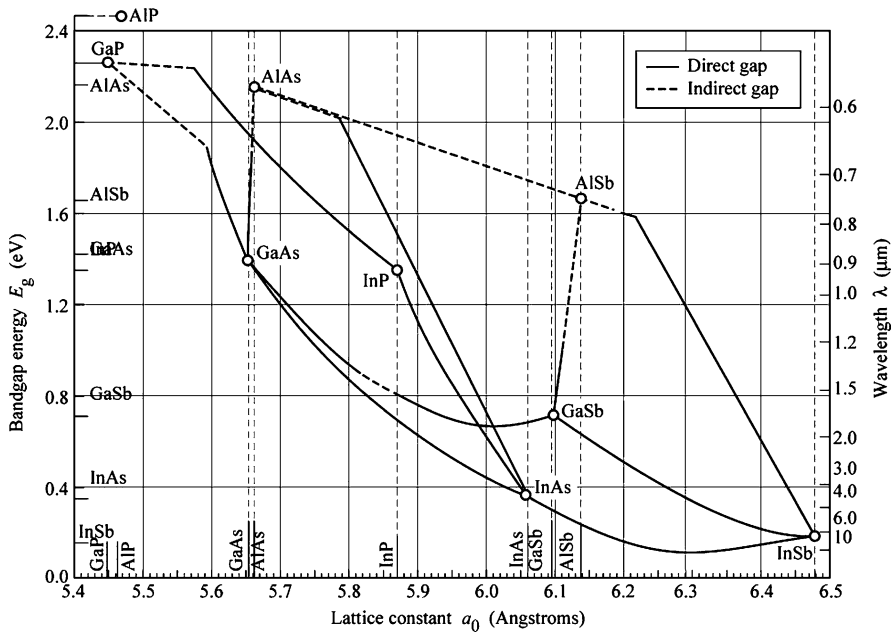


Fig. 36.1 Bandgap vs lattice constant for different compound semiconductors (Figure taken from [1])

Recently also medicine tends to use laser systems for new applications, such as imaging diagnosis, ablation and minimal-invasive surgery.

The advantage of semiconductor lasers compared to other laser systems is their small size of typically sub-millimeter dimensions per single emitter and their versatility. By combining different III-V semiconductor materials, lasers, covering a huge wavelength regime from UV (ultra violet) to FIR (far infrared) with output powers from some milliwatts up to several watts per single emitter can be fabricated (Fig. 36.1).

These features allow cost-effective packaging, cooling and housing of the lasers for generic purposes. Stacks of packaged laser bars offer output powers in the range of kilowatts, while having dimensions of a cup [2]. Furthermore, semiconductor lasers are the only type of laser, which can be driven directly by an applied current. Wall-plug efficiencies in the range of 40–60% are typical, rendering the systems both economically and ecologically interesting. Other types of laser, such as gas- or solid-state lasers only achieve around 1% efficiency. Lifetimes of qualified diode lasers are reaching up to hundreds of years. A clear disadvantage of semiconductor lasers is their beam profile. Since the output front of an edge-emitting diode laser is rectangular and very small, the beam profile is elliptic and has a large divergence angle. This creates problems while transporting the laser light to where it is needed or couple it into an optical fiber.

The first diode laser invented in 1962 by Robert Hall et al. was nothing else than a degenerately-doped p-n diode forward biased to flat-band conditions [3]. The basic design has changed in order to overcome the drawbacks like high threshold

currents, low output powers and life-times. Today a diode laser is comprised of a “p-i-n” structure with highly-doped p and n regions and an undoped i region. The i region consists of a low bandgap material while the p and n regions consist of high bandgap materials. This double hetero-structure (DH) design was first proposed by Herbert Kroemer in 1963 and then implemented by Alferov et al. in 1970 [4,5]. With this ground-breaking idea it was possible to fabricate diode lasers, which work at room temperature in continuous-wave (cw) mode. For their work both were awarded with the Nobel Prize in physics in the year 2000.

In the first diode laser, which was comprised of a normal p-n junction, electrons and holes could easily move through the junction and reach the opposite site instead of recombining and producing photons. The double hetero-structure principle used instead provides two features. First, electrons and holes face a barrier when reaching the opposite hetero junction and are thus confined in the i region, which reduces leakage currents and internal losses (see Fig. 36.2 taken from [6]).

Second, the refractive index profile of the DH structure forms a vertical waveguide for the produced photons. Moreover, the i-region is undoped which dramatically decreases impurity scattering and recombination with the dopants. These two points reduce the internal absorption inside the laser structure and make cw operation at room temperature possible [7]. In 1977 the first quantum well laser was fabricated by N. Holonyak and co-workers [8,9]. The DH structure is maintained. The difference is the actively light producing area. It is nothing more than a thin film with a thickness smaller than the De-Broglie wavelength of the charge carriers. Since the volume of the active region is dramatically decreased by this step, threshold currents of quantum well lasers are much lower than that of bulk lasers. This step stimulated the commercial success of semiconductor lasers. Alongside the progress of epitaxial growth methods like molecular beam epitaxy (MBE) or metal-organic vapor phase epitaxy (MOVPE), which are able to deposit single atomic layers of different materials, ongoing achievements in semiconductor structuring were achieved. This led to the fabrication of the first quantum dot laser in 1994 at TU Berlin [10]. A quantum dot laser has the same p-i-n structure as a quantum well laser except for the active region. The thin film is replaced by small boxes of a

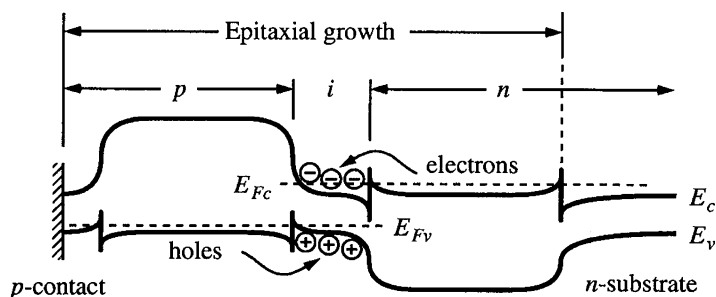


Fig. 36.2 Sketch of conduction and valence band of the double hetero-structure under bias conditions (taken from [6]). The p-i-n structure confines the charge carriers in the i-region, where they recombine instead of migrating to the electric contacts

material different from the surrounding material, called quantum dots. These quantum dots form three-dimensional potential wells, which completely confine the charge carriers. Together with other features quantum dots are proposed to have a huge impact on current applications and are likely to open up new ones, e.g. single-photon emission.

Semiconductor-based sensors are used in a variety of fields as many physical properties, such as temperature, pressure, chemical environment as well as electric and magnetic fields can be detected with tailored structures. However, this paper focuses on the utilization of semiconductor diode lasers for sensing applications. First, a short overview over the fabrication methods and physics of diode lasers will be given. A presentation of already existing as well as future technology is performed by exemplarily introducing typical applications.

Fabrication of Semiconductor Lasers

The fabrication of diode lasers is distributed into two parts. At first, the necessary epitaxial layers need to be deposited and complex structures such as gratings, ridges or photonic crystal structures are processed using lithographic methods and wet- as well as dry-etching techniques. Both steps offer several degrees of freedom to optimize the diode laser for different applications. During the epitaxial growth one is able to tailor the properties of the laser by bandgap engineering and the doping profile of the deposited layers. The active material inside the laser may be tailored by exploiting the unique features of structures, such as quantum wells or quantum dots. This engineering on the material level is continued by photonics engineering during the processing steps in order to fabricate a device completely tailored and adapted for a certain application. Of course, both fabrication steps are not independent of each other. Special etch processes may only work with specific materials, which limits the optimization potential on the material side.

Epitaxial Growth

The term “epitaxy” is a combination of two greek words “epi” (above) and “taxis” (in ordered manner). Hence, epitaxy describes deposition methods, in which the growing film adapts to the crystal structure of the substrate.

Usually semiconductor lasers are fabricated on single-crystal wafers of GaAs or InP. The layers that form the p-i-n structure of a laser are deposited using epitaxial techniques, such as MBE or MOVPE [11,12]. The use of such methods is unavoidable, since a well-defined crystalline structure free of defects and impurities is required to provide low carrier losses by non-radiative recombination, good electrical transport (low series resistance) and low optical absorption properties. The optical properties of quantum wells and quantum dots are very sensitive to the material composition

Fig. 36.3 Cross-sectional transmission electron microscopy (XTEM) micrograph of subsequently deposited layers of AlAs (dark rows) and GaAs (bright rows) demonstrating the monolayer precision of the MBE growth technique. Note, the AlAs layers are only one monolayer thick

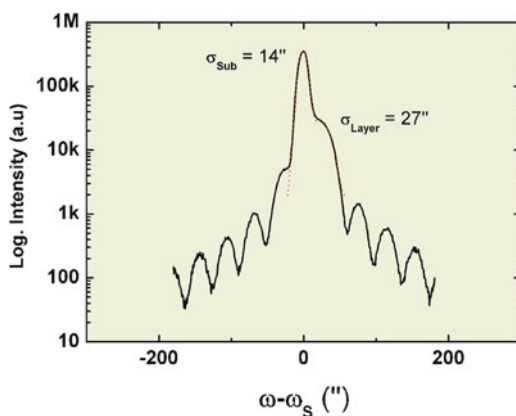
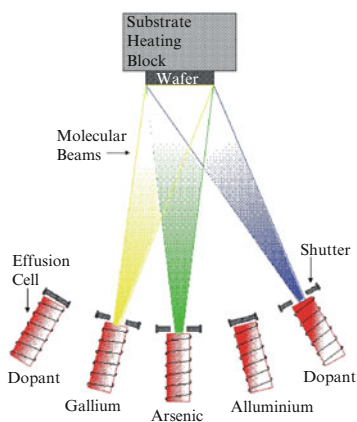
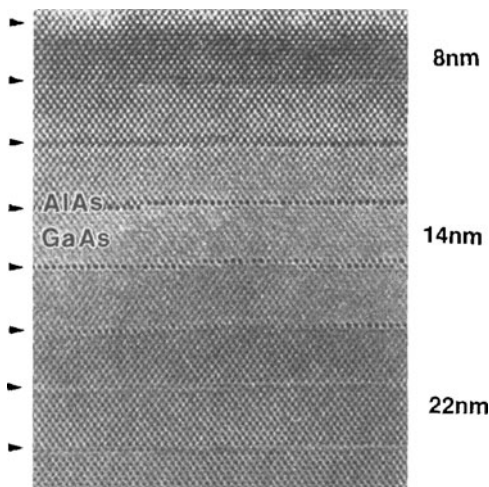


Fig. 36.4 *Left*: Sketch of an MBE chamber. The effusion cells are arranged around the rotating substrate. Due to the UHV conditions inside the chamber the molecules reach the surface without interference of residual gases. Opening and closing the shutters allows for a rapid change of the composition and enables sharp interfaces between different semiconductors materials. *Right*: XRD rocking curve of a 500 nm thick layer of $\text{In}_{0.528}\text{Al}_{0.238}\text{Ga}_{0.234}\text{As}$ grown on a $2''$ n-doped InP (100) wafer. The lattice-mismatch of the layer to the substrate amounts to $\epsilon = 10^{-5}$. Such low mismatches make the growth of crystalline layers with thicknesses of several micrometers possible

and thickness. MBE and MOVPE allow for precise control of these features. Layer thicknesses may be controlled down to single monolayers (see Fig. 36.3).

Figure 36.4 shows the x-ray diffraction rocking curve of a $0.5\ \mu\text{m}$ thick layer of $\text{In}_{0.528}\text{Al}_{0.238}\text{Ga}_{0.234}\text{As}$, grown lattice-matched to the substrate of InP by MBE. “Lattice-matched” means the lattice constants of both semiconductors are equal. Thus, no strain is incorporated into the layers, which would lead to formation of

misfit dislocations and crystal defects. The relative mismatch amounts to $\varepsilon = 10^{-5}$. The appearance of fringes next to substrate and layer peaks demonstrates their crystalline structure and a smooth InAlGaAs/InP interface with low roughness. The left side of Fig. 36.4 depicts a sketch of an MBE reactor chamber. The working principle is based on Knudsen effusion cells in which the materials are stored in elementary form and evaporated by thermal heating. These cells are nothing else than a long tube with a heating filament at the inside. The material is contained in a crucible of boron nitride. The cells are arranged in front of the substrate. The reactor chamber is evacuated down to ultra-high vacuum conditions (UHV). Pressures of 10^{-9} – 10^{-10} mbar are usually reached. Because of this huge difference in pressure, the vaporized material escapes the heated cell in form of a molecular beam directed onto the substrate. During growth, chamber pressures of 10^{-7} mbar are reached. Such pressures are still low enough to prevent scattering of the molecular beams with residual gas species in the chamber. In other words, the mean free path $\bar{L}$ is much longer than the distance l between the cells and the substrate.

$$\bar{L} = \frac{k_B T}{\sqrt{2\pi} d^2 p} > l$$

The UHV conditions allow for lower growth temperatures than in chemical vapor epitaxy. Impurity incorporation of outgasing hot components and interdiffusion of grown materials are reduced [13].

UHV also allows for in-situ monitoring of the growing layers by reflective high energy electron diffraction (RHEED). This technique provides information about the growth rate, structure and composition of the growing layer. Typical growth rates are around 1 $\mu\text{m/h}$ and lower, which gives the molecules the necessary freedom to adapt to the crystal structure of the substrate. Substrate temperatures are monitored by pyrometry. Growth temperatures for GaAs are in the range of 580–620°C. InAs and InP are grown between 450°C and 520°C.

The total thickness of layers for a complete laser structure ranges from 3 to 5 μm . However, special devices like Quantum Cascade Lasers (QCLs) require epitaxial structures with thicknesses of several tens of micrometers.

Processing of Diode Lasers

The easiest way to fabricate a diode laser of the grown wafer is to cleave bars of the wafer and evaporate metallic stripe contacts on the p- and n-side. The cleaved facets serve as mirrors due to the jump in refractive index at the semiconductor-to-air interface and thus define the laser cavity. The application of diode lasers for sensing requires more advanced processing, e.g. to obtain a very narrow line width of the emitted spectrum or a continuous tuning of the emission wavelength [14].

Figure 36.5 shows different types of structured semiconductor lasers having single-mode emission. The processing can include the etching of wavelength-selective

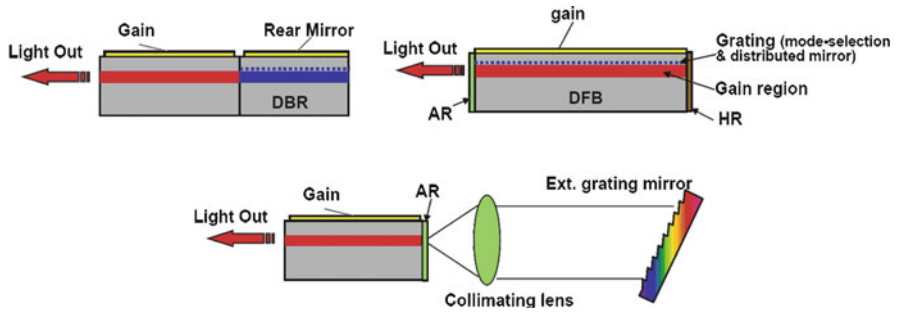


Fig. 36.5 Different kinds of processed single-mode semiconductor lasers. *Top left:* DBR laser. *Top right:* DFB laser. *Bottom:* Diode laser with external feedback. High-reflective (HR) and anti-reflective (AR) coatings can be applied on the cleaved facets to optimize the emission (Figure taken from [14])

elements, such as gratings for distributed Bragg reflectors (DBR) or distributed feedback gratings (DFB) as well as the application of anti-reflective (AR) or high-reflective coatings on the cleaved facets. In both types (DBR and DFB) the feedback is not restricted to two interfaces, but is distributed over a certain length. Each grating period reflects a part of the light resulting in an effective reflection. The advantage is that the emission wavelength can be selected by adjusting the reflectivity of the grating. In a DFB laser only the longitudinal mode, which matches the grating period will be reflected and can be amplified in the diode laser. The so-called Bragg wavelength λ_B is defined as

$$\lambda_B = \frac{2n_{\text{eff}}\Lambda}{m}$$

where n_{eff} denotes the effective refractive index of the grating structure, Λ the grating period and m the order of the grating.

For the fabrication, techniques such as e-beam lithography and dry-etching are deployed. The processing of a DFB grating involves two growth steps. The epitaxial growth is interrupted after the deposition of the active region and the material necessary for etching of the grating. Then, the structure is completed by overgrowth of the grating with the remaining epitaxial layers for the diode laser. The yield of these DFB processes is low and the devices are expensive, which is mainly caused by the overgrowth step. A way to get rid of the overgrowth is to apply surface-defined gratings. Such gratings are etched into the surface of the wafer after all epitaxial layers have been deposited. Epitaxy and processing are completely separated. This type of grating is also compatible with nano-imprint techniques. Nano-imprint has been introduced to the fabrication of diode lasers to overcome the serial processing bottleneck of e-beam lithography and to increase the throughput [16].

Etching precise surface grating structures is a very demanding task, since the feature sizes are in the range of several tens of nanometers. The period of a first order DFB is around 60 nm in the blue visible range for example. The required

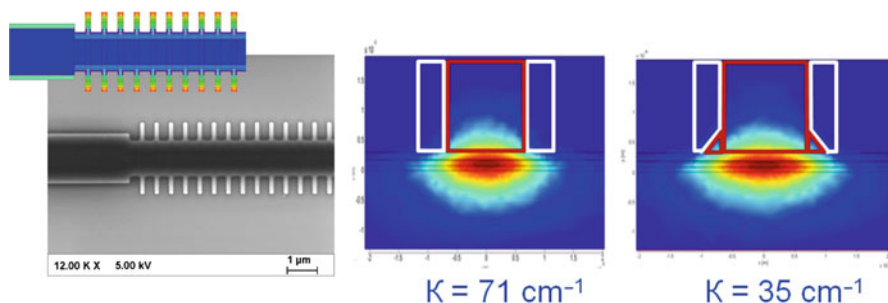


Fig. 36.6 *Left:* E-beam exposure simulation of a surface DFB grating and corresponding SEM micrograph of a processed grating. *Middle and right:* Simulation of a laser with a surface DFB grating having a perfect rectangular shape and an imperfect shape. The color code represents the light intensity. Imperfect etching leads to reduced coupling and feedback of the light and the grating (*Left* figure by S. Afzal (INA, University of Kassel), *middle and right* figures by P. Bardella and I. Montrosset (Politecnico di Torino) with kind permission)

depths are usually around 1 μm . This leads to width/height aspect ratios of 1:10 or more. Figure 36.6 shows a simulation of the emitting edge of a DFB laser [15]. With a perfectly rectangular etched surface-grating a coupling constant of 71 cm^{-1} is obtained. Slight imperfections in the etching process will severely reduce the overlap of the light wave (color code in Fig. 36.6) and the grating. Hence, the wavelength selection of the grating is reduced. Too low coupling will lead to laser emission of more than one mode making the systems useless for sensing applications. Well optimized DFB lasers are able to obtain single-mode emission with a line width of typically 1 MHz, which is considerably narrower than typical molecular absorption lines. For a near-infrared lasing wavelength such line widths are around 8 orders of magnitude lower than the carrier frequency.

Quantum Wells and Quantum Dots

With the introduction of quantum wells (QW) as active region of diode lasers their commercial breakthrough was set. A QW is a one-dimensional potential well that forms discrete energy states for the charge carriers inside the structure. The width of the potential well has to be in the range of the De-Broglie wavelength

$$\lambda = \frac{h}{\sqrt{2m^*E}}$$

of electrons and holes, where m^* denotes the effective mass and E the energy of the particle. For electrons in GaAs $\lambda \approx 5\text{ nm}$ at $T = 300\text{ K}$. The carrier motion is confined inside the structure. This results in an improved spatial overlap of the wave functions of both types of carriers. The transition matrix element and the probability

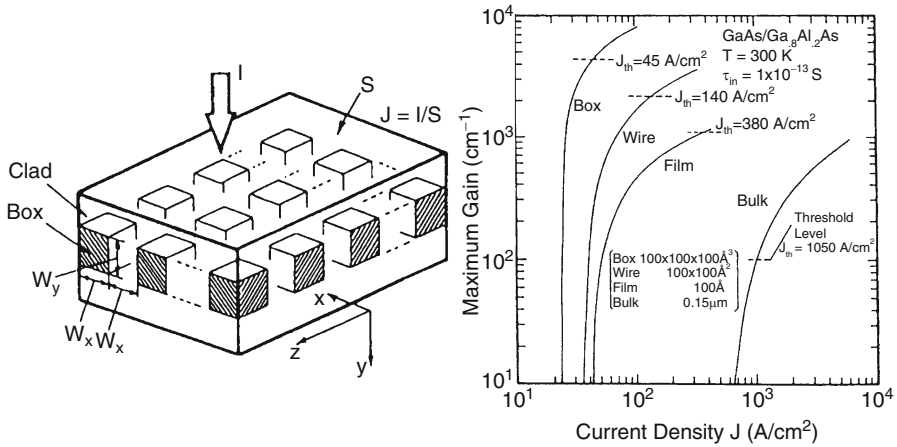


Fig. 36.7 Three-dimensional confining boxes embedded in surrounding material (*left*) and model calculations for diode lasers with different dimensionality in the active region. Model calculations predict a superior performance of boxes as active region (*right*) (Figures taken from [17])

of radiative recombination enhance. An escape of carriers due to thermal activation out of the active region is prevented by the confining potential. This improves the stability of the laser operation with varying ambient temperatures. Furthermore, the volume of the active region is largely reduced so the inversion conditions necessary for lasing are met at much lower currents. The total power consumption decreases, self-heating of the device is suppressed, which imminently raises the operation efficiencies. A QW is epitaxially formed by depositing a thin film of material ($\sim 10 \text{ nm}$) with a lower bandgap than the surrounding material, e.g. a InGaAs QW in GaAs barriers or a GaAs QW in AlGaAs. Theoretically the introduction of a three-dimensional potential well as active region should once again lead to a vast enhancement of the above described effects. Figure 36.7 shows corresponding model calculations by Asada and co-workers [17]. The confining 3D potential is modelled as cubes of low bandgap material embedded in a higher bandgap matrix. Note, that the threshold current density of a diode laser with such an active region is nearly a factor of 20 lower than a corresponding QW laser. At the same time the achievable gain is around one order of magnitude higher. Since now all three dimensions are smaller than the De-Broglie wavelength of the charge carriers, the boxes form a three-dimensional potential well. The allowed energies for carriers inside the boxes are discrete in all three dimensions of motion. Since all boxes are modelled as equal in size and geometry the ensemble possesses a delta-like distribution of the density of states (DOS) function, due to quantum mechanical principles. The luminescence of such an ensemble would show a very sharp line with a line width limited by the lifetime of the electron-hole recombination (homogenous broadening). A diode laser would work at exactly this luminescence energy with each box contributing to the laser gain.

Hence, a superior performance of nearly all important diode lasers parameters was predicted. The term “quantum dot” (QD) was introduced for these boxes, referring to quantum wells. However, the assumption of all QDs being equal in size is unrealistic. If the dots do not share the same size, their energy states are slightly different. These size fluctuations induce an inhomogeneously broadened luminescence that is composed of the overlap of all the homogeneously broadened lines of each single QD (compare Fig. 36.8).

One method to grow semiconductor quantum dots by epitaxial means is the Stranski-Krastanov growth mode (SK growth), also referred to as Asaro-Tiller-Grinfeld instability [18] (Fig. 36.9). It is a bottom-up method based on self-assembly. A lattice-mismatched layer structure is deposited by intention, for example InAs ($a = 6.0583 \text{ \AA}$, $E_g = 0.354 \text{ eV}$) on GaAs ($a = 5.6611 \text{ \AA}$, $E_g = 1.424 \text{ eV}$). The first few InAs monolayers will grow as a film on the GaAs substrate. The lateral lattice constant will adapt by building up strain energy. The growing layer is called wetting layer. At a certain critical thickness h_c the accumulated strain energy is minimized by

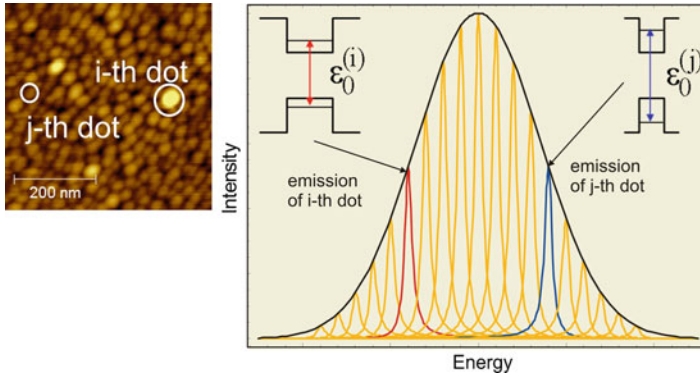


Fig. 36.8 $0.5 \mu\text{m} \times 0.5 \mu\text{m}$ AFM scan of an ensemble of InAs QDs on GaAs (*left*). The statistical size fluctuations cause different emission lines for each dot, because of shifts in the confined states. The resulting luminescence is the overlap of all the individual lines (*right*)

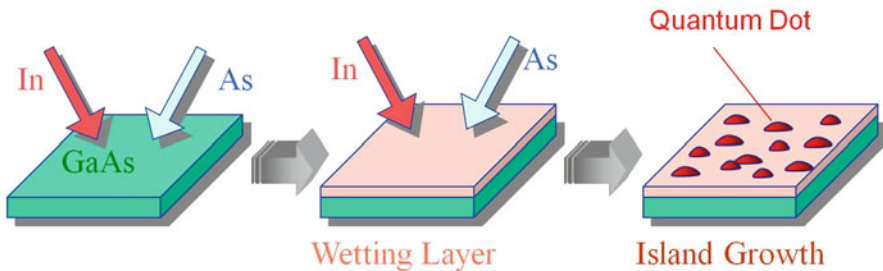


Fig. 36.9 Sketch of the Stranski-Krastanov growth mode

a transition from a monolayer-by-monolayer film growth to a three-dimensional island growth. With ongoing supply of material the islands grow in size. The lateral lattice constant relaxes slightly from the bottom of the island their top. If the islands grow too big, misfit dislocations and crystal defects will be incorporated, due to this relaxation. If one stops the growth of the dots and buries them by depositing another layer of lattice-matched material with a higher bandgap, the intended three-dimensional potential well will be formed. The buried quantum dots are elastically strained inside the surrounding matrix material. There have been attempts to create QDs by e-beam exposure and etching of a QW followed by a second growth process to deposit the upper layer structure of the laser [19]. However, this led to impractically high threshold current densities of 7.7 kA/cm^2 . SK growth has therefore become the most common method for the creation of semiconductor QDs.

As a self-assembly technique SK growth is also a statistical process. All islands dimensions, such as height and diameter are statistically (Gaussian) distributed. The size fluctuations can be directly identified in the inhomogeneously broadened luminescence. Typical ensemble line widths vary from 20 meV at 10 K up to 100 meV at 300 K. The ensemble fluctuations may be a drawback at first glance, but also offer new degrees of freedom for tailoring the QDs for specific needs [20]. Figure 36.10 demonstrates three parameters dependent on the dot morphology, which are important for device performance.

A high power laser for example requires a high dot density with a very uniform distribution to improve the output power and reduce gain saturation effects. A semiconductor optical amplifier on the other hand benefits from a high dot density with a less uniform distribution, because a much broader spectral range can be amplified [21].

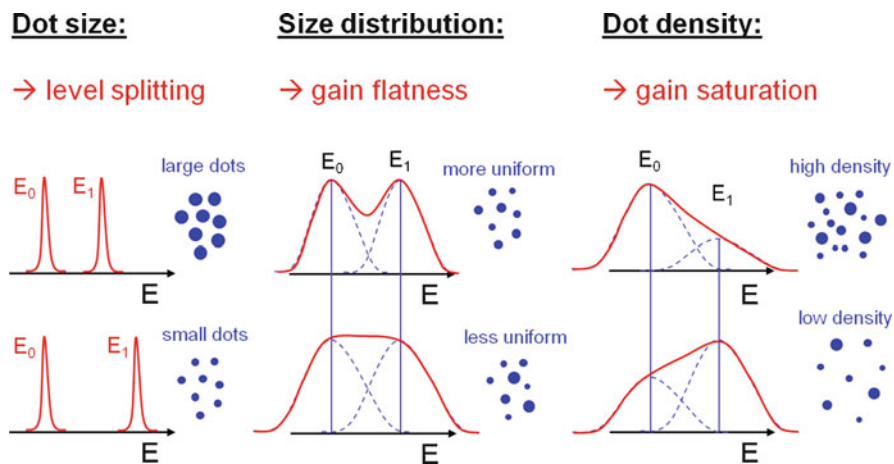


Fig. 36.10 Schematic diagrams showing the influence of the morphology on the optical properties of a QD ensemble

Semiconductor Lasers for Sensor Applications

Optical sensing of matter is based on the three properties reflection, transmission and absorption of light. Optical sensing is non-destructive, can be applied over far distances and is almost independent on the environmental conditions (high voltage, chemicals, bio-hazard). Sensitivities for gas sensing can be in the ppb range for example [22].

The areas of applications range from homeland security, military communications, infrared countermeasures, chemical warfare agent detection, explosives detection over civil use in medical diagnostics, industrial process controls, remote gas leak detection, pollution monitoring, real-time combustion controls and topology measurements. Markets for mid-IR sensors at \$70.2 million in 2008 are anticipated to reach \$2.5 billion by 2015 [23]. In the following section selected examples of laser sensor applications will be introduced.

Diode Lasers for Gas Sensing

Most gas sensing techniques that apply diode lasers are gathered under the term “Tuneable Diode Laser Absorption Spectroscopy” (TDLAS). This technique uses a diode laser tuneable in wavelength and the characteristic absorption lines of gases for detection [24, 25]. For the working principle it does not matter, which absorption lines are used. Absorption of electronic (NIR) as well as vibrational (MIR) or rotational (THz) transitions may be detected.

However, a direct absorption spectroscopy is often not suitable for high sensitivities. According to Beer’s law, the absorbed light intensity increases with increasing absorption path. Hence, sensitivity values are dependent on the length the laser light travels through the species to be detected. One way to improve TDLAS sensitivities is to couple the laser light into an external cavity that the light passes several times before detection. Techniques relying on such multi-pass configurations are gathered under the term “Cavity-Enhanced Absorption Spectroscopy” (CEAS). Multi-pass cells with total path lengths of 100 m have been developed allowing for sensitivities in the ppb range yet fitting in a tabletop set-up [22] (Table 36.1).

The gas species to be detected may also be introduced into the resonator of the laser system itself. Lasers are very sensitive on changes in absorption. Thus, by shifting the point of detection into the resonator, a vast improvement can be obtained. Methods relying on this feature are called “Intra-Cavity Absorption Spectroscopy” (ICAS). Since the resonator of a diode laser is usually formed in the semiconductor material itself, an external feedback cavity is required. ICAS systems offer various improvements over a conventional TDLAS set-up [26]. It consists of a conventional DFB laser with anti-reflection coatings. Due to the coatings the laser can be compared to a semiconductor optical amplifier (SOA) that

Table 36.1 Gas species, scan wavelengths and minimal detectable concentration (*MDC*) for a tabletop gas-sensing set-up based on a DBR and an external cavity diode laser (Data taken from [22])

Gas species	Scan center (μm)	MDC (ppb)
CO ₂	4.19	460
N ₂ O	3.89	95
H ₂ CO	3.53	54
HCL	3.52	9
NO ₂	3.47	259
CH ₄	3.30	23

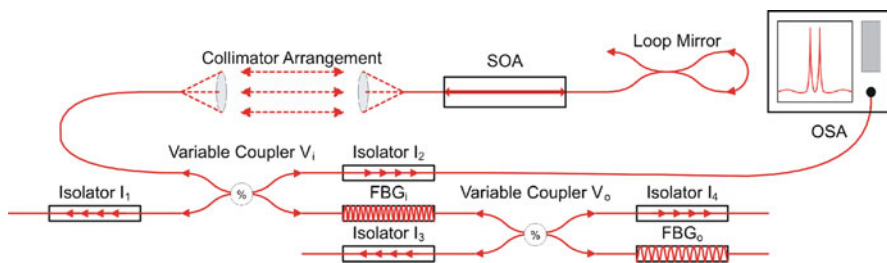


Fig. 36.11 Schematics of the two-mode ICAS setup at INA (Figure taken from [26])

only provides gain without forming a laser resonator. The laser is coupled to optical fibers. The feedback and thus the resonator is built by two fiber Bragg gratings included in the fibers. The DFB grating in the laser allows for emission of two laser modes. This two-mode approach is more effective in terms of sensitivity as a single-mode setup. One mode is tuned over the absorption line of the gas in the cavity and is absorbed while the other stays unaffected. This will immediately change the dynamics of the laser, because of mode competition. Figure 36.11 shows schematics of such a setup. Figure 36.12 presents a measurement in which one of the two modes is centered on a absorption peak of propofol.

Conventional multi-mode ICAS systems use a large set of modes, which makes calibration, handling and operation a delicate process. Furthermore, they are often driven by dye or fiber lasers that have low wall-plug efficiencies and can hardly be miniaturized.

The introduction of a diode laser as light source drastically decreases set-up complexity and cost. As only one mode is absorbed, a simple photo diode rather than a bulky and expensive optical spectrum analyzer may be used. There is even potential to completely change the detection to an electronic one. In a diode laser the electronic and photonic systems are directly coupled. Therefore the change in the photonic system induced by the gas is detectable in the electronic system. A cheap electronic RIN (relative intensity noise) measurement might be already suitable [26]. Despite the actual measurement method each TDLAS set-up sets certain requirements on the diode laser such as wavelengths in the NIR regime,

Fig. 36.12 Unmodified spectra of the two modes upon insertion of propofol. Please note that a configuration with a 5 cm long sample cell is used [26]

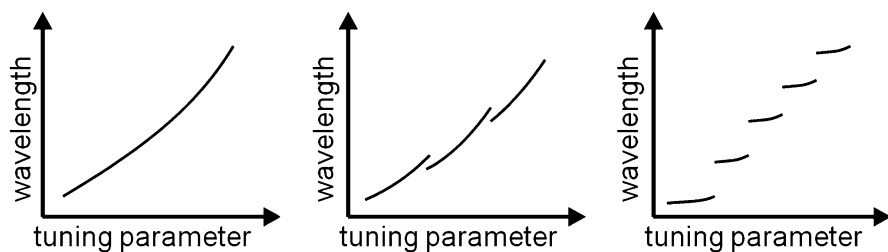
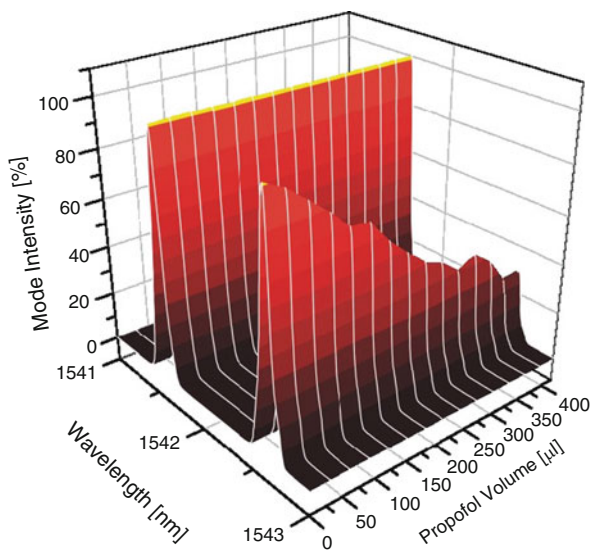


Fig. 36.13 Emission wavelength versus tuning parameter for continuous (left), quasi-continuous (middle) and discrete tuning (right). Note that the figure is not to scale

output powers of several milliwatts and a very narrow emission spectrum. All these are typical requirements for DFB lasers as introduced in section “[Processing of diode lasers](#)”. Diode lasers for gas sensing can therefore rely on a broad and profound technological base. This is also a reason, why the NIR regime is widely used in TDLAS, since this wavelength range can be covered by common diode lasers based on III-V semiconductors.

However, a tuneable diode laser is required. Several methods are applied to tune the wavelength of a DFB laser; they can be separated into three categories: continuous, quasi-continuous and discrete tuning (Fig. 36.13).

Continuous tuning is realized by thermal heating or carrier injection into the grating. This changes the effective refractive index n_{eff} of the grating material and thus the Bragg condition. The Bragg mode is shifted. The achievable wavelength shifts are typically around 5 nm. This range can be extended by using mode jumps

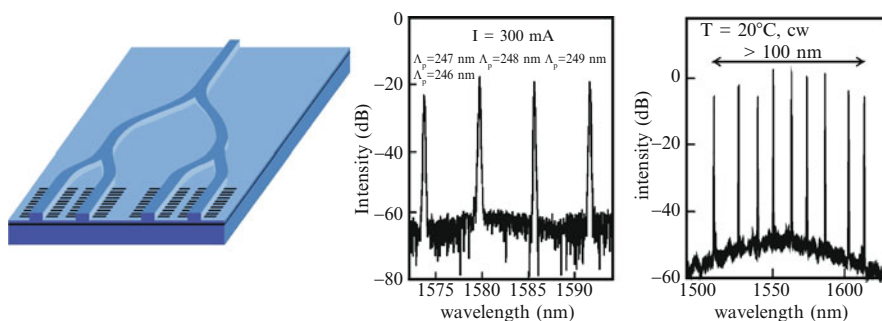


Fig. 36.14 *Left:* Example for an array of DFB laser with different grating periods. *Middle:* CW emission of several DFB gratings processed on the same wafer [27]. *Right:* If the active region is composed of quantum dashes, a wavelength range of more than 100 nm can be addressed with a almost constant level of output power [28]

(quasi-continuous tuning). A discrete tuning may be realized by combining the continuous tuning of the Bragg mode and mode jumps. Also external wavelength tuning can be applied by using a Littman-Metcalf set-up with an external blazed grating. All tuning techniques only work in the region of spectral gain of the active material inside the laser, of course. A flat and broad gain profile is desirable in order to have a near constant output power of the laser at all wavelengths. To exploit the complete spectral gain range of the active region, e.g., broadband quantum dots, several diode lasers with different DFB gratings can be fabricated and monolithically integrated on the same chip (Fig. 36.14) [27, 28]. In this manner the number of detectable gases can be extended easily. A coarse tuning is done by pumping the correct laser and a fine tuning can then be carried out by thermal heating, resulting in a quasi-continuous tuning scheme covering a very broad wavelength range.

Optical gas sensing in the MIR regime was based on lead salt diode lasers, since this wavelength range cannot be covered with conventional III-V semiconductors. Such systems are large in size and require cryogenic cooling below 90 K for sufficient operation. Nevertheless, the MIR wavelength regime is interesting for gas sensing as some gases don't show proper absorption lines in the NIR range. Furthermore, detection limits can be several orders of magnitude lower, which directly affects set-up dimensions. The development of quantum cascade lasers (QCL) was a tremendous step to robust lasers emitting in the MIR regime. Unlike conventional diode lasers QCLs are based on intra-band transitions of electrons in a QW. No holes are necessary and no p-n junction is required, rendering the devices uni-polar. The gain of such lasers is very low, so the active region is repeated several times to achieve sufficient gain ("cascaded").

The electron transport from one QW to the other is based on resonant tunnelling from the ground state of one QW to the excited state of the neighbouring QW (compare Fig. 36.15). Due to this cascade of QWs one electron will help in the emission of several photons. Prerequisite for such a working QCL is a very precise

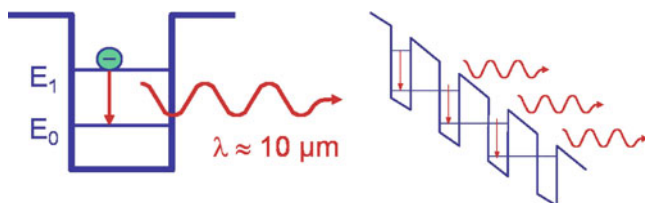


Fig. 36.15 Sketch of an QW intra-band transition leading to an emission in the MIR range (*left*). *Right*: Repetition of the active region to achieve sufficient gain. The band structure is bent due to the biasing of the device

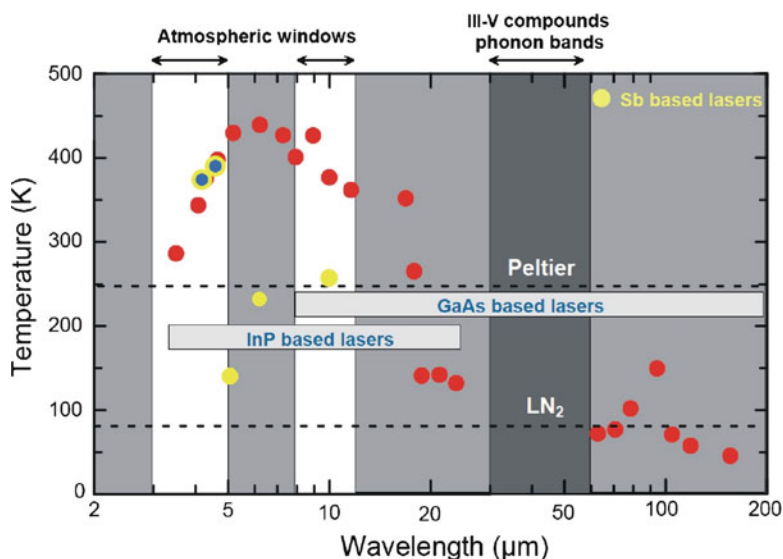


Fig. 36.16 Plot of operation temperature versus emission wavelength for several reported QCL devices (Graph by J. Kunsch (Laser Components GmbH, with kind permission) [29])

epitaxial growth to allow for efficient tunnelling. Accuracy of layer thicknesses and material compositions should be better than 1% for each individual layer. This demand is very challenging, since several tens of micrometers of epitaxial material need to be deposited to achieve sufficient gain.

For several years QCLs could only be operated at cryogenic temperatures, but recent developments and optimization of the active region and tunnelling schemes have led to QCLs working at room-temperature and above. Figure 36.16 depicts a plot of the emission wavelengths versus operation temperature for QCLs developed by several groups [29]. For the range of 3 to 10 μm QCLs with operation temperatures even exceeding room temperature are available.

For single-mode emission, DFB gratings are processed as already discussed [30]. Gas sensing applying DFB-QCLs has been demonstrated [31].

Generation and Amplification of THz Radiation by Diode Lasers

THz radiation has attracted lots of interest in recent years due to its potential applications in medicine, non-destructive material testing and law enforcement. In order to fabricate THz devices, several approaches have been discussed in literature. Two of these approaches will be introduced in this section: QCLs for THz emission and optically driven THz generation by conventional diode lasers. QCLs emitting in the THz regime ($\lambda \sim 100 \mu\text{m}$) have already been demonstrated as Fig. 36.16 shows. However, the operation temperatures are yet limited to the cryogenic range. This is mostly due to electron–phonon scattering at higher temperatures that prevents the desired intraband transitions. Highest operation temperatures are around 180 K [32]. New cascade schemes are constantly being developed to overcome these limitations [33].

Another method of THz generation is optical heterodyning. Here two laser beams are superimposed. The resulting optical signal is beating with the difference frequency of the two incident laser beams. A beating frequency of 1 THz with two lasers emitting at around $1.55 \mu\text{m}$ converts to a difference of around 8 nm in wavelength. The beating signal now needs to be coupled to a material with charge carrier lifetimes below 1 ps. This allows the carriers to be modulated by the beating frequency. The optical beating signal is converted into an electronic modulation in this so-called photomixer. A material that provides sufficiently short lifetimes is low-temperature grown GaAs for instance. The signal is then outcoupled by an antenna structure metalized on the GaAs. Figure 36.17 depicts a sketch of this scheme.

Since the emitted frequency is directly proportional to the incident beating frequency, tuning of the two emission wavelengths allows a continuous tuning of the generated THz frequency. The required wavelength differences are easily achievable by processing two DFB gratings on one wafer as shown above [27, 28]. Engaging diode lasers for the described THz generation scheme allows for a high level of integration. Moreover, it was demonstrated that quantum dots can also possess lifetimes on the sub-picosecond scale. Thus, the QDs could overtake two functions: provide the broad gain profile to allow for a broad tuning range and at the same time act as photomixer. An external photomixer is not necessary anymore, and a highly integrated device, a “THz diode”, could be realized (see Fig. 36.18).

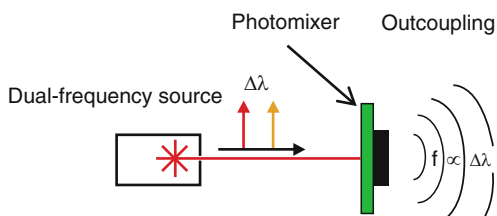
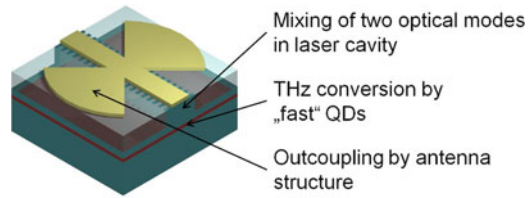


Fig. 36.17 Scheme of optical heterodyning and electro optical conversion in a photomixer to generate THz radiation

Fig. 36.18 Possible design of a fully integrated “THz” diode with quantum dots as gain as well as photomixer material and an evaporated antenna structure for outcoupling



The usage of surface-defined DFB gratings enables the introduction of nano-imprint techniques to increase the throughput of the fabrication process and makes the devices cheaper. Such a fully integrated device may be fabricated by transferring the knowledge and technology that is currently being developed for telecommunications lasers by our group [34,35].

LIDAR

LIDAR is the acronym for “light detection and ranging”. The name is derived from RADAR (“radio detection and ranging”) as it applies the same principles of measurement. Laser pulses are emitted and the light scattered back at objects in the beam path is detected. The pulses usually have a pulse length shorter than 10 ns and a repetition rate of 10 Hz. The pulse energies vary in the range of tens of millijoule to Joule, depending on the emission wavelength. The basic LIDAR equation may be written as

$$P(z, \lambda) = c_z \frac{\beta_m(z, \lambda) + \beta_p(z, \lambda)}{z^2} \exp \left\{ -2 \int_0^x [\alpha_m(z', \lambda) + \alpha_p(z', \lambda)] dz' \right\}$$

where $P(z, \lambda)$ denotes the LIDAR signal at wavelength λ at a distance z , α the absorption and β the backscatter coefficient. The indices “m” indicate the usual atmosphere and “p” the particles of interest. This can be solid objects, gases etc. As can be seen by the LIDAR equation the backscattered light contains information about location, velocity and qualitative structure of objects in the beam. A typical laser for LIDAR is a diode pumped Nd:YAG laser at $\lambda = 532$ nm, but also other sources, such as infrared lasers, may be used. For example, the toll charge system on German Highways is composed of a network of bridges that are equipped with LIDAR emitting at $\lambda = 905$ nm to automatically distinguish between passing cars and trucks. Figure 36.19 shows an example of a time-evolved LIDAR measurement in the atmosphere. The measurements were performed at the Ludwigs-Maximillian University of Munich on April, 23th 2010, 1 week after the eruption of the Icelandic volcano “Eyjafjallajökull” [36]. The detection wavelength was 1,064 nm. However,

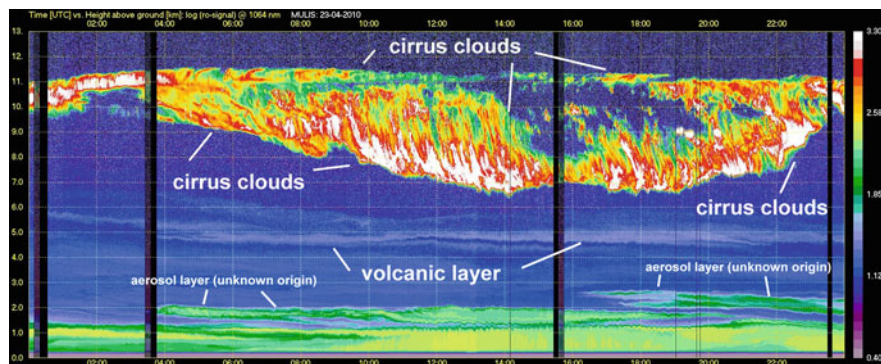


Fig. 36.19 Time-Height cross section of range-corrected LIDAR signal (1,064 nm) on 23 April 2010 at Maisach (25 km northwest of Munich, Germany). The applied “MULIS II” LIDAR system is part of the European EARLINET network for atmospheric aerosol detection [36]

any wavelength may be used as detection channel. Hence, elastically as well as inelastically scattered (raman-scattered) light may be detected.

Therefore, depending on the emission and detection wavelengths, the scattered light reveals information about concentration and structure of gas species. Consequently, different LIDAR techniques exist, such as, “Doppler Wind Lidar” (DWL) for measuring wind velocity and turbulences, “Differential Absorption Lidar” (DIAL) for ozone and water vapor detection or “Integrated Path Differential Absorption” (IPDA) for carbon dioxide and methane. This enables a complete profiling of gas concentrations, e.g., in the atmosphere.

Moreover, LIDAR systems can be installed in airplanes and satellites. Such air- or satellite-bourned systems are used to determine topology and vegetation on the surface of the earth.

Conclusions

After a short historical synopsis in which the advantages of semiconductor lasers over other types of lasers have been demonstrated the basic concepts behind diode lasers have been briefly discussed. The necessary fabrication techniques were introduced. It has been shown that sophisticated nanoscaled engineering allows to tailor semiconductor lasers can be tailored for specific needs, e.g., by using low-dimensional structures as active gain material. Furthermore, different types of diode lasers or QCLs are able to cover the whole wavelength range from UV over VIS, NIR to MIR. Many applications in these wavelength regimes can be addressed. Special operation and clever design even allow for generation and amplification of THz radiation (FIR regime). The small dimensions of diode lasers and the ability to be driven electrically makes them very attractive for integration

and economic operation. At the same time they are highly independent on the environmental conditions.

Acknowledgements The authors like to thank S. Afzal (INA, University of Kassel), P. Bardella and I. Montrosset (Politecnico di Torino) for their kind permission to use the graphs in Fig. 36.6, J. Kunsch (Laser Components GmbH) for the graph in Fig. 36.16 and M. Wiegner (Meteorological Institute, Ludwig-Maximilians-Universität München) for the LIDAR plot in Fig. 36.19. The financial support of the EU projects, “DeLight”, “Gospel” [37] as well as the project “Mitepho” of the Marie Curie training network is thankfully acknowledged.

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Chapter 37

Optical Characterization of Very Thin Films for Nanotechnological Basis of Sensors

Peter Sharlandjiev

Abstract Thin films and photonic crystals are used as elements of a nanotechnological basis for sensors due to their well-defined optical properties such as transmittance, reflectance, or diffraction. Key issue is the optical characterization of structures obtained by nanotechnological methods, i.e. a determination of the physical thickness of each individual layer, its dielectric permittivity, magnetic permeability as well as the evaluation of its homogeneity and corrugation. Herein, we focus on a specific problem of great importance to fundamental and applied science: we analyze the case of very thin films, meaning that the ratio ‘layer thickness to wavelength’ is much less than $1/50$. We also demonstrate the potential of a new direct approach developed by us to inverse optical problems, based on a position estimation of the probability density function of partial solutions.

Keywords Inverse optical problems · Thin films · Ellipsometry · Spectrophotometry

Introduction

Thin films, multilayer structures, and more complicated periodic stacks (photonic crystals) are the fundamental construction blocks for the design and production of many optical sensor devices. Important sensor features, such as resolution, sensitivity and detection range are related to the detectable modification of the optical response for a minimum magnitude of the input signal [1]. Optical sensors have a small size, a fast output, and the possibility to analyze the response at a remote location through optical fiber coupling. Sensor ‘blocks’, obtained by nanotechnological methods, have well-defined optical properties such as transmittance, reflectance, scattering or diffraction. Key issue is the optical characterization of the structures, i.e. the determination of the physical thickness of each individual

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layer, its dielectric permittivity, magnetic permeability, as well as an evaluation of its homogeneity and surface corrugation. Usually, these parameters are estimated from spectrophotometric (SPE) or ellipsometric (ELE) experiments. Herein, we focus on a specific problem of great importance to fundamental and applied sciences: we analyze the case of very thin films, meaning that the ratio ‘layer thickness to wavelength’ is much less than $1/50$ [2, 3]. By numeric simulations, we generate realistic spectrophoto- and ellipsometric data, which are later processed by mathematical deterministic and stochastic methods in order to extract the thin films parameters needed.

Model and Computational Procedures

We consider a stack of three very thin oxide films on a $\text{Si} < 100 >$ substrate. Structures of that type are of great importance for many applications and have serious potential for the development of new sensor devices. SiO_2 is naturally formed on Si substrates but if a metal oxide is deposited on it, an intermediate inhomogeneous layer is formed as well [4]. Our model consists of a Ta_2O_5 layer of thickness $D1 = 8$ nm; a second layer of 50% Ta_2O_5 and 50% SiO_2 , ($D2 = 2$ nm); and third layer of 97% SiO_2 and 3% a-Si, formed on the Si substrate. The permittivity of each material is taken from [4]. We choose the mixing rules for the inhomogeneous layers according to the filling factors of the oxides: Bruggemann for the second layer and Maxwell-Garnett for the third one [5]. The problem is to determine the physical thickness of each layer from experimental data by mathematical minimization techniques. We generate spectrophoto- and ellipsometric measurements by calculating observable quantities and adding random experimental noise with zero mean and variance, equivalent to that of high precision equipment (Cary5E (Varian Co.) spectrometer and VASE ellipsometer (Woollam Co.)). Wavelength spectra (WS) between 250 and 400 nm are considered for four incident angles: 20° , 40° , 60° , and 70° . Other data are generated as well: Angular spectra (AS) between 20° and 70° at wavelengths of 270, 290, 320, and 400 nm. The choice of these spectra is based on analysis of the experimental sensitivity to small perturbations of the model stack parameters. The estimation of the ‘unknown’ parameters can be regarded as heavily over-determined inverse problem [3].

Results and Discussion

Derivative Approach

We tested two derivative methods, which are very popular in inverse problem estimations: the classical Levenberg – Marquardt (LM) and the trust – region reflective (TR) method [6]. The LM method is based on the evaluation of the step

to the global minimum as a cross between the Gauss – Newton direction and the steepest descent direction. In our case LM gave unsatisfactory results. Calculating gradients based on finite difference methods can be unstable and the Jacobian can be ill conditioned leading to a lack of convergence in the numeric procedures. All results presented below are obtained with TR. The leading idea of this method is to find a region in the parametric space where the goal function F can be approximated by a simpler function, which evaluates the goal function in a satisfactory manner. Obvious candidates for this simpler function are the two terms in the Taylor approximation of F at the point of evaluation. We found that in our case the trust region is not spherical in shape but ellipsoidal, due to the strong correlation between the model parameters. TR is essentially a derivative method: the step to the global minimum (its direction and magnitude) is evaluated by the help of a Hessian matrix.

In Table 37.1 we present the results for the SPE with WS at four different angles of light incidence for both TE and TM light polarization. The fit is a multiobjective procedure for all the 4 incident angles and the two polarizations simultaneously. The residual of the fit is far below the experimental uncertainty, so the estimation $\{De1, De2, De3\}$ has to be accepted. We introduce an operational criterium for the goodness of the fit, defined as euclidian distance to the fit (EDF). EDF is the distance between the model point in the parameter space $\{D1, D2, D3\}$ and the point evaluated by the fit $\{De1, De2, De3\}$. For this SPE – WS data processing, EDF is 0.1458 nm. When we estimated the confidence intervals with a level of certainty of 95%, we found that $8.01 < De1 < 8.02$; $1.89 < De2 < 1.910$; and $1.09 < De3 < 1.11$ (all values in nm). Therefore, the confidence bound intervals do not contain the model thickness values $\{D1, D2, D3\} = \{8, 2, 1\}$ with 5% chance of being incorrect. We explain this discrepancy by the very strong correlation between the model parameters. In fact, the

Table 37.1 Results of the different approaches discusses in this paper

Method	Parameters	SPE-WS	SPE-AS	ELE-WS	ELE-AS
TR	EDF	0.146	0.146	0.198	0.285
	De1	8.02	8.02	8.08	7.86
	De2	1.89	1.89	1.84	2.23
	De3	1.09	1.09	1.08	0.91
GA	EDF	0.213	0.444	0.426	0.248
	De1	8.02	8.12	7.87	8.04
	De2	1.84	1.63	2.33	1.82
	De3	1.17	1.23	0.77	1.17
DS	EDF	0.141	0.141	0.141	0.250
	De1	8.00	8.00	8.00	8.00
	De2	2.10	1.90	2.10	1.85
	De3	0.90	1.10	0.90	1.20

Model parameters: $D1 = 8$ nm, $D2 = 2$ nm, $D3 = 1$ nm. All data are given in nm
Acronyms: *SPE* spectrophotometric experiment, *ELE* ellipsometric experiment, *WS* wavelength spectra, *AS* angular spectra, *TR* trust region derivative method, *GA* stochastic genetic algorithm, *DSM* direct search method, *EDF* euclidian distance from model to fit

correlation coefficients (CC) are very close to one: $CC(D1\_D2) = -0.973$; $CC(D1\_D3) = -0.923$; $CC(D2\_D3) = -0.986$.

Besides WS, we used angular spectrophotometric spectra between 20° to 70° (step of 1°) for the evaluation of the model parameters at four fixed wavelengths of 270, 290, 320, and 420 nm for TE and TM polarizations. The residuals are below the experimental uncertainty and $EDF = 0.1461$ nm, practically equal to the fit with WS data. Other details are shown in Table 37.1. The correlations are also very similar: $CC(D1\_D2) = -0.984$; $CC(D1\_D3) = 0.948$; $CC(D2\_D3) = -0.989$, but the sign of the CC between the first and the third film is opposite. The conclusion is that for spectrometric experiments both AS and WS data are equally acceptable for the solution of the inverse optical problem by the help of the TR derivative method. The choice is either arbitrary or can be based on experimental convenience.

Next, we treated the ELE data, keeping the other conditions very close to the SPE experiments described above. With WS as input data to TR processing, we obtain $EDF = 0.198$ nm, compared to $EDF = 0.285$ nm for AS data. Other details are given in Table 37.1. Although both residuals are somewhat lower than the corresponding values from SPE, both fits are perfectly acceptable within the corresponding experimental uncertainty. Although ellipsometry has a greater sensitivity, spectrophotometric data are reliable and no less informative – what really matters is the experimental accuracy of the data obtained. This is confirmed by our results obtained by stochastic and direct search methods as described below.

Stochastic Approach

There are two very popular stochastic approaches in global minimization techniques: the simulated annealing and the genetic algorithm. Both have many implementations and mathematical developments, which have two very important features in common. All of them make use of random number generators and they develop strategies for an evolution towards a global minimum. All stochastic methods are based on the Monte-Carlo approach. They are very effective in escaping local minima. We present here results obtained with the Genetic Algorithm (GA) from the same ‘experimental’ data for an estimation of the model parameters $\{D1, D2, D3\}$. There are three initial steps in GA: initiation, evolution and termination. The first stage is a choice of an ‘initial population’ of points in the model parameter space. This population has an ‘aim and aspiration’: to find a global minimum of the goal function(s) in the parameter space within the termination limits. The aim is reached after several ‘generations’ of the population by evolution and reproduction. The algorithm makes ‘evolution’ by selection rules (roulette, tournament, etc.). ‘Reproduction’ is done by crossover and mutation. It is obvious that the mathematics behind these intuitive descriptions is very complicated. From a user point of view, the problem is that there are over 30 features of the algorithm to be tuned before the start of the procedure in order to obtain a robust estimation of the unknown parameters. In Table 37.1 we present results from SPE (WS and AS) and ELE

(WS and AS) simulated experiments. The same data are used as in the derivative and direct search approaches. EDF and $\{De1, De2, De3\}$ show that there is no obvious advantage for SPE over ELE. The same is true for WS versus AS data. All residuals are well below the experimental uncertainty; the resulting EDFs are between 0.213 and 0.444 nm for the model in consideration.

Direct Search Method

Direct Search Methods (DSMs) are used in solving minimization problems because of their effectiveness, simplicity, and friendly use. They have a large area of applications even when the functional relation between the unknown parameters is not differentiable and even not continuous. For our specific problem, not all DSMs are effective. We used the simplex method – one of the most popular DSMs – just to find that it strongly depends on the initial guess (input of the unknowns, an obligatory step in the procedure) and couldn't find a robust estimation of the model parameters. Recently, we have developed a DSM, which has an efficient strategy for finding a global minimum. Our method is based on the probability density of acceptable solutions within the experimental uncertainties region in the observation space [3]. It can perform a multiobjective search, has no iterative procedures, and needs no initial guess. There are three steps in the algorithm: initiation, estimation, and decision-making. First, we define a range in the parametric space, where solutions will be searched. This can be based on some preliminary information of general character. The only condition is that the interval for each parameter (min to max value of each unknown variable) contains the 'true' value. For our problem, we fixed for the interval for the physical thickness of the first layer from 0 to 10 nm, and for the other two layers from 0 to 5 nm. Then a mesh grid is defined, where the step for a change of each variable must still have a physical meaning, simulating a quasi-continuous change in the measurable quantities. The steps in our case were equal to 0.1 nm. This initiation is not relevant for the numeric approach; it just limits the number of computer evaluations of the objective functions. Second, for each point of the variable mesh we calculate the measurable quantities. The calculated functions for a given mesh point are compared with the experimental values. If the differences between the calculated and measured values are *simultaneously* less than each one of the corresponding experimental uncertainties, the parameters are accepted and stored. In the other case, we retain all points from the parametric space that result in residuals that fall in the experimental joint confidence region. This procedure is rigorous but computer-time consuming; this is the price for making no linearization, neither on the goal functions nor on the model function, no derivatives, etc. Last, but not least, is the decision-making. It is a mathematical implementation of the intuitive picture that when we get closer to the 'true value' of an unknown parameter, the relative frequency of this parameter realization is asymptotically increased. Thus, for each experimental value, we obtain a set of parametric points. We proceed to remove the 'outliers' from the parametric data and make a

robust estimate of the unknowns. Here the main difficulty is that these outliers cannot be rejected as due to random errors. Besides, they do not have some predetermined statistical distribution, i.e. they are not just extreme values of random variables that occur naturally but infrequently. We use techniques related to distribution-free tests [3,6]. The median of the parametric set vector is evaluated. Then, by the help of an interquartile range of values of the sample realization, the upper and lower 25% of the data are eliminated. Keeping the 25–75% percentiles, we obtain an estimate of the parametric values spread. Results for the problem in consideration are presented in Table 37.1; all of them are robust and effective. They demonstrate that our DSM is competitive to TR and GA approaches.

Conclusions

We have presented numeric simulations for the determination of optical characteristics of a three-layers stack on Si substrate. The physical thickness of each layer is evaluated from SPE and ELE data, generated with experimental uncertainties equal to that of high precision instruments. We have shown that deterministic, stochastic and direct search algorithms can be applied with equal success. Our modelling showed also that the impact of systematic errors [7] in the measuring process could distort the physical picture of the investigations. We discussed also some features of a new direct search method. Although it consumes more computer power, it is very effective and can be easily implemented in grid cluster structures.

Acknowledgments This work was partially supported by the National Science Foundation at the Ministry of Education of Bulgaria by grant D01-377/2006.

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Part V.2

Gas Sensors

Chapter 38

Tellurium Thin Films in Sensor Technology

Dumitru Tsiulyanu

Abstract An extensive review of the application of tellurium thin films in sensor technology is reported and discussed. Along with the traditional use of Te films in photo and strain sensitive devices, their modern application in chemical gas sensors is considered in detail. Fabrication parameters such as the technology of preparation, the substrate material, the thickness and morphology of the samples are shown to influence the response to gases. The effect of these parameters as well as that of temperature and thermal treatments on sensitivity, response and recovery times is discussed with respect to the structural evolution of the films, studied by SEM, XRD and XPS analyses. Further, the characterization of Te thin films for the detection of NO₂, NH₃ and H₂S as well as their cross-sensitivity to the main components of the atmosphere (O₂, N₂ and H₂O vapor) at different temperatures is given. The sensing mechanism is explained and the state of the art in the development of Te-based gas sensors operating at room temperature is considered.

Keywords Sensor technology · Tellurium films · Gas sensors · NO₂ · NH₃ · H₂S

Introduction

Polycrystalline tellurium thin films were the subject of many investigations in the past due to their interesting electrical [1,2] and optical [3] properties. One of the advantages of Te films over compound semiconductors in sensor and other device applications is the exemption from stoichiometry problems. This advantage allows the use of a large variety of methods for their preparation including thermal evaporation, sputtering, chemical precipitation and hot wall epitaxy. Tellurium films show p-type conduction due to lattice defects acting as acceptors; the band

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gap is about 0.34 eV and the carrier concentration at room temperature is in the range of $(1-5) \times 10^{18} \text{cm}^{-3}$. The Hall mobility is temperature dependent, at room temperature it is typically in the range $20-50 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$. The grain sizes of Te film depends on the fabrication conditions, being usually less than 100 nm. The electrical conductivity may be influenced by localized surface states at the crystalline boundaries due to impurities and gas atoms adsorbed during and after the growth process.

These peculiarities were used for the development of diodes with rectification ratios of 10^6 , thin film field transistors [4] and optical recording media [5,6]. However, Te thin films are of main interest for sensor applications such as infrared [7] and UV [8] detectors, strain sensitive devices [9] and, particularly gas sensors [10–14]. In the present work a survey on this topic is given paying special attention to gas sensors operating at room temperature.

Structure and Electronic States of Tellurium

The structure and properties of tellurium thin films are firstly determined by the properties of element tellurium. The structure of tellurium consists of spiral chains of atoms with three atoms per turn and corresponding atoms forming a hexagonal network [15]. The bonds between the atoms of the same chain are covalent, whereas between the chains a mixture of electronic and Van der Waals forces is assumed to prevail. The distance between the atoms in the same spirals is 2.86 Å but 3.74 Å between the atoms in different spirals. Due to this large difference between these two distances there is a tendency for crystals to grow in the direction of the trigonal axis rather than in other directions.

Tellurium is in the VI.th group of the periodic table and has six outer electrons in the $5s^2 5p^4$ configuration. Two of these electrons are paired in the s -orbital, occupying the lower energetic level in the shell, but four electrons are distributed between three p -orbitals (Fig. 38.1a). As only two electrons are available for covalent bonding in the half filled p -orbitals, the Te atoms normally are twofold coordinated. The other two p -electrons remain unshared and form a nonbonding electron pair, the so-called lone-pair (LP) electrons.

As the atoms are brought together the formation of molecular states illustrated in Fig. 38.1b occurs. The strong overlap of the bonding orbitals leads to their splitting into bonding (σ) and antibonding (σ^*) states. The splitting appears to be symmetric with respect to original p -state energy. The LP orbitals overlap far less strongly, so their splitting is neglected.

The covalent bonded molecules form the chains. In its turn the chains becomes bonded together by the weak Van-der-Waals forces mentioned above which originate from LP interactions. In the solids, the molecular levels are broadened into bands (Fig. 38.1c). The LP electrons form a band situated between the valence and the conduction bands, which is normally filled.

Thus, the gap between the LP band and the conduction band of 0.34 eV appears to be the main forbidden band that controls the semiconductor properties of the solid.

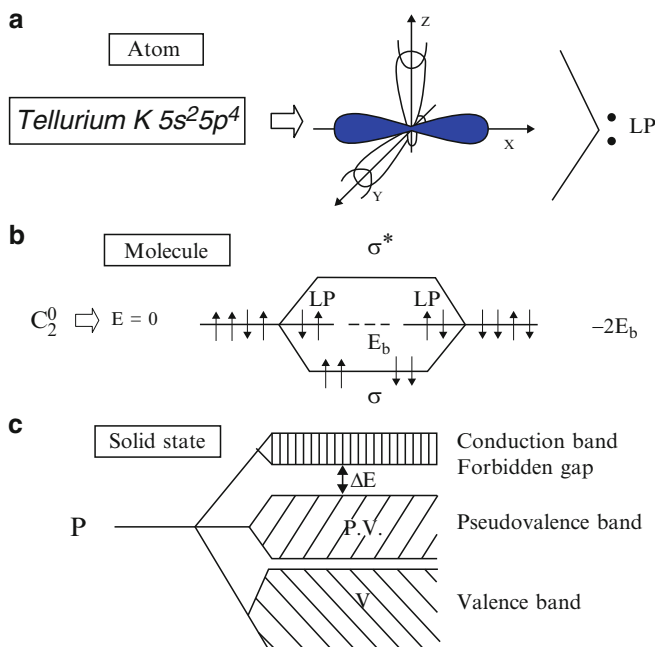


Fig. 38.1 Bonding in tellurium: (a) atomic states, (b) molecular states, (c) solids

Another peculiarity of the chalcogens including Te is due to the formation of localized charged atoms. Normally the neutral tellurium atom is twofold coordinated and labeled C_2^0 (the upper index shows the charge, the lower the coordination). The presence of LP electrons gives rise to a high negative effective correlation energy [16], which results in the transformation of two neutral chalcogen atoms C_2^0 to a pair of charged atoms with higher and smaller coordination (Fig. 38.2), respectively, by the reaction:



The threefold coordinated atom is a positively charged center, but the atom with the non-bonded covalent bond, trapping a free electron, is transformed to a negatively charged center.

The formation of such defects, which are called valence alteration pair (VAP) requires a minimum of energy, as by reaction (38.1) the total number of chemical bonds remains unchanged. Another reason for the formation of VAP is the existence of unsaturated chemical bonds, that is neutral C_1^0 centers (dangling bonds), especially at the surface. The dangling bond interacts with neighboring lone-pairs by the reaction (Fig. 38.3):



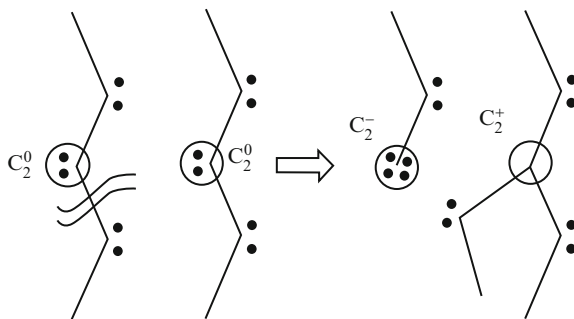


Fig. 38.2 Formation of valence alteration pairs in a chalcogen solid by bond switching

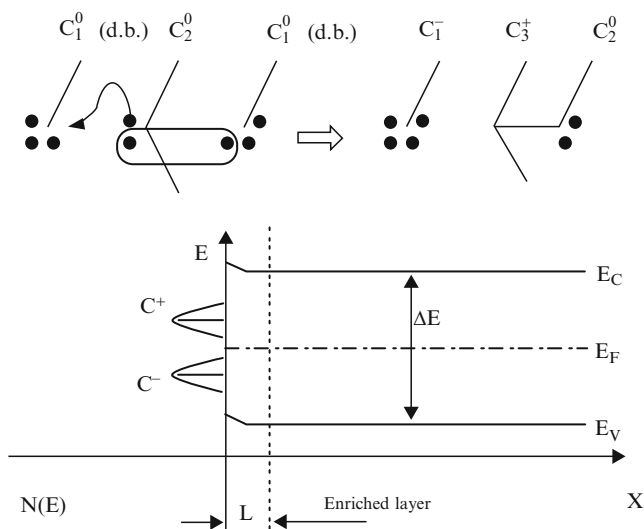


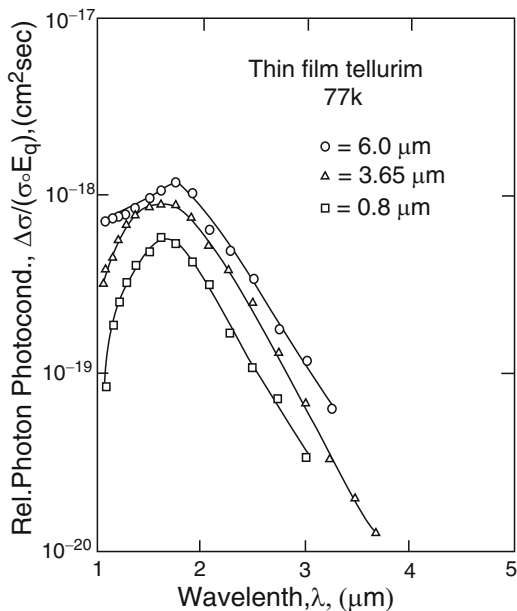
Fig. 38.3 A possible model of the dangling bond-LP interaction and the state bands at the surface

Each of these interactions releases two holes. Hence, a hole enriched region is formed at the surface and the grain boundary and intragrain regions. The energy of electrons in VAP states is higher than that of electrons in fundamental states. Hence the VAP defects can easily trap or release charge carriers, i.e. operate as acceptors or donors.

Photoelectrical and Strain Sensitive Devices

The first sensor devices based on Te thin films were infrared detectors. This application is due to the high photoconductivity around the band gap of 0.34 eV especially at low temperatures [7]. The maximum of the relative change of the

Fig. 38.4 Relative photon photoconductivity vs wavelength for tellurium thin films (Ref. [7])



conductivity per unit photon flux (Fig. 38.4) is found at a wavelength of ca. 2 μm ($h\nu = 0.62$ eV). The shift $h\nu > \Delta E$ is due to the small thickness of the films (condition $Kd \sim 1$, where K is the adsorption coefficient and d the thickness of the film).

An UV sensor can be fabricated by light treatment of Te films ($h\nu = 4.0\text{--}4.5$ eV) in air or oxygen atmosphere. Such a treatment leads to photooxidation of the surface (~ 25 nm TeO_2) [8,17]. Thus, a metal/oxide/semiconductor (MOS, adsorbed $\text{O}_2^-/\text{TeO}_2/\text{Te}$) structure forms on the Te surface. The subsequent illumination with UV light results in photodesorption of O_2^- on the TeO_2 , which bends the Te band near the interface upwards. This band bending increases the hole concentration, leading to the appearance of a photoconductivity.

The Te-based strain sensor (Fig. 38.5a) consists of an appropriate strain sensitive Te film and gold electrodes grown on a glass substrate of constant thickness, cut to a special shape so that stress and strain are the same everywhere at its surface [9]. The substrate is clamped along the line BC, and point A is deflected during the measurement. If a stress T is applied along the Ox direction, two strains are developed on the Oxy surface:

$$\varepsilon_{0x} = \frac{T}{E} \quad \text{and} \quad \varepsilon_{0y} = -\nu \frac{T}{E}, \quad (38.3)$$

where E and ν are the Young's modulus and Poisson's ratio of the substrate, respectively. Similar strains are developed in the tellurium film, which results in its electrical resistance change.

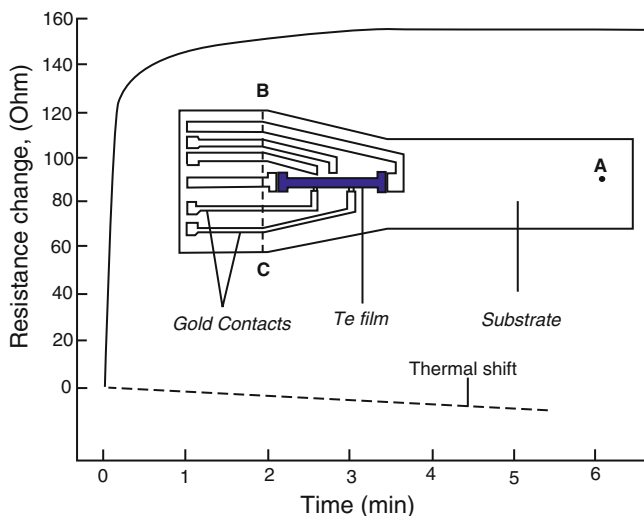


Fig. 38.5 Schematic view of a Te-based strain sensor (a) and the resistance change after application of a strain 292×10^{-6} as a function of time (Ref. [9])

Figure 38.5b shows the resistance change of a Te film after application of a strain of 292×10^{-6} as a function of time. It can be seen that 90% of the resistance change occurs during the first minute, whereas the remaining 10% of the change require more than 10 min. To reduce the time constant and the thermal sensitivity Sb, Bi or Ag impurities can be introduced into the Te film.

Gas Sensitive Devices

It has long been known that the electrical resistance of Te films is affected by the oxygen concentration in the ambient. This phenomenon was first observed by Tabatadze and Measnikov [18], who investigated the adsorption of both molecular and atomic oxygen. The chemical activity of the latter was found to be much more pronounced, which results in a higher change of the electrical conductivity of the films. Szaro reported [19] the effects of oxygen and nitrogen on the electrical properties of Te films. An increase in the hole concentration during the adsorption process was found but the changes of the electrical properties induced by the gases were irreversible and too small to achieve a useful sensor.

The real interest in Te thin films based gas sensors was initiated by Tsiulyanu and coworkers [10–12] who in the early 2000s showed that Te thin films exhibit a high sensitivity to nitrogen dioxide even at room temperature. This advantage allows a miniaturization of gas sensitive devices and a reduction of the power consumption.

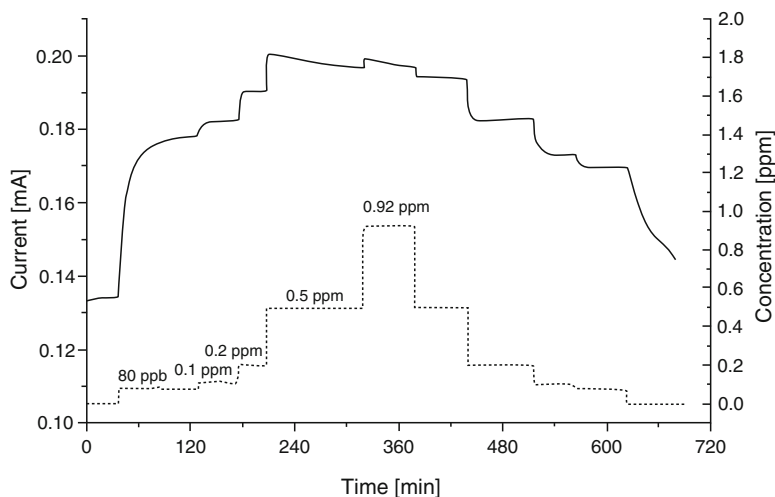


Fig. 38.6 Response of a Te thin film sensor to small concentrations of NO_2 at room temperature [11]

NO_2 Sensors

Tellurium-based gas sensors for nitrogen dioxide are intensively studied and characterized. The sensitivity of a conductive sensor is usually defined as the relative resistance variation expressed in percent. Response and recovery times are the times required to reach 90% of the steady-state value of the signal. Other important sensing parameters are: the dynamic range (the range of concentrations which can be detected), reversibility, selectivity (cross sensitivity) and stability. So far two main methods have been applied for the fabrication of NO_2 sensors: thermal vacuum evaporation [10–14,20] and rf sputtering [21]. Figure 38.6 shows the transient response of a Te thin film sensor fabricated by thermal vacuum evaporation to various small concentrations of NO_2 [11]. The sensor can obviously detect gas concentrations in the sub-ppm range i.e. below the limits of environmental standards.

Effect of Substrate Microstructure and Film Thickness

The substrate microstructure essentially influences the morphology and grain sizes of as-grown Te film prepared by both rf. sputtering [21] and thermal vacuum evaporation [20], which results in variations of the gas sensitivity. The grain size for films grown on glass substrates was found [20] to be the smallest, the grains were preferentially oriented along the substrate (100) direction [10] while those on alumina have a preferred (101) orientation.

As the films deposited on glass substrates show a maximum sensitivity to NO_2 , hereafter the sensors on glass substrates are considered unless otherwise specified.

Fig. 38.7 Effect of the thickness on (a) the electrical conductivity and (b) the sensitivity of Te thin films to 1.5 ppm of NO₂ at room temperature (Ref. [14])

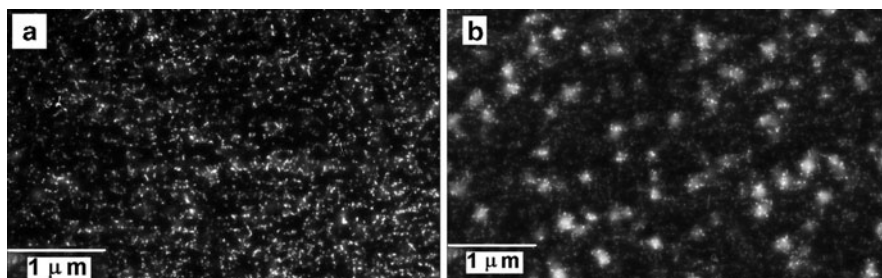
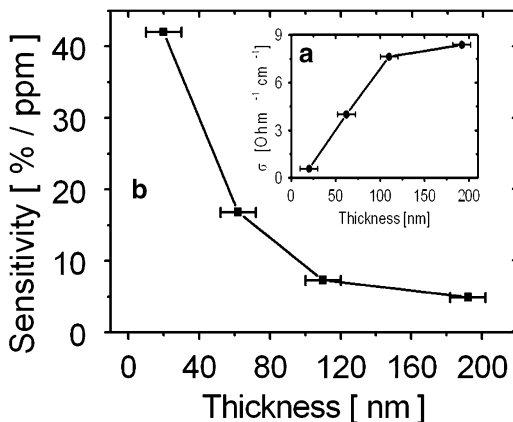


Fig. 38.8 SEM micrograph of a Te film: (a) as-grown; (b) annealed for 2 h at 200°C (Ref. [22])

The conductivity of Te layer increases with thickness [14], but above 100 nm saturation occurs (Fig. 38.7a). The sensitivity to NO₂ follows an opposite behavior: it strongly increases with decreasing thickness (Fig. 38.7b). The SEM image of an as-deposited Te film depicted in Fig. 38.8a elucidates a morphology typical for a compact layer. In such a case [23], the current flows through two parallel channels, one of them being the surface channel, which is affected by the reaction with the gas, and the other is the gas-unaffected bulk. Decreasing the layer thickness enhances the influence of the surface grain boundary resistance and diminishes the gas-unaffected parallel bulk resistance. Therefore the film conductivity decreases, while its sensitivity strongly increases with decreasing thickness.

Effect of Substrate Temperature and Annealing

The substrate temperature during thermal deposition has a very pronounced influence on the Te film texture as well as on the electrical and gas sensing properties [20,24]. High substrate temperatures were reported to result in an increase of the

grain sizes, but at temperatures above 343 K a dendritic growth of extended hexagonal prisms occurs. The gas sensitivity approximately doubles if the substrate temperature increases from 300 to 373 K.

Post-deposition annealing of Te films at temperatures above 100°C also noticeably influences their electrical conductivity and sensitivity to NO₂ [20,22] but at temperatures higher than 150°C the conductivity sharply increases simultaneously with the appearance and development of large-sized crystallites (Fig. 38.8b). The decrease of the gas sensitivity is due to this coalescence of crystallites.

Effect of Operating Temperature and Humidity

Figure 38.9a shows the sensitivity of a Te sensor towards 0.75 and 1.5 ppm NO₂ vs the operating temperature. The temperature reduces the sensitivity of the films, especially strongly at temperatures above 80°C. This is due to a decrease of both the total electrical resistance of the sensor and the number of adsorbed NO₂ molecules with temperature [22].

The humidity response of the Te films becomes important as water vapor is the main interfering gas during NO₂ monitoring in our environment. Figure 38.9b shows the typical response of a tellurium thin film to an impulse of humid air (58% RH) at 23°C, 50°C and 70°C. [25]. Synthetic dry air (1–2% RH) was used as a reference gas. Switching from dry to wet synthetic air slightly decreased the current flowing through the film, reaching the steady state at room temperature in approximately 45 min. The relative resistance of the film increased by this process by ca. 15%. Such an essential change will obviously result in a high cross-sensitivity to NO₂. On the other hand, as follows from Fig. 38.9b the humidity response of a sensor heated to 50°C becomes negligible. A RH of 58% leads at this temperature to an increase of the relative resistance of only with 3–4%. The dramatic influence of the temperature on the humidity response indicates that the effect of water vapor on tellurium films is due to simple physical adsorption.

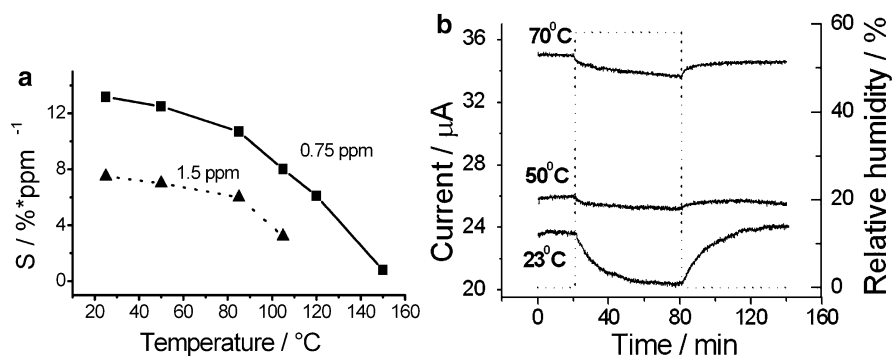


Fig. 38.9 (a) Sensitivity vs operating temperature (Ref. [22]); (b) effect of humidity on the sensor response (After Ref. [25])

Cross-Sensitivity to Other Gases

The cross-sensitivity to gases is one of the crucial sensor parameter, which determines its selectivity. Humidity is known mainly to disturb pollutants measurements if sensors operating at low temperatures are used. Figure 38.10 shows the influence of the humidity on Te films for NO_2 detection at 50°C [25]. At this temperature the best compromise between sensitivity, the effects of annealing, response and recovery times is achieved, and the humidity do not much disturb the conductivity. As one can see from Fig. 38.10, the humidity does not interfere with NO_2 reaction at this temperature. The inset of Fig. 38.10 illustrates the response of a Te film to 1.5 ppm NO_2 vs the relative humidity of the carrier gas at 50°C . It suggests that the influence of the humidity on the sensor sensitivity to NO_2 appears to be negligible at these conditions.

The others main components of uncontrolled atmospheres, which can disturb the detection of NO_2 , are oxygen and nitrogen. Figure 38.11 presents the time dependent current to pulses of 100% nitrogen, 100% oxygen and 1.0 ppm NO_2 diluted in dry synthetic air (used also as reference gas) at room temperature. It can be seen that the response to either 10^6 ppm O_2 or N_2 is far below the response to only 1.0 ppm NO_2 under the same experimental conditions, this means that the films exhibit a negligible cross-sensitivity to N_2 and O_2 which may interfere the measurement of the target gas NO_2 . This is due to different mechanisms of adsorption: “weak” chemisorption in the case of unpolar, symmetric molecules like N_2 or O_2 , and “strong” chemisorption of nitrogen dioxide molecules which involves interactions with the lone-pair electrons of the tellurium atoms.

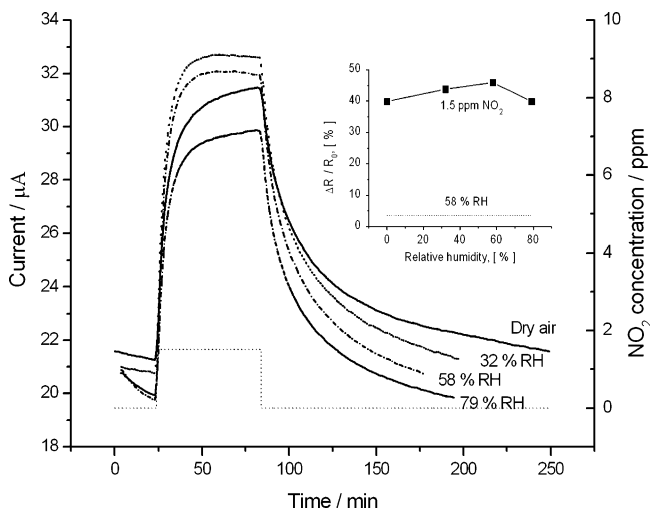


Fig. 38.10 Effect of humidity on Te films for NO_2 detection at 50°C . The inset illustrates the response vs RH (After Ref. [25])

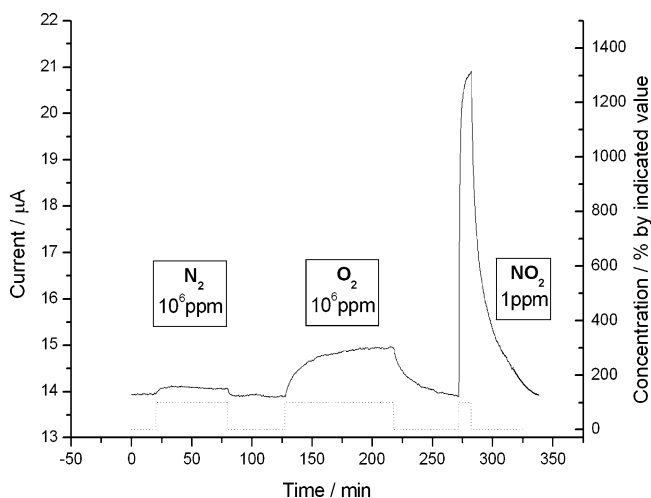


Fig. 38.11 Time dependent current for pulses of 100% O₂, 100% N₂ and 1.0 ppm NO₂ diluted in dry synthetic air (Ref. [25])

NH₃ Sensors

Ammonia sensitive Te films were prepared by thermal vacuum deposition on heated (370–430 K) alumina substrates fitted with gold or indium electrodes [13,26,27]. In contrast to NO₂, the resistance of the films was found to increase on exposure to NH₃. The response in dry air is linear in the range from 10–100 ppm (Fig. 38.12) and saturates at higher concentrations.

The transient characteristics (Fig. 38.13) essentially differ from that of NO₂. The response is only a few seconds (Inset of Fig. 38.13) but the recovery time is about 24 h. The effects of the operation temperature do not differ from that to NO₂. In spite of a strong cross-sensitivity to water vapor there is a good response to NH₃ in humid media [26].

H₂S Sensors

The resistance of Te films was observed [20,28] to increase reversibly on exposure to H₂S (Fig. 38.14a). This response, being much larger than to NH₃ (Fig. 38.14b), allowed the development of a hydrogen sulfide gas sensor. The sensing characteristics were found to depend on the substrate (material) microstructure, the deposition and operation temperature. The films deposited on glass substrate exhibits the maximum sensitivity [20].

Fig. 38.12 Sensitivity of Te films in dry air vs the ammonia concentration (Ref. [13])

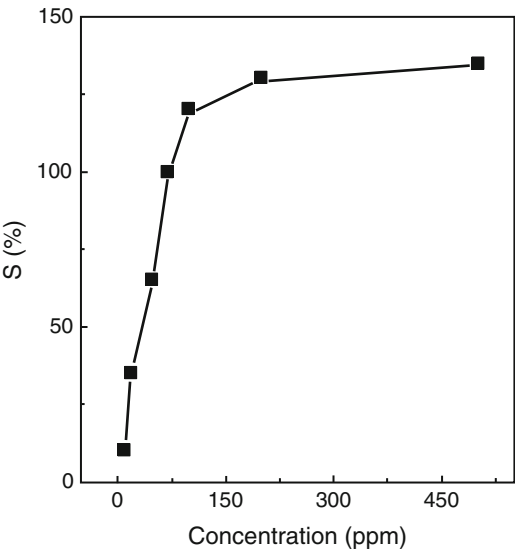
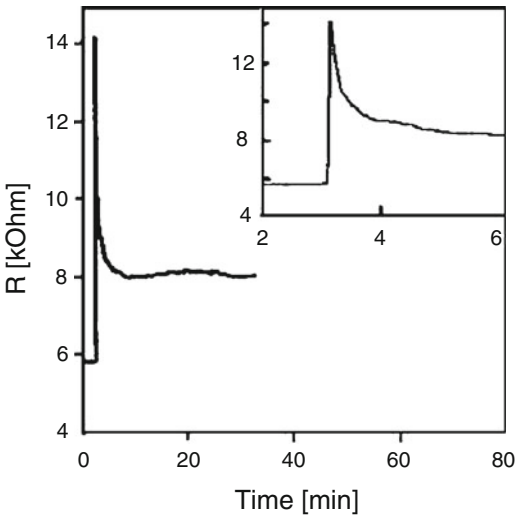


Fig. 38.13 Transient response of a Te film to 100 ppm of ammonia (After Ref. [13]). The inset shows the response of the film for the first few minutes after exposure to NH_3



Sensing Other Gases

Tellurium thin films exhibit also a sensitivity to a number of other toxic gases but much weaker. The comparison of the sensitivities to different gases (Fig. 38.15) can be only qualitative due to the very different dynamic ranges which are summarized in Table 38.1.

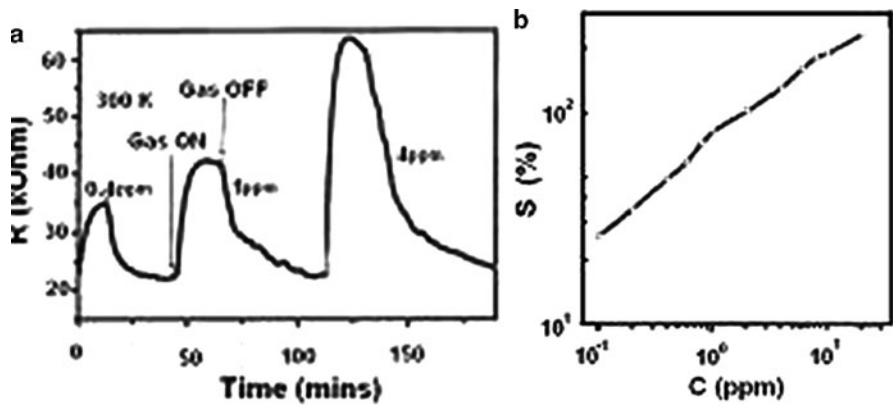


Fig. 38.14 (a) Transient response and (b) sensitivity of a Te film vs the H₂S concentration (Ref. [28])

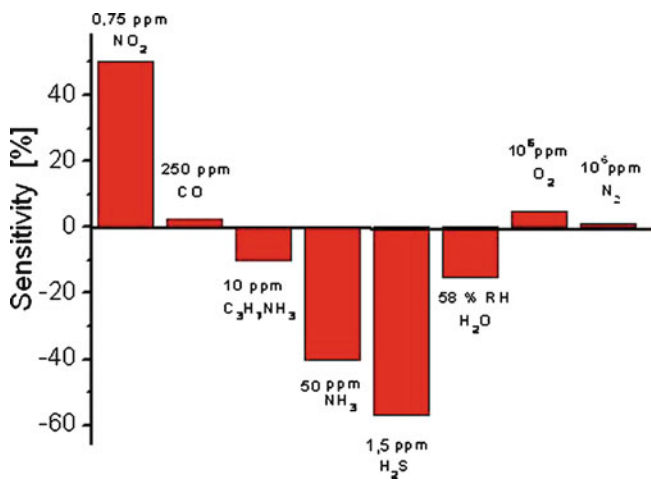


Fig. 38.15 The sensitivity of Te films on exposure to various gases at room temperature

Table 38.1 Gas response comparison of Te thin films

Gas	Technology of preparation	Dynamic range	Reference
NO ₂	Thermal vacuum evaporation	0.01–1.0 ppm	[10]
	rf sputtering	1.0–100 ppm	[21]
NH ₃	Thermal vacuum evaporation	10–150 ppm	[13]
H ₂ S	Thermal vacuum evaporation	0.1–1.0 ppm	[28]
CO	Thermal vacuum evaporation	50–400 ppm	[12]
	Te/Ti thermal vacuum evaporation	0.1% vol	[27]
C ₃ H ₇ NH ₂	Thermal vacuum evaporation	1.0–10 ppm	[12]

Sensing Mechanisms

Nitrogen Dioxide

The mechanisms of gas detection by Te thin films was investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD), Raman and X-ray photoelectron spectroscopy (XPS). XRD spectra of tellurium thin films either thermally deposited on unheated substrates (Fig. 38.16) or rf sputtered [10] comprise peaks corresponding only to elemental tellurium. No peaks corresponding to oxides of tellurium are visible in these spectra. Also no other peaks were observed in Raman spectra before (Fig. 38.17a) or after exposure to NO₂, apart to those corresponding to pure tellurium. Therefore the mechanism of gas sensing by Te films, being different from that for the metal oxides, is attributed to lone-pair electrons.

The nitrogen dioxide molecule comprises an odd electron, i.e. after covalently bonding of nitrogen to oxygen one of the atoms remains with a single unpaired electron. Being adsorbed on the surface of the Te grain, the NO₂ molecule acts as a dangling bond (Fig. 38.18) which can accept a LP electron to form an electron pair via the reaction:



This reaction occurs on the surface of metal oxides semiconductors (e.g. SnO₂) as well, but the difference between these two cases consists in the nature of the

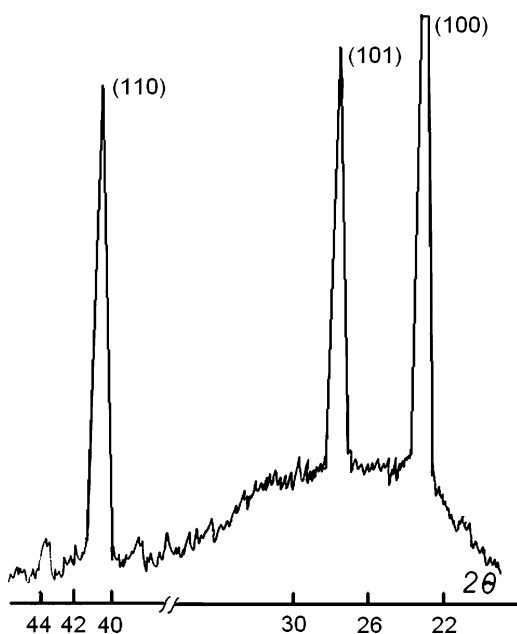


Fig. 38.16 XRD spectrum of a Te film thermally deposited at 300 K (Ref. [10])

Fig. 38.17 Raman spectra of (a) a sputtered Te thin film and (b) Te powder (Ref. [10])

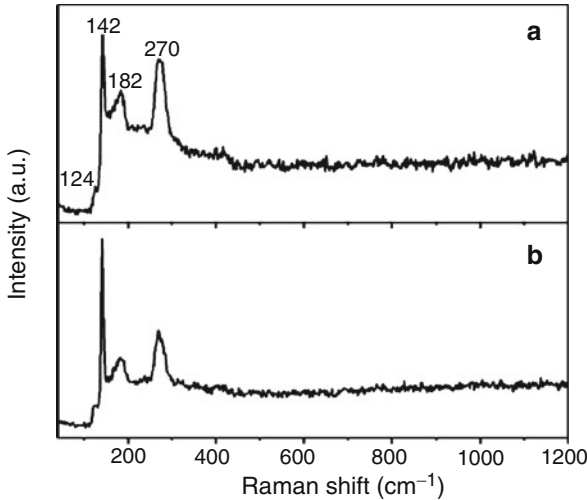
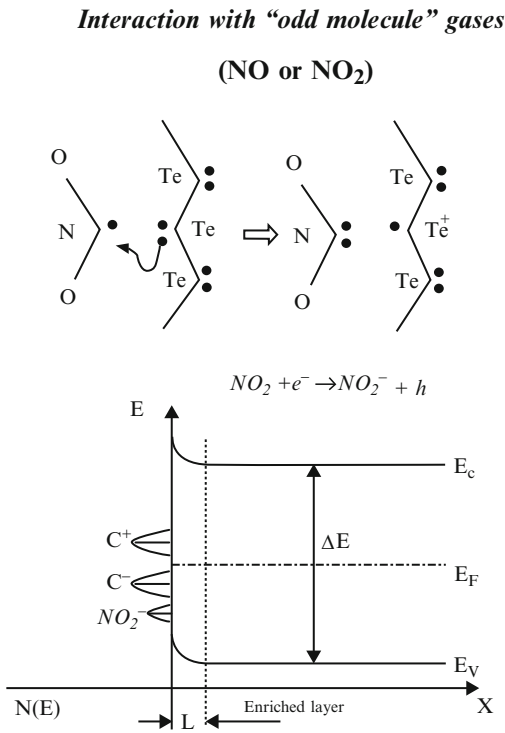


Fig. 38.18 Schematic diagram showing the dangling bonds – LP electrons interaction and the surface state bands



trapped electron. In SnO_2 the trapped electron comes from thermally generated oxygen vacancies and the surface reaction requires enhanced temperatures of 300–500°C.

In the case of Te films, the trapped electron originates from lone-pair orbitals, which form the upper part of the valence band. The capture of a lone-pair electron, i.e. the transition of an electron from the upper part of the valence band to a NO_2 acceptor level (accompanied with the release of an additional hole) occurs at lower temperatures, including room temperature. For this reason tellurium films offer excellent perspectives for the use as a main component in gas sensors which operate at room temperature.

Ammonia

The response of tellurium films to NH_3 differs essentially from the response to NO_2 which implies another mechanism of gas sensing. Ammonia does not have an odd electron, hence its molecule cannot act as dangling bond. Nevertheless, if the films are prepared on substrates heated up to 423 K they exhibit a sensitivity to NH_3 . The Raman spectra (RSP) of virgin films show peaks corresponding to TeO_2 , which disappears after exposure to NH_3 [13].

The absence of TeO_2 after exposure to NH_3 indicates the conversion of TeO_2 to elemental Te. XPS spectra (Fig. 38.19) of virgin films exhibit two peaks attributed to TeO_2 and TeO_3 , respectively [13]. No peak corresponding to metallic Te was observed for unexposed films. After exposure to 100 ppm NH_3 the peaks of TeO_3 disappeared, but a new one at 571.7 eV appeared, corresponding to pure Te $3d_{5/2}$. Both RSP and XPS analyses did not reveal the formation of any compound containing nitrogen.

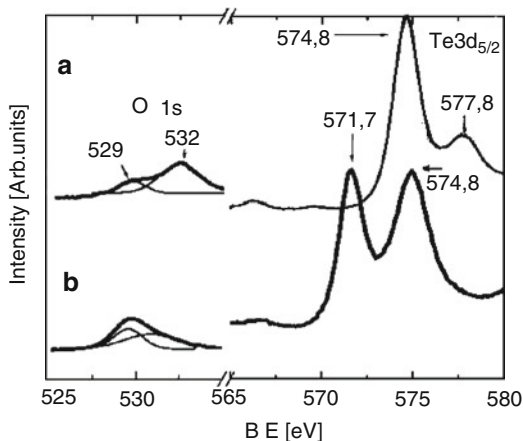


Fig. 38.19 XPS spectra in the O 1s and Te $3d_{5/2}$ regions for (a) unexposed and (b) NH_3 exposed Te films (Ref. [13])

These results indicate that the sensitivity of Te film to ammonia arises from an induced reduction of tellurium oxides to Te metal on the top surface of the grains. Probably, the oxygen in TeO_3 act as acceptors, which interact with LP electrons resulting in an increase of the hole density in accumulation regions and thus of the conductivity of the films. Removing this oxide by interaction with NH_3 diminishes the hole density on the grain surfaces and reduces the conductivity of the film.

Hydrogen Sulfide

Highly sensitive H_2S sensors were fabricated by thermal vacuum deposition of tellurium on alumina substrates heated up to 373 K [28]. The Raman spectra of virgin films also showed the peaks corresponding to TeO_2 . On exposure to H_2S , TeO_2 was observed to be reduced to elemental Te. This result was confirmed by XPS (Fig. 38.20). The Te $3d_{5/2}$ spectra of unexposed samples indicates the presence of both metallic Te and TeO_2 but the intensity of the last is much higher.

On exposure to 1,000 ppm H_2S , TeO_2 is reduced to elemental Te. Simultaneously two peaks appear which are attributed to S 2p and hydroxyl groups (OH). This is a reversible chemical reaction on the surface as the XPS recovers after removing the H_2S .

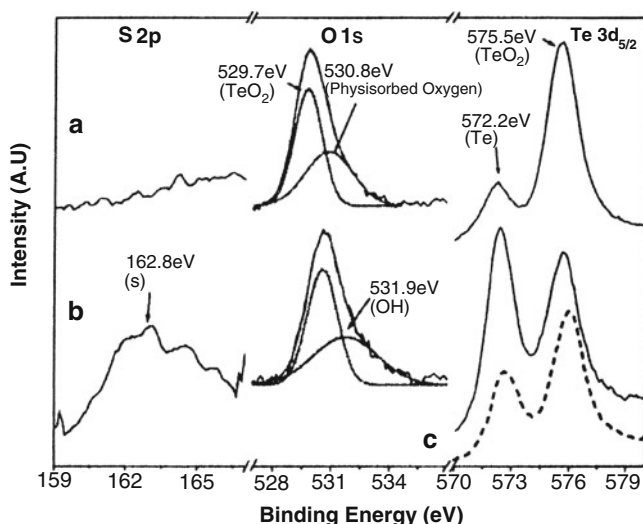


Fig. 38.20 XPS spectra in the S 2p, O 1s and Te $3d_{5/2}$ regions for (a) unexposed and (b) H_2S exposed films. The dotted line (c) stems from a film recovered after exposure to H_2S (Ref. [28])

Conclusions

Due to its special chemistry and structure, polycrystalline tellurium can be applied in the development of both effective physical and chemical sensors. The gas sensitive devices can operate at room temperature. They show considerably short response times and a good sensitivity in the ppm and sub-ppm concentration range. The flexible structure and the high ability for alloying allow variation of the properties of these materials in wide ranges and give the possibility to design of sensors selective to different gases for environmental monitoring and process control. Investigation of the gas sensing mechanism of Te thin films is still in progress but in principle it can be explained by direct or indirect interaction of adsorbed species with lone-pair electrons, which form the upper part of the valence band, and/or reversible chemical reactions on the grain surfaces.

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Chapter 39

Yttrium Nanoparticle Hydrogen Gas Sensors

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Abstract The preparation of new types of nanosystems based on metallic yttrium nanoparticles, which are difficult to produce by traditional methods due to the high melting temperature and the extremely high oxidizability of this metal, has been studied. The materials were prepared with an original high vacuum set-up (LUCAS) intended for the formation of metal nanoparticle beams by laser ablation. Yttrium nanoparticles were synthesized, and their chemical reactions with hydrogen were studied at room temperature. It was found that the reaction at low hydrogen pressures ($\sim 10^{-3}$ Pa) leads to the formation of YH_2 dihydride particles with metallic properties and optical plasmon absorption. An increase in the hydrogen pressure to ~ 100 Pa results in the transformation of metallic-like YH_2 nanoparticles to dielectric YH_{3-x} ($x < 1$) nanoparticles. It is shown that the last reaction corresponding to the metal–dielectric phase transition is reversible with respect to the hydrogen pressure. These experimental data demonstrate that yttrium nanoparticle materials can be effectively used as optical hydrogen gas sensors.

Keywords Hydrogen gas sensor · Yttrium-based nanoparticles · Yttrium dihydride · Laser ablation · Plasmon resonances

Introduction

At present, nanostructured materials, in particular metal nanoparticles (MNPs) or clusters, have been extensively investigated from fundamental and applied viewpoints. MNPs occupy an intermediate position between molecular species and bulk

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materials and exhibit new properties that arise either as a result of the small number of atoms in a particle (“size effect”) or due to the strong influence of the interface between MNPs and the environment (“surface effect”) [1]. The present work is devoted to the preparation of a new nanostructured material based on transition metal (yttrium) nanoparticles and, the study of surface effects in these MNP systems. It should be noted that metallic yttrium nanoparticles are quite difficult to synthesize by conventional physical methods, such as vacuum deposition, sol–gel synthesis, and other techniques, due to the high melting (1,522°C) and boiling (2,927°C) temperatures of yttrium, as well as the extremely high oxidizability. Moreover, as was shown in Refs. [2–5], bulk samples of metallic yttrium are characterized by a high chemical reactivity with respect to hydrogen. These physicochemical features of yttrium gave impetus to investigations of the synthesis of yttrium nanoparticles and the influence of hydrogenation of the nanoparticles on their optical and electrical properties.

Experimental Procedure

The high vacuum laser-based universal cluster ablation source (LUCAS) was designed for synthesizing yttrium nanoparticles with a high chemical reactivity [6]. Nanoparticles were produced using a LUMONICS JK 702H pulsed Nd:YAG laser operating at a wavelength of 1.064 μm . A beam of yttrium particles was generated by laser ablation of chemically pure metallic bulk yttrium in argon atmosphere at pressures of 6.0–1.2 Pa. The plasma generated by the laser pulses above the surface of the yttrium target was cooled by atoms of the inert gas fed in the chamber. The gas mixture of argon and yttrium particles was ejected from a nozzle with a diameter of 1.2 mm due to the pressure difference between source and deposition chamber produced by vacuum pumps. The pressure in the deposition chamber was approximately equal to 6.0×10^{-4} – 1.2×10^{-5} Pa. The laser ablations was performed using 500 pulses with an energy density of $\sim 4.7 \text{ J/cm}^2$, a pulse duration of 1 ms, and a frequency of 80 Hz. The MNPs were deposited onto quartz substrates or carbon thin films intended for electron microscopic analyses, which were carried out with a Philips EM 400T transmission electron microscope.

After deposition, the samples with the yttrium nanoparticles were exposed from 30 min to several hours to hydrogen atmospheres at pressures in the range from 5×10^{-4} to 500 Pa at room temperature. In order to provide in-situ chemical reactions between hydrogen and yttrium nanoparticles, the MNPs were coated in a vacuum chamber by a palladium thin film ($\sim 0.3 \text{ nm}$) by electron beam evaporation. The palladium served for the formation of a hydrogen solution, which favored the incorporation of hydrogen into the yttrium particles. The phase composition of the nanoparticles was controlled by measuring in-situ the optical extinction spectra with a single beam fiber-optic set-up based on a Zeiss MSC spectrometer in the range 250–1,000 nm. The electrical resistance of the samples containing

hydrogenated yttrium nanoparticles was in-situ measured according to the standard procedure by the four point probe method using a Keithley 236 source unit, which made it possible to measure currents from fA to nA. The voltage between the contacts was equal to 1 V, the distance between the gold contacts 4.5 mm.

Fabrication of Yttrium Nanoparticles

Electron micrographs of yttrium nanoparticles with two scales and the corresponding histograms of their size distributions are shown in Fig. 39.1 for different argon pressures. It can be seen that the nanoparticles are almost spherical. Data on the average size d of the nanoparticles and the standard deviation σ from the average are also presented in figure. It was revealed that larger nanoparticles with a narrower size distribution are formed at the higher argon pressure (1.2×10^5 Pa). The average sizes of yttrium nanoparticles synthesized at pressures of 6.0×10^4 and 1.2×10^5 Pa are 25 and 30 nm, respectively. The observed dependence of the size of yttrium nanoparticles on the gas pressure is qualitatively in agreement with the results of investigations of the formation of semiconductor particles [7] and silver and copper nanoparticles [8] formed by laser ablation. However, in our case, the value of σ obtained at a pressure of 1.2×10^5 Pa appears to be considerably lower than those determined in [7,8]. An interesting feature, which was observed in the case of yttrium nanoparticles but not in earlier experiments, is that the surface of the nanoparticles is covered by a shell (Fig. 39.1b). It was established that this shell appears on the MNPs at argon pressures above 6×10^4 Pa and that the shell thickness increases with increasing pressure. A high resolution electron micrograph of yttrium nanoparticles with shells of varying thickness is displayed in Fig. 39.2. It can be seen from this figure that the shell thickness can be as large as $\sim 4\text{--}6$ nm. It should also be noted that, since the shell between yttrium particles in direct contact is absent, the inference can be made that the shell is formed within a certain time after the formation of the MNPs. Since the shell appears for nanoparticles synthesized at high pressures of the seeding gas, we can assume that the MNPs undergo surface oxidation due to the presence of residual oxygen in the gas phase.

In this case, we can expect the formation of a dielectric phase Y_2O_3 , which is known easily form on the surface of metallic yttrium films in air [6]. To check this assumption, we performed in situ measurements of the absorption (optical density) of yttrium nanoparticles without and with shells, which were prepared at low and high argon pressures, respectively. Figure 39.3 shows the experimental optical density spectra of the nanoparticles. The absorption spectrum of yttrium particles exhibits the well-known band with a maximum in the range of ~ 380 nm due to the surface plasmon resonance in MNPs [1,9]. Unlike yttrium nanoparticles, the absorption spectrum of particles with shells is characterized by a considerably broader band that covers almost the entire visible range with the maximum shifted toward longer wavelengths to approximately 650 nm. Moreover, an enhancement

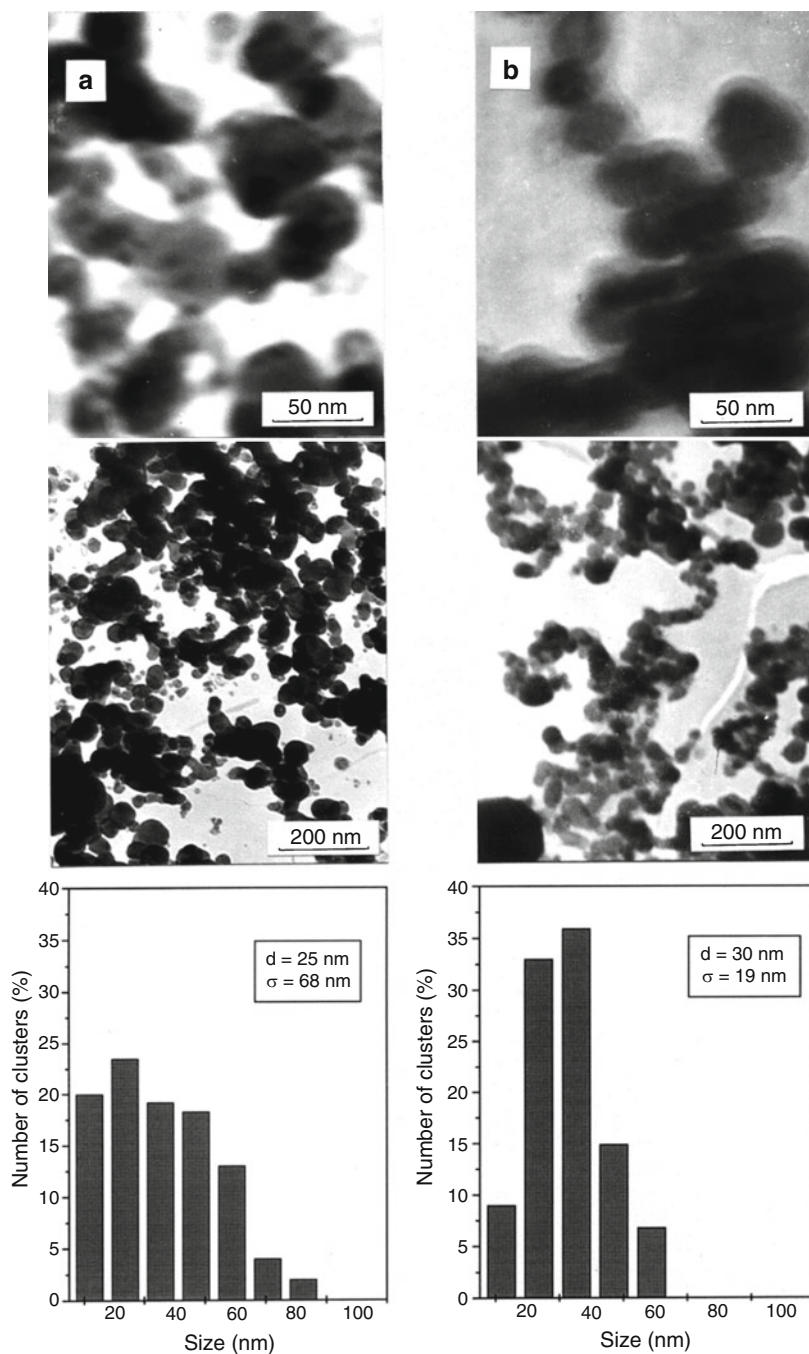


Fig. 39.1 Electron micrographs and histograms of the size distributions of yttrium nanoparticles synthesized at argon pressures of (a) 6.0×10^4 and (b) 1.2×10^5 Pa

Fig. 39.2 High resolution electron micrograph of yttrium nanoparticles with shells of different thickness

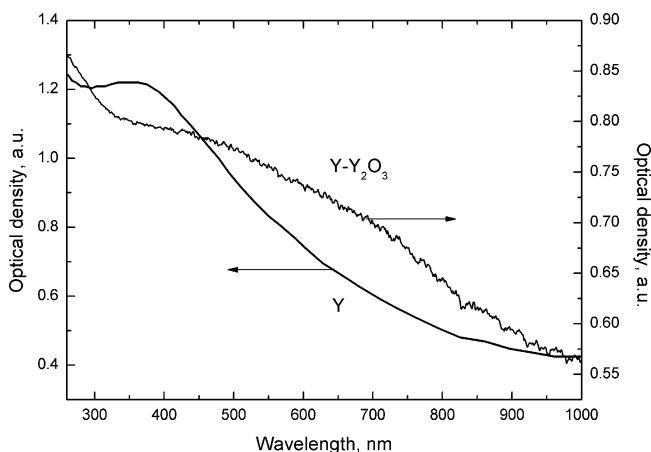
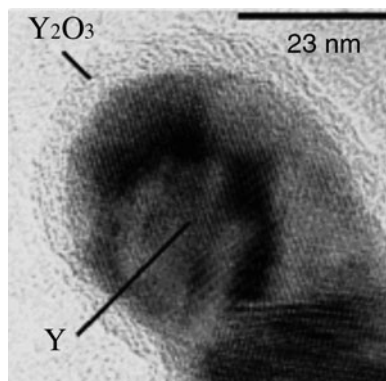
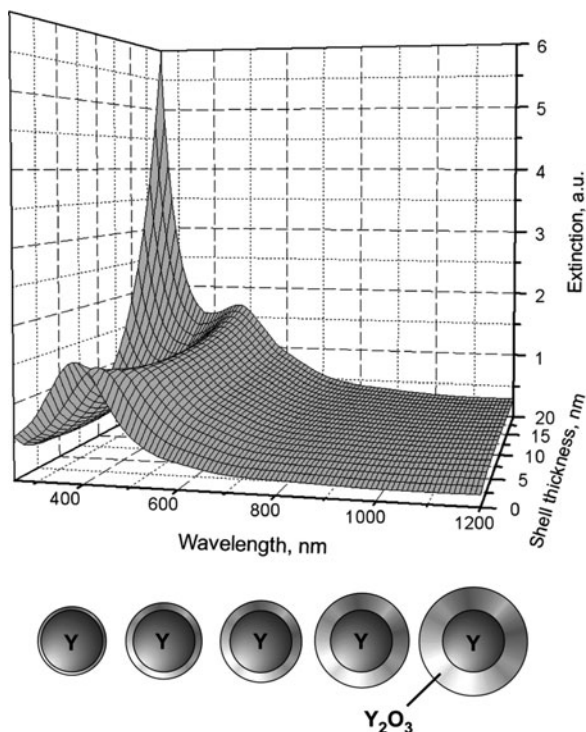


Fig. 39.3 Experimental optical density spectra of yttrium nanoparticles without and with shells, synthesized at argon pressures of 6.0×10^4 and 1.2×10^5 Pa, respectively

of the absorption in the UV spectral range below 300 nm is observed in the spectrum. In order to explain these experimental results, the extinction spectra of complex particles consisting of an yttrium core and an yttrium oxide shell were simulated using the electromagnetic theory of Mie [10,11]. In our calculations, the thickness of the Y_2O_3 shell varied from 0 to 20 nm, whereas the core size remained constant (30 nm). The permittivities of Y and Y_2O_3 required for the calculations were taken from Ref. [12].

The calculated spectra are shown in Fig. 39.4. It can be seen from this figure that the presence of Y_2O_3 shells on the surface of yttrium nanoparticles leads to a shift in the extinction maximum toward the red spectral range and, in addition, to an increase of the absorption in the UV range. Although the experimental and simulated spectra are only in qualitative agreement (this can be associated with

Fig. 39.4 Calculated optical extinction spectra of yttrium nanoparticles with Y_2O_3 shells as a function of the shell thickness



difficulties encountered in calculating the particle size distribution and the variable thickness of the shells), we should note two coinciding spectral features: the shift of the maximum to longer wavelengths and the increase in the absorption intensity in the UV range in the presence of oxide shells. This circumstance gives ground to suggest that the surface shells observed for yttrium particles in the micrographs (Figs. 39.1 and 39.2) are caused by the oxidation of the MNPs.

Fabrication of Hydrogenated Yttrium Nanoparticles

Since, as was shown in the previous section, yttrium nanoparticles are prone to oxidation, we chose samples synthesized at a low argon pressure (6×10^4 Pa) for hydrogen experiments. The average size of the nanoparticles in these samples remained almost unchanged after the chemical reaction with hydrogen. Previously, in experiments on hydrogenation of bulk yttrium thick films, the types of crystal structures corresponding to the yttrium phase and the newly formed yttrium hydride phases were determined using X-ray diffraction [5]. Furthermore, for the same hydrogenated yttrium films, these authors determined the dielectric constants of [5]

which were subsequently used in [13] to calculate the optical extinction spectra of nanoparticles of different phase compositions Y and YH_{3-x} (from $x < 1$ to $x \ll 1$) in the framework of the Mie theory. In this respect, the available calculated spectra can be used for determining the phase composition of the hydrogenated nanoparticles produced in our work.

In order to hydrogenate yttrium nanoparticles, the samples were coated by a thin continuous palladium film in which a hydrogen solution was formed. It was revealed that the presence of the palladium film does not substantially affect the initial optical spectra of the yttrium nanoparticles. Exposure of the yttrium nanoparticles to different hydrogen pressures results in a significant change in their optical extinction spectra (Fig. 39.5). Exposure of yttrium to low hydrogen pressures ($\sim 10^{-3}$ Pa) leads to the formation of particles of a new yttrium dihydride (YH_2) phase with a face-centered cubic lattice due to the occupation of face-centered cubic interstitial positions in the hexagonal close-packed yttrium lattice by hydrogen atoms [4]. According to earlier calculations [13], only in the case of small particles (Fig. 39.6, hydrogen pressure 5.0×10^{-4} Pa) the YH_2 phase is characterized by two spectrally resolved bands of optical Mie resonances (400 and 960 nm), which are considerably narrower than those for yttrium nanoparticles. The YH_2 particles also exhibit metallic properties and have a stable structure. Since a decrease of the hydrogen pressure (complete evacuation of hydrogen from the chamber) does not result in any change in the optical spectrum of the YH_2 nanoparticles, we can assume that their phase composition is retained. As for the bulk materials [5], in the case of the nanoparticles the chemical reaction $\text{Y} \rightleftharpoons \text{YH}_2$

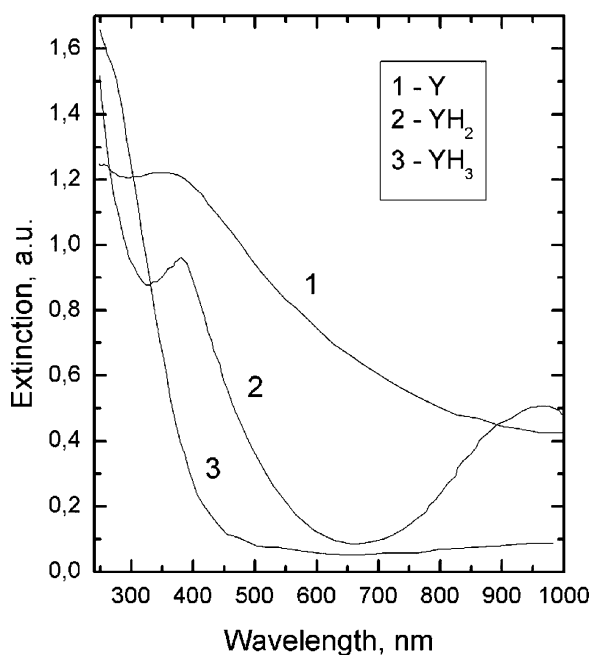
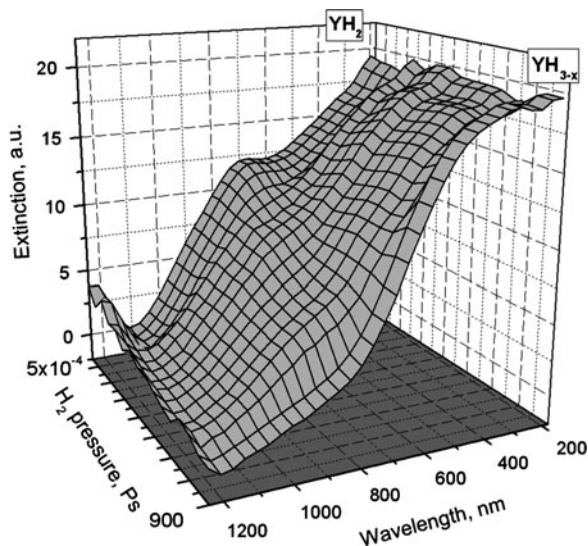


Fig. 39.5 Experimental optical extinction spectra measured in situ for (1) Y, (2) YH_2 , and (3) YH_3 nanoparticles

Fig. 39.6 Experimental optical extinction spectra measured in situ and illustrating the reaction $\text{YH}_2 \rightleftharpoons \text{YH}_3$ at different hydrogen pressures



is irreversible. The optical reflection from deposited YH_2 particles is characterized by a metallic surface, as is the case of yttrium nanoparticles.

Figure 39.6 shows a series of extinction spectra measured in situ for samples in hydrogen atmosphere as a function of the hydrogen pressure. The spectrum of yttrium nanoparticles is not shown in this figure. As can be seen from Figs. 39.5, 39.6, a gradual increase of the hydrogen pressure leads to a monotonic change in the optical spectra, which manifests itself in a smooth decrease of the intensity of the selective extinction bands down to their complete disappearance. By analogy with a study of bulk yttrium films [4], we can suggest that an increase in the hydrogen pressure (in our experiment to a level of ~ 100 Pa) results in a change in the phase composition with the formation of nanoparticles of yttrium trihydride YH_{3-x} (from $x < 1$ to $x \ll 1$) due to the incorporation of hydrogen atoms on interstitial positions the hexagonal close-packed crystal lattice of the YH_2 phase. In this case, the metallic luster of the YH_2 nanoparticles disappears. Curve 3 in Fig. 39.5 and the curve corresponding to a hydrogen pressure of 900 Pa in Fig. 39.6 characterize the YH_{3-x} nanoparticles, which have a hexagonal close-packed structure. The optical density spectrum of these particles is typical of small dielectric particles [1]: the absence of selective absorption bands in the visible range and a monotonic increase of the absorption in the UV range. The chemical reaction $\text{YH}_2 \rightleftharpoons \text{YH}_3$ turns out to be reversible at room temperature with respect to the hydrogen gas pressure. This effect manifests itself as a reversible change in the optical spectra upon sequential multiple (no less than ten times) increase and decrease of the hydrogen pressure in the deposition chamber of the set-up, which is also confirmed by reversible changes in the electrical conductivity. Such a change in the phase composition of hydrogenated yttrium particles seems to be promising from the

standpoint of the design of optical or electrical hydrogen gas sensors and detectors, because the observed phase transition is accompanied by a substantial change in both the optical spectrum (from absorbing to transparent in the visible range) and the conductivity of the sample. Composite materials based on these nanoparticles possess a number of obvious advantages over, for example, thick brittle yttrium films [5]. The first is the more developed surface of small particles, which increases the efficiency of the interaction with hydrogen. Second, the nanoparticles are less prone to mechanical stresses and damage that arise because the transition $\text{YH}_2 \rightleftharpoons \text{YH}_3$ is accompanied by a change in the lattice constant by up to 10%.

Acknowledgements The author is grateful to the Alexander von Humboldt Foundation (Germany) and the Austrian Scientific Foundation in the frame of the Lise Meitner program for financial support. This work was partly supported by the Russian State Contract No. 02.740.11.0797.

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Chapter 40

Conductive Gas Sensors Prepared Using PLD

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Abstract This contribution deals with conductive thin film gas sensors fabricated using laser technology. The principles of the pulsed laser deposition (PLD) technology is explained. Hybrid PLD systems, based on a combination of PLD and magnetron sputtering, PLD and RF discharges, and PLD with two laser targets are also presented. The growing layers can be modified by an ion beam. Organic films can be grown using the cryogenic MAPLE technology. Nanocrystalline and nanocomposite thin films for gas sensors can be deposited. Examples of layer fabrication and testing of layer properties for gas sensors are given.

Keywords PLD · Hybrid PLD · MAPLE · Gas sensors · Thin film sensors

Introduction

The working principle of sensors is based on the detection of changes of their physical, chemical or biological properties under the influence of the quantity to be detected. Here, two principles of detection complying with these requirements are considered: thin film gas sensors based on the detection of resistivity changes or on changes of the refractive index under the influence of selected gases.

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Various basic materials and their combinations were tested and studied for these purposes. The following overview includes only the most important semiconductive materials:

- inorganic: SnO_2 , In_2O_3 , Fe_2O_3 , TiO_2 , WO_3 , MoO_3 , ZnO , NiO , AgWO_3 , BaSnO_3 , SnO_2/NiO , $\text{SnO}_2/\text{Fe}_2\text{O}_3$;
- organic: metal acetylacetonates (MeAcAc: SnAcAc , FeAcAc , InAcAc , TiOAcAc , $\text{SnAcAc}/\text{FeAcAc}$, $\text{SnAcAc}/\text{PdAcAc}$, $\text{InAcAc}/\text{CeAcAc}$), metal phthalocyanines (MePc: FePc , CuPc).

All of these organic materials have delocalized π -electrons in their molecules. The sensor structure usually contains an active layer, suitable dopants (materials containing Ni^{2+} , Fe^{3+} , Cu^{2+} etc.), catalysts (Pt, Pd, Ni, Fe etc.) and surface membranes (SiO_2 , polytetrafluoroethylene etc.).

For thin film sensor fabrication various methods can be used, e.g. thermal evaporation, RF sputtering, ion assisted deposition, spray pyrolysis, the sol-gel method, chemical vapor deposition, thermal oxidation, spin coating, etc. A very flexible method with a wide range of deposition conditions, a wide choice of applicable materials and high deposition rates is the Pulsed Laser Deposition (PLD). It can be used for the deposition of both organic and inorganic substances. The high flexibility of PLD enables to carry out the deposition of multilayered structures in situ in a single technological step. Using hybrid laser-magnetron deposition systems layers with variable dopand concentrations and a variable composition along the layer thickness can be created. By deposition from a frozen target (MAPLE technique) layers composed of large organic molecules can be formed.

In the last years the interest has been focused on oxides, acetylacetonates and phthalocyanines. Systems based on Sn, Zn, Fe, Ti, Ce were investigated for detectors for reducing gases (hydrogen, alcohol vapours, alkanes, aldehydes, ketones) while In and W based systems aimed at oxidizing gases (ozone, nitrogen dioxide).

In this article we report on thin film gas sensors based on the detection of resistance changes. First an overview of laser techniques for the creation of thin films such as PLD, hybrid PLD for the deposition of inorganic films, and MAPLE (Matrix Assisted Pulsed Laser Evaporation) for the creation of organic films is given. The principles of conductive gas sensors and experimental results are presented.

Laser Technology for Thin Film Synthesis

Lasers are unique devices which can be used for the fabrication of thin films of multicomponent materials, thin nanocomposite films, amorphous, nanocrystalline, polycrystalline or monocrystalline films, and multilayers and superlattices.

A real laser deposition system consists of a laser and a deposition chamber. In the last years mainly excimer lasers were used, due to the high output energy and the short wavelength of the radiation. The method is called pulsed laser deposition (PLD). The absorption coefficient of materials increases for shorter wavelengths;

consequently, the laser radiation is absorbed in a thinner surface layer of the irradiated material. Higher absorption coefficients at shorter wavelengths result in a decrease of the ablation threshold. A homogeneous laser spot is required for the target; hence the quality of laser beam and focusing optic is critical. The laser beam has to be focused directly, without any limitations on the target placed in a vacuum chamber. The chamber input window has to possess a large diameter to be able to scan the laser beam over the target to ensure the same conditions for material evaporation on each point. The stream of material from the target (plasma plume) is very directional and perpendicular to the target normal. Easy deposition of multi-layers is one of the advantages of PLD. Several targets are placed in a deposition carousel. The substrate is usually heated during the deposition process. For the majority of materials the substrate temperature is not higher than about 800°C. Another advantage of PLD is that only a relatively simple and economical pumping system is required (10^{-3} Pa). The PLD deposition scheme and a photo of a real deposition chamber is shown in Fig. 40.1.

Hybrid PLD: The spectrum of materials which can be created by PLD is very wide; it includes the majority of inorganic materials and composites. But in some cases it is better to use a combination of PLD with some other deposition techniques or discharges; in these cases one speaks of hybrid PLD. For example, when we tried to synthesize the β -phase of C_3N_4 (which was calculated that to possess extreme mechanical, electrical, chemical and optical properties) we were not able to reach the required high content of nitrogen in the layers. Using combinations of PLD and discharges we managed to obtain it, since an additional RF source for higher excitation of the nitrogen was used. Hybrid PLD can be used for the creation of nanocrystalline diamond embedded in a carbon matrix, for the formation of crystalline BN or TiO_2 layers at low substrate temperatures, etc. Another example of hybrid PLD it is the combination of PLD and magnetron sputtering (PLDMS deposition, Fig. 40.2). Streams of materials from the PLD target and the MS target

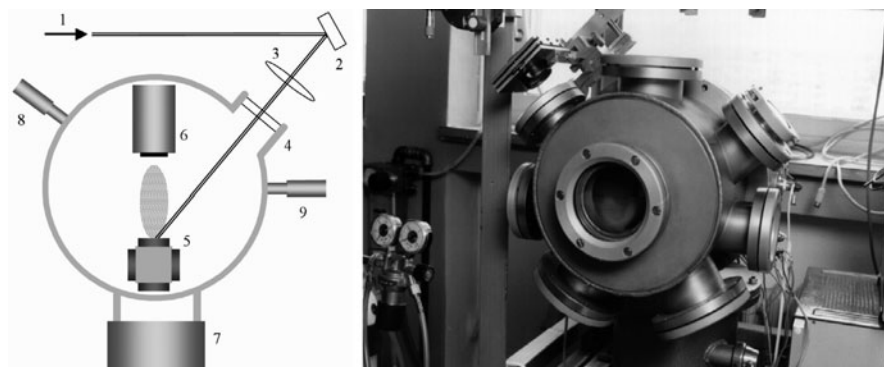


Fig. 40.1 Scheme of a PLD deposition chamber (*left*) and photo of a real chamber (*right*) (1: laser beam, 2: reflecting mirror, 3: focusing lens, 4: window, 5: carousel with four targets, 6: heated substrate holder, 7: vacuum system, 8, 9: vacuum gauge)

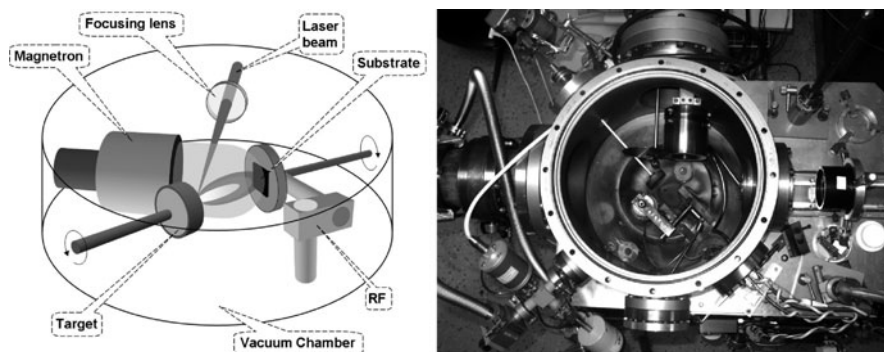


Fig. 40.2 Scheme of a hybrid PLD /magnetron deposition system (*left*) and a photo of real chamber (*right*)

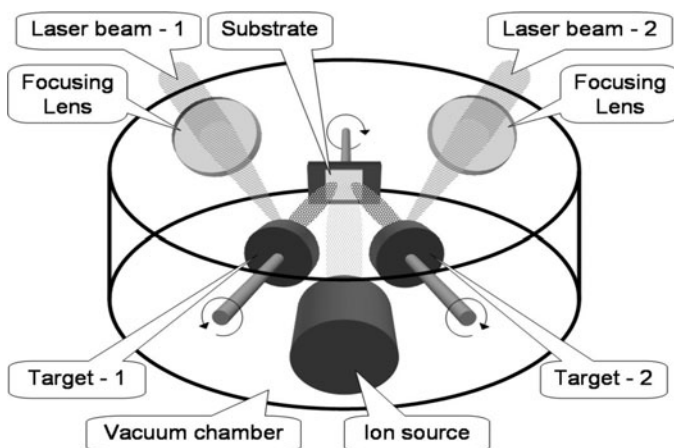


Fig. 40.3 Scheme of hybrid PLD with two laser targets and an ion beam gun

intersect on the substrate. The combination of high energetic PLD material and low energetic MS species makes it possible to synthesize materials with new properties at technologically reasonable conditions. Varying the laser repetition rate and the magnetron power allows to modify the flows of materials on the substrate and to create gradient layers with a special material distribution as a function of the thickness.

Another type of hybrid system is based on the combination of two lasers, depositing material from two targets (Fig. 40.3). By changing the repetition rate of the lasers multilayers can be easily fabricated. Such a system with an additional ion gun, is under development in our laboratory. The ion gun will be used to modify the growing film (to increase film density, crystallinity, or to improve the morphology, etc.).

MAPLE (Matrix Assisted Pulsed Laser Evaporation): Basically MAPLE is similar to PLD. It is a relatively new PVD method for the fabrication of organic layers. Various materials solved in different solutions were tested up to now [5].

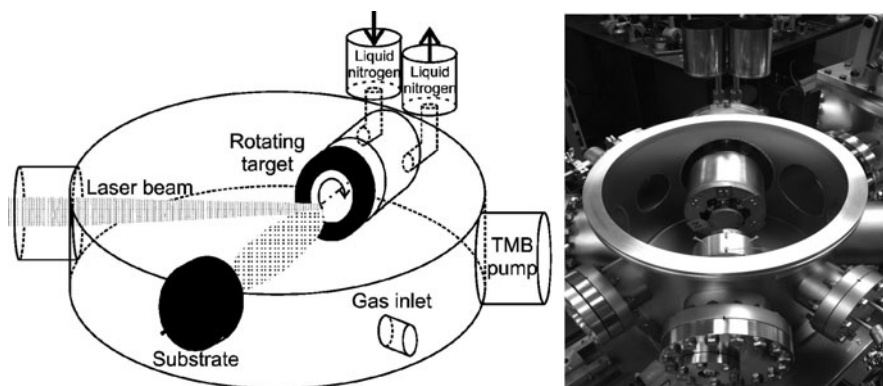


Fig. 40.4 Scheme of a cryogenic MAPLE deposition system (*left*) and photo of a real MAPLE deposition chamber (*right*)

A drawback of using standard PLD for film formation is that direct ablation of the target can be destructive to organic materials. To decrease the photochemical damage caused by direct interaction of the UV laser light with an organic or biomaterial target, a novel deposition technique, known as MAPLE was invented. It was developed to overcome the difficulties in solvent-based coating technologies such as inhomogeneous films, inaccurate placement of material, and difficult or wrong thickness control. The process uses a low fluence pulsed UV laser and a frozen composite target consisting of a diluted mixture of the material to be deposited and a high vapor-pressure solvent. The low-fluence laser pulse interacts mainly with the volatile solvent, causing its evaporation. During the process, the solute desorbs intact, i.e. without any significant decomposition, and is then uniformly deposited on the substrate. A scheme of MAPLE and a photo of a real MAPLE deposition system are shown in Fig. 40.4.

Conduction Type Gas Sensors

Principle

Conductive gas sensors are frequently used for thin film gas sensing. They have small sizes, a simple principle of operation, a low power consumption and can be easily integrated into other devices. The basic part of this sensor is the active layer. It often contains a basic material, dopants and a catalyst. Dopants have influence on the resistivity and crystallinity of the active layer. Catalysts are noble metals in form of small, non-aggregated particles. They reduce the activation energy of chemisorption and shift the Fermi level of the active layer surface.

During detection an exchange of electrons between molecules of the detected gas and the surface of the active layer takes place. The conductivity of this layer is

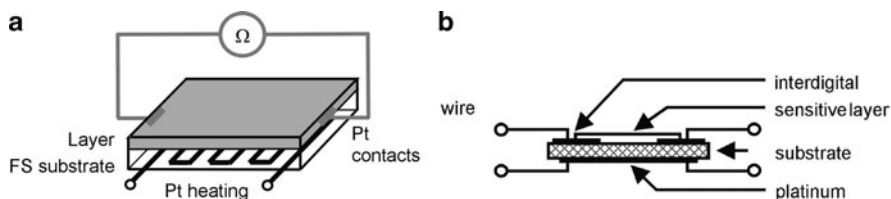


Fig. 40.5 (a) Substrate, deposited layer and heating system and (b) connection of the electrodes of a conductive gas sensor

controlled by these exchanged electrons. The quality of detection depends on many factors: (i) the thermodynamical stability of the active layer; (ii) a large gas/ solid interaction surface, (iii) the rate and reversibility of sorption/desorption processes. These factors predict the physical parameters of the sensor: (i) working temperature, (ii) sensitivity, (iii) response and recovery time, (iv) operating point stability. The active layer of conductive gas sensor is deposited onto two electrodes (Fig. 40.5).

By setting the layer temperature by heating from the opposite side, the layer sensitivity can be tuned to various gases. The sensitivity S_i of an active layer is usually evaluated for a given working temperature T_m and concentration of the detected gas component c_i as ratio of layer resistance in air R_{air} and that in the atmosphere the containing detected gas at this temperature R_{gas} :

$$S_i(T_m, c_i) = R_{\text{air}}(T_m)/R_{\text{gas}}(T_m, c_i) \quad (40.1)$$

For sensor applications, it must be taken into account that this quantity also depends on the humidity. Other definitions used are $S_i = ((R_{\text{air}} - R_{\text{gas}})/R_{\text{air}}) \times 100(\%)$ [1], $S_i = ((G_g - G_0)/G_0)$, where G_g is the sample conductance in the presence of the test gas and G_0 is the sample conductance in dry air [2], $S_i = R_{\text{gas}}/R_{\text{air}}$ [3], etc.

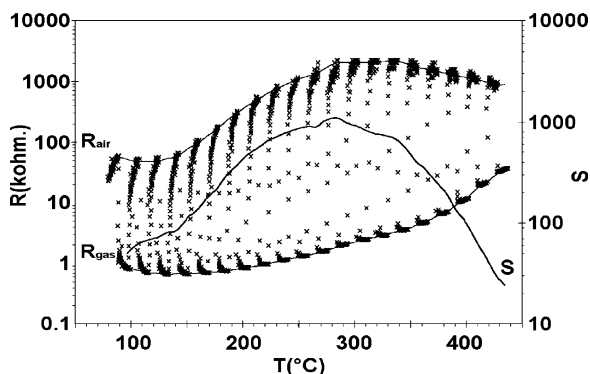
Experimental Results Using Laser Methods

In the last decade we fabricated and tested a wide scale of organic and inorganic layers and multilayer systems [4–18]. The films were prepared by PLD or MAPLE using a KrF excimer laser (LUMONICS, 248 nm). This technologies ensures a high porosity of the deposited layers (“mushroom-like” layers with a larger gas absorbing volume), resulting in a higher sensor sensitivity. The focus was mainly on SnO_2 , SnAcAc , PTFE, NiAcAc , In_2O_3 and InAcAc -based systems.

The films were deposited on small alumina plates with dimensions of $2.5 \times 1.5 \text{ mm}^2$. On one side of the plate interdigital Pt electrodes were fabricated. The as-deposited layers were exposed to special heat treatment in order to activate them, namely to form a crystalline structure, to stabilize them thermodynamically and to form an ohmic junction between the platinum electrode and the active layer.

A typical output of a dc-sensitivity measurement is presented in Fig. 40.6. It was performed in a flow system (gas flow 40 ml min^{-1} , dead volume $\sim 20 \text{ ml}$), while the

Fig. 40.6 Sensor resistivity R and dc sensitivity S vs temperature for a SnO_2/Pd sensor. The maximum dc-sensitivity $S = 1,093$ was achieved at 284°C (1,000 ppm H_2 , clean air as reference gas)



temperature of the sensor was gradually increased from 80 to 450°C for 2 h and the atmosphere periodically changed from “pure” synthetic air to synthetic air with 1,000 ppm of hydrogen and vice versa.

The resistance of samples in “pure” synthetic air R_{air} decreases (typical for semiconductors) with increasing temperature up to $\sim 100^\circ\text{C}$. In the range from ~ 100 to $\sim 300^\circ\text{C}$ there is a significant increase of R_{air} . This effect is probably caused by further chemisorption of oxygen to the SnO_2 surface connected with the bonding of free electrons.

The sensitivity and operation temperature of thin film resistive gas sensor is influenced by many parameters (layer thickness, morphology, composition, crystallinity, dopants, etc.). We also studied some sensors with inorganic-organic compound active layers. The composition of the layer was $\text{SnO}_2/\text{SnAcAc}$ (90/10 wt%) /Pd catalyst (equivalent thickness 1 nm). This composition achieved extremely short response and recovery times (i.e. very good dynamic properties) even at 80°C . Another part of our investigation was focused to the detection of oxidizing gases, namely ozone and nitrogen dioxide. In our experiments significant sensitivities to 100 ppb ozone were achieved for WO_3 ($S = 8$) at 180°C and In_2O_3 ($S = 3.5$) at 100°C . The material InAcAc was investigated. A very high sensitivity ($S = 470$) of this material was observed at 120°C .

The InAcAc layer yielded the highest response ($S = 50$) to 130 ppm of NO_x at 270°C . The selectivity between O_3 and NO_x can be “set” by controlling the operating temperature.

Conclusion

In this work the basic principles of laser thin film deposition methods such as PLD, hybrid PLD, MAPLE and the deposition of doped films were described and the basic principles of conductive detection of gases explained. Films for conductive detection must have a proper thickness as their maximal resistance has to be several megaohms. Higher resistances cannot be measured reproducibly under the given

conditions. Due to this fact materials with a high specific resistivity (e.g. TiO_2) cannot be used for thin active layers of about 200 nm thickness. Sensors with thicker active layers ($\sim 1 \mu\text{m}$) are more stable, but they have worse dynamic properties and their deposition is time consuming. The as-deposited layers used for resistive detection were exposed to a special heat treatment to activate and stabilize them, since the selectivity and sensitivity can depend on surface reactions with oxygen. The selection of the gases detected can be influenced by tuning the sensor temperature. The working of the sensors strongly depends on the material properties of the layers. There are also many experimental possibilities by using the influence of various dopants and catalysts (Pd, Pt, Ru, Cd) or metal oxides (Bi_2O_3 , TiO_2 , MoO_3 , Fe_2O_3) [5] with varying concentrations and positions in the layer (multilayers structures).

With the conductive detection sensitivities as high as $S = 2,820$ were reached (for 1,000 ppm hydrogen) with a $\text{SnO}_2/\text{NiO}/\text{Pd}$ multilayer system deposited by PLD. The aim is not only to find possibilities to detect low concentrations of gases, but also to increase the sensor selectivity and stability, to decrease the operation temperature and to reach fast responses.

Acknowledgements We thank for grants from the Ministry of Education, Youth and Sports of the Czech Republic MSM6840770012 and the Institutional Research Plan (AVOZ 10100522).

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Chapter 41

Electrochemical Sensors for the Detection of Hydrogen Prepared by PLD and Sol–Gel Chemistry

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Abstract Two different series of H₂ sensors were prepared. The first series was based on n-type semiconducting SnO₂ thin films, prepared by the sol–gel method. The effect of Au and Pt nanoparticles in SnO₂ was investigated for gas sensor applications. The second series was based on p-type NiO thin films, which were grown by pulsed laser deposition on microscope glass or (100) Si substrates. The effect of substrate temperature and O₂ pressure during the deposition process on the morphological and sensing properties of the films has been investigated. The films were fully characterized. A significant response to a broad range of hydrogen concentrations was demonstrated for both series of films at operating temperatures lower than 200°C.

Keywords SnO₂ · NiO · Thin films · Au · Pt nanoparticles · Hydrogen sensor

Introduction

Nowadays the development of solid-state gas sensors for the detection of inflammable and toxic gases such as hydrogen, carbon monoxide, etc. is a major concern for both human and environmental protection.

Hydrogen is an abundant, renewable, efficient, clean energy source, which produces zero emissions [1]. In the near future it could be used as a city gas or to power cars in the same way as natural gas is used. As an industrial gas, it is currently used in a large number of areas, e.g. chemistry (crude oil refining, plastics, as a reducing environment in float glass industry, etc.), food products (hydrogenation of oils and fats), semiconductors (as a processing gas in thin film deposition and annealing atmospheres), and transportation (as fuel in fuel cells and space vehicle rockets).

All these applications require the development of hydrogen sensing devices that allow safe control of the gas usage. Devices capable of detecting hydrogen

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concentrations below the lowest explosion limit (LEL) of 40,000 ppm [2] have become indispensable to prevent explosions. A promising approach in the field of solid-state sensing devices is to use electrochemical gas sensors based on semiconducting metal oxides (MO), utilizing novel gas sensing materials [3].

Metal oxides, in particular tin dioxide, are widely used as a basic material for the preparation of gas sensing devices [4]. The effect of the addition of metallic particles on the gas sensing properties of metal oxides has been widely studied, but the results depend on the experimental conditions and method of fabrication [5]. Although n-type transition metal oxide semiconductors (such as SnO_2 and ZnO) have already been investigated as gas-sensing materials, the sensing properties of p-type semiconducting oxides have received significantly less attention.

Nickel oxide (NiO) is widely considered as a model p-type semiconductor. Due to its excellent chemical stability, NiO films have a broad range of applications as catalysts [6], electrochromic display devices [7] and fuel cells [8]. Moreover, recent studies have shown that NiO thin films are attractive sensing materials in gas and humidity detection devices [9].

MO thin films can be deposited by different techniques, including chemical self-assembling, sol-gel, rf sputtering, dc sputtering and pulsed laser deposition (PLD). We have used an alkoxide sol-gel method to prepare SnO_2 thin films, undoped or doped with Au and Pt nanoparticles. Additionally, undoped NiO thin films were prepared by PLD. All films prepared were tested as H_2 sensors, and the influence of preparation conditions to the sensing properties were studied.

Experimental

Synthesis of SnO_2 Films

Starting point was a mixture of tin isopropoxide in isopropanol and an ethanolic solution of HAuCl_4 (or H_2PtCl_6) [10]. This solution was hydrolyzed and aged by stirring at room temperature (r.t.) for 24 h. After spin-coating on glass or Si substrates, the tin oxide gel films were dried at r.t. for 1 day and heat-treated for 2 h at 510°C in air. The content of the metals (Au and Pt) in the SnO_2 matrix was 5 wt%.

Synthesis of NiO Films

Undoped NiO films were grown by PLD in a stainless steel vacuum chamber [11]. A Ni foil (purity 99.999%) was used as a target, placed on a movable vacuum-compatible, computer-controlled XY translator and irradiated by a Quantel Nd:YAG laser ($\lambda = 355$ nm) at a repetition rate of 10 Hz. The NiO films were

deposited on heated Si or glass substrates. Two series of films were grown. The first was deposited at an O₂ pressure of 10 Pa at room temperature, 200°C and 400°C, the second at 400°C and O₂ pressures ranging from 5 to 50 Pa.

Characterization and Sensing Studies

The films were characterized by thermogravimetric analysis (TGA), scanning electron microscopy (SEM), X-ray diffraction (XRD) and ellipsometry.

Hydrogen sensing tests were performed in an aluminum vacuum chamber [12]. The chamber was evacuated down to 1 Pa, filled with dry air at atmospheric pressure. The samples were resistively heated to operating temperatures of 147–180°C. The films were tested at hydrogen concentrations in the range of 10,000–500 ppm. The hydrogen concentration was calculated based on the partial pressures of the sensed gas and air inside the chamber. A bias of 1 V was applied, and the current through the film was measured with a Keithley Mo. 485 Picoammeter. The response r is defined as $r = (R_o - R_s)/R_o = (I_s - I_o)/I_o$, where R_s and R_o are the sensor resistivities with and without gas, respectively. Current changes are therefore a measure for hydrogen sensing.

Results and Discussion

SnO₂ Films

Structural and Morphological Properties

Thermogravimetric analysis showed that heating at 500°C evaporates or burns all the organic components and reduces the H₂AuCl₄ or H₂PtCl₆ to metallic Au or Pt. XRD characterization of the films revealed that both types of SnO₂ samples are polycrystalline. The presence of Au and Pt clusters in the films seems to induce some changes in the texture of the films [10]. SnO₂–Au films have a clear tendency of texturing in the [101] and [200] crystalline directions of the tetragonal rutile structure. SnO₂–Pt films show a weaker tendency for texturing with a preferred orientation towards the [200] direction [10].

According to scanning electron microscopy (SEM) characterization, all SnO₂ samples show the presence of a granular film structure with randomly distributed and shaped particles on the surface. In the case of the SnO₂–Au sample, the particles are mostly irregularly shaped with dimensions of a few hundred nanometers, as shown in Fig. 41.1 (ignoring some quite big features of μm dimensions attributed to dust formation and impurities during sample preparation for SEM). In the case of SnO₂–Pt, the top features are clearly hexagonal faceted (Fig. 41.1. insert).

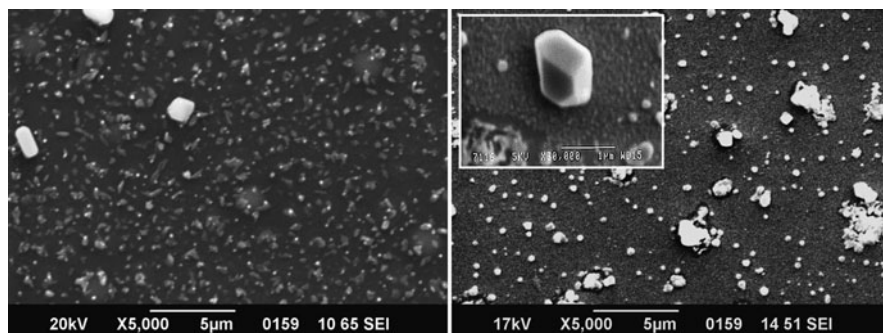


Fig. 41.1 SEM image of $\text{SnO}_2\text{-Au}$ (left) and $\text{SnO}_2\text{-Pt}$ (right) thin films

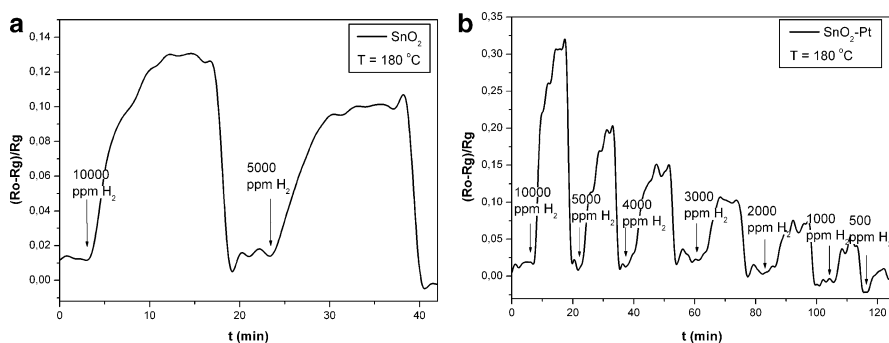


Fig. 41.2 Response of SnO_2 and Pt-SnO_2 thin films at 180°C

Hydrogen Sensing

SnO_2 films without metal nanoparticles respond only at temperatures above 180°C and hydrogen concentrations higher than 5,000 ppm (Fig. 41.2a). The presence of Pt in modified $\text{SnO}_2\text{-Pt}$ films distinctly enhanced the relative response, the detection limit was lowered down to 500 ppm (Fig. 41.2b). The $\text{SnO}_2\text{-Au}$ sensor response exhibits a dramatic increase by 50 times at the same temperature (Fig. 41.3a). Furthermore the working temperature can be lowered down to 85°C (Fig. 41.3b).

NiO Films

Structural and Morphological Properties

XRD analysis of the samples prepared at r.t., 200°C and 400°C showed that the film deposited at r.t. is poorly crystallized. When increasing the substrate temperature, the NiO lines become narrower and their intensities increase, indicative of an

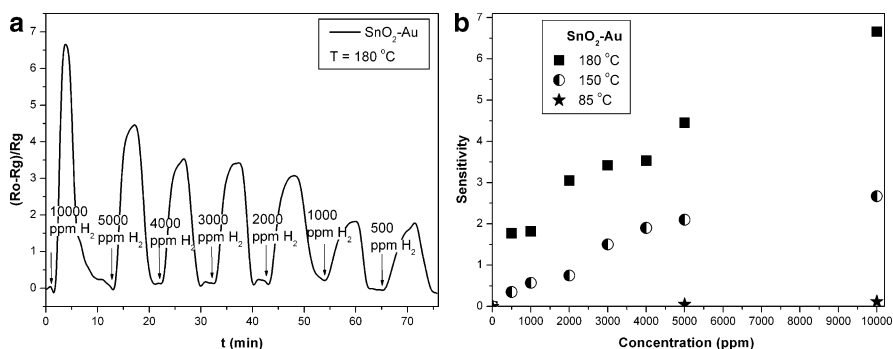


Fig. 41.3 (a) Response of Au-SnO₂ thin films at 180 °C for 10,000–500 ppm H₂; (b) at different temperatures for 10,000 ppm H₂

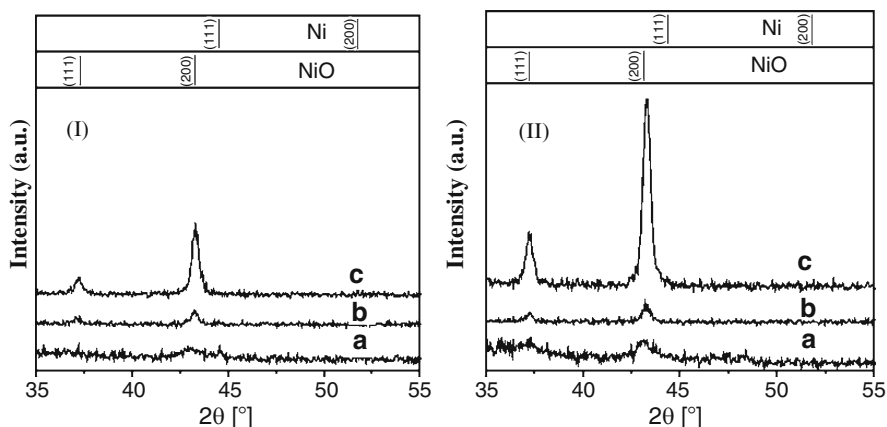


Fig. 41.4 X-ray diffractograms of NiO thin films grown on Si at r.t. (a), at 200 (b) and 400 °C (c); (I) without postdeposition heat treatment; (II) after post-deposition heat treatment at 500 °C for 3 h

improved crystallinity (Fig. 41.4I). Annealing at 500 °C for 3 h increases the crystallinity mainly for the films prepared at 400 °C (Fig. 41.4II). Similar results were obtained by AFM.

Ellipsometric measurements of the NiO films prepared at 400 °C at different O₂ pressures showed that by increasing p_{O2} the thickness of the film decreases while the roughness increases (Fig. 41.5a). SEM images showed that at low p_{O2} Ni nanoparticles are present due to an incomplete reaction of Ni with O₂ (Fig. 41.5b).

Hydrogen Sensing

All films responded to the presence of H₂ at 180 °C. The response of the first group of NiO films depends strongly on the preparation temperature (Fig. 41.6a). The best response was observed for the samples prepared at 400 °C (Fig. 41.6a). According to

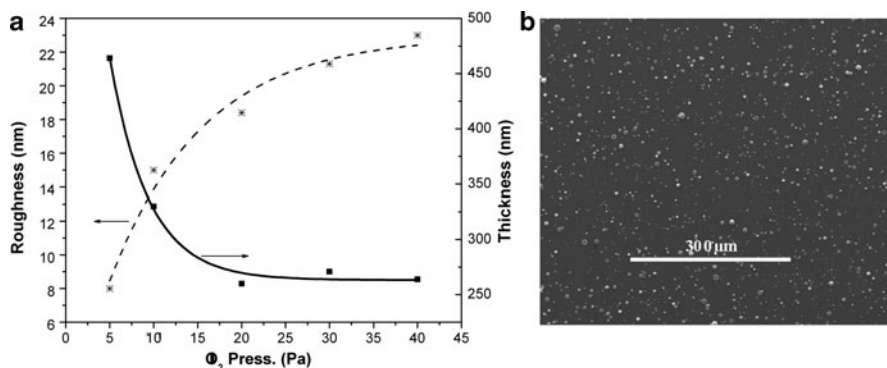


Fig. 41.5 (a) Plot of roughness and thickness of NiO films as a function p_{O_2} ; (b) SEM image of a NiO film prepared at 5 Pa O_2 pressure

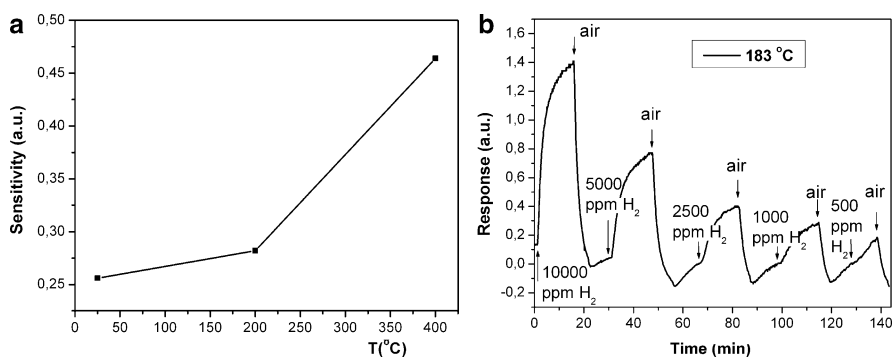


Fig. 41.6 (a) Response of NiO thin films at 180 $^{\circ}C$ to 10,000 ppm H_2 as a function of the preparation temperatures; (b) Response of NiO thin films prepared at 400 $^{\circ}C$ and 40 Pa O_2 pressure at 180 $^{\circ}C$ operation temperature to 10,000–500 ppm H_2

previous result and the structural and morphological studies of the second group the best sensor was deposited at 400 $^{\circ}C$ and 40 Pa O_2 pressure. This film showed a very good linear response at 180 $^{\circ}C$ for H_2 concentrations of 10,000–500 ppm.

Conclusions

The introduction of Au and Pt nanoparticles in SnO_2 thin films increase their H_2 sensing properties. In particular, Au nanoparticles decrease the working temperature of the sensor to 85 $^{\circ}C$ while the response increases more than 50 times. NiO thin films can also be used as H_2 sensors. Their sensing properties, crystallinity and morphology strongly depend on the growth conditions. Optimized sensing properties can be achieved by deposition at 400 $^{\circ}C$ and 50 Pa O_2 pressure.

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Chapter 42

Acetone Sensing by Modified SnO₂ Nanocrystalline Sensor Materials

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Abstract A complementary gas sensor and gas chromatography/mass spectrometry study was performed to investigate the chemical basis of acetone vapor sensing via semiconductor metal oxide gas sensors. The effect of additives to nanocrystalline SnO₂-based sensor materials was analyzed. The main process that contributes to the electrical yield of this interaction and thus to the sensor response is a complete acetone oxidation to CO₂ and H₂O. At the same time it is clearly shown that this sensor response is severely limited by the rate of desorption of the reaction products. The main contributors to this negative influence on the sensor response are heavy organic compounds with molar masses larger than that of acetone. It is also shown that their negative effect could be mitigated by the incorporation of catalytic clusters of gold on the surface of SnO₂ based sensor materials. This kind of catalyst acts either as a preventor of the formation of heavy and complex organic molecules on the sensor surface or as a combustion catalyst, which facilitates their decomposition.

Keywords Semiconductor sensors · SnO₂ · VOCs · Sensing mechanism · Surface modification

Introduction

Acetone is a widely used solvent and synthetic precursor in housekeeping and industry [1], but its prolonged influence on the human organism leads to several serious damages [2]. Acetone vapor also can serve as a disease marker in the air

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J.P. Reithmaier et al. (eds.), *Nanotechnological Basis for Advanced Sensors*,
NATO Science for Peace and Security Series B: Physics and Biophysics,
DOI 10.1007/978-94-007-0903-4_42, © Springer Science+Business Media B.V. 2011

exhausted from human lungs [3]. Currently there are no reliable, fast, simple and cheap commercial techniques suitable for continuous monitoring of possible acetone contaminated areas or for medicine diagnostics uses [4]. Nanocrystalline SnO_2 -based sensor materials are advantageous for volatile organic compound (VOC) vapor detection in terms of sensitivity, stability of the electrophysical parameters, response and recovery times and range of working temperatures [5,6]. They are highly sensitive to a large variety of oxidizing and reducing gases and organic vapors [7–9] and thus could be recommended for acetone sensing. Unfortunately such sensors require an improvement of the selectivity of their response towards different VOCs; this remains a serious obstacle for wide applications of such sensor systems.

Partly this drawback hasn't been solved yet due to the lack of solid data on particular chemical and physical processes, which lead to a sensor response to acetone and other VOCs [10]. One simple and reliable way of improving the selectivity of SnO_2 -based sensor materials is adding catalytic clusters of noble metals and metal oxides to the semiconductor matrix. It leads to the formation of active adsorption sites having a selective "receptor" sensitivity of either chemical or physical nature to the molecules of different gases [11,12]. In this work we have studied the dependence of the sensor response towards acetone vapor of chemically modified SnO_2 -based materials on their composition, surface properties and solid-gas interaction parameters, evaluated by means of a gas chromatography/mass spectrometry device. The type of the SnO_2 modifier was chosen in such a way that it allowed the investigation of the influence of additional acid or basic sites on the surface or the modified redox properties on the sensor response.

Experimental

Material Synthesis

Nanocrystalline pure tin dioxide was obtained by the conventional sol–gel technique via hydrolysis of an aqueous solution of SnCl_4 by $\text{NH}_3 \cdot \text{H}_2\text{O}_{\text{conc.}}$ with subsequent washing off the Cl^- ions, drying and calcination. Chemical modification of the SnO_2 was achieved by means of impregnation. Aqueous solutions of HAuCl_4 , $\text{Ni}(\text{NO}_3)_2$, $\text{NH}_4\text{Mo}_7\text{O}_{24}$, $\text{La}(\text{NO}_3)_3$ and an ethanol solution of $\text{Pd}(\text{AcAc})_2$ were used as precursors. The impregnated powders were annealed at a fixed temperature in the range 300–700°C for 24 h to ensure a total decomposition of the precursor. These techniques were described in detail in our previous works [11]. Thus materials modified with catalytic clusters of Mo, La and Pd oxides or double-modified with NiO and gold were obtained. Their parameters are summarized in Table 42.1.

Table 42.1 Parameters of the synthesized materials

Sample	T _{an.} , °C	[M]/[M] + [Sn], at. %	d _{XRD} (SnO ₂), nm	S _A , m ² /g	Acidity, uM/m ² NH ₃ -TPD
SnO ₂	300	–	4 ± 1	65	3.5
SnO ₂ -PdO	300	0.4	4 ± 1	61	3.81
SnO ₂ -NiO-Au	350	0.4 (Ni); 0.75 (Au)	5 ± 1	75	3.51
SnO ₂ -La ₂ O ₃	700	5.0	5 ± 1	27	2.14
SnO ₂ -MoO ₃	500	5.0	5 ± 1	75	3.9

XRD

The phase composition of the materials was investigated by means of the XRD technique with a DRON-3 and Rigaku D/MAX 2500 diffractometer (Co K_{α+β}, λ = 1.7903 Å). The diffraction peaks were analyzed with the use of ICDD database.

The XRD data were used to evaluate the grain sizes by means of the Scherrer equation:

$$D = \frac{0.9\lambda}{\beta \cdot \cos \theta} \quad (42.1)$$

where β is the diffraction peak broadening value.

TEM

The microstructure of the samples was investigated by means of high resolution transition electron microscopy with a LEO 912 AB Omega microscope. The powders were suspended in hexane and deposited on grafitized copper plates. The suspensions were treated in an ultrasonic bath before deposition to avoid the formation of large agglomerates.

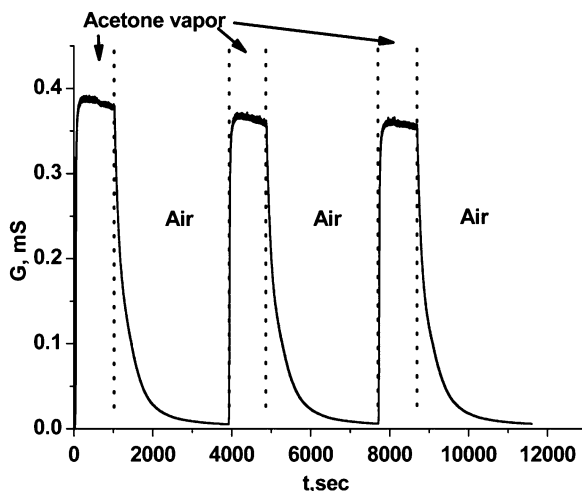
Effective Surface Area Measurements

The effective surface area of the synthesized samples was measured by means of low temperature nitrogen adsorption with a Micromeritics Chemisorb 2750 device with further analysis via the BET model.

In-Situ Conductivity Measurements

The materials obtained were deposited in form of thick films on dielectric micro-hotplates with a Pt heater and contacts for conductivity measurements. The sensors

Fig. 42.1 Conductance change of a pure SnO_2 -based sensor during cycles of exposure to diluted acetone vapor (1,800 ppm), interrupted by the flow of pure dry air through the sensor chamber. The working temperature of the sensor was $T_w = 350^\circ\text{C}$



were placed in a hermetic chamber with flows of either pure air or acetone vapor/dry air mixtures. A pure air generator was used as an air source for both air and gas mixture flow. The precise concentration of acetone vapor in the air was obtained by means of airflow saturation at a fixed temperature (0 – 25°C) with subsequent flow diverting and dilution. The sensor chamber was exposed to the gas mixture for 20 min followed by a pure air flow for 1 h during each sensor signal measurement cycle. The conductivity of the sensor materials was measured in situ with working temperatures in the range of 200 – 500°C . When measuring the sensor signal response to acetone vapor at 400°C , the exposition and recovery times were shortened down to 15 and 30 min, respectively. Figure 42.1 represents the sensor conductance during exposure to diluted acetone vapor followed by the recovery to the basic conductance in the flow of pure dry air.

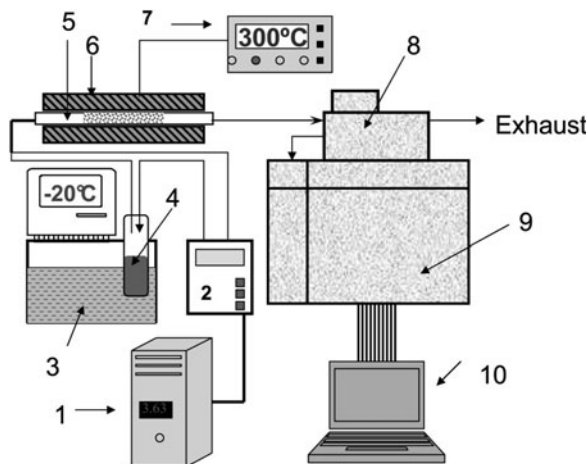
The value of the sensor signal to acetone at any given working temperature was calculated as the ratio between the conductivity increase during exposure to the gas mixture and the conductivity at the end of the recovery step.

$$S = \frac{\Delta G}{G_0} \quad (42.2)$$

Investigation of the Products of the Interaction between Sensor Materials and Acetone

A scheme of the set-up designed to investigate the products of the acetone vapor/sensing film interaction is presented in Fig. 42.2. It consists of a tube oven with a 3 mm diameter quartz reactor filled with 100 mg of the sensing material in the form

Fig. 42.2 Gas chromatography/mass spectroscopy set-up: 1. pure air generator; 2. mass flow controller; 3. cryostat; 4. acetone flask; 5. tube reactor; 6. tube oven; 7. temperature controller; 8. automatic dosing apparatus; 9. gas chromatograph with FID/mass spectrometer; 10. PC



of compacted granules of 0.25–0.5 mm diameter. The powders were compacted at a pressure of 1 t/cm². The gas mixture scheme was designed to provide a flow of air with a fixed acetone vapor concentration. After the interaction the flow with the residual amounts of acetone and the interaction products is passed to an automatic sampler to prepare a fixed volume (0.5 ml) dose for gas chromatography analysis. Gas chromatography was with a Chromatek Crystall 5000.1 apparatus with a flame ionization detector (FID) and a Perkin-Elmer Clarus 600 gas chromatograph coupled with a Perkin-Elmer Clarus 600 S mass spectrometer. A silica capillary column of 50 m length and 0.22 mm inner diameter with a 50 µm thick SE 30 phase (dimethyl silicone elastomer SE-30) was used in the procedure. Chromatograms were recorded with a temperature ramp with a 4 min step at 40°C and a further increase of the temperature up to 250°C at a rate of 30°C/min.

Results and Discussion

XRD

X-ray diffraction of all tested samples showed the presence of the crystalline cassiterite SnO₂ phase. XRD did not show any phases involving the components of the modification. This might be due to their low amounts in the sensor materials, partial formation of solid solutions or formation of quasi-2D structures of segregations on the grain surfaces, which could not be detected by means of X-ray diffraction. The distribution of additives in the SnO₂ matrix is thoroughly discussed in our previous work [11]. The size of coherent-scattering regions d_{XRD} and the effective surface areas S_A of the synthesized materials are given in the Table 42.1.

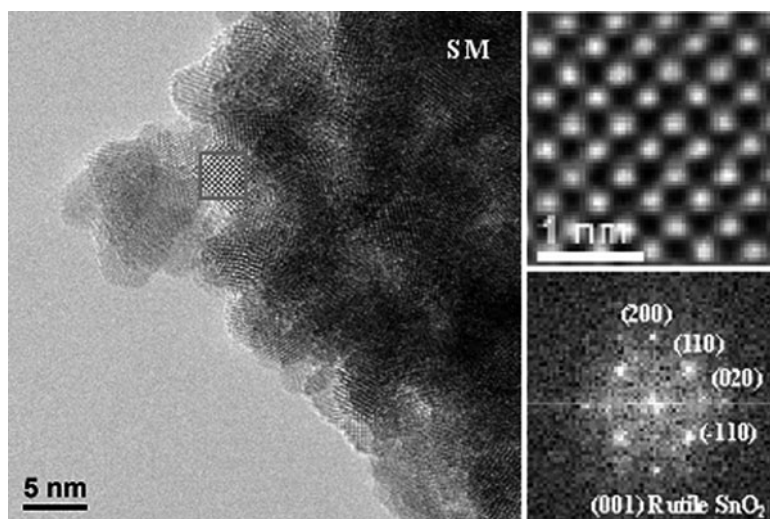


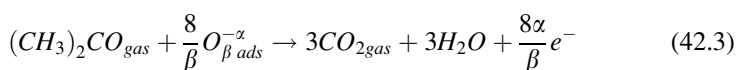
Fig. 42.3 HRTEM detail of one of the SnO_2 nanoparticles showing the rutile tetragonal structure

Transition Electron Microscopy

The transition microscopy study of the materials obtained did not allow us to detect any clusters of the additional components on the surface of SnO_2 grains. The average grain size, calculated from TEM images (Fig. 42.3) coincides with the coherent-scattering region size, which was estimated on the basis of the XRD peaks broadening.

Sensor Property Measurements

The increase of the conductivity during exposure to acetone (Fig. 42.1) occurs due the consumption of reactive oxygen species (ROS). Being initially chemisorbed on the surface of the grains they serve as electronic traps, depleting the semiconductor band of electrons which leads to an increase of the resistance of the materials. The chemical reaction producing the electronic yield can be written as [13]:



The following conductance decrease is due to the desorption of products of the acetone/sensor material interaction and reoccupation of the surface by ROSs.

Fig. 42.4 Temperature dependence of response of synthesized materials to 1,800 ppm acetone

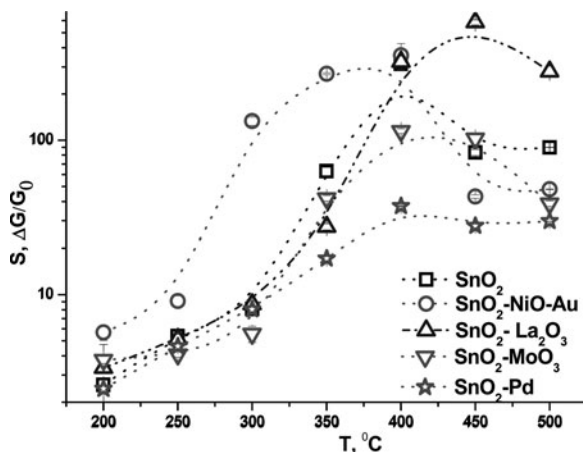


Fig. 42.5 Relationship between sensor response and acetone concentration at a working temperature of 400°C

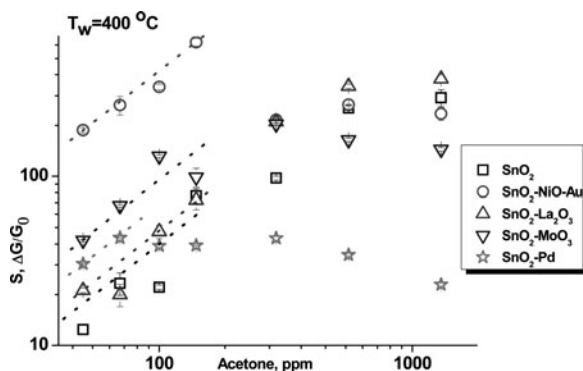


Figure 42.4 shows the temperature dependence of the sensor signal to 1,800 ppm of acetone in dry air calculated as mentioned above for all materials presented in this study.

In all cases there is a pronounced sensor signal increase starting at 300°C. This increase is most pronounced in the case of SnO₂-NiO-Au. The maximum of the sensor response is reached at 400°C for all materials except SnO₂-La₂O₃, which shows this extreme at 450°C. On the basis of literature analysis, showing the same shape of temperature dependence for metal-oxide-semiconductor acetone sensing materials [14–17]; owing to these preliminary results, a working temperature of 400°C was chosen for the evaluation of the relationship between the vapor concentration and the sensor signal dependence. This dependence is shown in Fig. 42.5.

It can clearly be seen that the sensor materials obey the power law of metal oxide semiconductor gas sensors proposed by Yamazoe et al. [18] only in a limited range of acetone concentrations below 200 ppm. At higher concentrations this linear relationship breaks; the sensor response even decreases with a further increase of

the vapor concentration. It should also be noted that the double modification of the surface of nanocrystalline SnO_2 by simultaneous addition of catalytic gold and nickel oxide clusters leads to a pronounced sensor response increase of one order of magnitude for low acetone concentrations compared to the other materials. At the same time the acidity level of the surfaces, which has already been shown to be very important in the case of ethanol sensing [19], does not seem to have any significant influence on the sensor response. The origin of such material behavior, which is different from the detection of simple gas molecules, can be explained.

Gas Chromatography/Mass Spectrometry Study

The mixture of interaction products exhausted from the reactor was analyzed 20 min after the start of the interaction. This procedure most closely resembles the desorption product mixture at the beginning of the recovery step during the sensor response measurements. A quantitative analysis of the chromatograms obtained shows that at 1,800 ppm acetone its conversion on the surface of the materials obtained generally coincides with an increase of the sensor response (Fig. 42.6).

At this point it is easy to see (Fig. 42.6) that the onset of the sensor response increase at about 350°C could be related to an increase of the acetone conversion rate. At the same time the origin of the differences in the performance of selected sensor materials demands deeper analysis of the gas chromatography data.

Figure 42.7 illustrates the chromatogram and the relative amounts of each kind of identified compounds observed during the acetone/sensor material interaction.

A qualitative analysis of the mixture components showed the presence of two groups of products. The first are light products with chromatography retention times shorter than that of acetone, the second heavy compounds with retention times significantly higher than that of acetone.

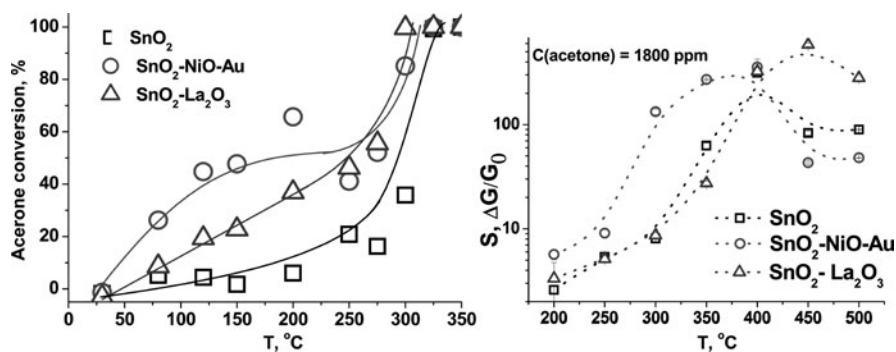


Fig. 42.6 Temperature dependence of the acetone conversion (1,800 ppm) and the sensor response

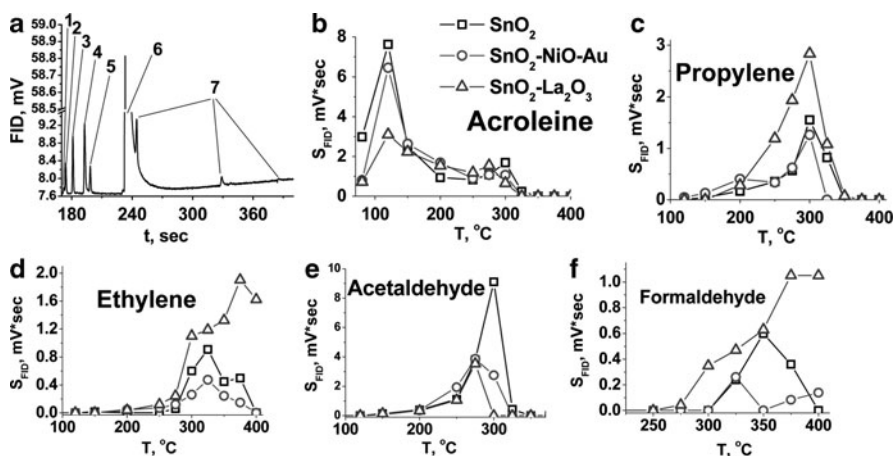
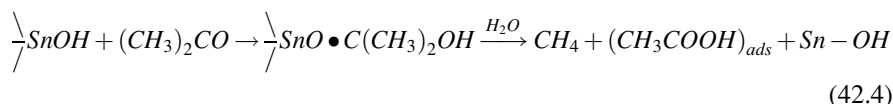


Fig. 42.7 (a) Chromatogram obtained for pure SnO₂ at 1,800 ppm acetone and 300°C working temperature. The *highlighted peaks* correspond to 1 formaldehyde, 2 ethylene, 3 propylene, 4 acetic aldehyde, 5 acrolein, 6 acetone, 7 unidentified compounds with high retention times. (b–f) temperature dependence of the signal of selected compounds

Mass spectrometry, coupled with gas chromatography analysis allowed us to identify all light organic compounds occurring after the reaction, which are represented by alkenes (ethylene, propylene), aldehydes (formaldehyde, acetaldehyde), and acrolein. The nature of these compounds gives us cues about the acetone conversion reaction at the surface of the sensor material: dehydration, coupled with carbon chain cleavage. It can also be seen that these processes play a minor role in the sensor response since the temperature at which these products are detected does not coincide with the increase of the sensor response. The drop of these compounds with temperature increase shows that reaction (42.3) indeed describes the process responsible for the sensor response, but these considerations does not give any cues on the origin of the difference of the sensor properties of the materials.

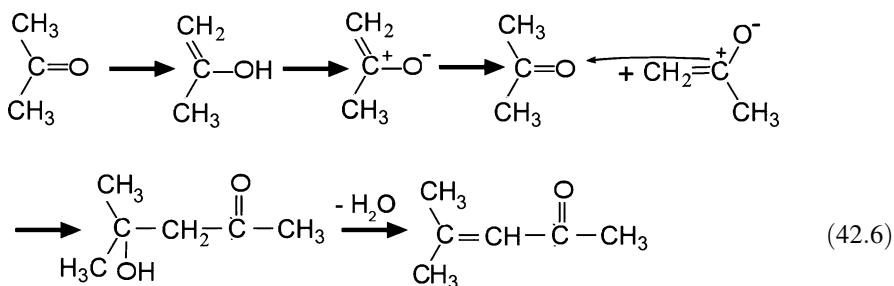
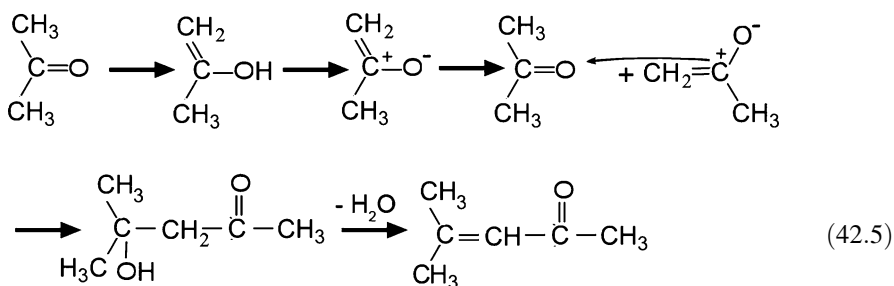
This leads us to refer to second group of compounds with high molar masses. It is accepted [20,21] that saturated ketones can participate in various reactions of oxidation, partial oxidation, chain cleavage and even reduction and reductive coupling on the surface of metal oxides [22]. This process might also lead to the formation of carbonic acids, which occupy adsorption and reaction centers and therefore reduce the performance of the sensor material [23]:



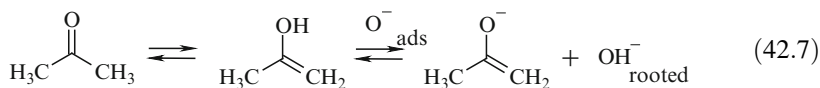
These reactions take place due to the formation of various coordination complexes on the surface through unshared carbonyl oxygen electron pairs with uncoordinated surface metal cations and/or through hydrogen bonding to the surface

lattice or chemisorbed oxygen. Thus the acetone molecules can be activated in such reactions to serve either as weak Lewis bases or weak Bronsted acids; the result of this interaction depends on the surface properties of the oxide and the temperature.

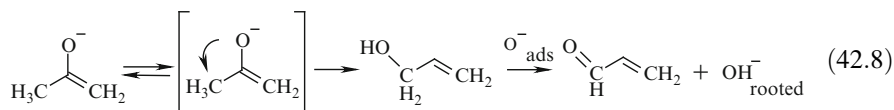
Due to the low amounts of heavy components in the mixture we were able to identify only two of them: 2,4-dimethylfuran (5) and 3-pentene-2-on (6). The reactions leading to their formation could be following:



These reactions are very characteristic since they show us the type of acetone molecule transformations on the surface. Either in the case of these heavy organic compounds or that of acroleine these transformations start with the enol form of adsorbed acetone for further dissociation:



The acrolein formation is indicative of further enol transformations:



The reactions presented take place without consumption of adsorbed ROSs and thus do not lead to a considerable sensor response. Despite this fact the formation of

heavy organic substances may have a pronounced effect on the sensor response. These compounds may have a very low rate of desorption from the sensor surface during the sensing measurements. This obstacle may increase the recovery time and lower the sensor response. According to their chemical nature furan derivatives and other heavy organic compounds may be very stable; their accumulation on the surface may lead to a blockage of adsorption sites for reactive oxygen species as the surface electric conductance decreases during the recovery step.

To examine this possibility we plotted the conductance of the sensor materials at the very beginning of the recovery step and at its end. The former shows the extent of electronic yield during the acetone conversion on the surface of the sensor while the latter gives cues about the extent of resistance recovery after exposure to acetone. It can be seen (Fig. 42.8) that either for pure SnO₂ or SnO₂ – La₂O₃ or SnO₂-NiO-Au the decrease of the acetone concentrations during the measurements leads to a decrease of the electronic yield. At the same time SnO₂-NiO-Au seems to be advantageous in acetone sensing due to the lower decrease of the electronic yield compared to the other materials. This material also demonstrates a pronounced elevation of the rate of resistance recovery below 200 ppm acetone concentration.

This means that during exposure to acetone the catalytic additives of the SnO₂-NiO-Au material (i) boost reaction (42.3), and (ii) prevent the formation of heavy organic compounds, poisonous for the sensor material and inhibitory for the recovery of the sensor surface. The first statement could not be tested by gas chromatography since the amounts of CO₂ and H₂O, which are the main products of reaction (42.3), could not be evaluated via FID or mass spectrometry on the background of the ambient air. At the same time it is possible to test the second hypothesis via a calculation of the relative amounts of substances with chromatography retention times greater than that of acetone. Given the same nature of these

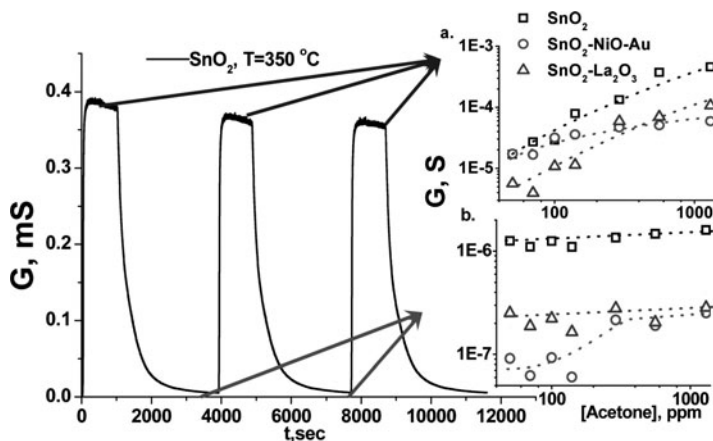


Fig. 42.8 Extent of electronic yield during sensor measurements and sensor resistance recovery in pure dry air flow, evaluated from conductance data

Table 42.2 Sum of chromatography peak areas for heavy organic products of acetone vapor interaction with sensor materials

T, °C	FID ΣS_A , mV•sec					
	Acetone 1,800 ppm			Acetone 200 ppm		
	SnO ₂	SnO ₂ -NiO-Au	SnO ₂ -La ₂ O ₃	SnO ₂	SnO ₂ -NiO-Au	SnO ₂ -La ₂ O ₃
80	31.37	18.05	24.32	15.437	11.944	40.636
150	14.46	11.94	10.35	13.093	5.811	28.077
200	15.25	2.931	1.173	28.766	5.979	39.121
250	15.05	0.134	0.913	6.05	5.831	30.523
300	8.024	16.45	3.217	11.499	0.342	6.761
350	12.34	3.724	2.923	49.395	8	34.684

products for each material we can directly compare the sum of the peak areas. This comparison is given in Table 42.2.

One can see that in the range of low acetone concentrations (200 ppm or lower) the amount of such heavy compounds is in the case of SnO₂-NiO-Au lower than in the case of the other materials tested. This evidence strengthens our hypothesis on the influence of catalytic additives on the sensor response of nanocrystalline SnO₂-NiO-Au towards acetone. This kind of positive influence could be achieved by additional reactive oxygen species provided by enhanced adsorption and dissociation of oxygen molecules on the surface of the catalytic gold clusters [24].

Conclusions

The sensor response of oxide semiconductor materials to acetone vapor is governed by several chemical reaction paths on the surface. These processes include full and partial oxidation of acetone molecules, reductive coupling, condensation and organic chain cleavage. These kinds of interactions lead to various products which could be referred to as “light” with molecular masses below acetone and “heavy” having significantly higher molecular masses. We have shown that the rate of these reactions is governed not only by the surface temperature, but also affected by chemical surface modifications with catalytic clusters of gold and nickel oxide. We presented evidence that this kind of additives may prevent the formation of heavy organic compounds on the surface during sensor measurements and guide interaction pathways to complete the acetone oxidation to CO₂ and H₂O. These chemical phenomena give rise to higher electronic yields during the sensor response measurements and enhances the recovery the conductance of the sensor material. Both processes lead to a superior sensor response towards acetone of nanocrystalline SnO₂-based sensor material modified with gold and nickel oxide.

Acknowledgements The authors wish to thank Professor Dr. Jordi Arbiol who effectuated TEM experiments at the University of Barcelona, Spain. The reported research work has been supported by the FP7-NMP-2009 EU-RU project 247768S3 and the Russian Agency “Rosnauka” under project 02.527.11.0008.

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Chapter 43

Gas Sensor Based on Chalcogenide AgI-Containing Glasses

Boris Monchev, T. Petkova, Cyril Popov, and Plamen Petkov

Abstract Layered Ge-S-AgI material was used as a sensitive layer in cantilever gas sensors. The proposed sensor system was exposed to different vapour analytes: water, acetone, ammonia. The sensor studied works on the principle of a resonance microbalance and showed the best response to ammonia vapours. The chemisorbed ammonia on the surface of the exposed material caused an increased sensitivity towards water.

Keywords Gas sensors · Chalcogenide glasses · Cantilever · Ammonia

Introduction

A relatively new method of gas sensing and monitoring is to observe the change of the resonance frequency of micromechanical cantilever-based chemical sensors [1]. The mechanism of gas sensing is related to the sorption of gas molecules onto the sensitive layer and relies on the effective mass of the cantilever/coating structure. The changes in the effective mass are registered as a shift of the resonance frequency.

The nature of the active sensitive layer in such gas sensor system is crucial. A variety materials [2,3] could be used but extremely promising are amorphous chalcogenides, which possess long-term stability and life cycle, good selectivity and stability in basic and acid media, a high reproducibility of the analyzed characteristics,

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and the possibility for a wide compositional variation as compared to their crystal analogues [4]. A wide spectrum of applications has been reported up to now such as optical storage media, memory devices, solid electrolytes etc. [5], but reports on the use of chalcogenide glasses in sensor systems [6] are pretty scarce which motivated us to perform research in this field.

Experimental Details

Priorly synthesized bulk materials [7] were used for the deposition of the layers. The thin films were deposited on Si/SiO₂ cantilevers and on monocrystalline silicon substrates in order to monitor and control their properties. The deposition was performed in a Leybold LB 370 vacuum system with a residual gas pressure of 1.33×10^{-4} Pa and a source-substrate distance of 12 cm [8]. The composition of the layers on the surface and in depth was determined by Auger analysis (LAS 3000 Riber), the surface topography by scanning electron microscopy (Hitachi S-4000) and atomic force microscopy (AFM XE-100).

The cantilevers used in this study were fabricated by a double-sided micromachining process developed for the manufacturing of piezoresistive AFM sensors as described in Ref. [9].

The set-up for the sensors measurements consists of a cell with a gas-handling system and an electrical measurement circuit [10]. The experimental process, i.e. the control of the gas-flow rates and the data acquisition, is fully automated. The gaseous analytes were introduced into the chamber using dry nitrogen as a carrier gas and a flow rate of 150 ml/l [10]. Each analyte was injected into the chamber with decreasing concentrations; between the measurement cell was purged with a dry inert gas.

Results and Discussion

The uniformity of the surfaces of the deposited materials was proven by AFM. No visible large features were observed on the surfaces. In addition, SEM studies were performed which also confirmed the uniformity of the deposited layers.

The dynamic response (the resonance frequency) of the microcantilever sensor (Fig. 43.1) functionalized with a thin Ge-S-AgI thin film was investigated upon exposure to acetone, water and ammonia vapours with concentrations between 8 and 54 vol.% in the gas flow mode. The sensor is most sensitive towards ammonia while the response to the other analytes, which is due to physisorption, is negligible (10–30 Hz). Exposure to ammonia leads to a tremendous shift of the resonance frequency (Fig. 43.2) on the order of 360 Hz. Initially, the baseline was established by purging the measurement cell with dry nitrogen for 7 min; thereafter exposure to ammonia vapour with a concentration of 54 vol.% was carried out. A new purging with nitrogen was not able to recover the initial baseline, which was now shifted by

Fig. 43.1 Cantilever sensor functionalized with a thin $\text{Ge}_{30}\text{S}_{60}(\text{AgI})_{10}$ layer

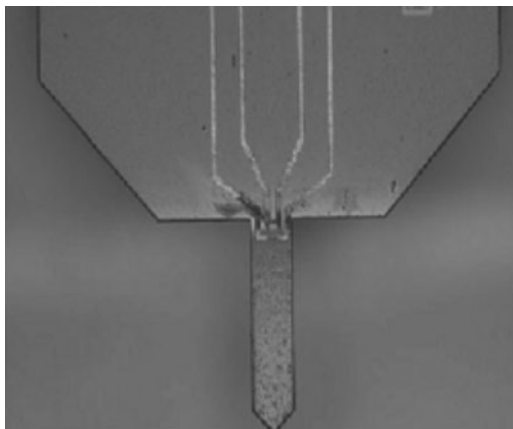
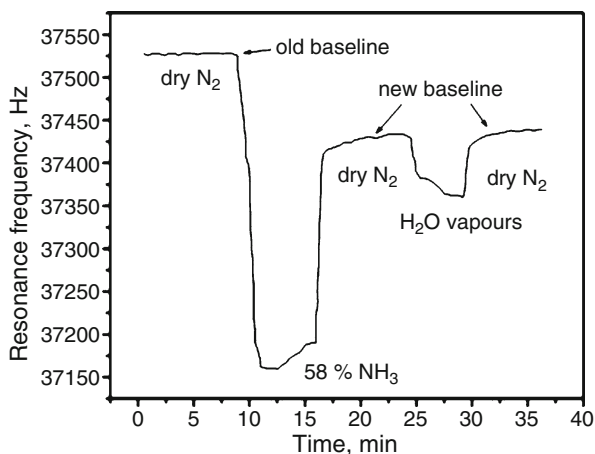


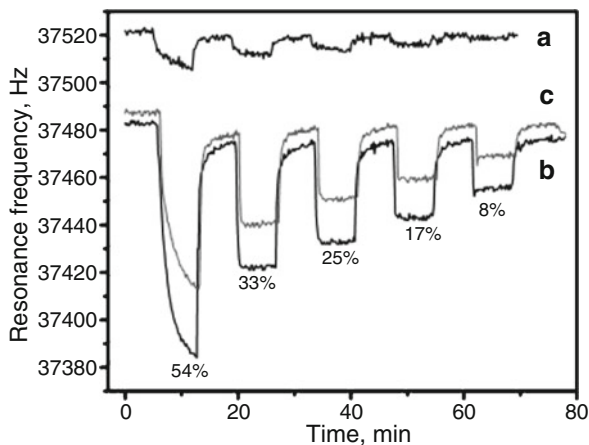
Fig. 43.2 Dynamic time response upon exposure to ammonia



about 90 Hz. We tried to recover the sensor with water vapour and dry nitrogen, but the new baseline appeared to be very stable, even after several days of purging with water vapour and nitrogen in different concentrations. It can be supposed that ammonia molecules were chemisorbed on the surface of the sensitive coating, leading to a decrease of its resonance frequency. Surprisingly, the chemisorbed ammonia modified the chalcohalide surface and rendered it more susceptible for the physisorption of analytes, especially for water molecules. An increased sensitivity towards water (Fig. 43.3b) was registered, shown in Fig. 43.3 in comparison to the initial measurement data for water vapor (Fig. 43.3a).

After a few days of continuous measurement cycles, the surface became slightly 'exhausted', i.e. some ammonia molecules were purged from the cantilever and the sensitivity slightly decreased, probably due to the lower number of binding sites (Fig. 43.3c).

Fig. 43.3 Dynamic time response upon exposure to various water concentrations: (a) as-deposited, (b) after chemical modification with ammonia, (c) after “exhaustion” of the modified surface



Conclusions

The response of thin Ge-S-AgI films coated on cantilever-based gas sensors to exposure to acetone, water and ammonia vapours was studied; it turned out that the sensor acts like a resonance microbalance showing the highest sensitivity towards ammonia. A modification of the surface of the sensitive layer after the exposure to ammonia can be associated with chemisorption of the analyte molecules. The result is an increased sensitivity towards water due to the chemisorbed NH_3 molecules.

The necessity of ammonia sensors applied in the automotive industry was pointed out by Timmer et al. [11] which is most promising for the sensor system reported here.

Acknowledgments The work was financially supported by the World Science Federation (National Scholarship) to whom Dr. Boris Monchev is deeply indebted.

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Chapter 44

Photocatalytic Oxidation of Toluene on Modified TiO₂ Nanoparticles

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Abstract Surface modification of TiO₂ nanoparticles with sodium silicate significantly influences their photocatalytic properties towards oxidation of volatile organic compounds (VOC) in the gas phase. Raman spectroscopic studies showed that surface silicates form isolated nanoislands on the TiO₂ particles. Addition of silicates significantly increased the intensity of surface water and hydroxyl group in infrared spectra. The efficiency of photocatalytic oxidation of air pollutants strongly depends on the relative humidity. During the reactions, water forms hydroxyl radicals which are very important as they act as a primary oxidant. They disappear and have to be renewed in order to keep an acceptable catalytic activity. The photocatalytic destruction of toluene over differently modified TiO₂ catalysts was investigated using an annular reactor. A model for the oxidation of VOCs in this reactor was used to obtain the kinetic constants. Small quantities of silicates (around 5%) promote the photocatalytic activity towards toluene oxidation due to their hydrophilic properties. During the oxidation, small quantities of benzoic acid are formed which are responsible for the deactivation of the TiO₂. Surface modification with sodium silicate also leads to an increased stability of the catalyst.

Keywords Photocatalytic oxidation · TiO₂ nanoparticles · Toluene

Introduction

Volatile organic compounds are an important class of pollutants usually found in the atmosphere of all urban and industrial areas. Photochemical oxidation has become increasingly popular as an alternative for environmental VOC

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decontamination. TiO_2 is one of the most commonly used functionally active matrices in semiconducting catalysis due to its chemical stability, non-toxicity, high refractive index, high dielectric constant and low price as well. There is a substantial interest in nanostructured titania films, especially for photocatalytic and photovoltaic applications. The optical gas sensing properties of TiO_2 thin films have been studied using optical absorption in the presence of different concentrations of alcohol vapours [1,2]. TiO_2 microsensors produce unique signatures in the presence of UV light and VOCs due to their electrical characteristics [3]. TiO_2 -mediated heterogeneous photocatalysis for the oxidation of VOCs at low concentrations has been extensively studied [4]. Photocatalysis on TiO_2 is advantageous compared to other oxidation methods as it takes place at room temperature, thus no thermal activation is necessary, and only a low-intensity UV lamp is needed (the band gap of anatase TiO_2 is 3.2 eV). A large variety of organic compounds can be oxidized by TiO_2 nanoparticles in the presence of UV light, O_2 and/or water [5]. By choosing precursors with suitable physicochemical properties, it is possible to exert a fine control on the formation of complex architectures of nanostructures. Improving the efficiency of TiO_2 -based photocatalysts has been attempted by increasing the surface area, modifying the structural, morphological or surface properties, or modifying the catalyst with metals and coupling semiconductors such as titania–silica. Although SiO_2 does not have a significant photocatalytic activity (the band gap of crystalline SiO_2 is 8.9 eV), it influences the activity of TiO_2 [6].

Experimental

Materials

As a reference, TiO_2 nanoparticles were obtained from two different producers: Millenium PC105[®] (Cristal) and Aeroxide P25[®] (Degussa). Several modifications of these nanoparticles were made with saturated sodium silicate solution (Sigma Aldrich), which has density $\rho(\text{SiO}_2\cdot\text{NaOH}) = 1.390 \text{ kg dm}^{-3}$. According to the required stoichiometry, small volumes of this solution (50–500 μl) were inserted into TiO_2 suspensions (1 g TiO_2 /100 ml water) to modify the TiO_2 nanoparticles with different SiO_2 coverages (5–30%). Aeroxide P25 was used for this purpose due to its superior catalytic activity. To produce thin catalytic films of porous TiO_2 nanoparticles, the spin-coating technique was used. Homogeneous suspensions were made by consecutive stirring in an ultrasonic bath (to dissolve agglomerations of particles) and a homogenizer. The samples were dried overnight at room temperature and calcinated in an oven at 400°C for 1 h. The catalyst samples will be referred to *TP1*, *TP2* for references, and *TS1*, *TS2*, *TS3*, *TS4*, for modifications, respectively (see Table 44.1). Modifications were performed only on *TP2* or P25 TiO_2 which show catalytic properties superior to that of *TP1* or PC105.

Table 44.1 Physical properties of the catalysts

	Catalyst	$S_{\text{BET}}/\text{m}^2 \text{ g}^{-1}$	$V_{\text{pore}}/\text{cm}^3 \text{ g}^{-1}$	$\bar{r}/\text{nm}$
TP1	TiO ₂ (PC105)	83.63	0.3027	7.09
TP2	TiO ₂ (P25)	58.16	0.1374	4.725
TS1	5% SiO ₂ -TiO ₂	53.73	0.2168	8.07
TS2	10% SiO ₂ -TiO ₂	49.20	0.1794	7.295
TS3	20% SiO ₂ -TiO ₂	37.84	0.1316	6.96
TS4	30% SiO ₂ -TiO ₂	24.39	0.0790	6.48

Characterization

The BET surface area of the photocatalyst, S_{BET} was measured using the N₂ physisorption technique (Micromeritics ASAP 2010) after outgassing in vacuum at 523 K for 3 h. From these measurements the volume of the pores, V_{pore} and the mean diameter of the particles, $\bar{r}$ of the photocatalysts can be extracted. Raman spectra were measured with a KAISER.XNR1 (Optical Systems Inc.) spectrometer using a 785 nm laser with a resolution of 4 cm⁻¹. Diffuse reflectance Fourier transform infrared (FTIR) spectroscopy was performed with a Perkin Elmer Spectrum One spectrometer. The scans were collected between 4,000 and 450 cm⁻¹ (resolution 4 cm⁻¹).

Reactions

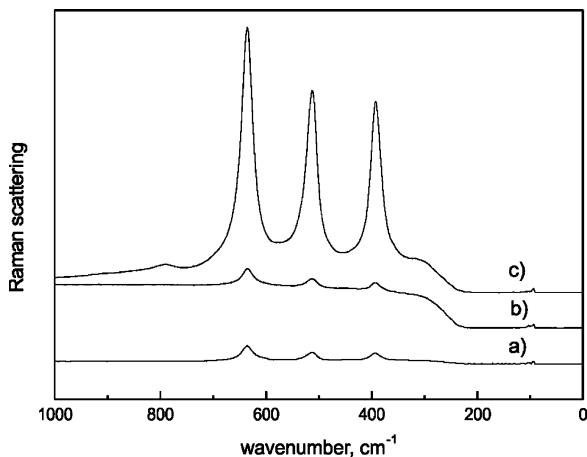
Photo-oxidation of toluene over the catalysts was carried out in a conventional gas-circulation system with an annular reactor (volume = 61 cm³) and a 8 W fluorescent lamp (Sylvania) as a light source which efficiently emits from 315 to 400 nm [7]. The toluene inlet concentration was set to 2.68 g m⁻³ in a 41 cm³ min⁻¹ air stream. The relative humidity was 50%, defined as the saturated vapor pressure of water at 20°C. Prior to switching on UV or visible light illumination, the catalyst was first exposed to the polluted air stream until dark adsorption equilibrium was reached. The toluene concentrations were measured on-line by a gas chromatograph.

Results and Discussion

Characterisation

According to expectations, TiO₂ nanoparticles should exhibit a higher specific surface area than the bulk material. Most of the experiments described in the

Fig. 44.1 Raman spectra of reference TiO₂ samples: (a) *TP1* (anatase); (b) *TS1*; (c) *TP2* (mixture of anatase and rutile)



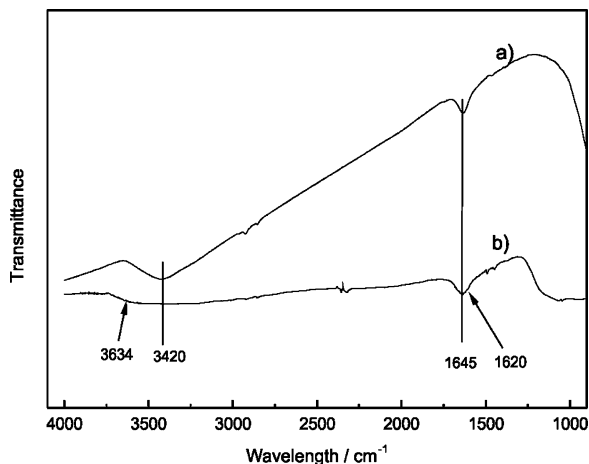
literature are based on the synthesis of mesoporous titania by sol–gel procedures. The one described by Bosc et al. [8] yields non-microporous specific surface areas of 180–190 m²g^{−1} with a mean pore diameter of 4–5 nm. Nanostructured TiO₂ prepared by different crystallization and pretreatment procedures produce specific surface areas of 90–242 m²g^{−1} with typical crystal sizes of 5.1–10.8 nm [9].

If silica gels with a surface area of 415 m²g^{−1} are used as a TiO₂ carrier, an increase of the TiO₂ content in the silica decreases the specific surface area [10]. Similarly, an increase of the SiO₂ content on TiO₂ nanoparticles decreases the real surface area (Table 44.1), which is not desirable for catalytic purposes. Figure 44.1 shows the Raman spectra of the reference TiO₂ samples and the modified TiO₂ nanoparticles *TS1*. All samples show three strong anatase-related Raman bands at 392, 512 and 635 cm^{−1}, with an additional very weak peak at 787 cm^{−1} for *TP2* [11]. The intensity of the former bands is extremely strong; their presence is an indication of the formation of anatase in the case of *TP1* nanoparticles, while the very weak in the case of *TP2* is due to rutile. The spectrum of the catalyst sample *TS1* indicate that the surface modification of TiO₂ with silicates does not lead to a solid solution due to the lack of Ti–O–Si bands. The Raman spectrum indicates small islands of silicates which are present on the TiO₂ surface.

Different studies showed that the enforcement of photocatalytic reactions on TiO₂ catalysts requires the presence of water [12]. As the water molecules are continuously consumed during the photocatalytic reaction, the formation of hydroxyl radicals requires the continuous presence of water in the system, which is secured by humidifying the reaction mixture. The surface of the TiO₂ nanoparticles is suited for the adsorption of different groups of organic molecules. During the photocatalytic oxidation of toluene competitive adsorption of water molecules, aromatic rings and/or methyl groups proceeds.

The presence of water adsorbed on various catalysts (*TP2*, *TS1*) was detected using IR analysis (Fig. 44.2). Peaks at 1,645 and 1,620 cm^{−1} show adsorbed water or water bound to Ti–OH group [13]. The increase in the intensity of the absorption peak at

Fig. 44.2 IR transmission spectra of: (a) *TP2* and (b) *TSI* nanoparticles (in the region of surface hydroxyl bands)



1,620 cm⁻¹ is caused by OH groups due to the presence of SiO₂. The 3,420 cm⁻¹ peak which appears in the case of *TP2* indicates the type of bond between OH groups on the rutile crystal form [13]. In the case of *TSI*, the bridging type of water is present on the TiO₂ nanoparticles. The configuration and type of surface OH group affects the activity of photocatalysts due to steric reasons.

It was experimentally found that with frequent use of the same catalyst (for a few days) or during prolonged or continuous use of a catalyst, there is a complete decline of the activity, i.e. its deactivation. According to literature [6,14], after the photocatalytic oxidation of toluene many peaks appear in the FTIR spectra in the range from 1,900 to 1,100 cm⁻¹ (Fig. 44.3). These peaks are associated with adsorption of intermediate oxidation products of toluene on the catalyst surface. According to literature, in the case of *TP2* the vibrations of carbonyl groups in aldehyde group appear at 1,689 cm⁻¹. The peaks at 1,641 cm⁻¹ and 1,595 cm⁻¹ are the consequence of different vibrations originating from aromatic rings. These results indicate that catalysts *TP2* and *TSI* probably adsorb molecules with a benzene nucleus, which is responsible for the deactivation of the catalysts. The peaks at 1,718, 1,689, 1,640, 1,569, 1,459, 1,405 and 1,284 cm⁻¹ appearing in the case of catalyst *TP2* occur due to the adsorption of benzaldehyde. These peaks are also observed on catalysts *TSI*, so it can be assumed that toluene or benzoic acid is also responsible for the deactivation, as indicated by the peaks at 1,569 and 1,331 cm⁻¹. According to literature, these peaks hint at carboxyl anion (COO⁻) groups and CO bonds in carboxylic acid, so it can be assumed that silicate modified catalysts deactivate due to the adsorption of benzoic acid on the surface.

Photocatalytic Performance

Photocatalytic oxidation of toluene over different TiO₂ catalysts was carried out in a photocatalytic annular reactor. In this paper the intrinsic activity of the

Fig. 44.3 IR transmission spectra of deactivated: (a) *TP2* and (b) *TS1* nanoparticles (in the region of surface organic bands)

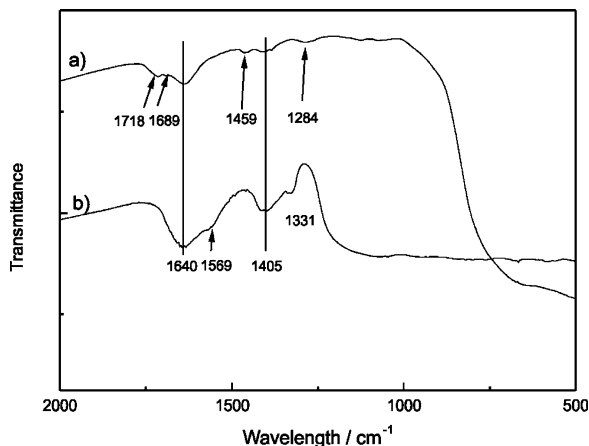


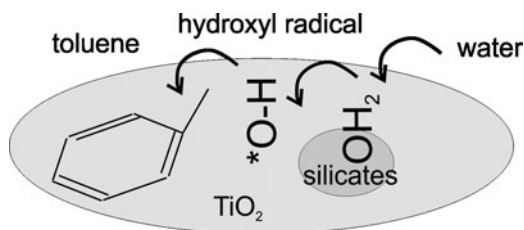
Table 44.2 Catalytic properties of TiO₂ modified nanoparticles

	k_A/min^{-1}	$SD \times 10^2$	k_d/min^{-1}
TP1	1.95	1.51	0.216 ± 0.025
TP2	2.82	1.07	0.153 ± 0.019
TS1	13.58	4.24	0.012 ± 0.001
TS2	3.28	4.12	–
TS3	1.82	2.29	–
TS4	0.63	1.70	–

catalyst is determined by mathematical modeling of the experimental results. Details about this mathematical modeling can be found elsewhere [14]. Generally, a one-dimensional (1D) heterogeneous model of the reactor is used, and a pseudo-first reaction order rate is used, in which the reaction rate constant (k_A) is estimated by the Nelder-Mead algorithm, with the agreement criteria of the root mean square deviation (SD). At the same time, the differential equation is solved by the Runge–Kutta algorithm. The case of photocatalytic oxidation of toluene leads to a model of parallel deactivation: the constant of deactivation (k_d) can be extracted by linear regression. Table 44.2 summarizes the results.

It can be seen that the activity of the catalyst increases with the increase of silicate to 5%, while a further increase does not lead to increased activity of the catalyst (Table 44.2). The activity increase can not be linked to changes of the specific area, but to a change in the electronic characteristics of the catalysts that has a positive impact on the formation of hydroxyl radicals needed for the reaction. In the literature, this change was confirmed for metal oxides with pyridine adsorption by IR measurements, in which it was found that SiO₂ in combination with TiO₂ strongly increases the Brønsted acidity [6]. Xie and co-authors also confirmed that the crystal structure of mixed oxide does not affect the photocatalytic activity of the

Fig. 44.4 Possible surface reactions in photocatalytic oxidation of toluene



obtained catalyst [15]. Comparing the activity of the catalysts and the results of IR analysis of freshly prepared catalysts and those after their use in catalytic experiments (i.e. after deactivation), an appropriate correlation is observed, which indicates the considerable influence of the hydroxyl groups in the process studied. This influence can be explained by their direct participation in the reaction mechanisms and their effect on the adsorption of reactant molecules (Fig. 44.4).

The synergistic effect of the silicates can be explained by their promotional influence in the photocatalytic oxidation. During the reaction hydroxyl radicals are spent. Due to the fact that SiO₂ is hydrophilic, it binds water molecules to the catalytic surface, which reacts with the holes on the surface of the TiO₂. SiO₂ has a large band gap width (> 8 eV), so it cannot attract UV light. The stability of the catalyst, i.e. its resistance to deactivation, is in our case improved by the modification of TiO₂ nanoparticles with sodium silicate. The deactivation rate constants (k_d) obtained for *TSI* are ten times lower than those for the base catalyst *TP2*.

Acknowledgement The authors highly appreciate the financial support by the Ministry of Science, Education and Sport of Republic of Croatia.

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Chapter 45

Impedance Spectroscopy of Tellurium Thin Films Sensitive to NO₂

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Abstract Impedance spectra of tellurium thin films with interdigital platinum electrodes have been measured in dry synthetic air and gaseous media with nitrogen dioxide. Analyses of Cole-Cole plots allowed to evaluate the characteristic frequency, time constant, resistance and capacity of the film in dry air and a mixture containing NO₂. It is shown that the impedance spectra, being strongly influenced by the gaseous environment, do not change their general shape. The effect of NO₂ is mainly a variation of the resistance of the while the capacitance does not vary significantly. The sensitivity of the impedance or its imaginary part depends on the frequency and is on the order of $\sim 50\%/ppm$. It is suggested that the effect of NO₂ results from “strong” chemisorptions of NO₂ molecules on the surface and the intragrain regions of the Te film.

Keywords Gas sensors · Impedance spectroscopy · Tellurium · NO₂

Introduction

Tellurium based films may be used for the detection of harmful gases at room temperature. This possibility was first pointed out for NO₂ [1]; thereafter, similar sensors have been reported for the detection of CO [2] and NH₃ [3]. Although the cross sensitivity to these gases is essentially different, it is important to detect namely the target gas. One possibility to obtain a selective detection of these gases has been proposed by Sbeveglieri [4] and consists in a fast sweeping of the sensitivity of a single sensor at different frequencies. That is, by monitoring the a.c. conductance at a specific frequency, the sensitivity to different gas components can be enhanced [5]. Moreover, a.c. measurements allow to obtain impedance or admittance spectra of a sensor, to calculate an equivalent circuit and to distinguish between contributions from the surface, bulk or contacts to the film conductivity [6].

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Experimental

Te thin films of about 100 nm thickness were prepared by thermal vacuum evaporation (10^{-4} Pa) from a tantalum boat onto ceramic substrates with previously deposited platinum interdigital electrodes (Fig. 45.1a).

A NO_2 mixture with a concentration of 1.5 ppm was obtained by using a calibrated permeation tube (Vici Metronics, USA), which was incorporated into the experimental set-up described in Ref. [7].

Results and Discussion

Impedance Behavior Under Dry Air

Before checking the effect of NO_2 , a.c. measurements have been performed under synthetic dry air. Figure 45.1b shows the typical complex impedance diagram obtained in pure synthetic dry air from a thin film device at room temperature (22°C) in the Cole-Cole presentation (Nyquist diagram). The diagram shows a slightly depressed semi-circular arc with the center placed below the real axis, owing to the presence of different circuit elements in the tellurium-based device [6]. The simplified equivalent circuit in Fig. 45.1c can interpret the Nyquist plot. The frequency independent serial resistance R_0 is due to the sum of the Ohmic resistances of the electrical connections, but the resistance R_ω and the capacity C_ω are due to other contributions; among them the grain boundary resistance and capacity seems to be the most important. The circle of the Nyquist diagram shown in Fig. 45.1b is depressed owing to the dependence of both R_ω and C_ω on the

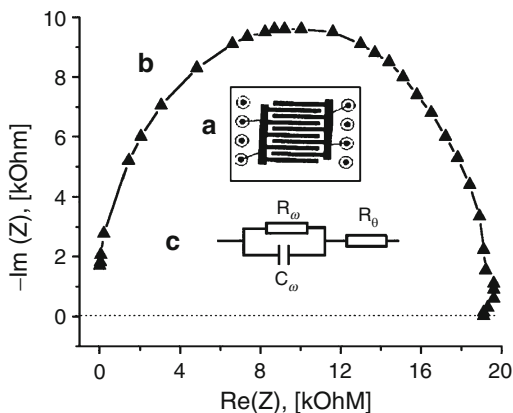


Fig. 45.1 (a) Interdigital electrode structure used to measure the a.c. conductivity; (b) Cole-Cole plot of a tellurium thin film in pure synthetic dry air; (c) suggested equivalent circuit

frequency. For a simple parallel $R_m C_m$ circuit, the relaxation time (time constant) is given by:

$$\tau_m = \omega_m^{-1} = \frac{1}{2\pi f_m} = R_m C_m \quad (45.1)$$

where f_m is the characteristic frequency at which the imaginary part $I_m(Z)$ reaches its maximum value, while R_m and C_m are the resistance and capacity of the film at the characteristic frequency f_m .

The impedance and time constant τ_m at the characteristic frequency of the sample in dry synthetic air are listed in Table 45.1, together with the parameters obtained for other environmental conditions.

For a parallel $R_\omega C_\omega$ circuit the real and imaginary parts of the impedance have the following form:

$$\text{Re}(Z) = \frac{R_\omega}{1 + \omega^2 R_\omega^2 C_\omega^2} \quad (45.2)$$

$$\text{Im}(Z) = \frac{\omega \cdot C_\omega R_\omega}{1 + \omega^2 R_\omega^2 C_\omega^2} \quad (45.3)$$

The resistance R_ω and capacity C_ω of the film at the characteristic frequency, i.e. R_m and C_m , as calculated from Eqs. 45.2 and 45.3 are listed in Table 45.1.

Impedance Behavior in a Mixture of Dry Air with NO₂

The values of the characteristic frequency, and the impedance and time constant τ_m of the film at this frequency, for 1.5 ppm NO₂ at room temperature are summarized in Table 45.1. From this table it can be seen that, as the environment is changed from dry air to the NO₂/air mixture, the resistance R_m decreases considerably while the capacitance C_m does not vary significantly.

Figure 45.2 presents the complex impedance spectra of Te films upon exposure to NO₂. It can be seen that the addition of NO₂ to dry synthetic air does not change the general shape of curve, i.e. it influences only the parameters of the equivalent circuit elements.

Table 45.1 Impedance and R-C values at characteristic frequency for different environments

Environment	f_m [kHz]	Z [k Ω]	$\tau_m 10^{-7}$	R_m [k Ω]	C_m [pF]
Dry air	900	13.3	1.8	19.2	9.6
1.5 ppm NO ₂	1,500	7.5	1.1	11.8	9.3

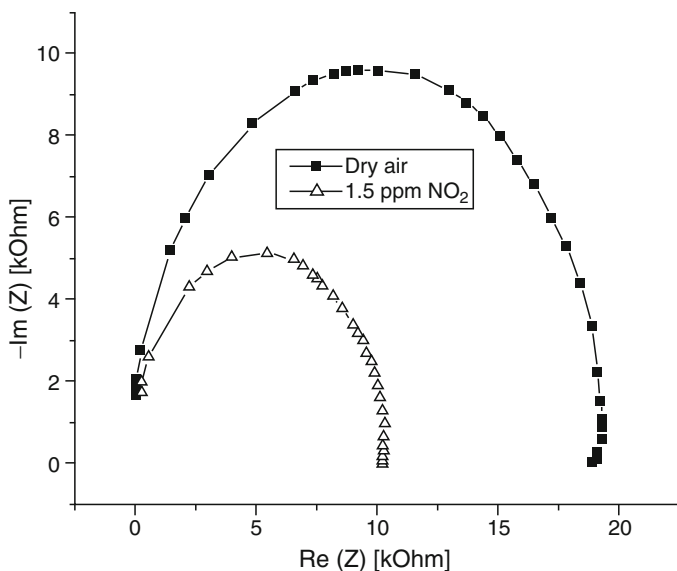


Fig. 45.2 Nyquist diagrams of tellurium thin films in different environmental conditions

Conclusions

Impedance spectra of thin Te films are strongly influenced by the composition of the gaseous environment. The effect of NO_2 on the impedance is mainly due to a variation of film resistance while the capacitance does not vary significantly. The response curves (sensitivity) for either impedance or its imaginary part strongly depend on target gas (NO_2) and frequency.

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Chapter 46

Piezoelectric Crystal Sensor for Ammonia Detection

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Abstract Piezoelectric quartz sensors (AT-cut, 5 MHz) with vacuum evaporated electrodes (Cr, Ni and Ag) were developed. Active NiCl_2 and AgCl films were chemically deposited onto the Ni/quartz//Ni/Ag structures. The sensors were tested at ammonia concentrations of 6.63; 31.32; 99.73 and 320.47 μgcm^{-3} and their calibration functions were taken. It could be established that the sensor with an active Ag film deposited on a Ni electrode is most suitable for the detection of high ammonia concentrations ($\geq 30 \mu\text{gcm}^{-3}$), while the NiCl_2 /Ni/quartz//Ni/AgCl structure shows the best characteristics for the detection of low NH_3 concentrations ($\leq 30 \mu\text{gcm}^{-3}$).

Keywords Piezoelectric crystals · Ammonia sensor

Introduction

The main advantages of microgravimetry with quartz crystal microbalances (QCM) over conventional analytic techniques (gas and liquid chromatography) are the high sensitivity and the minimal response time. Most often quartz resonators modified with active films are used [1]. The selectivity of QCM-based chemical sensors is tightly related to the selectivity of this chemical layer. Regretfully, there is no material, which is selective enough to absorb or react with only one component of the gas phase.

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Ammonia belongs to the group of secondary air pollutants. Investigations show that ammonia contents in the air of about few ppb is enough to form aerosol pollutants [2].

The first QCM sensor for NH_3 detection was proposed by Guilbault and Karmarkar [3]. Subsequently QCM sensors with active organic films [4-7], metal oxide films [8-11] and thin films of $\text{Ag}_2\text{S}_{1-x}\text{Te}_x$ [12] have been developed.

The aim of the present work was the development of quartz piezoresonator sensors with various metallic electrodes and functional layers for ammonia vapour detection and the measurement of their main analytic characteristics.

Experimental

The QCM structures based on AT-cut quartz plates were prepared using the classical technology for the production of 5 MHz quartz piezoelectric resonators. Two types of electrodes were used, Ni and Cr.

Silver, AgCl and NiCl_2 were used as materials for the sensitive layer. The active silver film was thermally evaporated (Hochvacuum B 30.2) at a pressure of 5×10^{-4} Pa, while AgCl and NiCl_2 were chemically deposited using FeCl_3 . The thicknesses of the Ni and Cr electrodes were 100–200 nm, that of the Ag films 80–100 nm.

Results and Discussion

The sensor structures with different electrodes and modified active layers are listed in Table 46.1 and marked with numbers from 1 to 5.

The sensor structures were placed above 50 ml ammonia solutions with different concentrations in glass containers at room temperature and air atmosphere. They were connected to the oscillator circuit, and their analytic characteristics were measured using a frequency meter.

A series of NH_3 solutions with concentrations decreasing by a factor of 2 were used: 25.0, 12.5, 6.25%, etc. The frequency/time characteristics $\Delta f(\tau)$ are shown in Fig. 46.2 ($\Delta f = f_i - f_o$ = frequency change; τ = time; $\Delta\tau = 10$ s).

Table 46.1 Structure and specifics of QCM sensors

No	Structure and material	Specifics of the QCM sensors
1	Ni	The active layer is the Ni electrode
2	Cr	The active layer is the Cr electrode
3	Ni//Ni/Ag	The active layer is Ag, deposited on one Ni electrode (Fig. 46.1a)
4	Ni//Ni/AgCl	The Ag film is deposited on one Ni electrode, which was treated with FeCl_3
5	NiCl_2 /Ni//Ni/AgCl	The Ag film and the Ni electrode were treated with FeCl_3 (Fig. 46.1b)

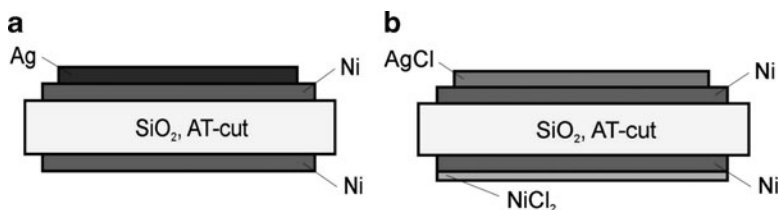
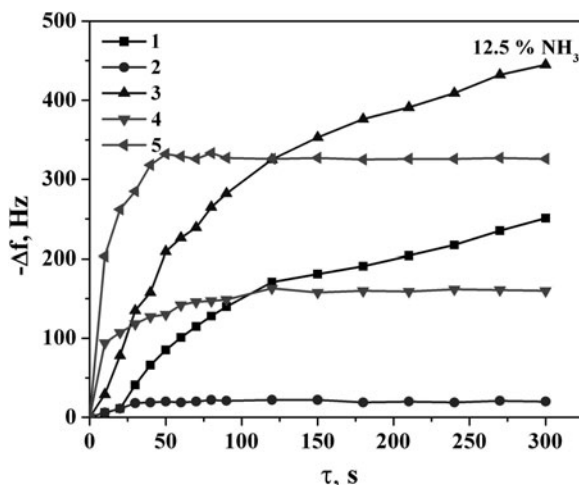


Fig. 46.1 Sensor structures 3 (a) and 5 (b)

Fig. 46.2 Frequency/time dependence for sensors 1–5 (τ = NH₃ exposure time)



An analysis of the results (Fig. 46.2) shows that the sensor structures 2, 4 and 5 are characterized by well expressed saturation regions, which means that their response time is about 30–90 s. The frequency deviations of sensors 1, 3, 4 and 5 for 60 s exposure time were taken for saturation with NH₃ vapour. The highest $-\Delta f$ values were obtained for sensors 3 and 5. For these structures $\Delta f(C)$ dependencies were recorded, where C is the ammonia concentration in the air, expressed in μgcm^{-3} (Fig. 46.3).

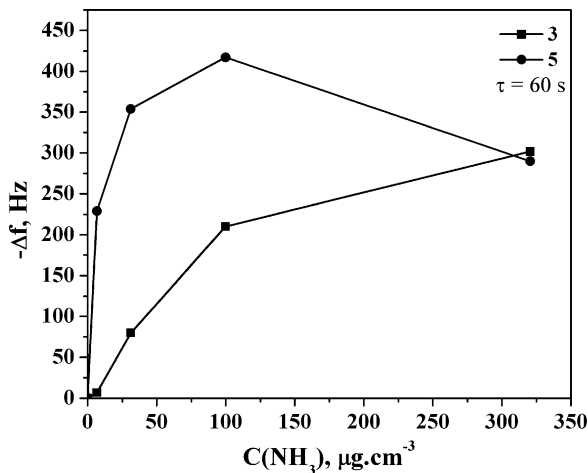
A promising characteristic of all sensors investigated is that they restore to their initial frequency f_0 in air (without forced convection) after no more than 5 s.

On the surfaces of the Ag films and the Ni electrodes always very thin oxide films exist, as a result of which the following reactions are taking place: $\text{Ag}_2\text{O} + \text{FeCl}_3 \rightarrow \text{AgCl} + \text{Fe}_2\text{O}_3$ and $3\text{NiO} + 2\text{FeCl}_3 \rightarrow 3\text{NiCl}_2 + \text{Fe}_2\text{O}_3$.

It is well-known that Fe₂O₃ and NiO have defect-rich structures with high porosities, which together with the formation of Ag and Ni complexes (AgCl:3NH₃ and NiCl₂:6NH₃) explains the good adsorption properties of sensor 5.

The $-\Delta f(C)$ dependence goes through a maximum for sensor 5 (Fig. 46.3). This characteristic is related to the properties of the ammonia complexes which

Fig. 46.3 Dependence $-\Delta f$ (C) for sensors 3 and 5



actually have the composition $\text{MeCl}:n\text{NH}_3$ (for the Ag-complex $n = 1, 2, 3$, for the Ni-complex $n = 1, 2, \dots, 6$). At low NH_3 concentrations (up to about 10–12 wt.%) they catch the maximum number of NH_3 molecules, but at higher concentrations they catch less NH_3 molecules, most probably because it is difficult to acquire thermodynamic equilibrium or due to saturation. Besides, at high NH_3 concentrations the probability of formation of complexes with larger average radius increases, which hinders adsorption in the pores of the active layer.

The Ag layer with thickness over 80 nm is characterized by a high porosity, therefore it has a high adsorption ability (sensor 3).

The results presented above give reason to propose the usage of sensor 3 for detection of high ammonia concentrations ($\geq 30 \mu\text{gcm}^{-3}$), while for lower concentrations ($< 30 \mu\text{gcm}^{-3}$) sensor 5 should be used.

Conclusion

Five quartz piezoresonator structures for the detection of NH_3 vapours have been developed. Based on the analytic characteristics investigated, two structures were proposed for applications: the Ni electrode with an active Ag layer (sensor 3) and the $\text{NiCl}_2/\text{Ni}/\text{Ni}/\text{AgCl}$ structure (sensor 5). Sensor 3 is favorable for detection of higher NH_3 concentrations ($\geq 30 \mu\text{gcm}^{-3}$), but sensor 5 for concentrations below $30 \mu\text{gcm}^{-3}$.

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Part V.3

Biosensors

Chapter 47

Nanocrystalline Diamond Films for Biosensor Applications

Cyril Popov and Wilhelm Kulisch

Abstract Diamond is a material with quite a number of excellent properties, like extreme hardness, high elastic modulus, high wear resistance, optical transparency in a broad spectral range, resistivity controllable by the level of dopants, etc. which make it a promising candidate for different sensor applications, e.g. for X-ray detection. Due to its outstanding electrochemical properties, superior chemical inertness and biocompatibility, artificially grown diamond has been recognised as an extremely attractive material for both (bio-)chemical sensing and as an interface to biological systems. This holds for all forms of diamond: monocrystalline (natural or artificial) and poly- (PCD), nano- (NCD) and ultrananocrystalline (UNCD) films. This paper is devoted to possible biosensor application of NCD and UNCD films. The first part will briefly introduce UNCD films (composed of diamond nanocrystallites of 3–5 nm diameter embedded in an amorphous carbon matrix with a grain boundary thickness of 1.0–1.5 nm), their deposition by microwave plasma chemical vapour deposition, their growth mechanisms and the characterization of their bulk properties, comparing them with other types of diamond films. The second part deals with surface modifications of UNCD films, which is the first step towards preparation of a biosensor, including different plasma and chemical processes, the thorough characterization of the resulting surfaces by a variety of techniques (AFM, XPS, ToF-SIMS, contact angle measurements, etc.) and the possibility to pattern the surface properties. The third part will describe possible pathways for the immobilization of biomolecules (proteins, DNA) on UNCD surfaces and the techniques for the characterization of this step, including force measurements,

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AFM and spectroscopic analyses. In the final part, different examples of biosensors based on UNCD as well as on NCD will be demonstrated in order to reveal the potential of diamond (films) in this field.

Keywords Nanocrystalline diamond films · Surface modification · Surface functionalization · Surface characterization · Biosensors

Diamond is an Outstanding Material!

For the public the word “diamond” conjures up images of gemstones, wealth and social occasions, but for the scientists diamond is a material with outstanding properties. Diamond is the hardest known materials, it possesses a low friction coefficient, chemical inertness, high electrical resistance, excellent thermal conductivity and good biocompatibility [1]. Upon doping it becomes a large band-gap semiconductor with an extremely high breakdown voltage and a high carrier mobility. It is transparent over a wide wavelength range and can withstand high electromagnetic radiation power fluxes from X-ray or laser sources. These unique properties of diamond and diamond films (poly- (PCD), nano- (NCD) and ultra-nanocrystalline (UNCD), depending on the size of the crystallites) make them of potential interest for a wide spectrum of applications including wear resistive and transparent protective coatings for optical components, heat spreaders, novel semiconductor devices, etc.

Due to its high electrochemical potential window and high chemical stability diamond is an ideal candidate for platforms for biosensors [2,3] and DNA-chips [4–8]. In almost all cases, after growth the surfaces of diamond films are hydrogen terminated [2,9,10]. These surfaces are chemically very stable and require photo-, plasma-, electro- or thermochemical processes to change the termination or to attach desired surface functionalities [9,10]. On the other hand, applications of diamond surfaces in biosensors require a variety of different functionalities in order to immobilize biomolecules.

This manuscript gives a brief overview of the pathway for the preparation of biosensors based on diamond films, taking as an example UNCD/a-C films. Different steps like deposition of the films, characterization of their bulk and surface properties, surface modification and functionalization, and interaction with bioentities will be considered. Finally, several examples of biosensors based on NCD and UNCD taken from literature will be presented.

Synthesis of Diamond and Deposition of Diamond Films

Although it was well-known for many years that diamond possesses outstanding properties, their exploitation was difficult due to the high costs and limited sizes and shapes of natural diamonds. In addition, the synthesis of synthetic diamond faced

technological problems since diamond is a thermodynamically unstable phase at normal temperature and pressure, and a large activation barrier has to be overcome in order to transfer e.g. graphite into diamond. To overcome these problems, researchers realized that in order to synthesize diamond, conditions are needed where diamond is the stable phase but not graphite. The knowledge of the conditions under which natural diamond is formed deep underground suggested that diamond could be formed by heating graphite under extreme temperatures and pressures. This process forms the basis of the so-called high-pressure high-temperature (HPHT) synthesis reported for the first time in 1950s. As a precursor graphite is used, which in the presence of metal catalysts (Ni, Fe, Co) at pressures of several GPa (i.e. several ten thousands atmospheres) and temperatures usually on the order of $1,500^{\circ}\text{C}$ is converted into diamond. However, the drawback of the HPHT method is that it still produces diamond in the form of single crystals ranging in size from nanometers to millimeters, which limits the range of applications for which it can be used. A further step in diamond technology was reached with the development of chemical vapor deposition (CVD) techniques for the preparation of diamond films, which was reported at the end of the 1960s. For CVD hydrocarbons are used as precursors, e.g. mixtures of methane (CH_4) and hydrogen (H_2) (1:99), which are introduced at low pressures (1–30 kPa) into a reactor, activated by hot filaments, microwave plasmas, arc discharges or laser beams, leading to the deposition of diamond films on substrates heated to temperatures of $500\text{--}1,000^{\circ}\text{C}$ (Fig. 47.1). Depending on the deposition conditions and the pre-treatment process (necessary to enhance the nucleation of diamond on non-diamond substrates), diamond films with different crystallite sizes (PCD, NCD and UNCD films), with or without the presence of an amorphous phase as a matrix (especially in case of UNCD) can be obtained.

The diamond coatings discussed in this paper, namely UNCD/a-C nanocomposite films, were grown by microwave plasma CVD from gas mixtures containing 17% CH_4 in N_2 . The substrate temperature was kept at 600°C , the working pressure was 2.2 kPa, the MW power 800 W and the deposition time 360 min. A detailed description of the MWCVD set-up is given in Ref. [11]. Monocrystalline silicon

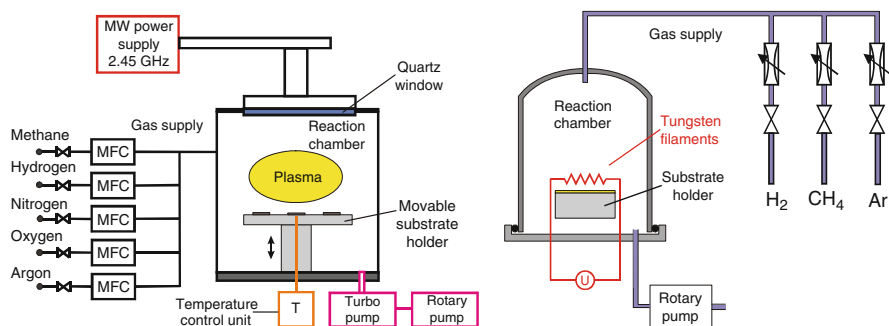


Fig. 47.1 Set-ups for chemical vapour deposition of diamond films: microwave plasma CVD (left) and hot filament CVD (right)

wafers were used as substrates which were ultrasonically pretreated in a suspension of diamond powders with different diameters in n-pentane prior the deposition. Such coatings can be prepared also on a number of other materials of technological interest, like Si_3N_4 , TiN, Ti-alloy, etc. [12].

Bulk and Surface Properties of As-Grown UNCD/A-C Films

The UNCD/a-C films deposited under the conditions described above have been comprehensively characterized with respect to their crystallinity, composition, topography and bonding structure [13–16]. X-ray diffraction (XRD) and selected area electron diffraction (Fig. 47.2) revealed patterns characteristic for the diamond phase. Furthermore, the size of the diamond crystallites was determined from the XRD peaks to be on the order of 3–5 nm. These nanocrystallites are embedded in an amorphous carbon matrix (a-C) with a grain boundary width of 1–1.5 nm, as shown by transmission electron microscopy [13]. The ratio of the volume fractions of the two phases (crystalline and amorphous) estimated from the density of the coatings and from the total crystallinity is close to unity [14]. Investigations of the UNCD/a-C films with Raman spectroscopy, X-ray photoelectron spectroscopy

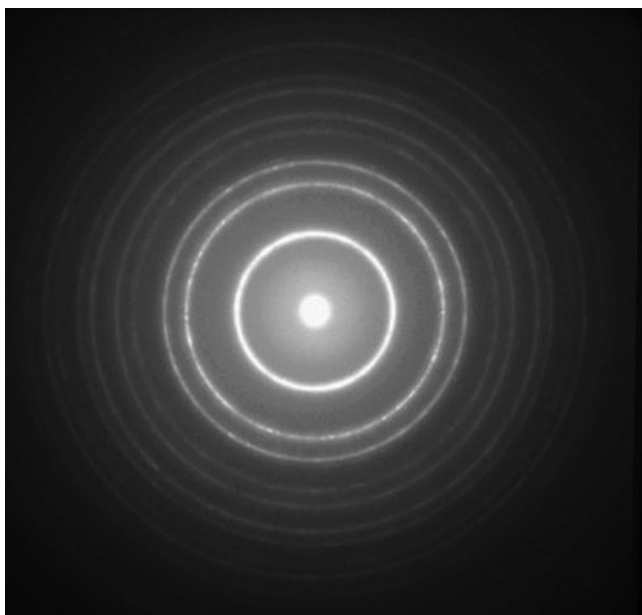


Fig. 47.2 Selected area electron diffraction of a UNCD/a-C film

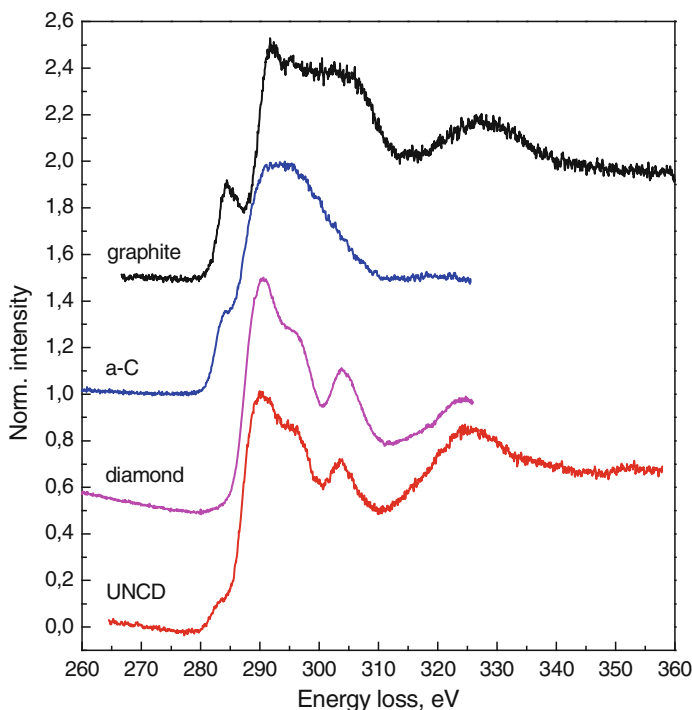


Fig. 47.3 Electron energy loss spectra of different carbon materials

(XPS), electron energy loss spectroscopy (EELS, Fig. 47.3) and Auger electron spectroscopy (AES) showed the presence of sp^2 -bonded carbon atoms (up to 15 at %) localized in the amorphous matrix [14,15]. Although no H_2 was added to the precursor gas mixture, the UNCD/a-C films contain about 8–10 at% H in the bulk, as revealed by elastic recoil detection (ERD) analysis, originating from the CH_4 molecules. Fourier transform infrared (FTIR) spectroscopy showed that the hydrogen is bonded predominantly in sp^3-CH_x groups [16].

Atomic force microscopy (AFM) studies showed for all investigated samples the characteristic topography of UNCD/a-C films, composed of structures with diameters of several hundreds nanometers, which themselves possess a substructure (Fig. 47.4). The rms surface roughness values lie in the narrow range of 10–14 nm [17]. The surface composition of as-grown UNCD/a-C films (**AG** in the following) was investigated by XPS showing that the as-grown surfaces are very clean, with oxygen and nitrogen concentrations of about 2 and 1 at%, respectively. From the depth profiles of hydrogen concentration in the UNCD/a-C films obtained by nuclear reaction analysis (NRA) surface H concentrations of 12–14 at% can be determined hinting at a hydrogen surface termination (Fig. 47.5) [18].

Fig. 47.4 AFM image of the surface of an UNCD/a-C film revealing the typical topography of the coatings

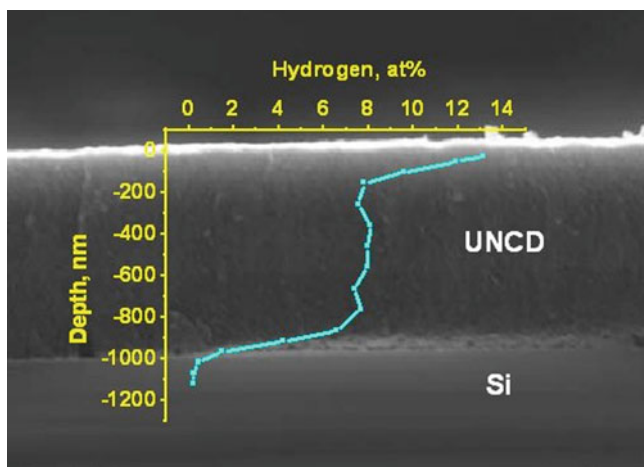
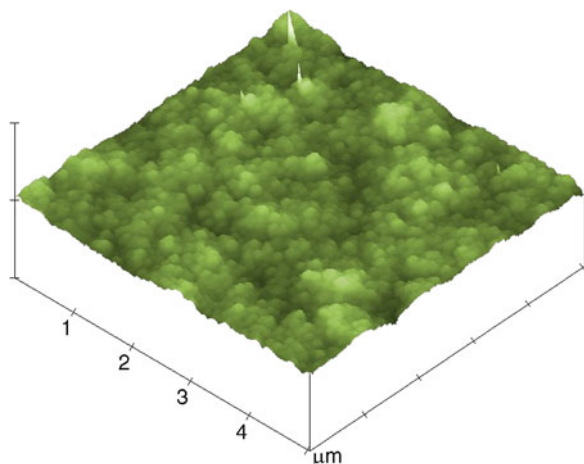


Fig. 47.5 Hydrogen depth distribution determined by NRA and a SEM cross section micrograph of an UNCD/a-C film

Surface Modification and Functionalization of UNCD/A-C Films

The next step in the preparation of a biosensor is the surface modification of the UNCD/a-C films in order to increase their versatility for tailoring the surface properties. For this purpose a number of surface modification processes have been investigated including: (i) H_2 MW plasma at 400°C in the deposition set-up (in the following: **HP**); (ii) O_2 MW plasma treatment at room temperature (**OP**); (iii) CHF_3 plasma treatment in a 13.56 MHz parallel plate reactor also at RT (**FP**);

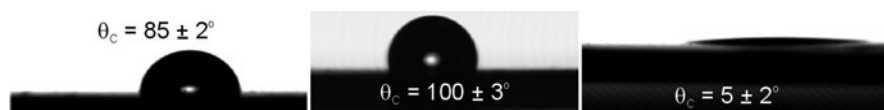
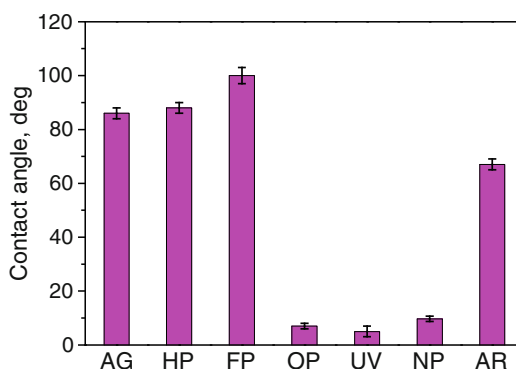


Fig. 47.6 Contact angles and water droplet profiles on UNCD/a-C films: as-grown (*left*), after F-containing plasma modification (*middle*) and after UV/O₃ treatment (*right*)

Fig. 47.7 Contact angles of UNCD/a-C surfaces after different treatments



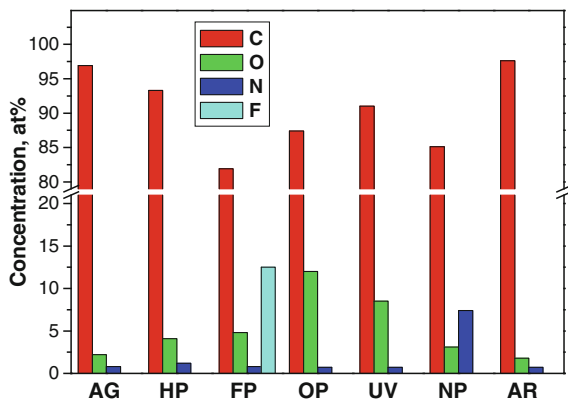
(iv) NH₃/N₂ plasma in a 13.56 MHz plasma enhanced chemical vapour deposition set-up at RT (*NP*); (v) UV/O₃ photochemical treatment at RT (*UV*) and (vi) chemical treatment with aqua regia (HCl/HNO₃ with a ratio of 3:1) at RT (*AR*). Further experimental details can be found in Refs. [19–21].

The wettability of the differently treated UNCD/a-C surfaces against purified water were examined by contact angles measurements. The results presented in Figs. 47.6 and 47.7 shows that all applied treatments have resulted in modification of the original surface.

Three types of surfaces can be differentiated: hydrophobic (*AG*, *HP*, *FP*) and hydrophilic (*OP*, *NP*, *UV*) ones, with surface *AR* in between the two groups. The contact angles θ_C of the three highly hydrophobic samples are in the order *AG* < *HP* < *FP*, varying between 85 and 100°, while for the hydrophilic samples θ_C < 10°. The contact angle of *AR* is 67 ± 1° showing also a hydrophobic character.

The surface composition of UNCD/a-C films with different terminations has been investigated by XPS and time-of-flight secondary ion mass spectroscopy (ToF-SIMS) [19]; the results from XPS are summarized in Fig. 47.8. As already mentioned, the *AG* surface is very clean; the same holds for *AR*. The sample *NP* exhibits an increase of the surface nitrogen concentration from 1 to 7.4 at% after ammonia treatment [21]. It was found that the oxygen content of the O₂ plasma treated surface is about 12 at% (*OP*) and about 8.5 at% for the UV/O₃ treated sample (*UV*), in contrast to 2 at% for *AG*, indicating an oxidation of the surface by both processes. The plasma treatment with CHF₃ leads to a surface fluorine concentration of almost the same value (ca. 12 at%) showing that a fluorination process has taken place on the surface. Having in mind that the hydrogen surface

Fig. 47.8 Surface composition of UNCD/a-C films after different treatments



concentration of as-grown samples is about 14 at% [18], the XPS results indicate a change of the surface termination by the plasma processes.

ToF-SIMS results gave further insight into the surface termination of the differently treated coatings, registering the count ratios C_xH/C_x ($x = 2, 4, 6$) as a measure for the hydrogen termination. These ratios were normalized by setting the values for the **AG** sample to unity. The values for the **HP** surface are slightly higher than 1, indicating an improvement of the H-termination as compared to non-treated surfaces. On the other hand, this shows that despite the hydrogen-poor gas mixture used in our deposition process, the as-grown surfaces are also hydrogen terminated, confirming the NRA results. The values for the **AR** sample are considerably lower, indicating that the H-termination has been partially destroyed although at the present time the mechanism is not clear. Finally, for the O_2 and CHF_3 plasma treated samples **OP** and **FP**, the values are very low (ca. 0.25–0.3). This implies that in both cases the same amount of C–H bonds has been replaced by C–O and C–F bonds, respectively, in agreement with the XPS observation that the O and F concentrations, respectively, are about 12% for the two samples. Closer analyses of the XPS peaks combined with ToF-SIMS results additionally revealed that in the case of the oxygen plasma treatment the terminating hydrogen atoms are replaced by O and OH groups rather than by carboxylic acid groups [19]. CHF_3 plasma treatment has led to a substitution of the C–H bonds by C–F rather than to the deposition of a $C_xH_yF_z$ polymer [19].

The UNCD/a-C surfaces with different terminations can be subjected to further processes of modification and functionalization aiming at the attachment of functionalities which will form the sensitive part of a biosensor. Different terminations offers different routes for further modification. The modification of H-terminated diamond is not possible by simple chemical treatment but requires either photo-, thermo- or electrochemical processes. For example, as-grown UNCD/a-C films have been functionalized by a sequence of steps including: (i) photochemical attachment of amine-containing molecules; (ii) deprotection of the amine group which renders the surface NH_2 -terminated; (iii) attachment of linker molecule SSMCC, sulfosuccinimidy 4-(N-maleimidomethyl)cyclohexane-1-carboxylate; (iv) functionalization with thiol-terminated DNA and (v) attachment of dsRNA [22]. The successful attachment

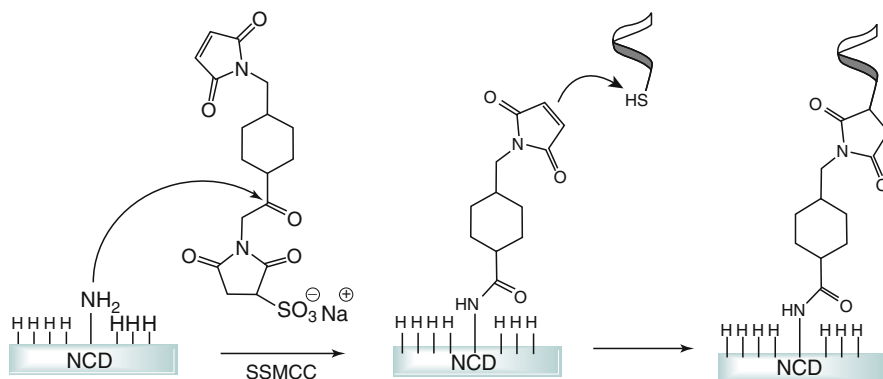


Fig. 47.9 Scheme of the surface functionalization of amine terminated UNCD/a-C film

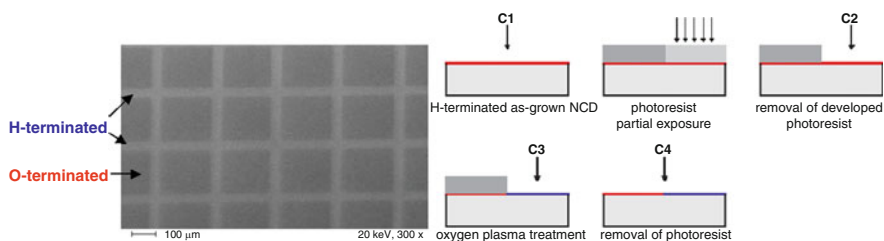


Fig. 47.10 Pathways for patterning of the surface termination of UNCD/a-C films: using a mask (*left*) or applying lithography (*right*)

of RNA molecules was revealed by AFM. If we consider O-terminated diamond surfaces which are more versatile in their chemistry, modifications can be realized, e.g. by Mitsunobu reactions or by silanization to introduce maleimide or amine surface groups, respectively [23]. These surfaces can further interact with linker molecules finally aiming at the attachment of biomolecules. Such a scheme starting from a NH_2 -terminated surface is schematically shown in Fig. 47.9.

In order to prepare areas with different functionalities on the sensor the surface termination can be patterned. For this purpose two approaches can be applied:

- Use of a mechanical mask (Fig. 47.10, left) which is placed on the UNCD/a-C surface. The areas of the surface exposed to the treatment through the holes of the mask are modified. This approach has been successfully tested for UV samples; the result can be visualized by SEM images due to the different surface conductivity of H- and O- terminated areas.
- Application of lithographic techniques (Fig. 47.10, right) including the following steps: (i) characterization of the AG surface before the process by contact angle measurements, ToF-SIMS, XPS; (ii) application of photoresist, exposure and removal of the resist after which the surface should still be H-terminated;

(iii) exposure to O₂ plasma of the area not protected by the photoresist followed by surface characterization; (iv) removal of the remaining photoresist and characterization. The photoresist, the exposure process and the two removal processes must not destroy the initial H-termination of the surface. In addition, the second removal step must also not attack the adjacent O-termination. These requirements demand careful selection of removal processes and chemicals.

After patterning, those parts of a biosensor which are supposed to remain inactive must be non-fouling, i.e. must not interact unspecifically with biomolecules contained e.g. in the analyte solution. Although UNCD/a-C surfaces are not prone to such unspecific interactions, as discussed in the next chapter, they will nevertheless adsorb heavily fouling proteins such as bovine serum albumin (BSA). This can be counteracted e.g. by deposition of anti-fouling layers such as polyethylene glycol (PEG) and related materials. First experiments to graft polyethylene glycol methacrylate (PEGMA) directly onto UNCD film by applying an atom transfer radical polymerization process using α -bromoisobutryl bromide as an initiator have been successfully performed; detailed description of the process and the results are given in Ref. [24].

Interactions with Proteins

The interaction of a biosensor with biological fluids, e.g. blood plasma, is usually dominated by adhesion of proteins onto the biomaterial surface, which occurs rather rapidly. For this reason it is important to study the interactions of proteins with UNCD/a-C surfaces and to tailor them if necessary by suitable surface modifications. Up to now, three series of experiments have been carried out to investigate the UNCD/protein interactions.

In the first series, scanning force spectroscopy measurements have been performed with as-grown UNCD/a-C films and glass (as a reference). A silicon cantilever functionalized with bovine serum albumin (BSA) has been used for this purpose (Fig. 47.11, left). One hundred and twenty single measurements at different positions have been performed for each of the two samples. On the UNCD/a-C sample none of 120 measurements indicated any interaction; all force curve had the structureless shape shown in Fig. 47.11, right. In contrast, for the glass sample in 38% of all force/distance measurements an interaction between the BSA-functionalized cantilever and the surface was observed, which gave rise to structures in the force curves. Thus it can be concluded that the UNCD/a-C surfaces are not prone to unspecific interactions with proteins [25].

On the other hand, even on such inactive surfaces there will be adhesion of highly fouling proteins such as BSA. In order to investigate whether the BSA adhesion on UNCD/a-C films is influenced by the surface termination, several of the above discussed surfaces have been subjected to BSA exposure in the second series of experiments. Immediately after this exposure the surfaces were investigated by ToF-SIMS and XPS [26]. According to the ToF-SIMS analysis, all surfaces were

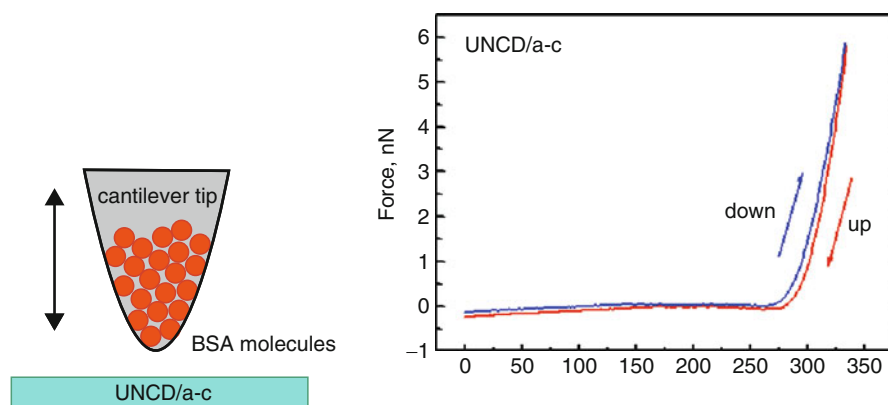
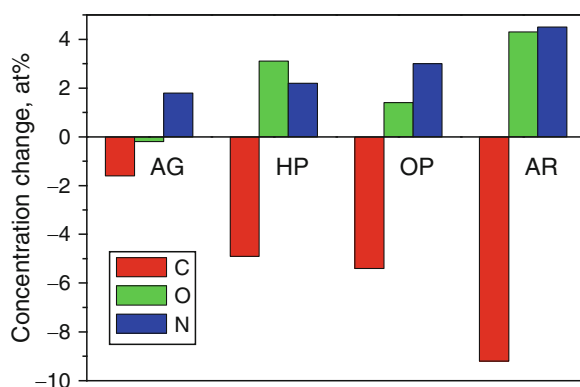


Fig. 47.11 Force measurements with UNCD/a-C films: scheme of the experiment (*left*) and the resulting force/distance curves (*right*)

Fig. 47.12 Relative changes of the surface composition caused by the exposure of the samples to BSA



covered by a BSA layer approaching a monolayer but it turned out to be impossible to quantify the adhesion and to evaluate differences between the various surfaces. More insight into this question was brought by XPS measurements. The surface composition of all samples investigated was far from that of a thick spin-coated BSA layer on a silicon substrate, taken as a reference, indicating that the BSA coverage on the UNCD/a-C surfaces is limited. As the composition of the starting surfaces is different as discussed above in Chap. 4, it seems to be more useful to look at the compositional changes inferred by the BSA exposure which are shown in Fig. 47.12. From this figure it is evident that the changes of the surface composition of the as-grown **AG** surface is only marginal. They are more pronounced for the H_2 and O_2 plasma treated samples (**HP** and **OP**). The largest changes, and thus the highest adhesion of BSA, were observed for the chemically aqua regia treated surface **AR**. A possible reason is the partial loss of the hydrogen termination caused by the treatment as discussed above. Summarizing, it can be stated that the unspecific adhesion of biomolecules such as the highly fouling bovine serum albumin on UNCD/a-C surfaces can be influenced by the surface termination.

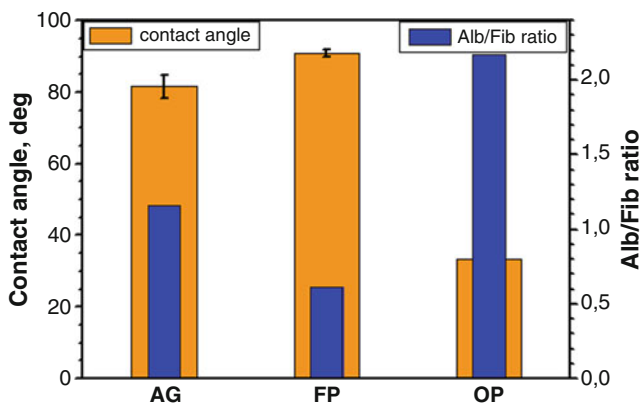


Fig. 47.13 Contact angles and BSA/fibrinogen adsorption ratios on differently terminated UNCD/a-C surfaces

In the third series of experiments, the protein adsorption on UNCD/a-C surfaces with different terminations was studied by an inverted enzyme-linked immunosorbent assay (ELISA) with albumin and fibrinogen [27]. The ratio of albumin to fibrinogen adsorption was calculated from the individual levels of both proteins adsorbed on the surfaces (Fig. 47.13). The oxygen terminated layers exhibit a higher albumin to fibrinogen ratio as compared to fluorine and hydrogen terminated films. It has been pointed out that the variation of the albumin and fibrinogen adsorption ratio is strongly related to the associated wettabilities since fibrinogen, being itself hydrophobic, preferentially adsorbs on hydrophobic surfaces, but albumin (with a hydrophilic nature) on hydrophilic surfaces during competitive binding [28]. The O-terminated UNCD/a-C layers have a hydrophilic surface with a contact angle against water of 33° which is higher than the value reported in the previous section. This difference is most probably due to the different method of measurement (static mode in the previous case and dynamic sessile drop mode in the current one) and, more probable, the sample storage history. The hydrophilic **OP** surface leads to a higher albumin/fibrinogen ratio. The F-terminated films show the Alb/Fib protein ratio, which is related to the hydrophobic nature of these surfaces (contact angle of water 91°). Therefore the albumin adsorption is much more pronounced on the oxygen terminated surfaces; vice versa the fibrinogen is preferentially adsorbed on the hydrophobic fluorine and hydrogen terminated surfaces.

Sensors Based on NCD and UNCD Films

In this chapter different approaches for the realization of biosensors on diamond platforms taken from the literature are presented. One example is a MEMS biosensor based on UNCD for the detection of specific biological compounds present in a gas or liquid [29] (Fig. 47.14). The sensor includes a micro-cantilever made of UNCD

Fig. 47.14 Schema of a BioMEMS sensor based on UNCD [29]

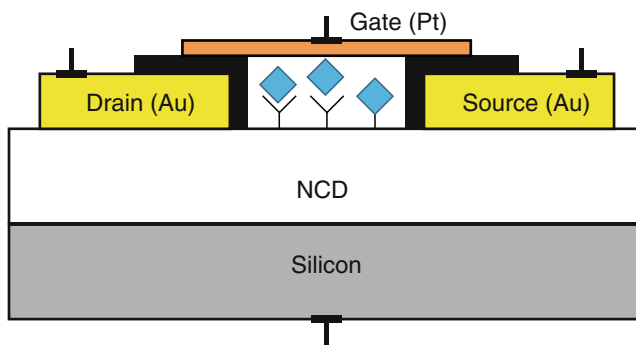
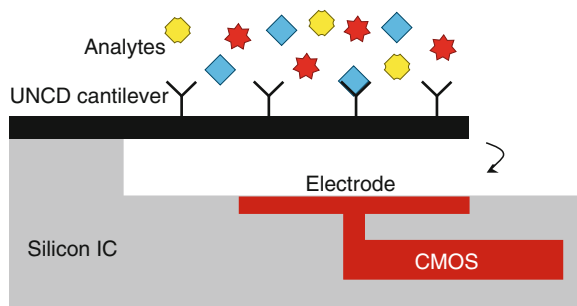


Fig. 47.15 Schema of a BioFET sensor based on NCD [30]

film onto which receptor biomolecules, e.g. antibodies, are attached. The cantilever is integrated with silicon-based CMOS electronics and vibrates excited by an electrical field at a definite resonance frequency. The sensor is exposed to a gas or liquid mixture containing biological toxins. The latter are selectively captured by the receptor biomolecules, which increases the mass of the cantilever and changes its resonance frequency. If different receptor molecules are attached to the cantilever, different biological toxins and other biomolecules can be selectively detected.

Another possibility includes the integration of a NCD film in a field effect transistor (FET) [30] (Fig. 47.15). The film is modified for biomolecular recognition following the major steps described in the previous chapters: plasma H termination, UV photochemical attachment of organic monolayer films, deprotection of the NH_2 group, reaction with glutaraldehyde resulting in a diamond surface functionalized with aldehyde groups. Immunoglobulin G (IgG) is bound to the modified diamond surface and this represents the active area of the sensor. Gold drain and source electrodes are deposited on the diamond and protected by an epoxy. A platinum gate electrode is placed above the active area of the sensor. Measurements with different electrolyte solutions containing two antibodies, anti-IgM (which does not bind to IgG) and anti-IgG, were performed. No changes in the drain-source current was observed, irrespective of the gate current, when the

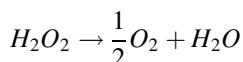
solution contained only anti-IgM due to the absence of binding. In contrast, when the solution contains anti-IgG selective binding occurs and the positive charges of anti-IgG, molecules decrease the drain-source current. In such a way specific responses of the NCD film-based BioFET are observed.

NCD-based glucose biosensors have also been demonstrated [31]. The starting NCD films was hydrogen terminated in a MWCVD reactor, followed by electrochemical functionalization in CH_3COONa for the attachment of $-\text{COOH}$ groups, onto which the enzyme *glucose oxidase* (GOX) molecules were immobilized. The electrochemical behaviour of the sensor was tested upon exposure to glucose solutions, using the electroactivity of H_2O_2 obtained after the following chemical reaction in the presence of GOX



to gain a measurable current signal. Cyclic voltammograms of the GOX-modified NCD electrode in solutions with different concentrations of glucose were recorded. A peak current proportional to the glucose concentration was observed, and a linear calibration curve up to 13 mM glucose was established (the normal concentration of glucose in blood is less than 6.1 mM and higher than 7.0 mM in the case of diabetes).

The last example demonstrates an enzyme-based amperometric sensor prepared on UNCD [32]. The technological steps of its preparation include the patterning of the UNCD surface by lithography and oxidation, followed by biofunctionalization with the enzyme *catalase*. Cyclic voltammetry of the current between the electrode and the electrolyte was performed in solutions containing hydrogen peroxide H_2O_2 , and an increased current was observed. This is related to the *catalase* catalyzed decomposition of H_2O_2



with the participation of Fe^{3+} from the *haem* group of the *catalase*, revealing that the immobilized enzyme molecules are fully functional and active.

Summary

Diamond is an attractive material for the preparation of biosensors because, in addition to having good mechanical, electrical and optical properties, it is biocompatible, chemically stable and possesses a large electrochemical potential window. Smooth and uniform diamond films can be deposited on silicon or other microelectronic compatible substrates which makes the further processing for device fabrication technologically possible. The surface of the diamond films has to be modified, functionalized and patterned in order to tune the surface hydrophilicity/

hydrophobicity which can promote specific biomolecule adsorption and/or suppress biofouling. Biomolecules (DNA, proteins/enzymes, etc.) immobilized on the diamond surface form the active part of the biosensor. Furthermore, in contrast to other microelectronic compatible materials, like silicon, gold or glass, no degradation of the biointerface occurs upon long-term exposure to biological fluids. Diamond films have been already successfully tested as platforms for the fabrication of BioMEMS, BioFET and DNA chips.

Acknowledgements We would like to thank all our partners and friends from different institutes and universities who contributed to the results presented in this manuscript: from the University of Kassel: S. Bliznakov, S. Boycheva, C. Sippel, H. Koch, N. Anspach, C. Hammann, W. Nellen; from the European Commission Joint Research Centre, Ispra, Italy: G. Ceccone, D. Gilliland, T. Sasaki, P.N. Gibson, L. Sirghi, F. Rossi; from the Institute of Molecular Biology, Bulgarian Academy of Sciences, Sofia: M. Apostolova and N. Milinovic, from Research Center Karlsruhe, Germany: H. Vasilchina and S. Ulrich; from AIST, Tsukuba, Japan: K. Yamamoto and Y. Koga; from the Research Center Rossendorf, Germany: D. Grambole.

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Chapter 48

Surface Functionalization of Plasma Treated Ultrananocrystalline Diamond/Amorphous Carbon Composite Films

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and Johann Peter Reithmaier

Abstract Diamond possesses a number of outstanding properties which make it a perspective material as platform for preparation of biosensors. The diamond surface needs to be activated before the chemical attachment of crosslinkers with which biomolecules can interact. In the current work we have investigated the modification of ultrananocrystalline diamond/amorphous carbon (UNCD/a-C) films by oxygen and ammonia plasmas. Afterwards the layers were functionalized in a further step to obtain thiol-active maleimide groups on the surface. We studied the possibility for direct binding of maleimide to terminal OH-groups on the UNCD surface and for silanization with 3-aminopropyltriethoxysilane (APTES) to obtain NH₂-groups for the following attachment of sulfosuccinimidyl 4-(N-maleimido-methyl)-cyclohexane-1-carboxylate (SSMCC). The thiol-bearing fluorescein-related dye 5-((2-(and-3)-S-(acetylmercapto) succinoyl) amino) fluorescein (SAMSA) was immobilized as an model biomolecule to evaluate the achieved thiol-activity by fluorescence microscopy. The results of the above mentioned surface modification and functionalization steps were investigated by Auger electron spectroscopy (AES) and contact angle measurements.

Keywords Ultrananocrystalline diamond/amorphous carbon composite films · Surface modification · Surface functionalization · Surface characterization

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Introduction

Diamond thin films with different crystallinity (single-, poly-, nano- or ultra-nanocrystalline [1, 2]) have evolved as ideal biomaterials, especially for applications in biosensors [3–5]. In almost all cases, after growth the surfaces of diamond films are hydrogen terminated [3, 4, 6]. These surfaces are chemically very stable and require photo-, plasma-, electro- or thermochemical processes to change the termination or to attach desired surface functionalities [3, 4]. On the other hand, applications of diamond surfaces in biosensors require a variety of different functionalities in order to immobilize biomolecules. In the present work the surface modification and functionalization of UNCD/a-C films by several plasma and chemical methods were studied as intermediate steps for sensor realization.

Experimental

Deposition and Modification of UNCD/a-C Films

UNCD/a-C nanocomposite films were grown by microwave plasma chemical vapor deposition (MWCVD) from a gas mixture containing 17% CH₄ in N₂ (sample **AG** in the following). The substrate temperature was 600°C, the working pressure 2.2 kPa, the MW power 800 W and the deposition time 360 min. Details about the basic properties of the films can be found in Refs. [7, 8]. In order to change the H-termination of **AG** samples to an OH one, they were subjected to O₂-plasmas in a incinerator set-up applying a microwave power of ca. 40 W, a gas flow of ca. 200 sccm and a working pressure of 62 Pa; the treatment time was varied between 5 and 1,200 s (60 s for sample **O**). Oxygen plasma treated samples were chemically modified by the Mitsunobu reaction (sample **M**) and by silanization (sample **A**) in order to introduce surface maleimide or amine groups, respectively. For the Mitsunobu reaction the samples were immersed in a 3% solution of diisopropyl azodicarboxylate (DIAD) in 0.15 M triphenylphosphan (Ph₃P) diluted with tetrahydrofuran (THF) at 0°C. 0.15 M N-substituted maleimide was added to the mixture under stirring. After the maleimide was dissolved, the reaction solution with the UNCD/a-C samples was left at ambient temperature for 15 h. For silanization, 2% 3-aminopropyltriethoxysilane (APTES) in toluene was used; the samples were immersed for 1 h. The possibility for direct amination through application of NH₃ containing plasmas was also investigated. For this purpose the UNCD/a-C samples were exposed to NH₃/N₂ plasmas in a plasma enhanced chemical vapour deposition set-up (PECVD, Oxford Instruments, Plasmalab 80 Plus) with a capacitively coupled 13.56 MHz discharge using gas flows of 39 sccm NH₃ and 740 sccm N₂, 39 Pa pressure; 30°C substrate temperature and 20 W rf power. The process time was varied between 15 s and 10 min (60 s for sample **N**).

Table 48.1 List of the samples investigated in this study

Surface treatment		SSMCC	SAMSA
As-grown	AG		
O ₂ -plasma treatment	O		
NH ₃ -plasma treatment	N	NS	NSF
Mitsunobu reaction	M		MF
Silanization	A	AS	ASF

In order to investigate the activity of the aminated UNCD surfaces towards a standard crosslinker like SSMCC (sulfosuccinimidyl 4-(N maleimido methyl) cyclohexane-1-carboxylate), which possesses an N-hydroxysuccinimide (NHS) ester group which could react with surface NH₂ groups, samples **A** and **N** were exposed to a 4.6 mM SSMCC solution in PBS-EDTA buffer (50 mM phosphate, 10 mM EDTA, 0.15 M NaCl in deionized water, pH 7.2) for 1 h (samples **AS** and **NS**, respectively). These samples as well as sample **M** were additionally exposed to the thiol-bearing SAMSA fluorescein (5-((2-(and-3)-S-(acetylmercapto)suc-cinoyl) amino)fluorescein) to examine the thiol activity towards the bound crosslinker and the maleimide modified surfaces (samples **ASF**, **NSF** and **MF**). The experimental details for the interaction with SAMSA are given in Ref. [9]. Table 48.1 lists the samples used in this study.

Characterization Methods

Static contact angles against purified water were measured with a CAM 100 (KSV Instruments) set-up by manual one-touch drop displacement of 1 μ l water at room temperature. The drop shape was calculated with the CAM 100 software applying the Young-Laplace equation. The surface composition was studied by Auger electron spectroscopy (AES, Las3000, Riber). The Auger analysis was performed in differential mode with a primary electron energy $E_p = 3$ keV ($I_E = 0.07$ μ A, $V_{mod} = 4$ V_{ptp}, $\Delta E/E = 0.3\%$); the most intense Auger peaks of C (272 eV), N (381 eV) and O (510 eV) were monitored. In order to obtain fluorescence microscopy images, the samples were placed in a fluid cell with 83 mM sodium phosphate buffer (pH = 7). The light source was a mercury gas lamp (X-Cite 120, EXFO). The pictures were taken with ca. 20% of the maximum possible intensity of the source, the exposure time was 2 s. The pictures were obtained with a fluorescence microscope (Axio Observer D1, Zeiss) with the filter set 09(488009-9901-000) and a 20 $\times$ objective lens. They were taken in grey-scale without gamma correction with a CCD camera (ProgRes MFcool, Jenoptik) with a resolution of 1,360 $\times$ 1,024 pixels. Histograms of the normalized brightness were obtained by the ImageJ 1.42q program.

Results and Discussion

The contact angles θ_C of O_2 and NH_3 plasma treated samples are below 10° in all cases which is an indication of a successful oxidation/amination of the surface (Fig. 48.1, left). For O_2 plasmas the values are identical within the range of error for all exposure durations, indicating that the surface modification was completed even after 5 s. For the plasma amination the contact angle decreases with increasing exposure time, reaching ca. 8° after 60 s, after which it remains constant.

Figure 48.1 (right) shows the contact angles of all samples under investigation for comparison purposes. It can be seen that the hydrophobic **AG** sample is rendered hydrophilic upon plasma treatment (**O** and **N**). The Mitsunobu modification and the silanization of **O** samples lead to increase of θ_C to ca. 31 – 32° revealing surface modification after these steps (**A** and **M**). The attachment of SSMCC to amine-terminated surfaces results in change of θ_C ; it decreases for **AS** and increases for **NS**. This can be attributed to the different chemical nature of the substrate on which the process takes place. In the first case the silanization results in an attachment of silanoether aminopropyl group, while the plasma treatment leads only to replacement of the surface terminating H atoms by NH_2 groups. Further reason could be the different SSMCC coverage. Finally, the exposure of sample **M** to SAMSA leads to only marginal change of the contact angle, most probably due to absence of interaction of the chemically modified surface with the fluorescein (sample **MF**).

The AES results revealed that the relative O/C ratio increases after O_2 plasma treatment of UNCD/a-C films (Fig. 48.2, left). Even after 1 min treatment the ratio increases almost three times indicating a change of the surface termination. This trend is preserved for longer treatment durations but no direct dependence of the O/C ratio on the time can be observed. The information obtained by AES supports the results from the contact angle measurements: the oxygen plasma treatment changed the surface termination from H to OH, and subsequently the wettability from hydrophobic to hydrophilic. Figure 48.2 (right) shows the relative N/C and

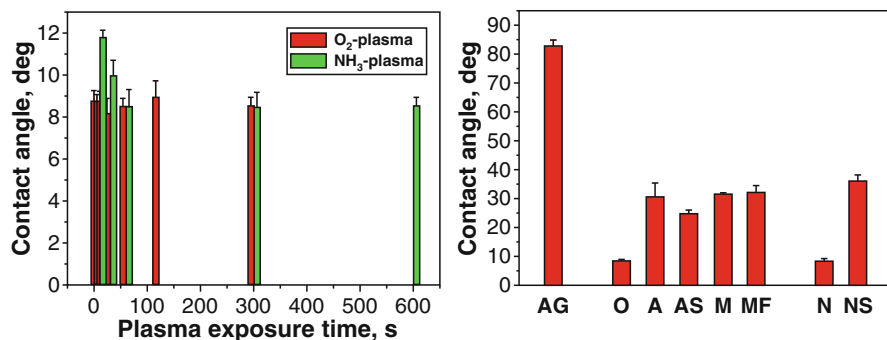


Fig. 48.1 Contact angles of UNCD/a-C surfaces after oxygen and ammonia plasma treatments with different durations (*left*) and after different surface treatments and modifications (*right*)

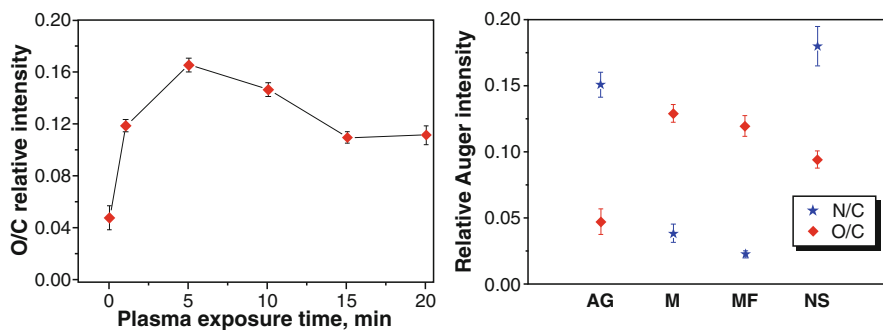


Fig. 48.2 Dependence of the relative intensity of the O/C Auger signal on the plasma treatment time (*left*) and O/C and N/C intensity ratios for differently treated samples (*right*)

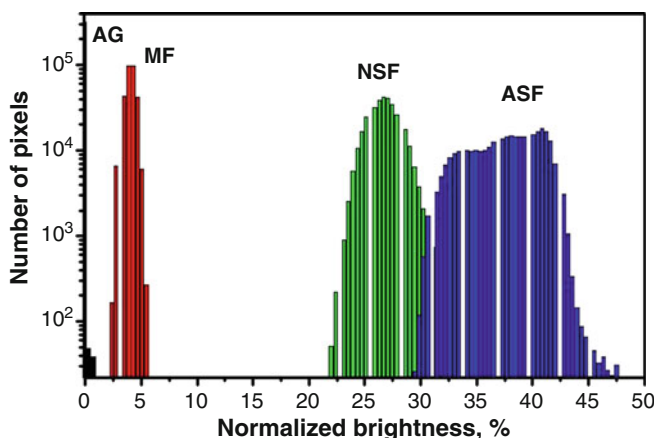


Fig. 48.3 Histograms of the normalized brightness of the samples under investigation

O/C ratios of several samples. It reveals higher oxygen contents of samples **M**, **MF** and **NS** as compared to sample **AG**. This is due to the additional O atoms brought to the UNCD surface by the maleimide, SSMCC and SAMSA molecules. Samples **M** and **MF** samples exhibit only marginal differences of O/C and N/C which suggests that the surface after the Mitsunobu modification interacts rather weakly with the SAMSA fluorescein. The highest N/C ratio is observed for sample **NS**. This is due not only to the introduction of N atoms from the SSMCC molecules but also to the NH₂-termination obtained after NH₃ plasma treatment.

Figure 48.3 shows histograms of the normalized brightness of several samples under investigation. In general, for samples **AG**, **O**, **N**, **M**, **AS** and **NS** no fluorescence signals have been detected as they have not been exposed to the fluorescein. In agreement with this observation the histogram of sample **AG** in Fig. 48.3 shows sharp peaks at low brightness values. In contrast, for samples **NSF** and **ASF** the histograms exhibit peaks at ca. 24% and 38% of the normalized

brightness, respectively. Therefore it can be concluded that the SAMSA fluorescein is present on these surfaces. The analysis of the fluorescence microscopy images reveal that it is distributed rather homogeneously on sample *NSF*, while the fluorescence of *ASF* is inhomogeneous, most probably as a result of silane polymerization on the surface. For sample *MF* a weak fluorescence signal of ca. 4% of the normalized brightness is observed, indicating the presence of small amount of SAMSA on the surface of the chemically modified UNCD/a-C films. This observation supports the contact angle and AES measurements, according to which there are marginal changes in θ_C and N/C and O/C upon interaction of the surface with fluorescein.

Conclusions

Ultrananocrystalline diamond/amorphous carbon composite films have been deposited by MWCVD from CH_4/N_2 mixtures. The films were subjected to O_2 or NH_3 plasmas in order to render the as-grown hydrogen termination to a termination with OH or NH_2 groups. OH-terminated surfaces were subjected to a chemical modification with maleimide and to silanization with APTES. In addition, the latter and the NH_2 functionalized UNCD surfaces have been exposed to the heterobifunctional crosslinker SSMCC and thereafter tested for interaction with the SAMSA fluorescein. The differently modified surfaces were investigated by contact angle measurements, AES and fluorescence microscopy. The results indicate that exposure to O_2 or NH_3 plasma leads to the introduction of OH or NH_2 groups to the surface, and renders it hydrophilic. The interaction of aminated surfaces after plasma treatment or silanization with SSMCC molecules results in their attachment, as shown by θ_C and AES results. Further experiments revealed that the SAMSA fluorescein can be attached to SSMCC functionalized surfaces via reaction of its thiol-group with the maleimide group of the SSMCC, supported by fluorescence microscopy results. The direct interaction of SAMSA with maleimide groups after chemical modification is less expressed, most probably due to the marginal gain of genuine maleimide groups on the surface due to steric reasons.

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Chapter 49

Electrochemical Response of Biomolecules on Carbon Substrates: Comparison between Oxidized HOPG and O-Terminated Boron-Doped CVD Diamond

Claudia Baier, Hadwig Sternschulte, Andrej Denisenko, Alice Schlichtiger, and Ulrich Stimming

Abstract In this work, two types of electroactive proteins, namely azurin and ferrocene-labeled papain, were adsorbed on differently oxidized diamond and investigated by cyclic voltammetry. A comparison was made with oxidized highly oriented pyrolytic graphite (HOPG). A direct electron transfer to the biomolecules was confirmed for all oxidized carbon electrodes. A strong influence of the oxygen termination process of diamond on the charge transfer through the interface has been observed. This effect has been attributed to different defects and electronic states at the interface, as confirmed by capacitance-voltage measurements in electrolyte, electrical characterisation and X-ray photoemission spectroscopy (XPS). Wet chemical oxidized diamond was proved to be the most effective electrode material for biomolecule anchoring with an electron transfer rate higher by factor of three than that of HOPG.

Keywords Bioelectrochemistry · Diamond · XPS · Surface defects

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Introduction

In the last years the study and characterization of biomolecules has grown drastically in interest. Especially the mechanisms how enzymes operate are important questions for bio-mimetic approaches in catalysis and electrocatalysis for the search of new catalysts for alternative energy systems [1,2]. The electrode material used in the fundamental studies and finally in the application should fulfill several requirements such as chemical stability, a broad electrochemical window and biocompatibility. At the moment, graphite is usually the material of choice due to the fact that this material can be functionalized e.g. by electrochemical oxidation. However, during this process the surface evolves structural and morphological changes, e.g. the formation of blisters [3,4]. Diamond with its unique combination of properties such as chemical stability, low background current and broad potential window is a perspective electrode material to be used in electrochemistry and electrochemical engineering [5–8]. Due to the progress in the last years in the synthesis of this material by chemical vapour deposition, diamond is now available in various morphologies, dimensions and controlled doping concentrations [9–11]. Its biocompatibility and inertness towards fouling makes diamond also suitable for research in the field of bioelectrochemistry and applications in biomedical sensor techniques [12–18]. Similar to the pretreatment of HOPG for anchoring biomolecules, the sp^3 carbon based diamond surface has to be functionalized in order to create binding sites.

In this work we compare the electrochemical response of proteins on oxidized HOPG and diamond. As electroactive proteins, the copper containing metalloprotein azurin and ferrocene-labeled papain are adsorbed on the carbon surfaces. As boron-doped diamond electrodes, nanocrystalline diamond (NCD) as well as homoepitaxial grown single crystal diamonds are applied. The diamond surfaces have been pretreated by several methods to obtain an oxygen termination resulting in different structures of the carbon-oxygen bonds at the surface.

Experimental and Methods

Highly oriented pyrolytic graphite (HOPG, 10 mm × 10 mm × 1.2 mm, grade ZYB) electrodes were obtained from Mikromasch, USA.

Single crystal boron-doped epitaxial diamond layers were grown on (100)-oriented surfaces of high-temperature high-pressure synthetic diamond substrates (Sumitomo) by chemical vapor deposition (CVD) in a microwave-assisted reactor (ASTEX-1500) using a solid doping source for boron. The grown epi-layers were approx. 50 nm in thickness with a concentration of boron acceptors of $5 \times 10^{21} \text{ cm}^{-3}$. The surface roughness of the as-grown layers was below 1 nm (peak-to-peak) as measured by atomic force microscopy (AFM). Details on CVD diamond growth, doping and surface evaluation can be found elsewhere [19].

A set of highly boron-doped nano-crystalline (NCD) diamond samples grown on silicon substrates was prepared by hot-filament CVD. Boron doping above 10^{20} cm^{-3} was achieved using a trimethyl borate gas source. For details on the NCD growth see Ref. [20].

The solutions for electrochemical tests were prepared from perchloric acid (HClO_4 , 70%, Merck, Suprapur), di-sodium-hydrogen phosphate-dodecahydrate (Na_2HPO_4 , VWR, analytical grade) and di-hydrogen phosphate-monohydrate (NaH_2PO_4 , VWR, analytical grade) with clean water obtained from a Millipore-Milli-Q system ($18.2 \text{ M}\Omega \text{ cm}$, 3 ppm total organic carbon). Na_2HPO_4 and NaH_2PO_4 were mixed to obtain a 10 mM phosphate buffer solution (PBS) electrolyte with pH 7. Peroxymonosulfuric acid was prepared with H_2SO_4 (95–98%, Merck, p.a.) and H_2O_2 (33%, Merck, p.a.) with a volume ratio of 1:1. Azurin from *Pseudomonas aeruginosa* and papain from papaya latex were purchased from Sigma Aldrich. Papain was modified with a ferrocene-tagged affinity label in order to make the enzyme redox active [21].

All electrodes were electrochemically characterized and investigated in 10 mM PBS (pH 7) by cyclic voltammetry (CV) using a software controlled potentiostat HEKA PG 310 (HEKA Elektronik Dr. Schulze GmbH) with the data acquisition software PotPulse V. 8.77.

The surface termination of the HOPG and diamond electrodes was inspected using X-ray photoemission spectroscopy (XPS) measurements. Details on XPS calibration, data acquisition and fitting of the spectra can be found in Ref. [22].

Results and Discussion

Electrode Preparation and Initial Characterization

Electrochemical Oxidation of HOPG

Freshly cleaved HOPG offers only few active sites for protein binding as its surface is hydrophobic. In order to change hydrophobicity into hydrophilicity and to create binding sites for the enzyme molecules, the HOPG was electrochemically oxidized in 0.1 M HClO_4 by applying three potential sweeps from 0.2 to 2.1 V vs. NHE (normal hydrogen electrode; in the following all potentials are given with respect to NHE) with a sweep rate of 200 mV s^{-1} [23,24]. This treatment forms oxygen containing groups on the surface such as carboxyls, hydroxyls and carbonyls [25–28] and produces surface defects which improve the electron transfer between enzymes and electrode [29]. The corresponding CV exhibited a characteristic oxidation current at 2.1 V and a slightly diminished reduction peak at 1.8 V, as shown for instance in [30]. The oxidation is attributed to a combination of graphite oxidation and intercalation of anions such as ClO_4^- into the graphite lattice [31]. Therefore, the reduction peak can be attributed partially to the deintercalation of the

anions and partially to the reduction of the oxygen containing groups formed at the graphite surface. However, the reduction of the graphite is not fully reversible; thus, surface bonds are broken and the graphite structure is thought to be disturbed during the oxidation process leading to a residual oxide layer. The formation of the oxide groups occurs by means of a nucleation and growth mechanism [31] where the oxidation, i.e. the irreversible breaking of the C—C bonds starts initially at step and defect sites and proceeds along step and ridge sites and only to a lower extent also into the basal plane. However, also blister formation due to the intercalation of ClO_4^- has to be taken into account [3,4]. By performing in-situ electrochemical scanning tunneling microscope (EC-STM) studies Gewirth and Bard [31] found that the tunneling barrier height through the oxide overlayer is significantly lower than that of the bare HOPG surface; it decreased from 0.9 to 0.25 eV in 0.1 M H_2SO_4 . This indicates that the oxidation process also enhances the electron transfer between the electrode surface and surface bound species, making it suitable for electrochemical investigations of enzyme/electrode architectures.

Oxygen-Termination of Diamond and XPS Analysis

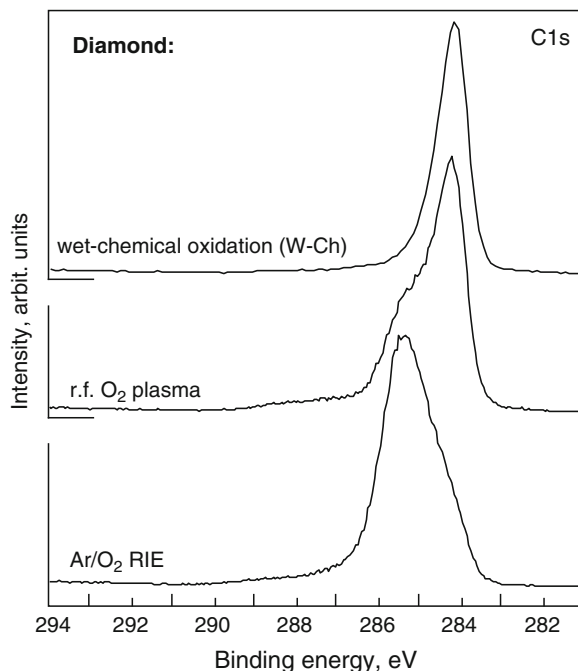
The oxygen-terminated diamond was prepared by (i) wet chemical oxidation (W-Ch); (ii) a low-pressure r.f. oxygen plasma in a barrel reactor (O_2 -plasma) and (iii) a reactive ion etching process (RIE) in Ar/O_2 atmosphere. According to the data in literature, the three methods result in different structures of carbon-oxygen groups and defect densities on the diamond surface [22,32,33]. In our study we applied these methods to both single-crystalline and also to nanocrystalline diamond electrodes.

The high resolution XPS spectra of the C1s core level taken from single crystal diamond are shown in Fig. 49.1 for the W-Ch, O_2 -plasma and RIE cases. For details on XPS calibration and fitting see Ref. [22]. The sample (#W-Ch) was treated in a hot chromium acid at 75°C temperature for 10 min, followed by dipping into $\text{HNO}_3 : \text{HCl}$ (1:3) solution for 120 s at room temperature to remove possible contaminations by chromium salts. The last step of this treatment was chemical oxidation in a $\text{H}_2\text{O}_2 : \text{H}_2\text{SO}_4$ (1:2) mixture at approx. 70°C for 10 min, followed by rinsing in de-ionised water. The corresponding spectrum in Fig. 49.1 exhibited a maximum at 284.1 eV binding energy related to the sp^3 bulk and small components at higher binding energies related to C—OH and C—O—C bond structures with a monolayer coverage [22]. These carbon-oxygen bonds induce electronic states pinning the surface Fermi level in diamond at about 1.7 eV above the top of the valence band edge.

A similar structure of the surface bonds was observed on the oxidized HOPG. Both HOPG and W-Ch-diamond samples exhibited similar features also in the energy range of 532 eV corresponding to the O1s core level (not shown).

Sample (# O_2 -plasma) was subjected to a r.f. oxygen plasma in a barrel reactor. The sample was on the grounded holder at room temperature with no self-bias. This plasma treatment was performed for 5 min at a pressure of 13 Pa and an r.f. power of 100 W. The XPS spectrum of this sample in Fig. 49.1 showed higher densities of

Fig. 49.1 High resolution XPS spectra of the C1s core level taken from single crystal diamonds exposed to wet chemical oxidation (W-Ch), r.f.-oxygen plasma (O_2 -plasma) and reactive ion etching (RIE) in Ar/ O_2 atmosphere



the C—O—C and also C=O bond structures corresponding to a surface layer of about 1 nm thickness [32]. Besides, exposure to the plasma generated a small signal below 284 eV of about 1% of the surface signal. This component can be attributed to an amorphous carbon (α -C) phase related to plasma-induced surface defects. The formation of the α -C phase was accompanied by an increased surface roughness of 0.7 nm (peak-to-peak by AFM), compared to 0.4 nm of the initial as-grown surface. According to a recent report [33], such defects may induce additional electronic states on the surface with positive charges and a density in the range of 10^{13} cm^{-2} . This leads to an increased depletion of boron-doped diamond at the surface.

The treatment in a reactive ion etching plasma (#RIE sample) was performed in an argon/oxygen environment with 10% oxygen in the gas phase (Perkin-Elmer 2400 sputter system, 13.56 MHz). The gas pressure during this process was 5.3 Pa, with gas fluxes of 17.6 sccm (argon) and 1.76 sccm (oxygen). The applied r.f. power was 25 W. The DC self-bias potential during this treatment was set to 100 V. The substrate was kept at room temperature. Due to radiation-induced defects, the C1s bulk component in the XPS spectrum in Fig. 49.1 was shifted to the higher binding energies of 285.3 eV. The spectral component at 284.3 eV is related to an amorphous carbon phase of approx. 4 nm in thickness, while the components at higher energies can be attributed to carbon-oxygen groups with a monolayer coverage [33]. The RIE-induced amorphous surface carbon produces an insulating layer on highly boron-doped diamond, resulting in non-ohmic characteristics of metal-diamond contacts.

Adsorption of Proteins on Carbon Electrodes

The oxidized HOPG and oxygen-terminated nanocrystalline and single crystal diamond electrodes were rinsed with Milli-Q water and immersed into a fresh protein solution (1 mg ml^{-1}) in 10 mM PBS for 2 h. According to the literature, the amine groups of the protein react with the carboxylic groups on the surface [34]. As electroactive proteins ferrocene modified papain (FcAL@papain) molecules, prepared according to [21], and the metalloprotein azurin were used in order to investigate the electron transfer between redox-active biomolecules and the different electrode support materials.

Electrochemical Characterization of HOPG and Diamond Electrodes

Initial Oxidized Electrodes

Prior to enzyme adsorption the NCD electrodes were studied by cyclic voltammetry in 10 mM PBS (pH 7). The cyclic voltammograms (CVs) were obtained at a sweep rate of 100 mV s^{-1} . In Fig. 49.2a the CVs of the HOPG surface (black curve) and a NCD film without subsequent surface treatment, i.e. an as-grown NCD electrode (grey curve), are shown. As-grown NCD films obtained directly from the CVD reactor are hydrogen terminated. It is clearly visible in Fig. 49.2a that the potential window is larger for NCD than for HOPG. While the CV of NCD is characterized only by a capacitive current at -0.4 V , a significant negative current is flowing at the HOPG electrode in this potential range. This current is caused by hydrogen evolution at the graphite surface. Figure 49.2b contains the CVs of the oxygen-terminated NCD samples prepared by the three different oxidation procedures

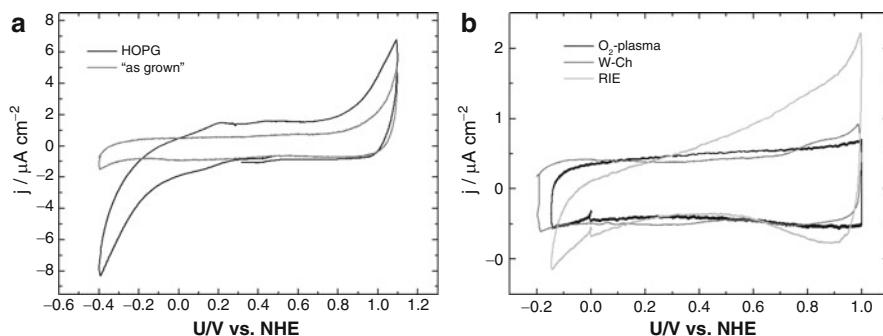


Fig. 49.2 Cyclic voltammograms of (a) HOPG and as-grown NCD electrodes and (b) NCD electrodes oxygen-terminated by different oxidation procedures, obtained in 10 mM PBS (pH 7) at a sweep rate of 100 mV s^{-1}

described in Sect. 3.1. The black curve corresponds to the NCD terminated by oxygen plasma, the grey curve to the wet chemical oxidation and the light grey curve to the reactive ion etching.

Except for the electrode terminated by RIE, all electrodes show a similar capacitive behavior in phosphate buffer according to a double layer capacity of approximately $4.5 \mu\text{Fcm}^{-2}$. This value is in good agreement with literature data obtained from electrochemical impedance spectroscopy [35]. The CV of the RIE treated NCD shows a positive current density starting at 0.3 V and steadily increasing up to 1 V and an increased negative current density between 1 and 0.7 V when sweeping backwards. The observed positive current density, which is higher than the negative current density, might indicate that an electrochemical process takes place at the electrode surface, which is only partially reversible. All other CVs show currents only determined by the double layer charging of the electrode, probably due to the fact that the oxidized surfaces are electrochemically not reactive.

Ferrocene-Modified Papain on HOPG and Diamond

Electroactive FcAL@papain molecules were adsorbed onto oxygen-terminated nanocrystalline diamond films. An as-grown NCD film served as reference electrode. For comparison FcAL@papain was also adsorbed on an oxidized HOPG (HOPGox) electrode surface. All electrodes were prepared freshly, being exposed to one adsorption procedure with 2 h incubation at room temperature and using the same enzyme solution of 1 mg ml^{-1} in 10 mM PBS at pH 7. Figure 49.3 shows the CVs obtained after the adsorption procedure obtained in 10 mM PBS at a sweep rate of 100 mV s^{-1} . Figure 49.3a presents the CVs of the reference electrodes FcAL@papain/HOPGox (black curve) and FcAL@papain/as-grown NCD (grey curve). The FcAL@papain/HOPGox electrode shows a significant redox behavior

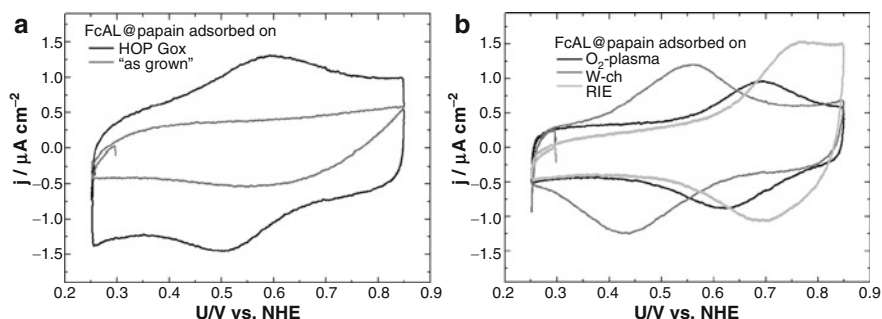


Fig. 49.3 Cyclic voltammograms of FcAL@papain adsorbed on (a) oxidized HOPG (black) and as-grownNCD (grey) and (b) differently treated oxygen-terminated NCD surfaces; O₂-plasma (black), wet chemical (W-Ch, grey), reactive ion etching (RIE, light grey). All CVs were obtained in 10 mM PBS (pH 7) at a sweep rate of 100 mV s^{-1}

with a redox potential at 555 mV. The untreated NCD as-grown shows no redox behavior. Untreated NCDs are usually hydrogen-terminated and thus hydrophobic. The lack of chemically reactive groups usually precludes the attachment of biomolecules to the surface [36], i.e. FcAL@papain molecules can not stably bind to the as-grown NCD electrode and thus no direct electron transfer is visible in the cyclic voltammogram. In contrast, the CVs of FcAL@papain adsorbed on oxygen-terminated NCDs (Fig. 49.3b) prove direct electron transfer between the electro-active biomolecules and the electrodes surface since a redox behavior can be observed.

While the electrodes FcAL@papain/NCD O₂-plasma (Fig. 49.3b, black curve) and FcAL@papain/NCD W-Ch (Fig. 49.3b, grey curve) show well pronounced redox peaks, a redox behavior of the FcAL@papain/NCD RIE electrode (Fig. 49.3b, light grey) can only be estimated to be in the range of 0.7 V. The oxidation and reduction peaks are superimposed by a background current which was already observed for the pure NCD RIE described in the previous section (see Fig. 49.2b).

The surface coverage and the redox potential of FcAL@papain adsorbed on different electrodes are significantly different. For all electrodes, the redox potential, the charge densities evaluated from the oxidation peak (q_{ap}) and the reduction peak (q_{cp}) as well as their ratio $q_{ap} : q_{cp}$ are given in Table 49.1. The lowest redox potential of 495 mV was found for the NCD treated by wet chemical oxidation. The redox potential for O₂-plasma NCD of 655 mV is more positive by 160 mV, and the redox potential for the RIE NCD, although only estimated, is even higher at 720 mV. The reaction potential is shifted to more positive values probably due to charged electronic states on the surface, which are related to the plasma-induced defects detected by XPS. The same tendency is observed for the O₂ plasma sample, but with a lower shift of the reaction potential. This is consistent with XPS: the lower intensity of the defect-related component in XPS means a lower density of charged states on the diamond surface compared to the RIE sample.

According to the charge detected, nearly the same amount of FcAL@papain molecules were adsorbed onto the oxidized HOPG surface and the O₂-plasma surface while the NCD modified by the wet chemical oxidation shows a 50% higher surface coverage. However, since the charge densities are based on the geometric surface area of the electrodes it is hard to compare these absolute values without knowing the roughness factor of the different surfaces. The ratio of the charge densities $q_{ap}:q_{cp}$ is for all electrodes close to unity indicating a completely reversible electron transfer process independent of the surface modification.

Table 49.1 Redox potential U_0 , charge density of the oxidation q_{ap} and the reduction peak q_{cp} evaluated from the CVs shown in Fig. 49.3, the ratio of $q_{ap}:q_{cp}$ and the surface coverage Γ

FcAL@papain on	U_0 (mV vs. NHE)	q_{ap} ($\mu\text{C cm}^{-2}$)	q_{cp} ($\mu\text{C cm}^{-2}$)	$q_{ap}:q_{cp}$	Γ (pM cm^{-2})
HOPGox	555	0.806	0.798	1.01	8.29
NCD W-Ch	495	1.196	1.225	0.98	12.5
NCD O ₂ -plasma	655	0.890	0.882	1.01	9.18
NCD RIE	720	–	–	–	–

Azurin on HOPG and Diamond

Since azurin is a well-known metalloprotein often described in literature to investigate the electron transfer between a redox active biomolecule and an electrode surface, it is used here to investigate the interfacial electron transfer to the oxidized electrode surfaces. (001) single crystal boron-doped CVD diamond was used in order to have smooth surfaces with sub-nanometer roughness, i.e. the geometric area is almost equal to the active surface area, comparable to HOPG.

In the previous section it was shown that wet chemical oxidation and the O_2 -plasma pretreatment promote the immobilization of biomolecules onto the diamond surface and enables a direct electron transfer. Therefore, single crystal diamond electrode surfaces were oxygen-terminated only by these two procedures. For comparison azurin was also adsorbed on NCD W-Ch and on oxidized HOPG electrode surfaces. All electrodes were freshly prepared, being exposed to one adsorption procedure with 2 h incubation time at room temperature using the same enzyme solution of 1 mg ml^{-1} in 10 mM PBS (pH 7). In Fig. 49.4a the cyclic voltammograms obtained for azurin/diamond W-Ch (black) and azurin/NCD W-Ch (grey), in Fig. 49.4b those for azurin/diamond O_2 -plasma (black) and azurin/HOPGox (grey) electrodes are shown.

All electrodes show observable redox peaks which can be attributed to the oxidation and the reduction of the adsorbed azurin on the surfaces. However, the redox behavior shows significant differences. Although the redox potential of azurin adsorbed on single crystal diamond W-Ch (Fig. 49.4a, black curve) and on NCD W-Ch (grey curve) is -150 mV for both electrodes, the azurin/NCD W-Ch electrode exhibits a peak separation of several hundred mV indicating a hampered electron transfer. In the case of the azurin/diamond O_2 -plasma electrode the redox peaks almost disappear in the background current, therefore, the redox potential can only be roughly estimated. Depending on the support electrode used the redox potential differs between -150 mV for azurin/diamond

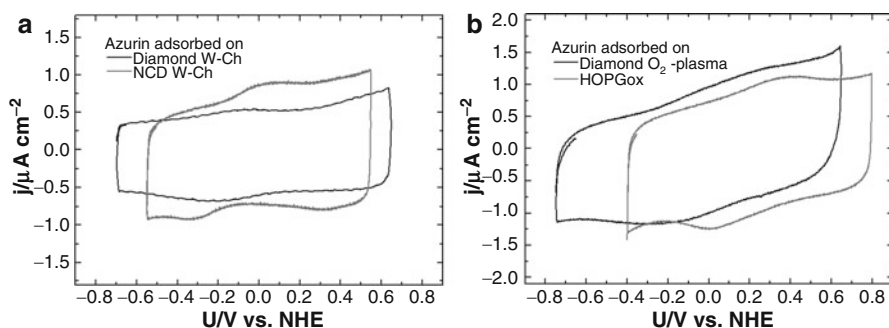


Fig. 49.4 Cyclic voltammograms of azurin adsorbed on (a) single crystal diamond W-Ch (black) and NCD W-Ch (grey) and (b) single crystal diamond O_2 -plasma (black) and oxidized HOPG (grey), obtained in 10 mM PBS (pH 7) at a sweep rate of 100 mV s^{-1}

Table 49.2 Parameters of azurin adsorbed on NCD W-Ch, single crystal diamond W-Ch and O₂-plasma and HOPGox: Redox potential U_0 , charge density of the oxidation q_{ap} and the reduction peak q_{cp} peak evaluated from the CVs shown in Fig. 49.4, the ratio of q_{ap} : q_{cp} , the surface coverage Γ and the apparent electron transfer rate constant k_{app}

Azurin on	U_0 (mV vs. NHE)	q_{ap} ($\mu\text{C cm}^{-2}$)	q_{cp} ($\mu\text{C cm}^{-2}$)	q_{ap} : q_{cp}	Γ (pM cm^{-2})	k_{app} (s^{-1})
NCD W-Ch	−150	0.334	0.312	1.07	3.75	–
Diamond W-Ch	−150	0.115	0.124	0.93	1.24	1.5
Diamond O ₂ – plasma	−60	0.659	0.590	1.11	6.47	–
HOPGox	215	0.492	0.497	0.99	5.13	0.43

W-Ch and azurin/NCD W-Ch (Fig. 49.4a), approximately −60 mV for azurin/diamond O₂-plasma (Fig. 49.4b, black curve) and 215 mV for the azurin/HOPGox (Fig. 49.4b, grey curve). These potential differences might be explained by the azurin molecules being located in different chemical environments depending on the kind of the oxide overlayer. Due to ligand effects the redox potential of a molecule can vary [37]. Especially the protonation and deprotonation of the molecule play an important role [38]. Table 49.2 summarizes the significantly differing redox potentials of azurin depending on the electrode material and the electrode pretreatment. Literature data [39,40] obtained for azurin in an acetate buffer with a pH 4.6 lie around 300 mV. While the redox potential found for azurin adsorbed on oxidized HOPG is around 80 mV lower due to deprotonation effects of the histidines within the molecule, the redox potential on the diamond electrodes can not be explained so far.

The surface coverage Γ , i.e. the number of redox active azurin molecules attached to the electrode surface was determined from the charge passed under the Faradaic peaks assuming a one-electron transfer process. Although the surface coverage obtained for azurin on the O₂-plasma treated diamond is higher by a factor of 5 than for azurin/diamond W-Ch (Table 49.2) the redox peaks are broad and almost superimposed by the capacitive current originating from the double layer charging of the electrode. The surface coverage of the O₂-plasma diamond is comparable to the coverage obtained for oxidized HOPG. For the diamond surface terminated by wet chemical oxidation the surface coverage amounted only 25% of the coverage obtained for oxidized HOPG or O₂-plasma diamond.

For the azurin/diamond O₂-plasma and azurin/diamond W-Ch single crystal diamond electrodes cyclic voltammetry at different scan rates was performed to calculate the electron transfer rate between the biomolecule and the electrode. However, due to the broad redox peaks the electron transfer rate could not be evaluated for the O₂-plasma diamond. The peak separation of approximately 400 mV indicates a sluggish electron transfer. The rate constant for electron transfer for azurin/diamond W-Ch was determined from the variation in peak position between the oxidation and the reduction peak as a function of the sweep rate and was compared to the electron transfer rate for the azurin/HOPGox electrode.

The separation of the peak potentials was fitted according to the Laviron theory [41,42], yielding an electron transfer rate $k_{\text{app}} = 0.43 \text{ s}^{-1}$ for azurin/HOPGox and $k_{\text{app}} = 1.5 \text{ s}^{-1}$ for the azurin/diamond W-Ch electrode. These values are given in Table 49.2. The apparent electron transfer rate of azurin/diamond W-Ch is by a factor of three higher than for the oxidized HOPG.

Conclusions

Electroactive proteins were adsorbed on differently functionalized carbon electrodes such as oxidized HOPG, hydrogen and oxygen-terminated single and nano crystalline boron-doped diamond. In the electrochemical investigation by cyclic voltammetry, all oxidized carbon electrodes confirmed a direct electron transfer between the surface and the biomolecules, only the hydrogen terminated as-grown NCD sample showed no signal. The procedure for the oxygen termination of the diamond samples has a strong influence on the formation of defects and electronic states at the interface as determined by capacitance-voltage measurements in electrolyte and electrical measurements which correlated to XPS results [22,32,33]. Therefore, the charge transfer through the interface is strongly dependent on the way, how the oxygen termination of diamond has been achieved. Wet chemical oxidized diamond is the most promising electrode material for biomolecule anchoring with an electron transfer rate higher by factor of three than that of HOPG.

Acknowledgements The authors want to thank Andrij Romanyuk from the Institute of Physics of the University of Basel for performing the XPS measurements.

This work was funded by the International Graduate School Materials Science of Complex Interfaces (ComplInt) in the framework of the Elitenetzwerk Bayern (ENB) and by Max-Buchner Forschungsstiftung (DECHEMA).

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Chapter 50

Impact of Nanotopography and/or Functional Groups on Periodontal Ligament Cell Growth

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Abstract The main purpose of this contribution was to obtain COOH functionalities and/or nanotopographic changes on the surface of 3D, non-woven polyester fabric (NWPF) discs (12.5 mm in diameter) by using low pressure water/O₂ plasma assisted treatments. The prepared discs were characterized by various methods after the plasma treatment. Periodontal ligament (PDL) fibroblasts were used in cell culture studies. The cell culture results showed that plasma treated 3D NWPF discs are favorable for PDL cell spreading, growth and viability due to the presence of functional groups and/or the nanotopography of their surfaces.

Keywords Polyethylene terephthalate · Low pressure plasma, nanotopography · Periodontal ligament fibroblasts

Introduction

The growing interest in synthetic polymeric materials for tissue engineering led to novel approaches to improve cell-biomaterial interactions, i.e. the development of new biocompatible/bioactive materials with the introduction of chemical functionalities, such as amine or carboxyl groups [1]. Plasma treatment, which is a surface modification technique, has been widely used to introduce functional groups onto the material surfaces (2).

In the present study, a low-pressure water/O₂ plasma was applied in order to obtain COOH functionalities and/or nanotopographic changes on the surface of 3D NWPF discs. The modified NWPF discs were biologically tested with PDL fibroblasts in cell culture experiments.

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Experimental Section

NWPF Discs

NWPF (Style # 2214) was used as 3D cell supporting material. It was obtained from Reemay (Old Hickory, TN, USA) in form of sheets and had a surface area of $1,200 \text{ cm}^2 \text{ g}^{-1}$, a Fraizer air permeability of $2.7 \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$ and a thickness of 0.23 mm.

The sheets were cut in the form of discs with diameters of 12.5 mm before the plasma treatment.

Cold Plasma Treatment Using Vacuum Environment

The NWPF discs were decontaminated and sterilized by an inductively coupled H_2 plasma (Plasma Term reactor; pressure 1.3 Pa; H_2 flow rate 1 sccm; time up to 10 min; power 200 W). The process is able to remove the silicone contaminations (due to shipping/storage/handling of samples) in 2 min, which was monitored by ESCA analysis (electron spectroscopy for chemical analysis).

Plasma assisted treatment of clean NWPF discs was carried out in a cylindrical capacitively coupled RF plasma reactor equipped with a 40 kHz power supply in three steps: $\text{H}_2\text{O}/\text{O}_2$ plasma treatment; in situ or ex situ gas/solid reaction (oxalyl chloride vapours; pressure 65 Pa; time 30 min); and hydrolysis (open laboratory condition; 2 h) for final $-\text{COOH}$ functionalities.

Characterization Studies

Experimental parameters such as the flow rates of water and oxygen, power, pressure and time of the plasma modifications were optimized according to a design of experiments (DoE) program (Design Expert 7, Stat-Ease, Inc., Minneapolis, MN). COOH and OH functionalities on the modified surfaces were detected quantitatively by using a fluorescent labeling technique and an UVX 300 G sensor. ESCA analysis was used to evaluate the relative atomic surface compositions and the carbon and oxygen linkages located in non-equivalent atomic positions. The surface morphologies of the NWPF discs before and after the decontamination process i.e. the hydrogen plasma treatment, were evaluated by scanning electron microscopy (SEM) using a LEO 1,530 field emission instrument (LEO Electron Microscope Inc., Thornwood, NY).

PDL Cell Culture

Cell culture studies were carried out with periodontal ligament (PDL) cells. The cells were obtained from the root surfaces of healthy premolar teeth extracted for orthodontic reasons as described by Nohutcu et al. [3]. They were cultured using Dulbecco's Modified Eagle's Medium supplemented with 10% (v/v) fetal bovine serum in 24-well polystyrene tissue-culture dishes containing NWPF discs. The discs were afore exposed to UV light for 30 min in order to sterilize them. An MTT assay was used in order to determine the proliferation of cells in the course of a 10-day cell culture period.

Results and Discussion

Plasma Treatment

According to the DoE response surfaces, the best conditions in order to maximize the OH fluorescence signals for NWPF discs were computed. The experiment with the conditions f (water flow rate) = 14 sccm, p (pressure) = 26.66 Pa, P (RF power) = 110 W, t (treatment time) = 3.5 min was chosen for further NWPF samples due to the fact that here the OH density possesses the highest value and the desirability is 1.000.

NWPF is sensitive to decarboxylation in a high energetic environment (e.g., pyrolysis, plasma). The oxalyl chloride treatment converts the OH groups to carboxyl functionalities but carbon in free carboxyl and in ester groups has pretty much the same binding energy so these groups are not differentiable in C1s high resolution ESCA spectra. SEM images (Fig. 50.1) show changes in the nanotopography of the filaments. The surface of fibers (Fig. 50.1a, d) is uniformly covered with features smaller than 100 nm after 2 min hydrogen plasma treatment (Fig. 50.1b, e). Extended hydrogen plasma treatment (8 min) is able to generate a complex topography bearing small features (less than 100 nm) into μm -size features (Fig. 50.1c, f), possibly very suitable for cell proliferation.

PDL Cell Cultivation

At the end of the culture it could be seen that decontaminated NWPF samples offered the highest PDL cell growth. It was considered that the incorporation of the polar, O-containing groups such as hydroxyl, carboxyl or carbonyl and peroxy, which are attractive for cell attachment to the surface of the polymer after the H_2

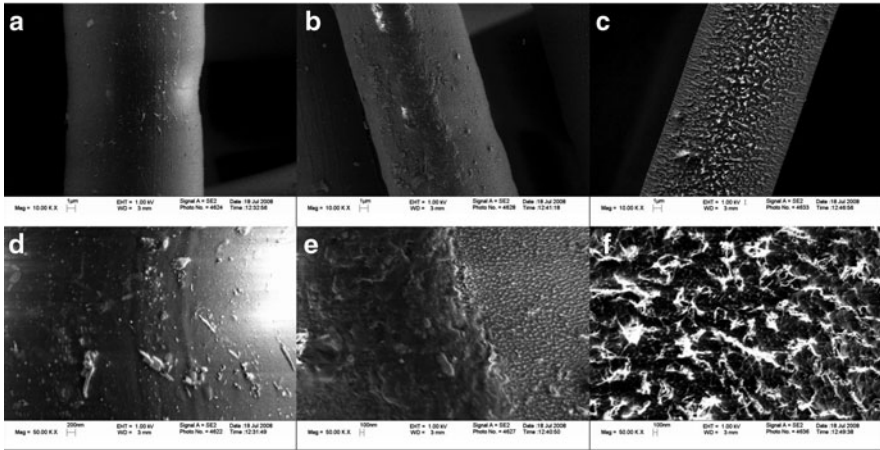


Fig. 50.1 SEM images of before (a and d) and after hydrogen plasma treated NWPf substrates. Treatment time: 2 min (b and e); 8 min (c and f). Magnification: $\times 10,000$ (A, B and C); $\times 50,000$ (D, E and F)

plasma treatment, might have caused surface morphology changes. A Nano-sized surface topography may render surfaces with special and favorable properties to a biological environment.

Conclusion

From the present study, it can be suggested that nano-structured surface topographies with increased surface/volume ratio can provide more binding sites for cells. Our suggestion for related future studies is the investigation of the effect of plasma created nanotopographies only on the cell growth in detail.

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Chapter 51

Effect of ZnO Nanostructured Thin Films on *Pseudomonas Putida* Cell Division

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Abstract In this report we study the interaction between the bacteria *Pseudomonas putida* and nanostructured ZnO and ZnO:H thin films prepared by magnetron sputtering of a ZnO target. The nanostructured ZnO and ZnO:H thin films possess some biological-active properties when in contact with bacteria. Our experimental data show that these films have no destructive effect on the cell division of *Pseudomonas putida* in poor liquid medium and can be applied in biosensor devices.

Keywords *Pseudomonas putida* · ZnO nanostructured film · Live/dead test

Introduction

The bactericide effect of some metal oxide nanoparticles, in particular ZnO, has recently received significant attention due to their potential application in pharmacology and medicine as antibacterial agents [1, 2]. It was found that the toxicity of ZnO particles and of ZnCl_2 is essentially due to dissolved Zn^{2+} ions [3]. Other

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group has reported that the concentration of ZnO nanoparticles is more important than the particle size, and the reason for the toxic effect is damaging of the cell membrane wall [4]. In this study results for the nondestructive influence of ZnO thin films on the cell division of *Pseudomonas putida* are reported encouraging the development of biosensors on the basis of ZnO thin films.

Experimental

Preparation of ZnO Nanostructured Thin Films

Two set of ZnO samples were used. ZnO and ZnO:H thin films were deposited on glass substrates by r.f. magnetron sputtering of a ceramic ZnO target in atmospheres of Ar (0.5 Pa) or Ar (0.5 Pa) + H₂ (0.1 Pa) at substrate temperatures T_s of 500°C and 400°C and a r.f. power of 180 W. The thickness of the films was about 600 nm. The optical and structural properties of the films were studied by transmittance and reflectance measurements, atom force microscopy (AFM), scanning electron microscopy (SEM) and X-ray diffraction (XRD).

Toxicity Test With Bacteria

To study the influence of the nano-size grained ZnO thin films on the bacterial activity of *Pseudomonas putida* cells two types of nutrient media were used: the rich natural and the poor synthetic medium ISO 12072.

The ZnO and ZnO:H films were sterilised by UV light for 30 min and put in the bacterial suspension in an exponential growth phase. The bacteria were prepared by inoculation in the solid rich medium and adapted to the poor mineral medium, as described in the ISO standard by three consecutive subcultivations. They were cultivated in aerated suspension in dark and light conditions at 25°C using an orbital benchtop shaker operating at 220 rounds/min. The light conditions were created by illumination with a tungsten lamp (100 W) at a distance of 1 m. The optical density of the bacterial suspension was measured. Then immediately tenfold dilutions were prepared, inoculated and cultivated on the rich medium. A suspension of 0.1 ml was formed and analysed by a fluorescence microscope.

The samples were collected after 3, 6, 9, 12 and 24 h. The bacterial abundance ranged from 10⁵ to 10⁸ cells/ml in the poor and rich media. The ZnO toxicity was measured by comparison of the ratio of live/dead cells by applying the special kit from Promega Live/Dead® BacLight (TM) with propidium iodide and SYTO 9. A fluorescence microscope (Leica DM5500B) was used to observe the samples. The image analysis was based on a two steps procedure: the recorded micrograph of

each microscopic field was first numerated and stored in the data base folder. In the second step the digitalized images were submitted an to the Image J. software. The background was subtracted manually. The manual counting of bacterial cells was performed by two independent operators. The percentage of living active cells was determined from the images by counting the green (live) and red cells (considered as dead or inactive). The quantity of living cells was determined by the most probable number method in the rich solid medium and by measurement of the optical density by Specol 11 at $\lambda = 600$ nm in the poor medium.

Results and Discussion

The optical properties of ZnO and ZnO:H films were studied by transmittance and reflectance measurements. The spectral dependence of $(\alpha E)^2$ versus the energy E is presented in Fig. 51.1 where α is the coefficient of absorption. The calculated energy gaps E_g between 3.27 and 3.33 eV are typical for ZnO. Our previously published data [5] show that hydrogen changes the stoichiometry of the sputtered species, so the growth conditions lead to a decrease of defects. The XRD spectra in Fig. 51.2 reveal the polycrystalline structure of the films with a preferential crystallographic (002) orientation with the c -axis perpendicular to the substrate surface.

The AFM pictures in Fig. 51.3a (ZnO) and b (ZnO:H) show rough top surfaces of the films. The grain size is about 100 nm for ZnO and 150 nm for ZnO:H films.

We observed that in all experiments the optical density of the suspensions with nanostructured ZnO and ZnO:H increases faster than that in the control experiment; thus the cells division of *Pseudomonas putida* is not inhibited (Fig. 51.4). This phenomenon was proven by classical cultivation methods. In the solid medium we counted only the active cells after 18–24 h of cultivation at 25°C. Under these conditions it seems clear that only the active dividing cells create visual colonies. The bacterial growth in contact with the samples is comparable with those for rich and poor liquid media. Cells exposed to ZnO in the poor medium divide faster than

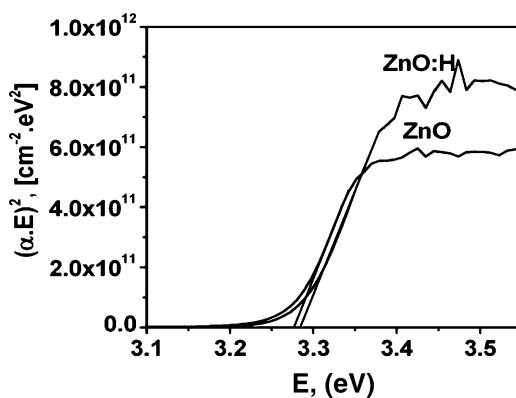


Fig. 51.1 Spectral dependence of $(\alpha E)^2$ versus the energy E of ZnO and ZnO:H thin films

Fig. 51.2 XRD spectra of ZnO ($T_s = 500^\circ\text{C}$) and ZnO:H ($T_s = 400^\circ\text{C}$)

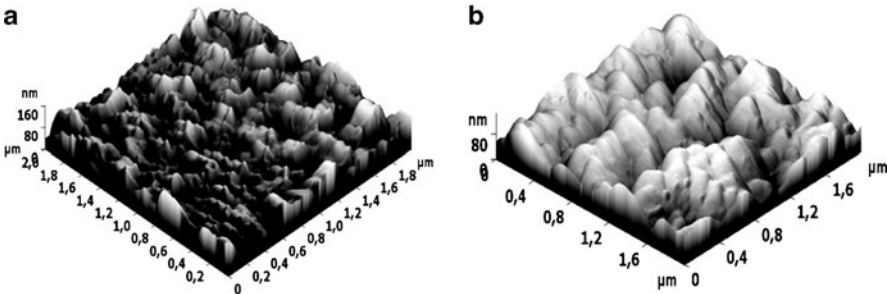
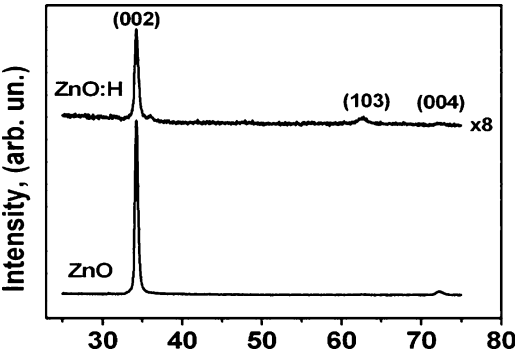


Fig. 51.3 AFM pictures (3D images, $2 \times 2 \mu\text{m}$) of a ZnO film (a) and a ZnO:H film (b)

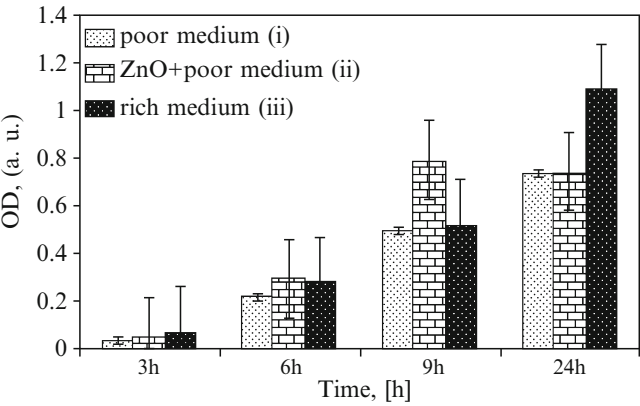


Fig. 51.4 Density of *Pseudomonas putida* bacteria grown in (i) poor medium as control experiment, (ii) poor medium with nanostructured ZnO thin films and (iii) rich medium

those from the control experiment under the same condition. However, the rates are close to the cell division rate in the rich medium. It was observed that the percentage of living cells having contact with the nanostructured thin film is more than 90% of the total amount of cells. In the control experiment the living cells were about 65%. This difference could be due to the activation effect of the ZnO nanofilms. We did not observe any significant difference between ZnO and ZnO:H nanofilms. The reason may be that the amount of Zn^{2+} , which is dissolved into the suspension, is equal. The presence of zinc ions even at very low concentrations in this poor medium influences on the cell division rate, leading to its increase. If the concentration is higher the effect is opposed, i.e., toxic. This hypothesis was tested by an additional control experiment. Our expectations are in congruence with the results from the image analysis.

We also found that in spite of the similarity between the division rates in the presence of ZnO and ZnO:H, the treated cells are much smaller in size than the cells in the rich medium. This fact may be explained by the presence of enough amounts of nutrients in the rich medium, which lack in the poor medium with the ZnO nanofilm.

Conclusions

This study report the influence of nanostructured ZnO and ZnO:H thin films on the cell division rate of *Pseudomonas putida*. Our experiments prove unambiguously that the presence of ZnO thin films is not toxic for the bacterial microsuspension. They activate the rate of the cell division and increase the percentage of live cells. There is no significant difference regarding effect between ZnO and ZnO:H nanostructured thin films. These results are encouraging for the development of ZnO based biosensor devices.

Acknowledgement This work has been supported by the Bulgarian Ministry of Science and Education, National Sci. Fund, Project: D002-207/2008 and by the Operative program "Human resources" (project BG 051PO001/07/3.3-02/58/17.06.2008).

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Chapter 52

Comparison of Photocatalytic Activity of TiO₂ Anatase Prepared by the Sol-Gel Technique and Chemical Vapour Deposition on Naphthalene in the Gas Phase

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Abstract In this study the gas phase photocatalytic oxidation of naphthalene in the presence of TiO₂-based photocatalysts prepared by chemical vapor deposition (CVD) and the sol-gel method is examined. As precursors for the photocatalyst preparation TiCl₄ was used for chemical vapor deposition (CVD), while for the sol-gel technique the precursor was titanium tetra-isopropoxide. The level of naphthalene degradation was examined with FTIR spectroscopy; the identification of the products obtained was performed by GC-MS measurements. The kinetics of the photooxidation reaction of naphthalene in excess of oxygen was investigated. It was found that the kinetics of naphthalene oxidation follow a first-order law; the rate constants were determined by means of mathematical modeling. Also, it was found that the rate limiting steps for naphthalene oxidation are diffusion of the components on the catalyst surface and transport through the films of the photocatalyst particles. The photocatalytic activity of TiO₂-based photocatalysts prepared by CVD as a gas phase method and the sol-gel technique as a liquid method are compared. The photocatalysts showed an excellent efficiency for naphthalene degradation in the presence of oxygen; a complete mineralization of the aromatic toxic compound to CO₂ and water was achieved.

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Keywords CVD · Sol-gel technique · TiO₂ photocatalysts · UV irradiation · Naphthalene

Introduction

Semiconductor photocatalysis is an advanced process based on photoinduced phenomena: the irradiation of a semiconductor catalyst with UV light carrying enough energy to overcome its band-gap results in the creation of electron-hole pairs. Excited conduction band electrons and valence band holes can react with electron donors or acceptors adsorbed on the catalyst surface and induced photocatalytic reactions. The most important field of photocatalysis is the photodegradation of organic compounds: the most widely used semiconductor is TiO₂. It acts as a photocatalyst in the environmental decontamination of a large variety of organics, viruses, bacteria, fungi, algae, and cancer cells, which can be totally degraded and mineralized to CO₂, H₂O, and harmless inorganic anions [1–4].

Naphthalene, a common polycyclic aromatic hydrocarbon (PAH), is found in many anthropogenic fluxes such as combustion fumes, used oils, bilge water, etc. It is considered as a carcinogenic compound with both acute and chronic effects on human and animal health [5]. Naphthalene photocatalytic oxidation has been investigated in aqueous phases [5–8]: these authors have shown that its degradation results in the formation of various compounds such as naphthols, naphthoquinones and cinnamaldehydes, and that naphthalene is finally mineralized to CO₂ and water.

Experimental

Naphthalene (99.9%) was purchased from Merck and used as received. TiCl₄ (99%), CrO₂Cl₂ (99.5%) and titanium tetraisopropoxide (99%) were purchased from Aldrich, SiCl₄ was taken from the laboratory stock, after vacuum distillation. Oxygen (99.99%, Linde) was used after drying by a molecular sieve.

An ArF excimer laser (193 nm) was used for the preparation of film substrates by a laser induced-CVD technique (TiCl₄ and oxygen as reactants, Cl₂ as product). The prepared films were annealed at 450°C for 2 h, in order to remove crystal defects. The thermal treatment was performed in a tube furnace 21100 (Thermolyne). The quartz tube with the deposit was evacuated by a turbopump (Pfeiffer Vacuum TCP 380); the temperature ramp was set at 10°C/min.

The sol-gel technique was used to prepare TiO₂ photocatalyst from titanium tetraisopropoxide, it has already been discussed in details elsewhere [8]. The prepared solids were placed on the glass substrate and annealed at 480°C for 2 h.

The thin films prepared were characterized by different techniques. Raman spectra were collected using a Nicolet Almega XR spectrometer (Thermo Electron) with 473 nm excitation. X-ray diffraction data were collected at ambient pressure

and temperature using a Philips X'Pert MPD system using the Co K_{α1} line ($\lambda = 0.17889$ nm, in the range $2\theta = 3^\circ - 85^\circ$).

The irradiation experiments were carried out in a 1,132 ml Pyrex cylindrical reactor with 55 mm diameter. It was equipped with two KRS-5 (thallium bromide-thallium iodide) windows, while a quartz window was used as an entrance for the UV irradiation. The glass substrates with thin TiO₂ film was placed at the bottom of the cylindrical reactor.

The light source was a 100 W middle-pressure mercury lamp emitting in the near-UV region (mainly around 365 nm). Using mirrors, the UV light was directed toward the reactor quartz window and to the surface of the photocatalyst. The irradiation time in all experiments was 3 h.

The progress of the photocatalytic oxidation was monitored by in situ infrared spectroscopic (Nicolet Impact 400) measurements in the region from 400 to 4,000 cm⁻¹; the decomposition was calculated using the absorption band of naphthalene at 781 cm⁻¹.

The reaction products were identified using FTIR and chromatography. The solid products of the reaction were washed with acetone and placed on a germanium window. After evaporation of the acetone, gas chromatography (GS, Shimadzu GC-14B with a flame ionization detector) and gas chromatography/mass spectrometry (GC/MS, Shimadzu GC-MS-QP5050) analyses of the gaseous mixtures were carried out after the irradiation. The GC/MS has a 50 m DB5 capillary column with He as a carrier gas.

Results and Discussions

In this work, three types of catalysts were used: photocatalytic system 1: anatase TiO₂ modified with SiO₂, prepared by CVD; photocatalytic system 2: anatase TiO₂ doped with Cr, prepared by CVD; and photocatalytic system 3: anatase TiO₂ prepared by the sol-gel technique.

In Fig. 52.1 Raman spectra of the final form (after annealing) of all photocatalytic systems investigated are presented. From the presence of Raman shifts centered at 634 cm⁻¹, 516 cm⁻¹, 392 cm⁻¹, and 142 cm⁻¹ it is obvious that the annealed materials possess the anatase TiO₂ crystal structure. Concerning the photocatalytic system 2 (line b), additional bands appear around 570 cm⁻¹ and from 700 to 810 cm⁻¹, proving the presence of Cr atoms in the system [8].

During UV irradiation of a naphthalene/gaseous oxygen mixture with photocatalysts, GC-MS analyses have shown the formation of water vapor, CO₂, ethanol, acetone, hexane, p-xylene, nonane, hexamethylcyclotrisiloxane, and decane. The presence of ethanol traces can be explained by residues of the cleaning of the photoreactor with ethanol prior to irradiation experiments. However, the occurrence of the other products reveals a partial mineralization of naphthalene.

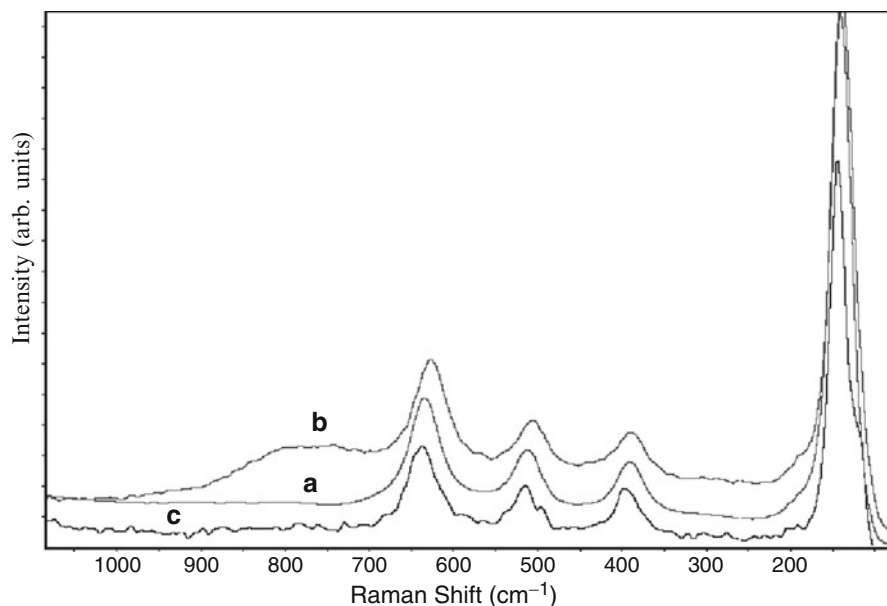


Fig. 52.1 Raman spectra of the annealed materials: (a) photocatalytic system 1; (b) photocatalytic system 2; (c) photocatalytic system 3

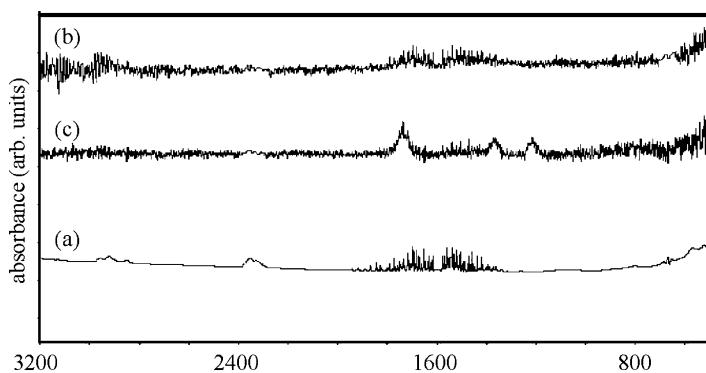


Fig. 52.2 FTIR spectra of solid product of naphthalene photocatalytic degradation in catalysts system1 (a), catalytic system 2 (b) and catalytic system 3 (c)

After finishing the photocatalytic experiments it was noticed that on the reactor walls there were some solid products. They were dissolved in acetone: after its evaporation they were analyzed by FTIR spectroscopy, as shown in Fig. 52.2a. The solid products have mainly vibrations in the C–H stretching region: $2,957\text{ cm}^{-1}$ (CH_3 stretching), $2,930\text{ cm}^{-1}$ and $2,920\text{ cm}^{-1}$ (asymmetrical CH_2 stretching) and $2,851\text{ cm}^{-1}$ (symmetrical CH_2 stretching). A very small

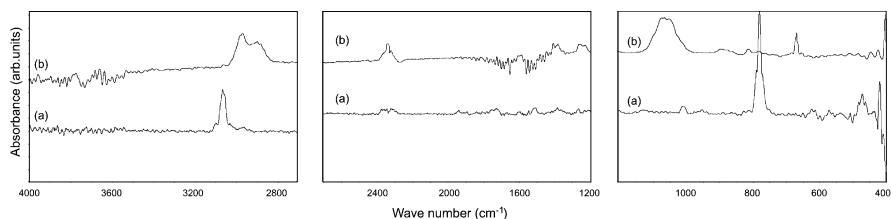


Fig. 52.3 FTIR spectra in characteristic vibrations regions of naphthalene before (a) and after (b) irradiation of 180 min in catalytic system 2

peak appeared at $1,260\text{ cm}^{-1}$, very probably from $\text{CH}_2\text{--CH}_2$ moieties. In the region from $1,140$ to $1,000\text{ cm}^{-1}$ a broad band with a maximum at $1,048\text{ cm}^{-1}$ has appeared, which was assigned to Si–O vibrations. Very probably, the deposition of C–H polymeric material was obtained with small amounts of Si–O moieties, coming from the catalyst or from impurities introduced from the reactor window.

After the irradiation of naphthalene in excess of oxygen with the catalytic system 2 (doped TiO₂ photocatalyst with chromium), GC-MS analysis detected that the main gaseous products after 180 min of irradiation were: CO₂ and water, although same traces of acetone and ethanol were also detected. Therefore, a complete degradation of naphthalene is achieved in this system.

In Fig. 52.3, the regions of characteristic FTIR peaks of the reaction mixture before and after the photocatalytic experiments are shown. It is clear that after 180 min of irradiation with the photocatalytic system 2, all characteristic vibration of naphthalene have completely vanished.

From the GC-MS analysis of the gaseous mixture after the photocatalytic experiments with system 3, the gaseous products of naphthalene degradation are mainly CO₂ and water, and traces of acetone, which is evidence for a total degradation of naphthalene in this system and for the effectiveness of the catalysts itself.

In Fig. 52.4, FTIR spectra of the reaction mixture before and after 180 min of photocatalytic reaction with system 3 are presented. The characteristic acetone vibration in the region from $1,110$ to $1,023\text{ cm}^{-1}$ are also present in Fig. 52.4, which is explained by introducing impurities during cleaning of the reactor.

Conclusions

It was shown that the way of preparation of TiO₂-based photocatalysts could highly influence the photocatalytic activity: the presence of different kind of supports or dopants. The photocatalytic activity of three different types of TiO₂-based photocatalysts was evaluated for naphthalene degradation in oxygen atmosphere.

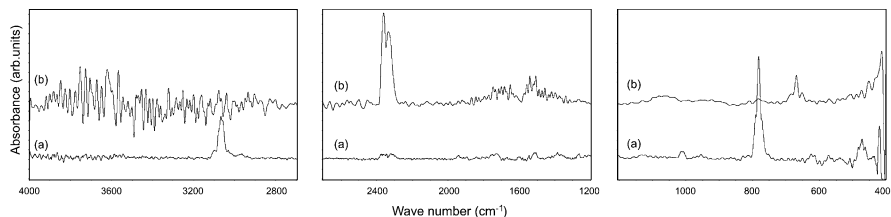


Fig. 52.4 FTIR spectra in characteristic vibrations regions of naphthalene before (a) and after (b) irradiation of 180 min in catalytic system 3

It was shown that two of the three used catalytic systems (system 2 (Cr doped TiO_2 prepared by laser induced CVD), and system 3 (TiO_2 prepared by the sol-gel-technique)) were very efficient and ensured a complete mineralization of naphthalene to CO_2 and H_2O . Even more with system 2 the reaction intermediates were also efficiently mineralized and no solid products were formed on the reactor walls.

Incomplete mineralization of naphthalene was obtained with catalytic system 1 (TiO_2 modified with SiO_2 , prepared by laser induced CVD), which was explained by a partial covering of TiO_2 particles surface with SiO_2 , which decreases the light absorptivity and surface area of the catalysts.

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Part V.4

Special Sensors

Chapter 53

Nanocomposite Sensors for Food Packaging

**Maurizio Avella, Maria Emanuela Errico, Gennaro Gentile,
and Maria Grazia Volpe**

Abstract Nowadays nanotechnologies applied to the food packaging sector find always more applications due to a wide range of benefits that they can offer, such as improved barrier properties, improved mechanical performance, antimicrobial properties and so on. Recently many researches are addressed to the set up of new food packaging materials, in which polymer nanocomposites incorporate nanosensors, developing the so-called “smart” packaging. Some examples of nanocomposite sensors specifically realised for the food packaging industry are reported. The second part of this work deals with the preparation and characterisation of two new polymer-based nanocomposite systems that can be used as food packaging materials. Particularly the results concerning the following systems are illustrated: isotactic polypropylene (iPP) filled with CaCO_3 nanoparticles and polycaprolactone (PCL) filled with SiO_2 nanoparticles.

Keywords Polymer nanocomposites · Food packaging

Introduction

Nowadays a wide range of polymer-based nanomaterials are used in applications which involve contact with food or beverages: particularly in foodstuff packaging applications, utensils, kitchenware and in processing equipment in food factories and other places where food is handled in large quantities [1].

The use of nanotechnology in food packaging is expected to grow rapidly in the next years, though its application in food packaging is at a developmental stage. Simple conventional packing is to be replaced by multi-functional intelligent

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packaging methods to improve the food quality thanks to the application of nanotechnology in this field. New packaging solutions will increasingly focus on food safety by controlling microbial growth, delaying oxidation, improving tamper visibility and convenience [2].

Generally nanotechnology offers three distinct advantages to food packaging:

- Barrier resistance and improvement of final properties;
- Incorporation of active components to provide functional performance;
- Sensing of relevant information about the food quality.

Applications in this area already support the development of improved taste, colour, flavour, texture and consistency of foodstuffs, increased absorption and bioavailability of nutrients and health supplements, new food packaging materials with improved mechanical, barrier and antimicrobial properties, and nanosensors for traceability and monitoring the condition of food during transport and storage. Particularly these latter are very interesting, since for example with embedded nanosensors in the packaging, consumers will be able to “read” the food inside. Moreover sensors can alarm us before the food goes rotten or can inform us the exact nutrition status contained in the contents.

Some examples of nanosensors applied to food packaging sector are reported as follows

Scientists at the University of Connecticut [3] are working on nanoparticle films and other packaging with embedded sensors that will detect food pathogens. Called “electronic tongue” technology, the sensors can detect substances in parts per trillion and would trigger a colour change in the packaging to alert the consumer if a food has become contaminated or if it has begun to spoil.

Researchers in the Netherlands [4] are going one step further to develop intelligent packaging that will release a preservative if the food within begins to spoil. This “release on command” preservative packaging is operated by means of a bioswitch developed through nanotechnology.

Developing small sensors to detect food-borne pathogens will not just extend the reach of industrial agriculture and large-scale food processing. In the view of the US military, it is a national security priority. With present technologies, testing for microbial food-contamination takes 2–7 days, and the sensors that have been developed to date are too big to be transported easily. Several groups of researchers in the US are developing biosensors that can detect pathogens quickly and easily, reasoning that “super-sensors” would play a crucial role in the event of a terrorist attack on the food supply. With USDA and National Science Foundation funding, researchers at the Purdue University [5] are working to produce a hand-held sensor capable of detecting specific bacteria instantaneously from any sample.

In the frame of nanostructured materials for food and beverage packaging applications, in this paper we report the results of our work concerning the preparation and characterisation of two new polymer-based nanocomposite systems that can be used as food packaging materials. Particularly the results concerning the following systems are illustrated: isotactic polypropylene (iPP) filled with CaCO_3 nanoparticles and polycaprolactone (PCL) filled with SiO_2 nanoparticles.

iPP/CaCO₃ Nanocomposites for Food Packaging

Isotactic polypropylene (iPP) is one of the most widely used plastic materials in the food packaging field [6]. Unfortunately, polypropylene shows a high gas permeability, which results in a poor protection of the packaged food thus limiting its usage [7]. One of the most used methods to improve these polypropylene drawbacks is to add a second component such as a polymer in blend or in a multilayer stack, micrometric fillers etc. [8]. Nowadays, nanocomposites based on a polypropylene matrix constitute a major challenge for industry since they represent the route to substantially improve the mechanical and physical properties of iPP [9–11]. The enhanced properties are presumably due to the synergistic effects of nanoscale structure and the interactions of fillers and polymers.

High performance iPP based nanocomposites filled with low-cost innovative calcium carbonate nanoparticles (CaCO₃) were prepared and the structure-properties relationships investigated and discussed in this paper. Peculiarities of the innovative tested nanoparticles are the very high specific surface area ($>200 \text{ m}^2/\text{g}$) and the elongated shape. This latter aims to merge the advantages of the well-assessed CaCO₃ know-how [12–15] with the properties enhancement attainable, for instance, by addition of clay platelets. In fact, in this way it should be possible to simulate the behavior of nanoclay, which reduces the gas permeability of polymers according to a tortuous path model, in which the platelets obstruct the route of gases and other permeants through the polymeric matrix. Moreover, in order to promote the polymer/nanofillers interfacial adhesion, CaCO₃ coated with a polypropylene-maleic anhydride graft copolymer (iPP-g-MA) or fatty acids (FA) as surface modifiers were tested. Structure-properties relationships were studied performing morphological and mechanical analysis and barrier tests.

Isotactic polypropylene (iPP) based nanocomposites were prepared by melt mixing. Elongated CaCO₃ nanoparticles coated with maleated polypropylene (iPP-g-MA) or fatty acids (FA) as surface modifier were tested as nanophase (coded as C-PPMA and C-FA, respectively). Particular interest was focused on the influence of the nature of the surface modifier on the polymer/nanoparticles interaction and consequently on the final material properties.

In order to evaluate the nanofiller dispersion into the polymeric matrix and the interfacial adhesion between the two components, morphological analysis was performed on fractured surfaces of the nanocomposites. As an example, SEM micrographs of nanocomposites containing 3 wt.% of C-FA and C-PPMA are shown in Fig. 53.1. As it is possible to observe, both C-FA and C-PPMA appear homogeneously dispersed into the iPP allowing to affirm that organic surface modifiers prevent nanoparticle agglomeration. Nevertheless, the strength of the polymer/nanoparticles interfacial adhesion depends upon the surface modifier nature. In fact, in the case of C-FA nanoparticles, the SEM micrograph reveals some areas in which debonding phenomena occurred after that a mechanical stress was applied (Fig. 53.1b). On the contrary, C-PPMA nanoparticles are completely

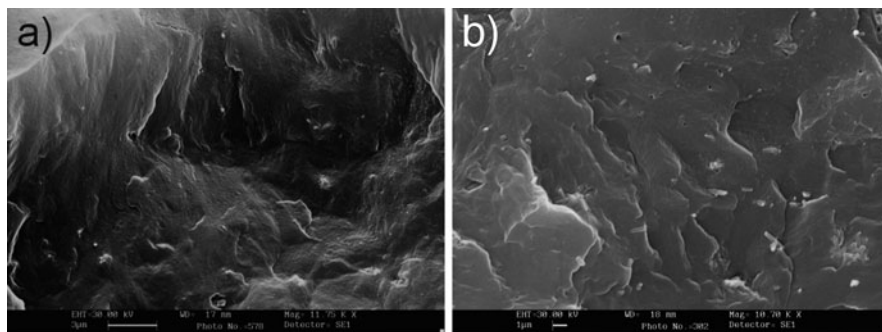


Fig. 53.1 SEM micrographs of cryogenically fractured surfaces of iPP-based nanocomposites containing 3 wt% of: (a) C-PPMA; (b) C-FA

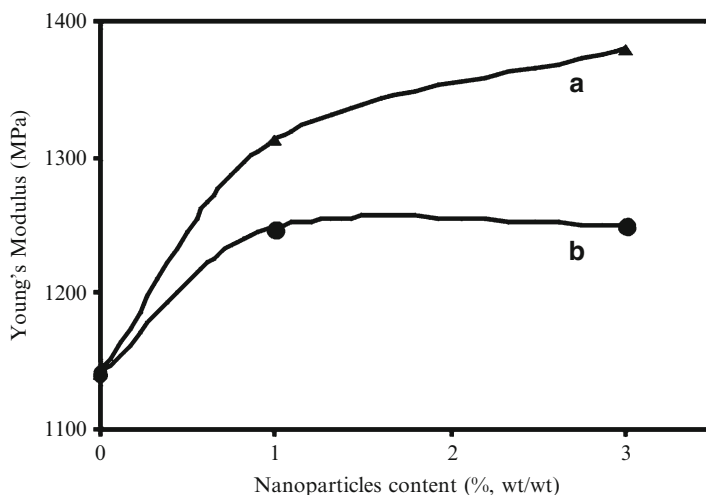


Fig. 53.2 Young's modulus of iPP-based nanocomposites containing: (a) C-PPMA; (b) C-FA

welded to the iPP phase. This result hints at a stronger adhesion between polymer and C-PPMA with respect to that obtained by using C-FA nanoparticles. It can be hypothesized that the presence of the iPP-g-MA modifier agent is responsible for strong physical interactions between the iPP-g-MA molecules and the polymeric matrix via entanglements. Interactions via entanglements can be only promoted if the molar mass of the surface modifier is quite high. It is known that the alkyl chains of fatty acids are too short to interact with matrix chains via the above described mechanism. Nevertheless, the presence of fatty acids reduces the polarity and the absorption surface energy of nanoparticles preventing their agglomeration.

The results of tensile tests performed with iPP-based nanocomposites are resumed in Fig. 53.2. As shown, the presence of nanoparticles increases the Young's modulus, while the extent of this improvement is strictly correlated to

the nature of the surface modifier. In fact, CaCO_3 coated with iPP-g-MA gave rise to a more pronounced modulus increase, up to 30% with respect to that of neat iPP and almost 20% higher than those obtained with nanoparticles coated with FA. Moreover, in the latter case the stiffness is slightly influenced by the filler content, reaching a maximum improvement by addition of only 1 wt% of C-FA nanoparticles, while in the case of C-PPMA a dependence of modulus value up on the filler content was observed.

These results allow assessing that there is a significant influence of the interaction nature between filler particles and polymeric matrix on the tensile properties of iPP-based nanocomposites. In fact, it is well known that in a multiphase system such as nanocomposites an external applied load can be transferred from the polymer to the reinforcement phase through the interphase region, obtaining mechanical improvements as a function of the polymer/nanoparticles adhesion level reached. As above described, C-PPMA nanoparticles permit to obtain a better interfacial adhesion between the components due to a strong surface modifier-polymer interaction, assuring, in this way, a larger increase of the Young's modulus.

In Figs. 53.3 and 53.4 the oxygen and carbon dioxide permeability coefficients are plotted versus the nanoparticles content. As reported, C-FA and C-PPMA nanoparticles are responsible for a decrease of the permeability of iPP either to oxygen or to carbon dioxide. Moreover, the surface modifier nature seems to play a key role in the extent of the iPP permeability improvement. In fact, while the C-FA nanoparticles lower the iPP permeability to oxygen up to 35% (Fig. 53.3b), in the case of C-PPMA nanofillers this decrease is around 50% (Fig. 53.3a). A similar trend was observed for the permeability to carbon dioxide as summarized in Fig. 53.4a–b. These results could be explained by considering that additional interactions generated between the surface modifier (PP-g-MA or FA) and either oxygen or carbon dioxide occur. Although the C-PPMA nanoparticles induce a

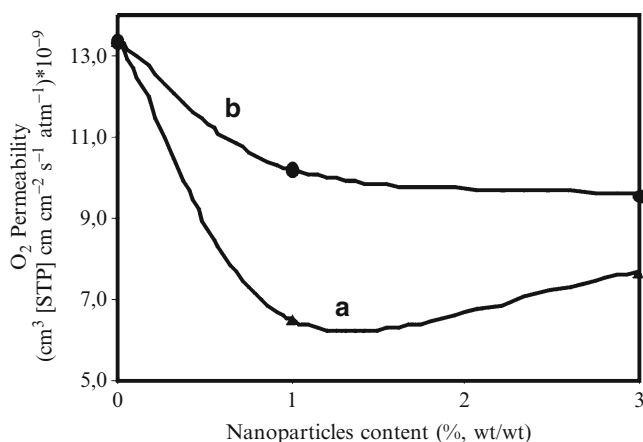


Fig. 53.3 Oxygen permeability of iPP-based nanocomposites containing: (a) C-PPMA; (b) C-FA

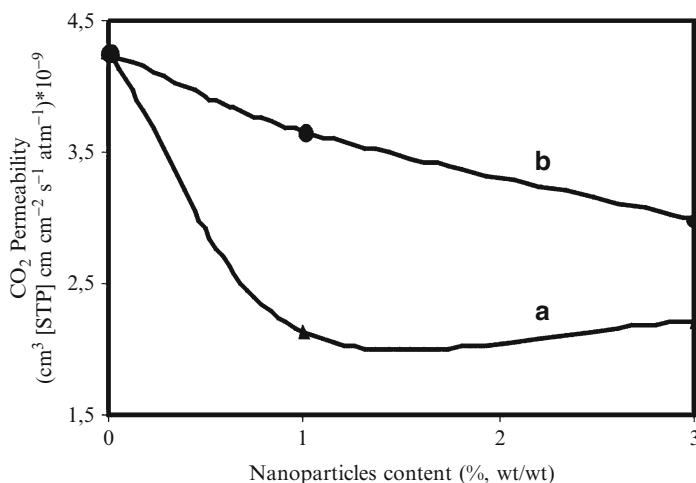


Fig. 53.4 Carbon dioxide permeability of iPP-based nanocomposites containing: (a) C-PPMA; (b) C-FA

stronger C-PPMA/iPP interfacial adhesion, the nature of the surface modifier is similar to that of the polymeric matrix regarding their permeability properties to oxygen and carbon dioxide. As a matter of fact, the barrier properties are influenced only by the tortuous path that diffusing molecules must bypass with a consequent improvement of polymer permeability.

Regarding C-FA nanoparticles, unsaturated fatty acids groups can be considered as potential sites of interactions with both oxygen and carbon dioxide molecules, thus an additional effect of hindering and slowing the diffusion of the gases through the nanocomposites.

In a previous work, it was demonstrated that spherical CaCO_3 nanoparticles also induce an improvement of iPP barrier properties, due to the high nanoparticles volume fraction occupied, the homogeneous CaCO_3 dispersion and the strong matrix-nanofiller interfacial adhesion reached [15]. However, the relevance of this phenomenon is less pronounced with respect to that discussed in this work. As a matter of fact, it can be assessed that elongated nanoparticles permit to magnify the well-known effect of CaCO_3 spherical nanoparticles on the permeability properties [16, 17].

PCL/ SiO_2 Nanocomposites for Food Packaging

Polycaprolactone (PCL) is a synthetic semicrystalline polymer which is characterized by a low glass transition temperature (T_g), low modulus and high elongation at break; moreover, it is biodegradable. The main disadvantages of PCL reside in its low melting temperature (around 60°C) and, mainly, in its low modulus and abrasion

resistance [18, 19]. The addition of silica nanoparticles should, in principle, be beneficial for all the above aspects, provided that no interfacial tensions are generated in the composite formation. A preliminary investigation on the chemistry of PCL grafting onto silica nanoparticles and on the influence of addition of modified nanoparticles into a high MW PCL matrix on the thermal, mechanical and morphological behaviour of nanocomposites is reported.

PCL-based nanocomposites filled with silica nanoparticles have been prepared by a reactive preparation methodology. Monodispersed silica particles have been prepared by the hydrolysis and polycondensation reaction of tetraethoxysilane (TEOS) [20].

The dried particles have been examined by transmission electron microscopy (TEM) and X-ray diffraction analysis. TEM analysis has revealed that the silica nanoparticles are nearly perfect with no agglomerated spheres and with an average diameter of 100–200 nm, while X-Ray analysis has shown that silica nanopowders are completely amorphous.

It is known that the presence of organic molecules on the nanoparticles surface improve the dispersion of the ultrafine particles in solvents and in polymer matrices. This is considered to be due to the fact that the grafted chains on the surface obstacle particles aggregation by increasing the affinity of particle surface towards organic solvents and/or polymeric matrices. In order to promote the polymer/inorganic nanofiller compatibility and to increase the interfacial adhesion between the two nanocomposite components, the silica nanoparticles surface has been functionalised by grafting a relatively low molecular weight PCL (~10,000 Da) onto it. A 10,000 Da PCL has been selected because higher values of the molecular weight would give some kinetic problems related to the efficiency of coupling reactions, while for lower values of molecular weight the compatibilization process to the polymeric matrix could be unfavourable due to thermodynamics problems; in fact, the homopolymer PCL used in the blend has a molecular weight of 60,000 Da.

PCL-based nanocomposites have been prepared by an extrusion process [21–24]. In particular materials containing 1.5 and 2.5 wt% of modified silica nanoparticles have been prepared. PCL filled with 2.5 wt% of non modified silica has been also prepared to evaluate the influence of the organic coating on the structure and properties of the nanocomposites.

To evaluate the state of dispersion of the silica nanoparticles within the polymeric matrix, the fractured surfaces of nanocomposites were observed by SEM analysis. The surfaces appear completely filled by the nanoparticles, and no pull-out phenomena are evidenced by the presence of voids. In the case of the nanocomposite containing modified silica, SEM micrographs show a fine and homogeneous dispersion of the nanoparticles in the polymeric matrix while as far as the nanocomposite containing unmodified silica, even though the nanofillers are embedded into the matrix many nanoparticles agglomerates are visible. The morphological analysis has thus revealed that the silica functionalization can provide a useful method of preparation of the nanocomposites with the achievement of a fine, good dispersion and strong adhesion levels. In Fig. 53.5 fractured surfaces of nanocomposites containing 2.5 wt% of neat and modified nanoparticles are shown.

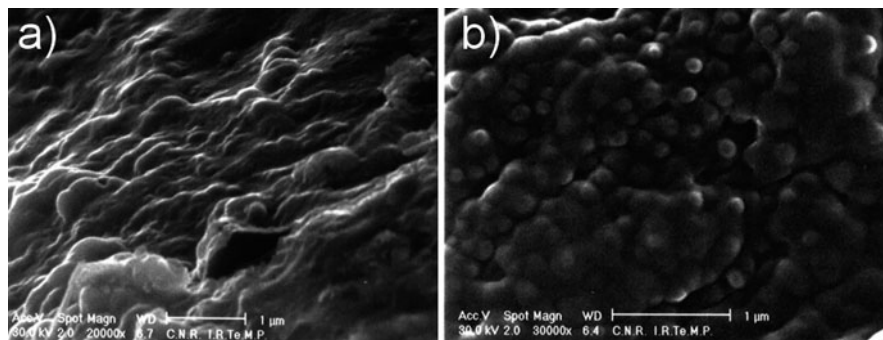


Fig. 53.5 SEM micrographs of cryogenically fractured surfaces of PCL filled with 2.5 wt% of: (a) unmodified silica; (b) modified silica nanoparticles

The thermal parameters were valuated by using the differential scanning calorimetry (DSC) analysis. It was seen that in the presence of 2.5 wt% of unmodified silica nanoparticles a slight decrease (about 5°C) in crystallization temperatures was recorded. The same effect was not observed for the compatibilized nanocomposites. Moreover, a slight decrease of the crystalline content was also seen for the samples containing neat nanoparticles. Finally, no influence on melting point with composition was observed.

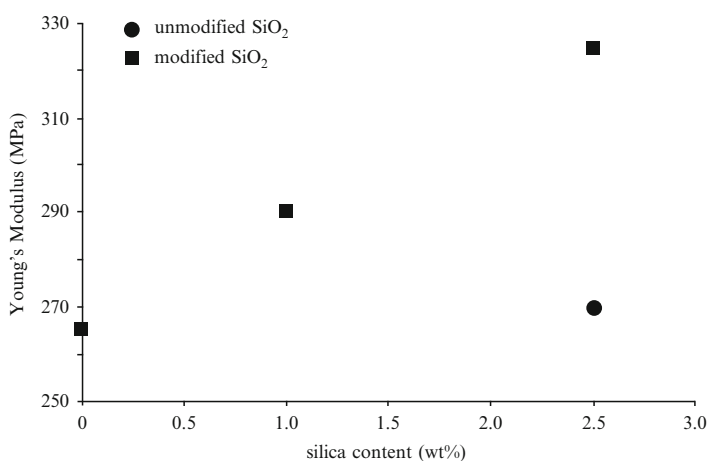
These results could be explained considering that in the compatibilized nanocomposites the dispersion of nanoparticles into the polymeric matrix appears fine and homogeneous while in the other case nanoparticles aggregation was evidenced. As a matter of fact, the dimensions of the individual nanoparticles are lower than the growth radius of the PCL spherulites. In the case no aggregation of nanoparticles occurs, the overall crystallization process of the polymeric matrix should not be disturbed by the presence of nanoparticles. When nanoparticles aggregates, as is the case of not functionalised nanosilica, the size of the cluster may be large enough to obstacle nucleation and growth of PCL spherulites, hence resulting in a lower crystallization temperature.

The thermal stability of the examined samples was investigated by using the technique of thermogravimetric analysis (TGA). In Table 53.1 the samples weight loss as function of the temperature is reported. As it is possible to observe, the presence of silica nanoparticles induces an increase of the starting temperature of the degradation process of the material. It can be outlined that only in the case of compatibilized nanocomposites this increase is a function of composition and it is kept during the entire degradation process. This improved thermal stability can be attributed to a restricted thermal motion of the PCL and to the hindered diffusion of volatile decomposition products within the nanocomposite due to homogeneous and fine dispersion of silica nanoparticles.

The mechanical performances of polymer composites are generally associated with the interfacial strength between the matrix and the reinforcing phase. If the interface between the two components is good, the external load will be transferred

Table 53.1 Results of thermogravimetric analysis of PCL based nanocomposites

Sample	Td (start)	Td (40 wt% loss)	Td (50 wt% loss)	Td (80 wt% loss)
PCL	343	410	414	428
PCL/2.5 wt% unmod SiO ₂	354	410	414	430
PCL/1.0 wt% mod SiO ₂	355	422	427	440
PCL/2.5 wt% mod SiO ₂	367	425	430	443

**Fig. 53.6** Young's modulus of PCL based nanocomposites containing unmodified and modified silica nanoparticles

from the polymer matrix to the reinforcement through the interface, and the mechanical performances of the composite increase. The same concept can be applied in the case of nanocomposites.

In our case (Fig. 53.6), PCL/modified SiO₂ nanocomposites have shown an increase of the Young's modulus of about 25% with respect to that found for the PCL homopolymer. On the contrary the Young's modulus measured for the PCL/unmodified SiO₂ sample is similar to that of neat PCL. These results can be easily attributed to the action of the compatibilizing agent that allows a better dispersion of nanoparticles and a good interfacial adhesion to the matrix, while in the case of unmodified nanocomposites these phenomena are limited.

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Chapter 54

Nanotechnologies and Nanosensors: Future Applications for the Conservation of Cultural Heritage

Maurizio Avella, Mariacristina Cocca, Maria Emanuela Errico,
and Gennaro Gentile

Abstract The most recent possibilities offered by nanotechnology for the conservation of historical and artistic objects and the control of the microclimate in which they are stored are summarized in this paper. Particular attention is paid to nanosensors, which are able to monitor relevant parameters for the durability of an artwork, such as temperature, relative humidity and pollutants. Furthermore, concerning the potential of nanostructured materials for stone conservation, a concise description of a new restoration treatment for silicate stones based on the application of perfluorinated nanodispersions, recently developed in our research group, is described in comparison with a TEOS treatment.

Keywords Conservation of cultural heritage · Stone conservation · Nanosensors · Nanostructured materials

Introduction

During time historical and artistic objects undergo an inevitable degradation due to physical, chemical, mechanical and biological deterioration of their constituent materials. The most important purpose of restorers and conservators is to set up efficient conservative interventions in order to slow down these degradation processes. In this respect, one of the most crucial decisions concerns whether and when a restoration intervention becomes necessary and how the treatment must be performed [1, 2].

In order to make the right choice, fundamental steps are represented by a periodic evaluation of the state of conservation of the mobile and immobile cultural heritage patrimony, and by the strict control of the microclimate in which these artefacts are or will be stored [3]. These actions help conservators to plan adequate treatments before further and severe degradation phenomena may occur.

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In the last decades the huge potential of nanotechnologies has been already exploited in several sectors of materials science [4–6]. Nowadays time seems ripe to apply the knowledge acquired on nanomaterials in the cultural heritage sector.

Concerning the need of keeping the degradation of historical and artistic artefacts under control, the availability of innovative sensors has created the possibility of significant improvements. In addition to periodic evaluations and microclimate surveys, a large number of parameters which can be related to the state of conservation of the objects (the presence of degradation products, the alteration of chemical or physical parameters) and to the microclimate in which they are stored (pollutants, relative humidity, temperature, irradiation) can be monitored continuously. In this framework, apart from traditional sensors, the set up of innovative and very effective nanosensors opens up new interesting applications for the conservation of cultural heritage.

Moreover, recent studies have been focused on the application of nanostructured materials for the conservation of wall paintings, stone and paper [7–9]. Due to their peculiar characteristics, in fact, nanomaterials seem to be very suitable for new conservation treatments.

In this paper, the most recent possibility offered by nanotechnology for continuous monitoring of the state of conservation of historical and artistic objects and the microclimate in which they are stored will be briefly described. Thereafter an innovative treatment for stone conservation based on the application of nanomaterials developed in our research group will be described.

Sensors and Nanosensors for Cultural Heritage

Degradation and conservation of cultural heritage is a widely debated subject involving many fields of research. First of all, it must be considered that the deterioration mechanisms strongly depend on the chemistry of the material constituting the object of historical/artistic interest. Therefore, factors affecting the degradation kinetics of an object will be different, as an example, for stone artefacts with respect to wall paintings, canvas, papers, textiles or metals. Nevertheless, it can be affirmed that there are a few main factors that can influence material degradation through similar mechanisms.

Relative humidity and temperature are amongst these factors. Water, in the liquid or the gaseous state, can induce dramatic dimensional changes in the structure of the material constituting an object; it can act as a solvent for soluble salts or for pollutants and can promote biological degradation.

Also temperature is a fundamental factor in conservation, because temperature variations can induce different thermal expansions in materials constituting works of art. In particular, temperature cycles induce a number of mechanical weathering mechanisms: the faster the temperature variations and the higher the temperature

gradients in an artwork, the faster is the ageing and the more dramatic the damage of the object. Furthermore, also temperature is able to promote biological degradation phenomena on several substrates.

Apart from relative humidity and temperature, a lot of several additional factors (e.g., radiation, pollutants) can influence and increase the degradation kinetics of objects of historical/artistic values. Therefore, keeping under strict control the microclimate in which the artworks are stored will allow conservators to carry out a precise diagnosis and to plan adequate treatments.

On the basis of these premises, the availability of innovative nanosensors, characterized by ultra-low dimensions, high sensitivity, low power dissipation and advanced non-contact or remote monitoring possibility offers possible significant advantages in this field [10].

Concerning the development of nanoscale thermal sensing devices, a remarkable review summarizes the most interesting results obtained in the last years [11]. Concerning nanoliterographic thermometry, for example, it has been reported that the characteristic response of a Pt/W nanoscale junction (with Ga impurities in both metals) yields a temperature coefficient of 5.4 mV/°C, which is 130-fold greater than conventional thermocouples.

Gao et al. [12] have reported a nanosized thermometer very similar in shape to that of a conventional Hg thermometer but a billion times smaller. It is composed of Ga-filled carbon/MnO nanotubes in which Ga serves as a temperature indicator by expanding and contracting inside the nanotube.

Kotov et al. [13] have developed a reversible nanothermometer comprised of a dynamic superstructure of two types of nanoparticles connected by polymeric spacers that act as a molecular spring in the aqueous state. The temperature data were determined from changes in the fluorescence intensity of the superstructure and showed reversible intensity dependence on temperature in an aqueous environment.

More recently, CN_x films and CoCl₂ nanocomposites have been prepared and used to realize prototype devices proposed for use in art conservation and museum applications. These nanosensors have been tested for temperature monitoring under controlled environmental conditions. In most cases, their performance are superior to solutions based on conventional sensor [14].

Concerning humidity sensors, the effect of pore size and uniformity on the response of nanoporous alumina, formed on aluminium thick films by an anodization process, has been reported by Dickey et al. [15]. A sensor with an average 13.6 nm pore size exhibited more than three orders of magnitude variation in the measured impedance over a relative humidity range from about 20% to 90%, with a response time of about 95s. More recently, a series of low cost prototype sensors based on nanoporous alumina and silica has also been proposed, with a reported response time of 4–8 min to changes of the relative humidity from 100% to 39% at room temperature [16].

Several nanosensors have been proposed in the last years for the monitoring of pollutants in the environment. A deep analysis of these systems is not within the

scope of this paper. For conductometric gas nanosensors there is a recent review reporting the last scientific and technological results in this field [17]. For gas monitoring, for example, a resistive device, realized by casting a dispersion of purified single wall carbon nanotubes (SWCNT) in dimethylformamide on a silicon substrate, is able to operate at room temperature and exhibits a very high sensitivity to nitrogen dioxide and nitrotoluene with detection limits of 44 and 262 ppb, respectively [18], thus once again demonstrating the extraordinary potential sensitivity of nanosensors with respect to traditional sensors.

Nanomaterials for Stone Conservation

For stone conservation one of the main prerequisites for a consolidating agent is the compatibility between the materials applied and the materials constituting the object. For silicate-based stone, for example, most of the treatments are based on the application of tetraethoxysilane (TEOS), which after hydrolysis and condensation leads to the formation of silica within the stone pores [19].

One of the most debated drawbacks of applications based on TEOS for this purpose is its lack of hydrophobicity, which means that the protective effect imparted to the treated stone is poor. Other solutions are based on the application of acrylate-based products [20, 21], but they show poor compatibility and durability and some difficulties related to the penetration depth of the materials into the stone [22, 23]. New techniques based on the application of monomers to solve the penetration problem, mainly centred on in situ polymerization techniques [24–27], are still under investigations.

Recently, in our research group, poly(tetrafluoroethylene) (PTFE) nanoparticles have been applied onto a silica stone as a pre-treatment followed by consolidation with TEOS with the aim of imparting a protective effect and improving the abrasion resistance of the treated substrates. For comparison, also samples treated only with TEOS have been tested.

Details on the experimental have been reported elsewhere [7].

Colorimetric analysis of untreated and treated tuff samples have shown very small differences. In particular, colour differences in the CIEL*a*b* space (ΔE_{ab}^* , CIE76) are in all cases lower than 4, thus indicating a negligible effect of the treatments on the chromatic parameters of the samples.

In Fig. 54.1 SEM micrographs of sections of tuff samples pre-treated with nano-PTFE dispersion and consolidated with TEOS are presented. The presence of spherical particles of nanometric size, attributable to nano-PTFE, is evident and demonstrates the ability of nanoparticles to penetrate well into the stone pores.

The water capillary absorption test is a very useful method in order to evaluate the protective effect of a treatment carried out for stone conservation: the larger the reduction of water capillary absorption, the higher is the protective effect of the treatment. As concerning untreated tuff, the water absorption tendency is very

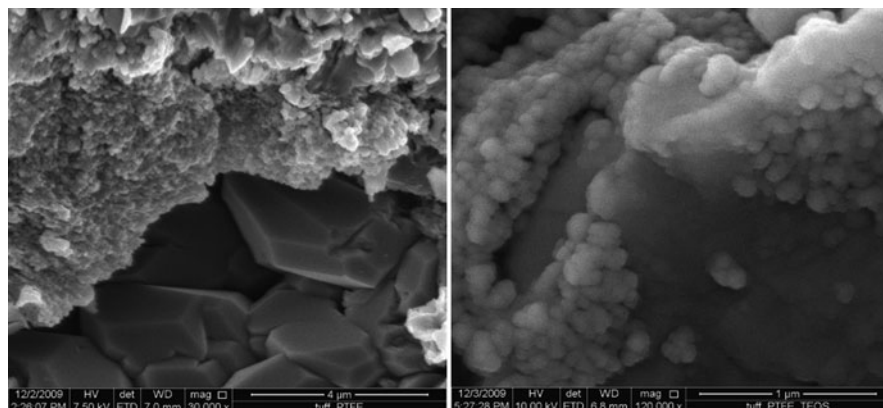


Fig. 54.1 SEM micrographs of tuff samples pre-treated with a PTFE nanodispersion and consolidated with TEOS

high and the maximum value of absorption is already reached during the first 10–15 min of the test; this is due to the extremely high porosity of tuff. Also tuff samples treated with TEOS shows high water capillary absorption rates, although a slight protective effect has been observed. On the contrary, the application of nano-PTFE + TEOS induced a dramatic reduction of the water capillary absorption rate. The water capillary absorption coefficient has been reduced from about $76 \text{ mg cm}^{-2} \text{ s}^{-1/2}$ (neat tuff) and $68 \text{ mg cm}^{-2} \text{ s}^{-1/2}$ (tuff treated with TEOS) to about $1 \text{ mg cm}^{-2} \text{ s}^{-1/2}$ for tuff treated with nano-PTFE + TEOS. This result indicates that this application can be considered as a potentially very effective method for stone protection.

Moreover, as it can be observed in Fig. 54.2, also contact angle evaluations have shown extraordinary results for the treatment based on PTFE nanoparticles.

Concerning the possible drawbacks of the proposed material, it is widely accepted that the basic requisite of a conservation treatment is that it must not induce a strong reduction of the water vapour permeability of the treated substrate, in order to prevent its insulation from the environment. Following the Italian Standard Norm 21/85, the water vapour permeability of untreated and treated tuff has been evaluated; it has been found that only a slight decrease of the water vapour permeability with respect to the untreated sample was observed for tuff samples treated with nano-PTFE + TEOS. This finding ensures that the PTFE-based treatment still allows the stone to “breathe”.

Finally, results of abrasion resistance tests are summarized in Table 54.1. As it can be observed, the nano-PTFE based treatment is able to significantly improve the abrasion resistance of the stone. This result can be easily explained by considering that PTFE is a very effective lubricant agent, able to significantly reduce the effects of the abrasion.

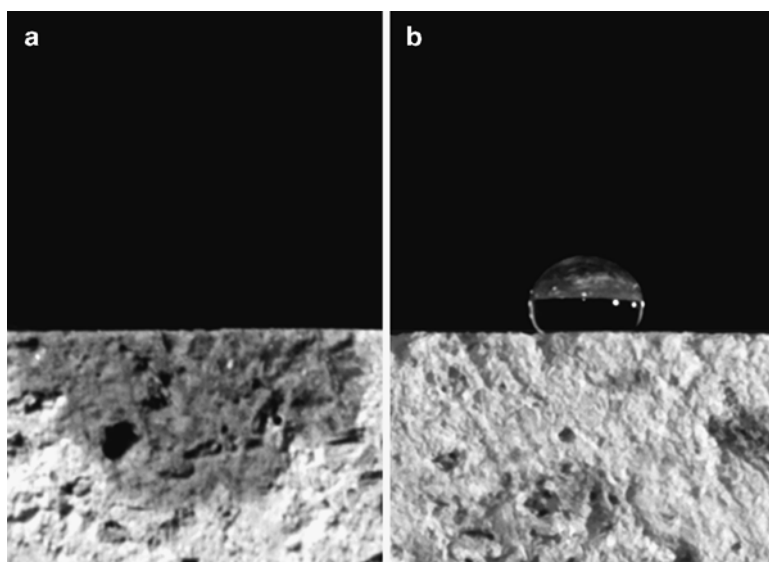


Fig. 54.2 Image of a water droplets on tuff samples after 10 s from its application: **(a)** sample treated with TEOS and **(b)** sample treated with nano-PTFE + TEOS

Table 54.1 Results of abrasion resistance tests on untreated and treated tuff samples

Sample	Weight loss (g/50 cycles)
Untreated tuff	1.62 ± 0.11
TEOS	1.20 ± 0.13
Nano-PTFE + TEOS	0.52 ± 0.05

Conclusions

The most recent possibilities offered by nanotechnology for the conservation of historical and artistic objects and the control of the microclimate in which they are stored have been summarized in this paper. Particular attention has been paid to nanosensors, able to monitor parameters relevant for the durability of an artwork, such as temperature and relative humidity.

Furthermore, as concerning the potential of nanotechnology for stone conservation, the first application of PTFE nanoparticles on stone substrats has been described. It has been observed that the pre-treatment with a PTFE nanodispersion do not induce alterations of the chromatic parameters of the stone. On the basis of water capillary absorption tests and contact angle evaluations, a high protective effect has been evidenced by stone samples pre-treated with nano-PTFE and

consolidated with TEOS. The water vapour permeability of the stone has not been significantly reduced. Finally, tuff samples pre-treated with PTFE nanoparticles have shown a pronounced increase of the abrasion resistance. In conclusion, the proposed treatment can be considered a very promising method for stone protection and consolidation.

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Chapter 55

Towards *In Situ*-Process Control in Tribological or Tool Applications: A Material Concept for the Design of Smart Thin Film Wear Sensors

Sven Ulrich, C. Klever, H. Leiste, K. Seemann, and M. Stüber

Abstract The optimization of processes for tribological or machining applications requires the development of (i) high performance substrate materials, especially ultra fine grain cemented carbides for cutting tools, (ii) complex tool geometries and (iii) innovative, nano-scaled hard and tough multi-functional protective coatings. Very important is also the in-situ process control which can be realized with (i) sensors which are embedded in the protective coating using microsystem technology or (ii) if possible, by using tailored coating designs which show itself both protective and sensor functionality.

Keywords Cemented carbides · Tool systems · Protective coatings · Wear sensors

Introduction

Modern high performance tool systems for turning, drilling, milling, threading and reaming in application fields like automotive, aircraft, mould and die, energy and general mechanical engineering essentially consist of four components: powerful structural materials for optimized insert shapes, multi-functional protective coatings, a system for effective status control of the cutting tool during operation as well as the tool clamping system. After an introductory description of a typical cutting process, an overview of different cemented carbides (WC, TiC, TaC, TiN, NbC, Co, Ni, Fe, Mo, ...) and cermets (Al_2O_3 , Si_3N_4 , ZrO_2 , TiC, WC, TiN, ...) as structural materials is given. Their constitution, microstructure, properties and behavior in cutting applications are discussed, particularly the role of nano- and microvoids and an ultra fine grain size. Thereafter, a detailed representation of the different

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industrially established protective coatings like nanocrystalline TiN, TiC, CrN, TiAlN, CrAlN, and amorphous carbon networks is given, and their modifications and combinations in specific coating concepts as well as new trends in coating developments are discussed. The in-situ control of the cutting process can be realized by optical methods, integration of sensors within the coating and protective nanocomposite coatings containing a ferromagnetic phase which allows contactless remote monitoring of a magnetic high frequency signal.

Cemented Carbides

Materials possessing high toughness in combination with high hardness are of great technological significance for manufacturing of highly exposed tools. A notably high toughness is usually found for pure metals as well as for metallic alloys (aluminum alloy (7075): $24 \text{ MN/m}^{3/2}$, steel alloy (4340): $50 \text{ MN/m}^{3/2}$, titanium alloy: $44\text{--}66 \text{ MN/m}^{3/2}$, 13Cr steel: $60 \text{ MN/m}^{3/2}$, Ti-6Al-1 V: $60 \text{ MN/m}^{3/2}$, 18Cr-8Ni: $200 \text{ MN/m}^{3/2}$, Cu-30Zn: $200 \text{ MN/m}^{3/2}$). On the other hand, hard materials show a high hardness and exist in quite different categories that can be classified according to their dominant chemical bonding into metallic, covalent, and hetero-polar hard materials. Cemented carbides are predominantly composed of metallic hard materials (WC, TiC, TaC, etc.), together with a metallic binder (Co, Fe, Ni, etc.) having a low solubility with the hard material basis. These cemented carbides combine high hardness of the most microcrystalline hard materials with the favorable toughness of the metallic binder. For example, the Vickers hardness of the metallic hard material WC amounts to 2,300 HV0.05 while the fracture toughness is $7.5 \text{ MN/m}^{3/2}$. As a metallic binder Co possesses a Vickers hardness of 104 HV0.05, but a fracture toughness of $37 \text{ MN/m}^{3/2}$. A typical cemented carbide consisting of 80 vol% WC and 20 vol% Co shows a low hardness of 1,000 HV0.05, its fracture toughness ($16.8 \text{ MN/m}^{3/2}$) is, however, more than twice as large as that of WC. For WC-, TiC-, TaC-, and Co-based cemented carbides, the content of Co is between 3 vol% and 25 vol%, and the defined ratio of the metallic hard phases $R_{\text{HM}} = ([\text{TiC}] + [\text{TaC}])/([\text{WC}] + [\text{TiC}] + [\text{TaC}])$ is between 0 vol% and 70 vol%. By appropriated tailoring of the Co content and R_{HM} the carbides are optimized for different types of cutting applications and classified into three groups (P, M, and K). The almost TiC- and TaC-free cemented carbides belonging to the K-series are preferably used for machining short-chipping materials like cast iron, non-ferrous metals, hardened steel, wood and plastic. The M-series is a crossover between P- and K-series type cemented carbides, often regarded as a multipurpose series being adequate for the machining of steel, austenitic steel, free-cutting steel, or austenitic manganese steel. The P-series type cemented carbides possess a relatively high volume fraction of TiC and TaC and are, as a consequence, suitable for long-chipping materials such as steel, cast steel, and long-chipping malleable iron. An index number specifying the materials' wear and toughness follows the series designation of K, M, or P. The smaller the number, the better the wear

resistance and the lower the toughness as well as the Co content (e.g. P01, M30, K05). The suffixes, F and UF, mean fine and ultrafine, respectively (e.g. K40UF).

Recent nanotechnology brings new chances for further enhancement of the performance of cemented carbides. At given elemental and phase compositions as well as identical microstructures of the individual phases, the Vickers hardness of all cemented carbides is known to increase with decreasing crystallite size. The typical crystallite sizes are between 1 and 7 μm for standard cemented carbides and in the sub- μm range for the so-called “fine-grained cemented carbides”. With nanotechnology, cemented carbides with crystallite sizes well below 100 nm can be realized through nanopowder development, as well as by novel synthesis routes and methods. On the other hand, the service life of cemented carbide tools depends drastically on the residual porosity of the hard-metal materials (with the same constitution, microstructure and distribution of crystallite sizes). This porosity lies between 0.001% and 1% for very high-quality cemented carbides. A reduction of the residual porosity by a factor of 10 typically results in a service-life increase by a factor of about 100. In this regard, advances in materials development of cemented carbides closely rely on an understanding, again through the nanotechnology, relating to the wetting behavior among the individual phases and interface reactions on the nanometer scale [1].

Cemented Carbide Based Tool Systems

The choice of materials for tools has evolved from tool-steels to high-speed steels and hard alloys, and then to cemented carbides due to an increasing demand in metal-cutting shape forming. An adapted surface coating can additionally improve the tool performance. A significant increase of tool costs is avoided either by soldering a cemented-carbide bit as a blade on a metallic body, or by upgrading to professional turning, milling and drilling modular tool systems consisting of exchangeable, coated cemented carbide inserts and metallic tool holders.

In the following, wear phenomena of cemented carbide inserts during steel machining as well as the reasons of wear are briefly discussed. The flank wear is typically abrasive in nature. Extremely fast processes including diffusion, welding, sticking, and flaking between the steel chip and cemented carbide insert are the reasons for the chemo-mechanical crater wear. The wear of cutting inserts will be influenced by the parameters of cutting processes (cutting speed, feed, and ambient medium), the selection of cemented carbide (K-, M-, and P-series), the geometry of cutting inserts (positive or negative cutting angle, with or without chip groove, nose angle, nose radius, etc.), fixing mode (negative and positive basic shape of holder, clearance angle, setting angle, edge fillet, chamfer, plain chamfer, etc.), the surface coating (materials, thickness, surface quality, coating concept, microstructure, coating properties), the cutting force, the chip formation, and the surface quality of working pieces. These seven main criterions (with numerous sub-criterions) are, however, interlinked in a complicated way.

Protective Coatings for Cemented Carbide Inserts

The service lifetime of cemented carbide tools can be considerably increased by applying appropriate protective coatings. This lifetime prolongation can be as high as up to 100 times the lifetime of the uncoated counterpart.

More than 80% of industrial protective coatings such as TiN, TiC, Ti(C,N), (Ti, Al)N, CrN, Cr₃C₂, Cr(C,N), (Cr,Al)N, (Ti,Cr)N, (Ti,Al,Cr)N, a-C:H, DLC, and diamond, are composed of the elements Ti, Cr, Al, C, and N. The range of elements is extended in the remaining 20% of coatings primarily to W, Mo, S, Si, and O, e.g. (Ti,Al,Si)N, a-C:H:metal, Al₂O₃ and MoS₂:metal. Different coating schemes including mono-, gradient-, and multi-layers are applied in practical applications, occasionally with an additional bonding layer if necessary. The predominant coating microstructures are nanocrystalline and amorphous, respectively. Because of a very high fraction of interfaces mostly appearing in nano-scaled coating structures, nanotechnology provides the key to the development of novel thin film materials [2–4].

Tools with Integrated Sensors Based on Micro System Technology

Recent advances in materials have led to a significant increase in the productivity of tools. Those tools could, however, become even more powerful when functioning jointly with integrated sensors. The surface sensors can be assembled onto the tools by means of microsystem technology, enabling real-time measurements of many process parameters, such as cutting force, torque, position, tool wear, temperature, etc. This does not only allow for real-time monitoring and recording of the machine state but an effective control of the tools to optimize their conditions during processing. Such smart tools result thus in improved processing quality and, furthermore, full exploitation of their potential.

The Fraunhofer Institute IST in Braunschweig, Germany, for example, has developed turning tools with disposable insert thin-film sensors for measuring temperatures, force, and wear [5].

Tough Protective Coatings with Intrinsic Remote Requested Sensor Functionality

In this section, the development of a tough, hard coating system with remote-sensing functionality will be illustrated. The goal was achieved through specific materials selection in combination with innovative coating design.

Specific Material Selection and Innovative Coating Design

Titanium nitride is a well-established metallic hard material. It has found numerous applications and, in particular, has been successfully deployed as a material for wear protective coatings in the tool industry. The coatings show high hardness, usually between 17 and 27 GPa, depending on their residual stress state and crystallite size, together with a sufficient toughness and excellent adhesion on metallic substrates.

Further improvement of the toughness of metallic hard materials can be realized, usually at the expense of their hardness, through a reasonable combination with an additional metallic materials. The metallic materials chosen should have a low solubility in the hard material. This represents the basis for the development of hard materials combining metallic Fe, Co, and Ni with WC, TiC, TaC, and TiN. Such combination may, however, bring about additional material innovation. For example, insertion of alloys from the Fe-Co system allows for the development of materials exhibiting excellent high-frequency magnetic characteristics. Therefore, tough protective coatings with intrinsic remote-sensing functionalities become possible when TiN- and FeCo-layers are combined in a multilayered coating system.

Experimental Details

Alternating TiN/FeCo multilayers were produced onto oxidized silicon substrates by magnetron sputtering using a lab coating device Leybold Z550, equipped with a rotatable substrate table. A TiN- and a FeCo-target, both with a diameter of 150 mm, were used as the sputter sources. The 6 mm thick TiN ([Ti] : [N] = 50 at.% : 50 at.%) target was operated by DC power at 700 W. The FeCo target ([Fe] : [Co] = 50 at.% : 50 at.%) powered by RF at 250 W was much thinner (1 mm thick) due to strong magnetic-shielding effect of the material. With the substrates being located 5 cm below the corresponding target, sputtering was conducted in non-reactive mode with Ar as the working gas at 0.2 Pa pressure. Neither substrate bias nor external heating was applied during deposition. In the present study, the resulting multilayers have a bilayer period of down to 2.6 nm. The growth times were the same for all individual layers using either the TiN- or the FeCo-target. Since the growth rates for the TiN- and FeCo-targets were 0.93 and 0.33 nm/s, respectively, the thickness ratio of the individual TiN- and FeCo-layers can be estimated to be approximately 3:1. After the deposition process, an uniaxial magnetic anisotropy was induced within the coatings by means of a 1 h heat treatment in vacuum at 600°C in a magnetic-field oven. The coatings were analyzed concerning their elemental composition by electron microprobe (type Cameca Camebox Microbeam) and Auger electron spectroscopy (AES, Physical Electronics, type PHI 680 Scanning Auger Nanoprobe). The crystalline structure was identified by X-ray diffraction (XRD, Seifert PAD II) and transmission electron microscopy

(TEM, Philips CM30). High resolution TEM (HRTEM, Philips CM30) as well as small-angle XRD (Seifert XRD 3003 HR) were used to evaluate the superlattice period, i.e. the bilayer period. The hardness and reduced Young's modulus were measured by nano-indentation using a UMIS-2000 device. The residual stress was determined from the bending of rectangular Si substrates measured by surface profilometry (type TENCOR P-10) before and after deposition. In addition, the frequency-dependent permeability was investigated.

Constitution

Two monolayer coatings (3 μm thick TiN and 2 μm thick FeCo, respectively) were grown onto oxidized Si substrates beneath the TiN- and FeCo-target with the deposition conditions identical to their counterpart in the TiN/FeCo-multilayer system. As indicated by microprobe analyses, the resulting TiN-monolayer film is nitrogen deficient, with $[\text{Ti}] = 54.77 \text{ at.}\%$ and $[\text{N}] = 45.04 \text{ at.}\%$. Traces of other elements originating from the FeCo-target, substrate, residual gases in the vacuum, as well as working gas (Ar) were also detected and can be considered as marginal ($[\text{Fe}] = 0.06 \text{ at.}\%$, $[\text{Co}] = 0.03 \text{ at.}\%$, $[\text{Si}] = 0.02 \text{ at.}\%$, $[\text{O}] = 0.04 \text{ at.}\%$, and $[\text{Ar}] = 0.02 \text{ at.}\%$). On the other hand, the FeCo monolayer film turns out to be almost stoichiometric: $[\text{Fe}] = 48.38 \text{ at.}\%$ and $[\text{Co}] = 51.55 \text{ at.}\%$. Nitrogen, oxygen, and silicon were not detectable; only very low concentrations of Ti (0.04 at.%), C (0.02 at.%), and Ar (0.01 at.%) are existent.

X-ray diffraction revealed the NaCl-type crystal structure of TiN (as evidenced by the (111) and (200) reflection signals) as well as the CsCl-type crystal structure of FeCo (by the (110) signal) to be present. Figure 55.1 illustrates two low angle X-ray diffraction (LA XRD) curves of a TiN/FeCo multilayer film consisting of 390 bilayers: one for the as-deposited, the other for a thermally annealed film (600°C, 1 h). Both curves exhibit two diffraction peaks at about 3.44 and 6.8 (2 theta)

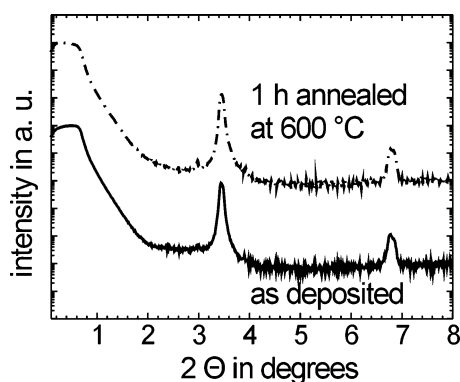


Fig. 55.1 Low angle XRD spectra of a TiN/FeCo multilayer film as deposited and after annealing for 1 h at 600°C in a magnetic field

indicating a bilayer period of 2.6 nm. This was additionally confirmed by HRTEM studies. Furthermore, the preservation of the multilayering was demonstrated by AES depth profiles [6].

Mechanical Properties

The hardness of the thermally annealed TiN/FeCo-multilayers with 2.6 nm bilayer period is $25.2 \text{ GPa} \pm 4.4 \text{ GPa}$, being larger than that of the TiN-monolayer (21.2 GPa) and the FeCo-monolayer films (8.5 GPa), respectively. Similarly, the annealed TiN/FeCo multilayer films show a larger reduced Young's modulus (267 GPa) than the TiN- (217 GPa) and the FeCo-monolayer films (170 GPa). This is attributed to an increased compressive stress of the TiN/FeCo-multilayers, possibly owing to diffusion processes between the individual layers: -4.4 GPa (TiN/FeCo multilayer films) in contrast to -1 GPa for TiN monolayer films and virtually stress-free FeCo monolayer films.

The mechanical properties are shown in Fig. 55.2 (hardness), Fig. 55.3 (reduced elastic modulus), and Fig. 55.4 (residual stress), respectively, for TiN and FeCo monolayer films, and $1 \text{ }\mu\text{m}$ thick TiN/FeCo multilayer films in dependence on the bilayer period (both as deposited and thermally annealed).

Fig. 55.2 Hardness of about $1 \text{ }\mu\text{m}$ thick TiN/FeCo multilayer films as-deposited (*squares*) and after annealing (*circles*) for 1 h at 600°C in a magnetic field in dependence on the bilayer period. The dotted horizontal lines represent the hardness of the TiN- and FeCo-monolayer films

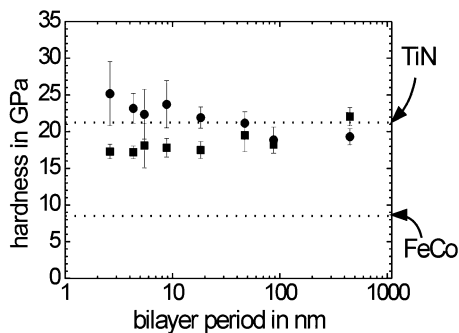


Fig. 55.3 Reduced Young's modulus of about $1 \text{ }\mu\text{m}$ thick TiN/FeCo multilayer films as deposited (*squares*) and after annealing (*circles*) for 1 h at 600°C in a magnetic field in dependence of the bilayer period. The dotted horizontal lines represent the reduced Young's modulus of the TiN- and FeCo-monolayer films

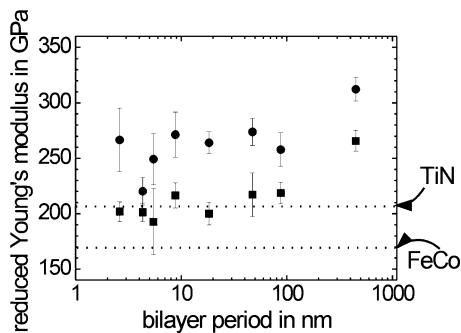


Fig. 55.4 Stress of about 1 μm thick TiN/FeCo multilayer films as deposited (*squares*) and after annealing (*circles*) for 1 h at 600°C in a magnetic field in dependence on the bilayer period. The *dotted horizontal lines* represent the stress of the TiN- and FeCo-single layers

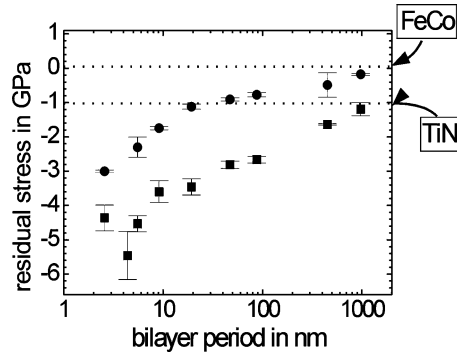
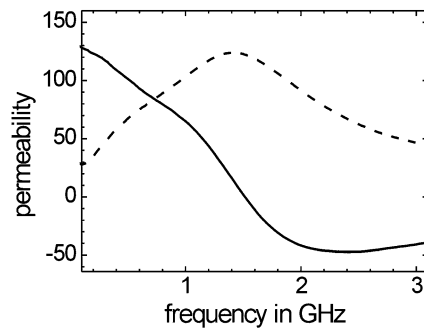


Fig. 55.5 Real part (*straight line*) and imaginary part (*dotted line*) of the complex permeability of a TiN/FeCo multilayer film with a bilayer period of 2.6 nm after annealing for 1 h at 600°C in a magnetic field



Magnetic Properties

The TiN/FeCo multilayer films show an in-plane uniaxial magnetic anisotropy field. The coercive field amounts to 0.30 mT, and the effective saturation polarization to 0.4 T. In Fig. 55.5 the complex permeability $\mu = \mu' + i\mu''$ in dependence on the frequency is displayed. The initial permeability (at 0.1 GHz) can be derived to amount to about 128. The real part of the complex permeability becomes zero at 1.51 GHz, whereas the imaginary part reaches its maximum at 1.42 GHz. This clearly proves that the permeability of the coatings can be remote-requested up to high frequencies in the 1 GHz regime.

Summary

Nano- and microsystem-technologies are doubtlessly the key technologies for future developments of cemented carbides (nanopowder technology), wear-resistant coatings and multifunctional coatings (nanoscale coating design, nanoscale structure, nanoscale interface engineering). An example has been illustrated

concerning the design and fabrication of wear-resistant coatings with integrated high-frequency magnetic characteristics. The magnetron sputtered, 1 μm thick TiN/FeCo-multilayer films with a 2.6 nm bilayer period and a volumetric ratio of 3:1 (TiN:FeCo) are harder than TiN-monolayer films and show a frequency-dependent permeability (about 100) up to 1 GHz. Moreover, enhancement of the coating toughness is reasonably anticipated on account of the high FeCo-content (about 25 vol%), the high interface portion in the 390-layer coatings favoring crack deflection and crack-energy dissipation, and the compressive stress for hindering crack propagation.

Outlook

Following the confirmed multilayer coating-concept, further optimization and development are still much promising relating, in particular, to the choice and processing of constituent layer materials. The hard TiN layer could be replaced, for example, by nanocrystalline, metastable fcc-like (Ti,Al)N or by low-friction carbon-based nanocomposites such as TiC/C, (Ti,Al)(C,N)/C, (V,Al)(C,N)/C. On the other hand, the issue of temperature stability (for FeCo: above 600°C) could be improved by synthesizes of magnetic-nanocomposites like FeCo-nanocrystals with TiN-, TaN- or HfN-grain boundary phases [7]. Hard, high-melting-point material phases enveloping the FeCo-nanocrystals are likely to reduce the grain growth of FeCo to lower the loss of high-frequency characteristics which results from the dominant anisotropy of large grains.

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Part V.5

Actuators

Chapter 56

Recent Developments and Challenges in Shape Memory Technology

Matthias Frotscher and G. Eggeler

Abstract Nickel-Titanium-based alloys (NiTi) represent structural materials with actuator and sensor functions due to their shape memory properties. This is especially useful for actuator applications, e.g. in valves or switches. A temperature sensor is no longer needed because the material can be set to exhibit the shape memory effect at a given temperature in a certain temperature range. High actuator forces and strains can be generated in a small material volume, which is ideal for the miniaturization of technical devices. Recent developments and technological challenges in shape memory technology with a focus on the research of the interdisciplinary Center for Shape Memory Technology (SFB 459 - Formgedächtnistechnik) at the Ruhr-University Bochum are discussed.

Keywords NiTi shape memory alloys · Actuator applications · Medical devices

Introduction

Shape memory effects are known to exist for a number of alloyed systems, including AuCd, FePt, NiAl, and CuZn [1,2]. However, the technologically most relevant shape memory material today is based on nickel (Ni) [3,4]. The main reasons for the success of NiTi are commercial availability and good mechanical properties. NiTi shape memory alloys (SMAs) feature interesting properties such as high reversible strains up to 8%, good corrosion properties, biocompatibility and the highest energy density (largest strains and forces in the smallest possible volume) of any actuator material used today [5,6]. A NiTi wire with a diameter

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of 0.2 mm can e.g. exert a force of 56 N or a reversible strain of 30 mm. Depending on the Ni-content of the alloy, three different shape memory effects can occur:

- Pseudoelasticity, where the material is initially in the austenitic phase and transforms into martensite due to an external mechanical load, allowing for high reversible strains;
- The One-way Effect, where initially martensitic material can be deformed at room temperature into a different shape and which transforms back to its original shape upon heating;
- The Two-way Effect, where initially martensitic material can switch between two shapes just by changing the temperature without applying an external load.

Medical Applications

Nowadays, one of the most important applications for NiTi SMAs is still medical technology. Prominent examples are stents, dental implants and files, arch- and guide wires, vena-cava filters or components used for artificial heart valves. An example of a new surgical instrument developed within SFB 459 applies a flexible shaft made of a NiTi wire. A bending radius of 60 mm is realized, making use of the pseudoelastic shape memory effect, which would not have been possible with a conventional metal. In this case, the SMA is used as a structural material, allowing for a significant miniaturization of the device without the need for transmission gears. The instrument can be used in oral- and maxillofacial surgery for cutting jaw bones under an angle of nearly 180° in the confined space of the mouth (Fig. 56.1) [7].

For the construction of the prototype, binary NiTi wires and ternary NiTiCr wires were examined for suitability. The microstructure of the wires was characterized in the as-received condition and after different heat treatments using scanning and transmission electron microscopy (SEM and TEM) [8]. A prominent feature of

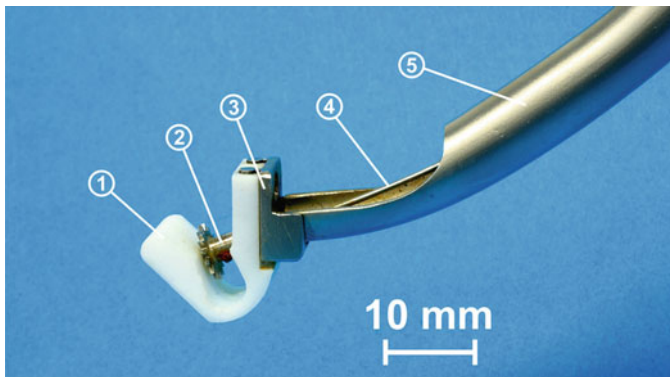


Fig. 56.1 Prototype of an instrument for oral- and maxillofacial surgery. (1) PTFE-head, (2) saw blade, (3) adapter, (4) flexible NiTi drive shaft, (5) handle piece

the microstructure are ultra-fine grains with a grain size on the order of 40 nm. Upon cooling from the high temperature phase, two sequential martensitic transformations occur: B2 austenite $\rightarrow$ R-phase followed by R-phase $\rightarrow$ B19' martensite. Upon heating, a two-step reverse transformation back to austenite takes place. The results were confirmed by X-ray and in-situ cooling experiments with electron diffraction in the TEM. Tensile cycling at temperatures ranging from 20°C to 80°C was performed to characterize the mechanical properties. The stress-strain behavior showed a strong temperature and strain rate dependence. Moreover, bending rotation fatigue tests (BRF) were conducted in air and in oil, and the influence of surface conditions on fatigue life was studied [9]. As a result, it was shown that NiTiCr is superior to binary NiTi under the projected mechanical loading conditions (longer service life, higher stiffness and torqueability) and that a significant service life increase can be achieved by electropolishing the surface of the shaft. Fatigue crack initiation was observed at surface defects, such as scratches, pores and intermetallic phases (titanium carbides of type TiC). It was shown that under bending rotation fatigue conditions the service life also depends on the wire diameter, the maximum strain amplitude in the bended shaft, the rotational speed, the temperature, and the surrounding medium. In addition, the influence of fatigue on the nanohardness was examined [10].

Actuator Developments

With regard to actuator applications, NiTi-based SMAs are promising because the forces and strains achievable are more than an order of magnitude higher than those of other actuator materials, such as bimetals or piezo-electric devices. System integration can be achieved by joining, using techniques such as laser welding or crimping [11–15]. It has to be mentioned that SMAs are not intended for high-frequency applications, due to the underlying phase transformation, which is in the case of actuators achieved through a temperature change. The limiting factor with regard to actuator frequency is not the heating (which is usually applied via electrical resistive heating), but the cooling of the SMA component. The effectiveness of cooling strongly depends on the system design within which the actuator is located (e.g. additional heat sources, availability of air convection or a cold liquid medium, etc.).

Challenges to be solved in order to achieve a widespread success of NiTi actuators are the engineering of a suitable design (e.g. simplification) including smart control systems, functional stability, higher phase transformation temperatures, a suitable structural fatigue life, and cost reduction [16]. Non-medical applications represent an important future market, promising access of shape memory technology to areas such as consumer products or the automotive industry with the potential for large-scale production [17,18]. The SFB has designed a variety of actuators using the one way effect. One example is a thermostat valve with a NiTi actuator spring for automotive preheating (Fig. 56.2) [19].

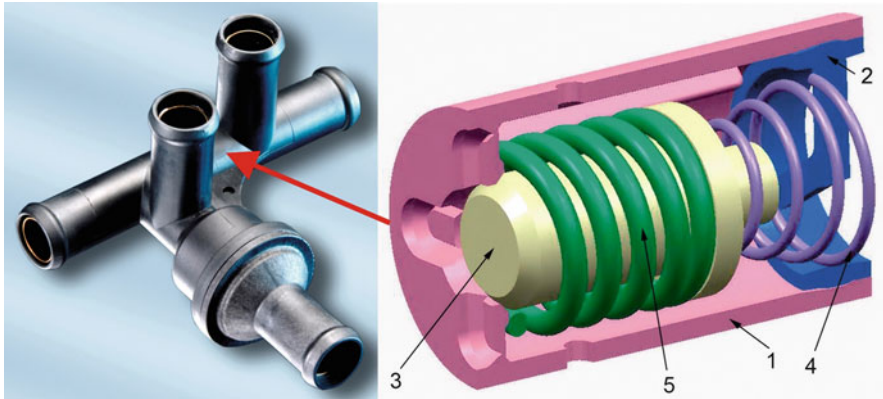


Fig. 56.2 Thermostat valve for automotive preheating. The position of the valve is indicated by the arrow. (1) case, (2) closing element, (3) plunger, (4) steel spring, (5) SMA spring [20]

Conventional preheating systems being applied in a simple in-line circuit in vehicles with large, heavy engines require dwell times longer or equal 50 min [20]. These systems can achieve a temperature of slightly above 30°C in 10 min during defrosting from 0°C, while the thermostat valve device being integrated into the heating circuit (between vehicle motor, heating system and recuperator) reaches 63°C in the same time. The major advantage is the reduction of the preheating time, making the system interesting for a wide range of car owners whose commuting distance is well below 45 min.

Conclusions

NiTi-based shape memory alloys have advanced to a level, where new fields of application besides medical engineering are opening up. The paper discusses two innovative examples for medical- and non-medical devices. The prospect of mass production of SMA components for automotive or consumer products has led to increased scientific research, with a focus on innovative actuator technologies. In addition, the potential for weight reduction, simplified designs due to a reduced number of components and the unique advantages of the shape memory effects (high actuator forces and strains) have also resulted in growing interest from industry. However, a higher operating temperature range, increased reliability (functional and structural stability), appropriate design tools and simulations, lower unit costs and a standardization of manufacturing processes and devices are required to achieve a breakthrough on the market. Especially the last-mentioned point would greatly contribute to overcome the inhibitions engineers might still have to apply an incontestably complicated material such as SMA.

Acknowledgments The authors acknowledge funding by the German Research Foundation DFG (Deutsche Forschungsgemeinschaft) and the State North Rhine-Westphalia in the framework of projects T3 and Z of the Collaborative Research Center SFB 459 (Shape-Memory Technology).

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Chapter 57

Micromachined Tunable Fabry-Pérot Filter Integrated into a Miniaturized Spectrometer for Low-Cost Applications

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Abstract Producing miniaturized and low-cost components of high precision optical sensors has attracted a wide variety of fields. Fabry-Pérot-based filters can be considerably miniaturized without decreasing high spectral resolution, compared to grating-based spectroscopic devices. The filters are assembled by using MEMS (micro-electro-mechanical-systems) technologies. Tunable Fabry-Pérot filters enable miniaturized sensor components for spectrometers covering a wide area of applications in the visible and near infrared range. We demonstrate a concept of micromachined tunable Fabry-Pérot filters, suitable for precisely selecting very narrow wavelength bands and, thus, by tuning for measuring spectra in the visible and infrared spectral range. These tunable filters integrated into optical devices act as sensors for process monitoring, color detection or medical applications. The design and the fabrication processes are compatible with nanoimprint requirements to assemble arrays of filters for increasing the spectroscopic range.

Keywords DBRs · Electrostatic actuation · Miniaturized spectrometer · Nanoimprint · Tunable Fabry-Pérot filter

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Introduction

Precise spectroscopic measurements improve the quality of many production lines because of enhanced process control. Due to their physical properties, grating-based spectrometers cannot achieve miniaturization while keeping a high spectral resolution. If the wavelength λ and the order is kept constant, a miniaturization of a grating spectrometer considerably decreases the number of illuminated lines and directly proportional to that the spectral resolution. Contrary, Fabry-Pérot (FP)-based spectrometers can be miniaturized and simultaneously afford high precision; by using low-cost materials this technology becomes more attractive also for the mass-market. The development of FP-based spectrometers is based on different methodologies to scan different wavelengths [1]. In this paper, we present a spectrometer consisting of electrostatically tunable FP filters in the visible range.

The presented tunable FP filters consist of two distributed Bragg reflectors (DBRs) with an air cavity in between. A single DBR highly reflects within a wide wavelength range, the so-called stopband. According to constructive interference which arises between the two DBRs and the cavity, only a narrow well-defined band of wavelength within the stopband of each filter passes through. By changing the cavity thickness the transmission wavelength can be precisely shifted spectrally: e.g. the narrow band of the filter is shifted to lower wavelengths for decreasing cavities. Figure 57.1 shows simulated spectra based on different cavity thicknesses expressed in optical thickness (0.5 for the case that the DBR and the cavity are calculated for the same central wavelength λ_D). The tuning is performed by applying of voltage to laminary contact electrodes. The electrostatic forces between these electrodes move the upper suspended DBR and alter the resulting cavity

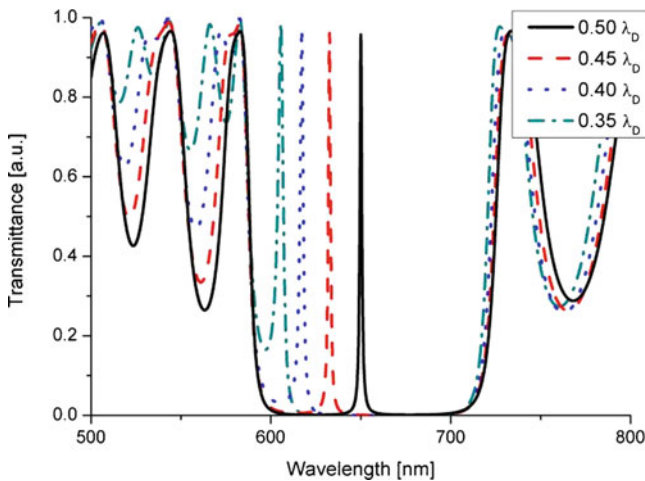


Fig. 57.1 1 Simulated transmission spectra of a $\text{Si}_3\text{N}_4/\text{SiO}_2$ Fabry-Pérot filter consisting of two 9.5 periods DBRs and different optical thicknesses for the cavity

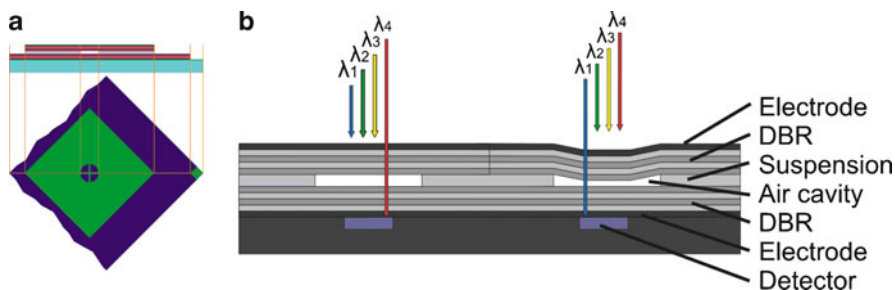


Fig. 57.2 Topview (a) and cross-section (b) of an untuned (*left*) and an actuated filter (*right*)

thickness appropriately. Microsystem technologies and sacrificial layer technologies are implemented to define the air cavities [2,3]. The deposition of the DBRs is performed by a plasma enhanced chemical vapor deposition (PECVD) process on glass substrates. The DBRs consist of multiple layers of $\text{Si}_3\text{N}_4/\text{SiO}_2$. The PECVD enables fast deposition and provides control parameters such as gas flow rate and radio frequency (RF) power to optimize the properties of the deposited material. The cavity layer is created by spin-coating the polymer mrUVcur06 on the bottom DBRs and then hardening it by UV light. The polymer used forms the so-called sacrificial layer since it is selectively removable by an oxygen plasma. In addition, mr-UVcur06 is convenient for ultraviolet-nanoimprint technology (UV-NIT) and, thus, can be used to form the three dimensional cavities by nanoimprinting instead of removing by O_2 -plasma [4,5]. Figure 57.2 schematically shows the cross-section of an untuned and a tuned FP filter on a detector which measures the intensity of the transmitted light. The filter thickness is less than $2.5\ \mu\text{m}$, the thickness of a single layer is around 100 nm.

The thickness of the cavity is maintained by adjusting the spin speed. Treatment of the polymer with N_2 during exposure is required to obtain a uniform surface profile. Subsequently, the top DBRs are deposited on top of the cavity layer.

The filters are vertically structured by reactive ion etching (RIE) with AZ1518 photoresist as etch mask. Etch rate and selectivity were investigated throughout the process. The etch rate is increased by a factor of 2.5 using an addition of SF_6 to the process gas mixture. The removal of the polymer layer underneath the filter membrane is obtained with an underetching rate of approximately $1\ \mu\text{m}/\text{min}$. The combination of actuation and optical transparency is solved by using indium tin oxide (ITO) as electrodes. The processes were monitored by surface profilometry, scanning electron microscopy and ellipsometry.

Results

First approaches to fabricate the tunable FP filter have been successfully achieved. Figure 57.3 depicts transmission spectra of a FP filter providing different transmitted wavelength depending on the applied tuning voltage. The spectral tuning range

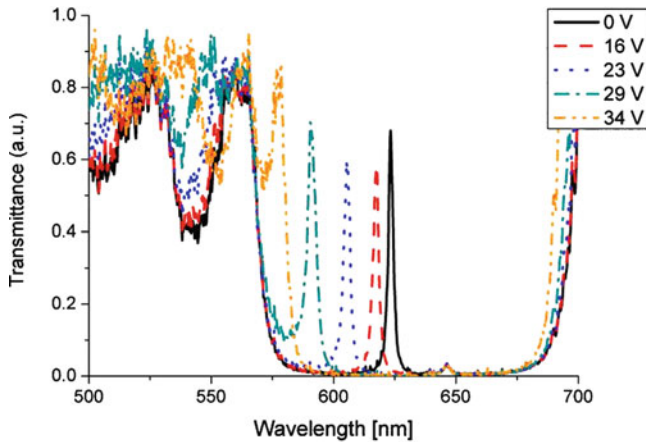


Fig. 57.3 Transmission spectra with actuated filter narrow bands at different voltages applied

of the filter is up to 47 nm at actuation voltages of 0–34 V. The filter narrow band has a full width at half maximum (FWHM) of 2 nm, and the spectral width of the stopband is about 120 nm at a central wavelength of approximately 630 nm.

The actuation of the FP filters was investigated in two different ways: First, geometrically by adding an aluminum layer for the measurement of the tuning range of the filter using white light interferometry (WLI). Second, optically with a microscope spectrometer set-up that is capable of direct spectroscopic measurement [6].

Outlook

Many steps are still required in order to combine a filter array with a detector array for the nanospectrometer. To obtain a broader stopband using a high refractive material, ZrO_2 , instead of Si_3N_4 as high refractive material increases the refractive index contrast. To structure the cavity layer for different central wavelengths of adjacent filters for improved tuning characteristics, nanoimprint technology saves time and cost.

Acknowledgments The financial support by the Federal Ministry of Education and Research (BMBF) is gratefully acknowledged. The authors thank W. Köcher and C. Sandhagen from Opsolution NanoPhotonics GmbH (OPN), M. Hornung and R. Ji from Süss MicroTec Lithography GmbH and I. Kommallein, D. Gutermuth and J. Krumpholz for their technological support.

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Part VI

Energy Economy Aspects

Chapter 58

Hydrogen Economy: The Role of Nano-scaled Support Material for Electrocatalysts Aimed for Water Electrolysis

Perica Paunović, Orce Popovski, and Aleksandar T. Dimitrov

Abstract The role and importance of support materials for electrocatalysts aimed for water electrolysis is given. Besides their superior support characteristics such as electroconductivity, a high developed surface area and chemical stability, support materials should be an active participant in the catalytic activity through strong metal-support interactions (SMSI) with the metallic catalytic phase. Subject of this paper are several support materials: (i) Vulcan XC-72, (ii) Vulcan XC-72 with TiO₂, (iii) multiwalled carbon nanotubes (MWCNTs) and (iv) Magneli phases, i.e. nonstoichiometric titanium oxides. A comparison of catalytic activity of Co-based electrocatalysts deposited on all support materials mentioned is given.

Keywords Electrocatalysts · Support materials · Vulcan XC-72 · Anatase · MWCNTs · Magneli phases · Hydrogen evolution

Introduction

The concept of a “hydrogen economy” [1–3] as a sustainable and secure energy system in the future has received considerable attention due to several reasons [4]. Firstly, it is **clean energy system**, where hydrogen can be generated by water electrolysis and further converted into electricity by fuel cells without pollutant emission. Water, hydrogen and oxygen appear as reactants and products within the hydrogen economy cycle. Thus, it has a **renewable nature**. This is of great importance taking the harmful effects of the present fossil fuel exploitation into consideration, articulated by the green house effect and the global warming of the earth.

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Further, hydrogen can be produced by and converted into electricity with a **high efficiency** ($> 60\%$). Hydrogen has a **high calorific value** and can be **transformed to energy by several ways** such as burning, electrochemical conversion and hydriding. Hydrogen can be **stored in all aggregate states**: in gaseous form for large-scale storage, as a liquid convenient for air and space transportation, and in the solid state as metal or chemical hydrides aimed for vehicles and other small-scale devices.

A very important issue within the hydrogen economy is the choice of the electrode materials in hydrogen electrolyzers/fuel cells, on which hydrogen evolution/oxidation and oxygen evolution/reduction occur. A high activity of the electrode material intensifies the electrode reaction, i.e. hydrogen evolution/oxidation, expressed by an increase of the current density and a decrease of the overpotential. As a result, the specific energy consumption for hydrogen production is lower, while the energy produced in fuel cell is higher. In other words, more active electrode materials mean highly cost-effective processes of hydrogen production/conversion.

Electrode materials for hydrogen evolution/oxidation have to satisfy technical, economical and environmental criteria. They have to be stable, thus showing no signs of corrosion or passivation in a long run, and must promote the electrode reaction. Economical reasons are in favor of cheaper materials, while the environmental concern requests the use of nonpolluting materials. Putting all together, these requests make the choice of proper electrode material not at all an easy task, due to the conflict of technical and economical issues. This conflict is evident: the best performing electrocatalysts, e.g. Pt, Pd, Ru, are expensive and scarce, while the cheaper substituents using less noble metals, e.g. Ni, Co etc., suffer of corrosion, passivation or similar problems. The need of active, stable and cheaper electrode materials induced an intensive research in the last few decades. Guided by the two main approaches (physical and chemical) to satisfy the above criteria, modern electrodes materials are multicomponent, where each component added to the basic catalytic metal improves its intrinsic catalytic activity or its surface characteristics.

In the next parts of this paper, physical and chemical approaches for the improvement of the catalytic activity of pure metals will be explained with particular turn on the role of support materials. Also, some results on the application of different support materials (Vulcan XC-72, mixed supports containing Vulcan XC-72 + TiO_2 , MWCNTs and non-stoichiometric titanium oxides (Magneli phases)) on catalytic activity of Co based electrocatalysts will be given.

Electrocatalytic Activity of Electrode Materials

The main role of the electrocatalytic electrode materials is to increase the reaction rate of the electrode reactions (hydrogen/oxygen evolution during water electrolysis). The reaction rate of a chemical reaction is defined as the quantity of products formed per unit time. In the case of electrode reactions, the products are formed by electron exchange between electrode and ion reactants. Thus the reaction rate can be defined as the number of exchanged electrons per unit time, that is the electric current i passing

through the electrode. The reaction rate of electrode reactions occurring at an electrode with a definite geometric surface area, i.e. the current density (amperes per geometric electrode surface area) is expressed by the following equation [5]:

$$i = j \cdot s \cdot m \quad (58.1)$$

where j is the **specific current density** (amperes per real electrode material surface area), s is the **specific surface area** of the electrode material (real surface area per g) and m is the amount of the loaded catalyst (g per electrode geometric surface area). The **Catalytic activity** of the electrode material is defined as $j \cdot s$. The specific current density j is the ability of the electrode material (electrocatalyst) to deliver electrons to the reactive ions, to adsorb discharged atoms at the electrode surface and to desorb gas products from the surface. It is an intrinsic property of the electrode material named intrinsic catalytic activity. A higher specific surface area s means a larger available surface for adsorbed species and, further, a higher reaction rate of the electrode process.

The crucial aim of electrocatalysis and material science is to increase the reaction rates through an increase of both j and s at a constant value of m , i.e. through increase of both the **intrinsic catalytic activity** of the electrode material and its specific surface area. The increase of the intrinsic catalytic activity of the electrode material is the **chemical aspect** of the improvement of the whole catalytic activity; the result of this improvement is called **intrinsic effect**. On the other side, the increase of the real surface area is the **physical aspect** of the improvement of the whole catalytic activity, and the result of this improvement is called **surface effect**.

Catalytic Activity of Transition Metals for Hydrogen Evolution Reaction

To understand the sense of the pathways for improvement of the catalytic activity of electrode materials, first the fundamentals of the catalytic activity of pure transition metals will be explained.

The hydrogen evolution reaction (HER) is a heterogeneous catalytic reaction including adsorption phenomena and the formation of intermediates between the reacting species and the electrode atoms/ions. Thus, the adsorptive characteristics of the electrode materials are of great importance for their electrocatalytic behavior. According to Sabatier's principle [6], an electrode material shows an optimal electrocatalytic activity when the strength of the adsorption bond between the electrode substrate and the H-atom has an intermediate value. A higher strength implies a high activation energy for further electrochemical transformation and desorption, or in other words, strong hydride formation. A weaker bond leads to premature desorption of the intermediate from the electrode surface, so no electrochemical transformation occurs.

Observing the electrocatalytic activity for HER as a function of the atomic number of elements of each transition series [7], one can notice that the electrocatalytic activity increases with the atomic number, achieves a maximum for group VIIIB of metals and sharply decreases to minimum values for group IIB of metals. The platinum group of metals (Ni, Pd and Pt) has the highest electrocatalytic activity. This behavior of the transition metals can be explained by the electronic configuration of metals.

Namely, the *d*-orbitals are responsible for the adsorptive/desorptive characteristics, while the *s*- and *p*- electrons are decisive for reacting and conducting features. Metals which have more paired electrons in the *d*-band have a higher percentage of the ***d*-character** [8,9]. On the other side, metals with more unpaired electrons, i.e. vacant orbitals in the *d*-band, interact with hydrogen adatoms, adsorbing them very strongly. Thus, the lower the percentage of the *d*-character, the higher the adsorption of H-adatoms, and further the more difficult the desorption, resulting in a slower reaction rate of the HER. Increasing the *d*-character leads to a decrease of adsorption, i.e. to an increase of the reaction rate of HER. After reaching the maximum of the reaction rate (Ni, Pd, Pt-group), a further increase of the *d*-character decreases the reaction rate due to a very weak adsorption of H-adatoms and premature desorption.

Considering these observations, the question that arises is: why is the electronic configuration of Ni, Pd and Pt (d^8) the optimal one?

The Balandin multiplet theory [10] can be used to answer this question. According to this theory, the reacting atoms (or molecules) are imposed upon a group of active atoms of the catalyst, and an adsorbed intermediate multiplex complex is formed. This formation is affected by short-range forces on different parts of the molecules and depends on the bond lengths and bond energy as well as on the geometrical shape and the space distribution of the reacting atoms (molecules), and the catalyst's crystal lattice. The short-range forces correlate with the atomic diameter of the catalyst and the metal-hydrogen atom distance involved in the multiplet. The smaller the catalyst atomic diameter and the shorter both the inter-atomic lattice distance of catalyst surface atoms and the M-H distance, the higher is the electrocatalytic activity of the metal catalyst. This theory points out that recombination of hydrogen multiplets (doublets) must take place upon a single atom of the metal catalyst for further release of hydrogen molecules. According to this consideration, at least two vacant unpaired *d*-electronic sites of the same catalyst atom are required for hydrogen adatom recombination. The platinum group of metals (d^8) has the optimal electronic configuration for this request.

As stabilization and exposition in the space of the *d*-electrons becomes higher from the 3d to the 5d transition series, platinum appears to be the most active individual metal catalyst. On the first glance, the Tafel reaction (second step in the mechanism of the HER: $M-H + M-H \rightarrow H_2 + 2M$) implies a recombination of H-adatoms from two different atoms, but, according to Balandin's theory, both Ms represent the same atom of the metal catalyst.

Concerning the electronic configuration, Sabatier's principle could be formulated as a follow: an electronic configuration with a lower electron concentration or

lower *d*-character leads to stronger metal-hydrogen bonding, even to hydride formation. On the other side due to many electrons in the *d*-bond or the higher *d*-character, there are no adsorption sites in the metal. In both cases there is no significant HER reaction rate. The optimal electronic configuration for a high HER reaction is that of the platinum group of metals.

The Pathways for Improvement of the Electrocatalytic Activity

The pathways to enhance the electrocatalytic activity of pure metals can be taken from Eq. (58.1). So, to improve the catalytic activity of a constant amount of electrocatalysts, the real surface area and the intrinsic activity should be increased. The first path (an increase of the real surface area of the electrode material) is based on **physical transformations** of the material such as a reduction of the particle size, which implies an increase of the surface area. The rise of the catalytic activity by such approach is called “size-effect”. The second path includes an increase of the intrinsic activity through **chemical changes** of the catalytic material through alloying of metals. The corresponding effect is called “intrinsic effect”.

The first path to solve this problem was to increase the ratio of the real surface area of the electrode vs its geometric surface (roughness factor S_R/S_G) or vs its mass (specific surface area, m^2g^{-1}). So, involving porous electrodes provides a considerable increase (10^3 – 10^4 times) of the limiting current density i_L and consequently of the power density [11]. The enhancement of these parameters makes fuel cells practically useful.

An increase of the real surface area of porous electrodes can be achieved by reducing the grain size of the electrocatalytic material. So, a maximum surface area can be reached by using **nano-scaled electrocatalysts**. Thus, **nanotechnologies** are priceless tools of modern electrocatalysis.

The need for active, stable and cheaper electrocatalysts motivated intensive research, resulting in the development of multicomponent catalysts. It was normal to start with combinations of the most active precious metals. So, electrocatalysts like Pt-Pd or Ir-Re [12,13] were prepared, but the resulting synergetic effect did not satisfy the expectations.

According to Jakšić's interpretation [14–16] of the Brewer resonance bond-valence theory [17] for intermetallic compounds, the combination of hyper *d*-electronic transition metals (having more electrons in the outer shell and being good individual catalysts) with hypo *d*-electronic transition metals (having less electrons in the outer shell and being poor catalysts as individual metals) exhibits a pronounced synergetic effect. He succeeded to obtain Co-Mo hypo-hyper *d*-electrocatalysts with a catalytic activity comparable with that of Pt [18].

Alloying of *d* metals from the opposite sides of the transition series occurs in accordance with the generalized Lewis acid–base theory by definite charge transfer. This transfer is in opposite direction to that expected from the electronegativities. In other words, the electron-donating metal is that of the right side with an excess of

electrons (hyper *d* element), while the electron-accepting metal is that of the left side with unused vacant orbitals (hypo *d* element). Thus, the hyper *d* element (Pt, Pd, Ni, Co, Ru, ...) behaves as a base and the hypo *d* element (Ti, Zr, Hf, W, Mo, ...) as an acid. Brewer has proposed a qualitative prediction for the expected trend of the stability of hypo-hyper *d* compounds. As the strength of *d* electron bonding rises from the 3*d* to the 5*d* transition series, the stability of intermetallics with 3*d* orbitals would be the lowest, that with 5*d* orbitals the highest. For example, the most stable intermetallic compounds would be Pt-Hf, Pd-Zr and Ni-Ti along each transition series, of which Pt-Hf compounds are the most stable.

Hypo and hyper *d*-components may be not only in the elemental state, but also in higher oxidation states. Depending on the valence state of the hypo and hyper *d*-components, we can distinguish more types of hypo-hyper *d*-electrocatalysts [19].

The Role of Support Material on Catalytic Activity

The very poor dispersion of metallic particles and their tendency to agglomerate to larger particles, lead to a degradation of the surface characteristics and consequently to a reduction of the utilization of the metallic electrocatalyst (pure metal or mixture of metals). For this reason the metallic phase can not be used as an electrocatalyst individually, but must be grafted on a so-called support material in order to avoid the above disadvantage. So, **the main role of the support material** is to provide a **good dispersion** of the metallic catalytic phase and **to avoid agglomeration** of the metallic particles. In this context, the support material should show superior physical surface characteristics. But this is not the only requirement for the support material. It has to assure some other requirements for better performances of catalytic electrode materials.

We already mentioned that during the electrode reaction a continuous electron exchange between ions and electrode occurs. So, the electrode material should be **good electronic conductor**. Because the ratio between support material and metallic catalytic phase is 4–5:1, the support material has the role of the main electron exchanger, thus it should have good electroconductive characteristics.

To provide long-term stability of the electrode material, the support material should be **chemically** and **mechanically stable**. This is very important for anodic processes (oxygen evolution in water electrolysis or hydrogen oxidation in fuel cells) within the oxidation processes occurring. So, the support material should be inert to these processes.

But on the other side, the support material should be “non-inert” to the metallic catalytic phase. Interactions between the metallic phase and the support material should improve the catalytic activity of the catalytic material through the so called **strong metal-support interaction (SMSI)**. In the case of support materials containing a hypo *d*-component (a metal or its compound, e.g. Ti or TiO₂), SMSI is achieved by the hypo-hyper *d*-interaction described above. As result of this interaction, a considerable rise of the catalytic activity of the metallic catalytic phase can be attained. In the case of carbonaceous support materials, SMSI is achieved by

surface acidic oxygen containing functional groups which act as anchoring centers for metal particles, limiting their growth, enhancing their dispersion and affecting the electronic nature of the metal sites. This effect is weaker than in the previous case. It is very important not only to enhance the surface and intrinsic properties of the metallic phase, but also to render the procedure of catalyst preparation easier, i.e. the grafting of the metallic phase onto the support material. For example, adsorption and dispersion of Pt metal precursors on carbon supports are largely influenced by the acid–base properties of the substrate and by the pH of the catalyst precursor solution [20]. A suitable surface-charge density on the support, in combination with the appropriate charge of the ionic precursor, favors the electrostatic interaction between the two phases, thus affecting the metal dispersion.

The most used support material for electrocatalysts aimed for water electrolysis/fuel cells is carbon black (Vulcan XC-7). Its distinctive properties such as a high degree of ordering, appropriate physical and chemical surface characteristics, and a high electron conductivity are responsible for that. The fact that carbon blacks with large volumes of mesopores with ($d > 10$ nm) and elongated aggregates of sub-micrometer sizes proved to be suitable as support material implies that other mesoporous carbons can be applicable [21]. So, the newer carbonaceous materials such as carbon nanotubes and nanofibers attract attention for this purpose [22–24].

Recently, non-stoichiometric titanium oxides known as Magneli phases (trade name Ebonex) impress as potential support materials [25], especially for electrocatalysts aimed for oxygen evolution/reduction [26–28]. Their appropriate conductive characteristics and high chemical stability make them suitable for this purpose. On the other side, they are hypo d -oxides which improve the intrinsic catalytic activity of the metallic phase through hypo-hyper d -interactions.

In the next parts of this paper, examples of the catalytic activity of Co-based electrocatalysts deposited on different support materials will be discussed. The electrocatalysts compared contain the same quantity of the metallic Co phase (10% Co + support material). The electrocatalysts studied were prepared by the sol–gel method using organometallic precursors for the metallic phase [29,30]. The performances of the electrocatalysts for hydrogen evolution reaction were investigated in an alkaline hydrogen electrolyzer (3.5 M KOH) using gas-diffusion electrodes [31,32] (GDE) prepared of the studied electrocatalytic material. As a reference, the traditional Pt electrocatalyst deposited on Vulcan XC-72 was used (10% Pt + Vulcan XC-72). The main idea was to produce non-platinum electrocatalysts deposited on a corresponding support material and to obtain catalytic activities comparable or even better than that of the traditional Pt/Vulcan XC-72 electrocatalyst.

Vulcan XC-72

In the first stage of this study, a non-platinum metallic phase (Co) was deposited on Vulcan XC-72. Its electronic conductivity of $4 \text{ S}\cdot\text{cm}^{-1}$ provides continuous electron exchange during electrode reactions. The surface area of $250 \text{ m}^2 \cdot \text{g}^{-1}$ and

appropriate physical and chemical surface characteristics provide a good dispersion of the catalytic phase over the support surface and avoid agglomeration of the catalytic metallic particles.

According to an XRD analysis (Fig. 58.1a), there are no well-shaped peaks, except those of the holder and the carbon phase. This points out that the Co phase is amorphous with very small particles of less than 2 nm size. The Co particles show the same size in all catalytic systems discussed below. Besides very small particles of the metallic phase, the support material used provides also a good dispersion of the metallic phase (see Fig. 58.2a). The catalyst particles deposited on Vulcan are of spherical shape. There is a grouping of the particles in clusters, so that a good adherence between the particles is achieved. There is a good uniformity of size and shape of the particles. The size of clusters is 100–120 nm.

The ratio of real vs geometric surface area S_R/S_G was determined by cyclic voltammetry [33,34]. The electrocatalyst shows a very high developed surface area with $S_R/S_G = 2,590$ calculated through the value of the double layer capacity $C_{dl} = 155 \text{ mF}\cdot\text{cm}^{-2}$ [35].

As a measure for the electrocatalytic activity, the overpotential at the reference current density of $60 \text{ mA}\cdot\text{cm}^{-2}$ was taken. The lower the overpotential, the higher

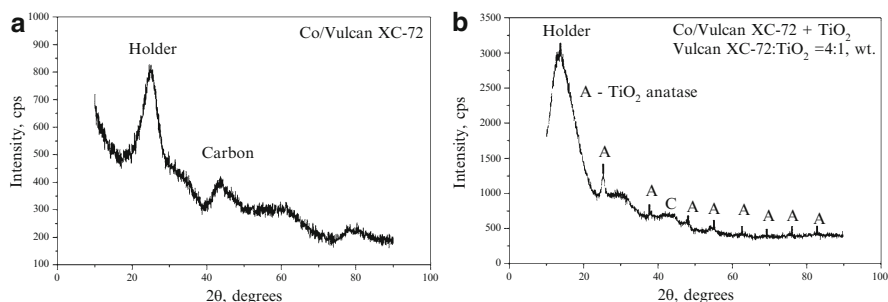


Fig. 58.1 XRD spectra of Co-based electrocatalysts deposited on (a) Vulcan XC-72 and (b) Vulcan XC-72 + TiO₂

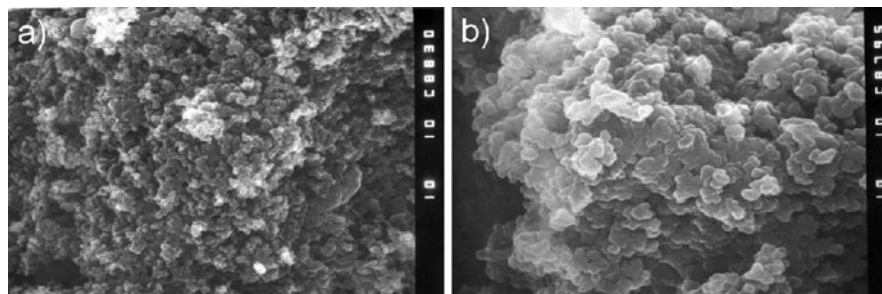


Fig. 58.2 SEM images of Co-based electrocatalysts deposited on (a) Vulcan XC-72 and (b) Vulcan XC-72 + TiO₂

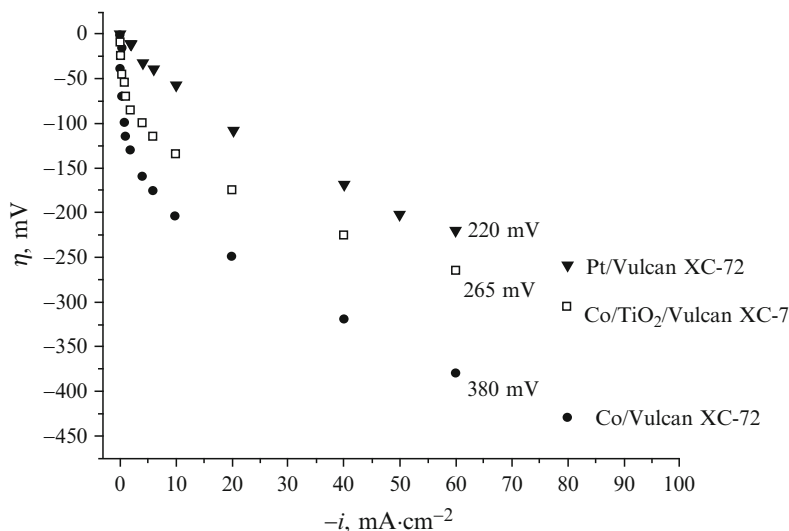


Fig. 58.3 Polarization curves of the electrocatalysts deposited on Vulcan XC-72

the electrocatalytic activity of the electrocatalyst. The electrocatalytic activity of this catalyst is much lower than that of the traditional Pt/Vulcan XC-72. The difference in the overpotentials is even 160 mV (380 vs. 220 mV, see Fig. 58.3).

So, this type of catalyst support is not suited to realize the main idea. The next step in the improvement of Co-based catalyst is the addition of the hypo *d*-phase TiO_2 to the catalyst support. The unique role of the anatase form of titania in the improvement of the catalytic activity in both heterogeneous chemical catalysis and electrocatalysis has been noticed elsewhere [36,37]. The weight ratio in the mixed support material is 4:1 Vulcan XC-72 vs TiO_2 . This ratio is the optimal one to keep the electric conductivity high enough for electron exchange processes and, on the other side, to improve the intrinsic catalytic activity of the metallic phase through hypo-hyper *d*-interaction.

The ratio of real vs geometric surface area is similar as in previous case, $S_R/S_G = 2,560$ ($C_{dl} = 154 \text{ mF} \cdot \text{cm}^{-2}$). Also, the structural characteristics of the Co phase are very similar (Fig. 58.1b). The size of the Co particles is near 2 nm, while that of the TiO_2 particles is 3–4 nm. The peaks present in the XRD spectra in Fig. 58.1b correspond to the anatase crystalline form of titania. Further, by depositing Co on Vulcan XC-72 + TiO_2 , the catalyst forms larger clusters that reach 150–200 nm (Fig 58.2b). The particles are not so uniformly distributed, and a number of holes exist between the aggregates. This contributes to the high specific surface area.

The electrocatalytic activity of this catalyst is considerably improved. The overpotential at the reference current density is 265 mV, even 115 mV lower than the corresponding one of the previous electrocatalyst. This activity is closer to that of the traditional Pt/Vulcan XC-72 electrocatalyst which shows 220 mV at the reference current density.

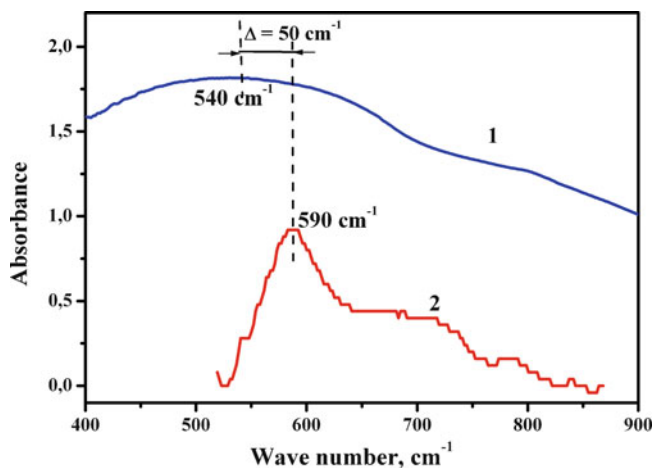


Fig. 58.4 FTIR spectra of pure anatase and Co/TiO₂/Vulcan XC-72 electrocatalyst

What is the cause for this considerable rise of the electrocatalytic activity if the size of the metallic catalytic phase, their dispersion and the real surface area of the catalysts are similar? TiO₂ as a hypo *d*-phase interacts with the metallic Co phase achieving a considerable synergetic effect of the electrocatalytic activity for hydrogen evolution. As result of this interaction, the intrinsic catalytic activity of the metallic phase increases. The hypo-hyper *d*-interaction was detected by FTIR spectroscopy shown in Fig. 58.4.

The only band of interest in the FTIR spectra of the catalysts originates from TiO₂ [38]. These bands are compared with the corresponding ones of pure TiO₂ produced under the same conditions as the catalysts. The peaks of the bands of TiO₂ from the catalysts are shifted to higher wavenumbers compared with the corresponding peak of pure TiO₂. This means that an interaction between the hypo *d*-oxide and the hyper *d*-metallic phase exists, i.e. a strong metal-support interaction (SMSI) is detected. The larger the wavenumber, the shorter the bonds between TiO₂ and the hyper *d*-metallic phase, i.e. the stronger the hypo-hyper *d*-interaction. The existence of a hypo-hyper *d*-interaction causes changes in the adsorption characteristics of the electrode materials and a synergetic electrocatalytic effect for the hydrogen evolution reaction [14]. The shift of the TiO₂ peak is 110 cm⁻¹ for the electrocatalyst related to the peak of pure TiO₂.

Carbon Nanotubes

The unique physical properties of carbon nanotubes (CNTs) such as electroconductivity, mechanical stability, surface area, porosity etc. make them very attractive as support material for electrocatalysts in the hydrogen economy. In comparison

with Vulcan XC-72, CNTs have a considerably higher electronic conductivity of $10^4 \text{ S} \cdot \text{cm}^{-1}$ [23], while the specific surface area is in range of $200 - 900 \text{ m}^2 \text{g}^{-1}$ [23]. Also, Vulcan XC-72 has micropores smaller than 2 nm, which is not the case with CNTs [22]. This is important for the electrocatalytic behavior, because small nano-structured metallic phases can sink into the micropores, reducing the number of three-boundary reaction sites. Another advantage of CNTs vs Vulcan XC-72 is the higher chemical, i.e. corrosion stability. This is a very important parameter for anodic reactions of oxygen evolution in hydrogen electrolyzers and hydrogen oxidation in fuel cells. Namely, the electrochemical degradation of carbon materials is considerably slowed by carbon graphitization [21]. This is explained by considering that electrochemical corrosion takes place at the edge planes of graphite, whereas the basal planes are relatively inert. Therefore, a considerably better corrosion resistance was detected in materials such as Pt/CNTs which are roll-ups of graphene sheets and possess a long-range order, as compared to Pt supported on carbon blacks which have a turbostratic structure and are composed of a mixture of graphite crystallites and amorphous carbon [39].

The next step of support material modification was the replacement of Vulcan XC-72 with multiwalled carbon nanotubes (MWCNTs). So, the new catalyst support consisted of MWCNTs with a corresponding amount of TiO_2 as in the previous case. The MWCNTs used were manufactured by Guangzhou Yorkpoint Energy Company, China.

Figure 58.5a shows a SEM image of the electrocatalyst in this stage. It possesses an intertwined thread-like morphology as a result of the presence of MWCNTs. This morphology is more appropriate than that of electrocatalysts deposited on carbon blacks. In this case, the catalyst's components are grouped into smaller clusters; there are more holes between them which leads to a better **inter-particle porosity** of the catalyst. Due to the intrinsic geometric shape of MWCNTs (see Fig. 58.5b), empty cylinders ordered one over the other, which possess inner holes, so the inner or **trans-particle porosity** of MWCNTs is considerably higher.

It should mention that the size of both Co and TiO_2 particles are the same as in previous cases (Co: 2 nm, TiO_2 : 3–4 nm) [40].

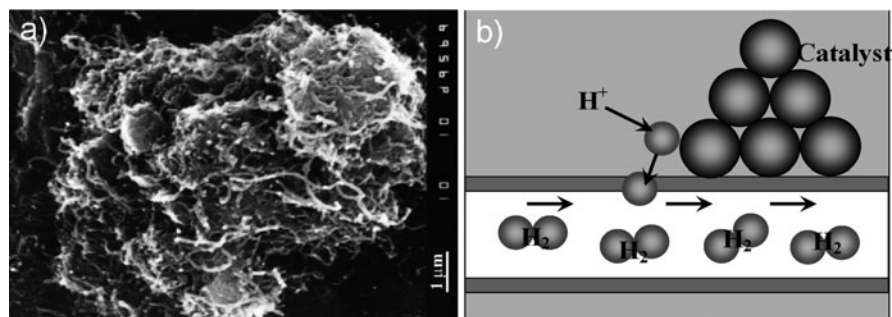


Fig. 58.5 (a) SEM image of a Co-based electrocatalyst deposited on MWCNTs + TiO_2 ; (b) sketch of a solid/gas boundary in the case when hydrogen passes through carbon nanotubes

The measurement of the double layer capacity for pure carbon phases (Vulcan XC-72 and MWCNTs) as well as for the electrocatalysts has been performed in order to determine the ratio of real vs geometric surface area [41]. These results are shown in Table 58.1. C_{dl} values of pure MWCNTs are almost twice as high than that of Vulcan XC-72. This means that the real surface area of carbon nanotubes is two times more developed. That implies a two times higher real surface area of the catalyst deposited on MWCNTs than that deposited on Vulcan XC-72.

A strong-metal support interaction expressed by the hypo-hyper d-interaction was detected by FTIR analysis. In this case, there is a higher shift of the peak maximum than in the previous case of the electrocatalyst deposited on Vulcan XC-72 (compare Fig. 58.4 and Fig. 58.6). This points out that when Co and TiO_2 are deposited on MWCNTs their interaction is stronger than in case when they are deposited on Vulcan XC-72. This is a result of the better chemical surface characteristics of MWCNTs vs Vulcan XC-72.

As result of the above explained improved surface characteristics and SMSI, it was expected that the electrocatalyst deposited on MWCNTs shows a better catalytic activity than the corresponding one deposited on Vulcan XC-72. So, the over-potential for hydrogen evolution at the reference current density of $60 \text{ mA} \cdot \text{cm}^{-2}$

Table 58.1 Double layer capacity C_{dl} and ratio of real vs geometrical surface area S_R/S_G

Sample	$C_{dl}/\text{mF} \cdot \text{cm}^{-2}$	S_R/S_G
Vulcan XC-72	179	—
MWCNTs (manufactured)	331	—
MWCNTs (activated)	355	—
Co/ TiO_2 /Vulcan XC-72	154	2,560
Co/ TiO_2 /MWCNTs (manufactured)	306	5,100
Co/ TiO_2 /MWCNTs (activated)	330	5,500

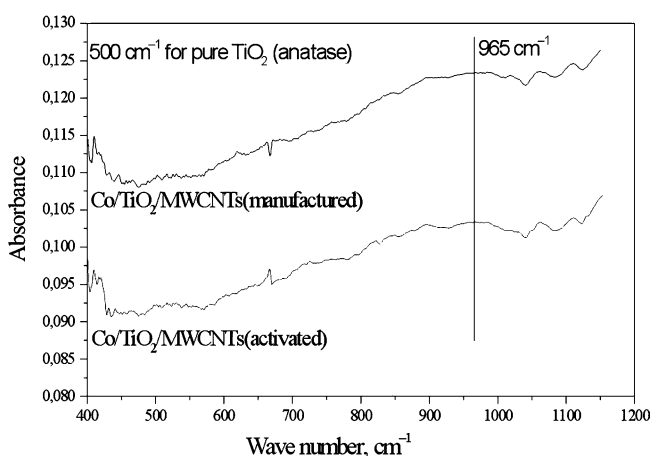
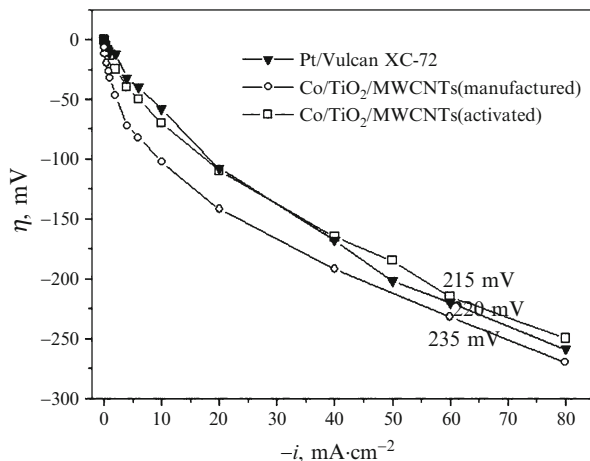


Fig. 58.6 FTIR spectra of Co/ TiO_2 deposited on manufactured and activated MWCNTs

Fig. 58.7 Polarization curves of the electrocatalysts deposited on MWCNTs



is 235 mV (see Fig. 58.7), i.e. 30 mV lower than that of the corresponding electrocatalyst deposited on Vulcan XC-72. This catalyst approaches the activity of the traditional Pt/Vulcan XC-72 electrocatalyst, but is still lower.

The next step for improvement of the electrocatalyst's performances by variation of the support material was an activation of the manufactured MWCNTs. This activation was performed in 28% (wt.) HNO_3 at ambient temperature for 4 h. So, the next electrocatalyst studied is composed of Co deposited on activated MWCNTs containing the corresponding amount of TiO_2 .

By chemical oxidation of the MWCNTs with HNO_3 three main effects are achieved: (i) functionalization of the graphitic network with functional hydroxyl groups which enable the formation of a well dispersed colloidal suspension; (ii) removal of disordered (amorphous) carbon from the MWCNTs; and (iii) an increase of the defect population/formation on the CNTs due to length shortening. The first one is an unavoidable process which can be easily detected and quantified by means of XPS and titration measurements [42]. The carboxylic groups surround both the outer and inner walls of the MWCNTs within the suspension, so the removal of some metal impurities is possible.

After removal of the amorphous carbon the level of crystallinity of the MWCNTs increases. On the other side, the increase of the defect sites causes a decrease of the crystallinity. The level of crystallinity, i.e. the graphitization of MWCNTs can be detected by means of Raman spectroscopy. Shown in Fig. 58.8 are Raman spectra of both manufactured and activated MWCNTs [43]. Both spectra are composed of two characteristic lines for nanotubes: the D and G bands. The D-line with a maximum of near $1,350 \text{ cm}^{-1}$ indicates disordered carbon atoms, defects such as pentagons and heptagons, edges of the graphite crystal, and mostly amorphous carbon [44,45]. The G-line with a maximum at $1,585 \text{ cm}^{-1}$ is related to highly oriented graphite [46]. In both cases, a shoulder appears to the right side of the G-line near $1,620 \text{ cm}^{-1}$; it is denoted as D'-peak. The appearance of the

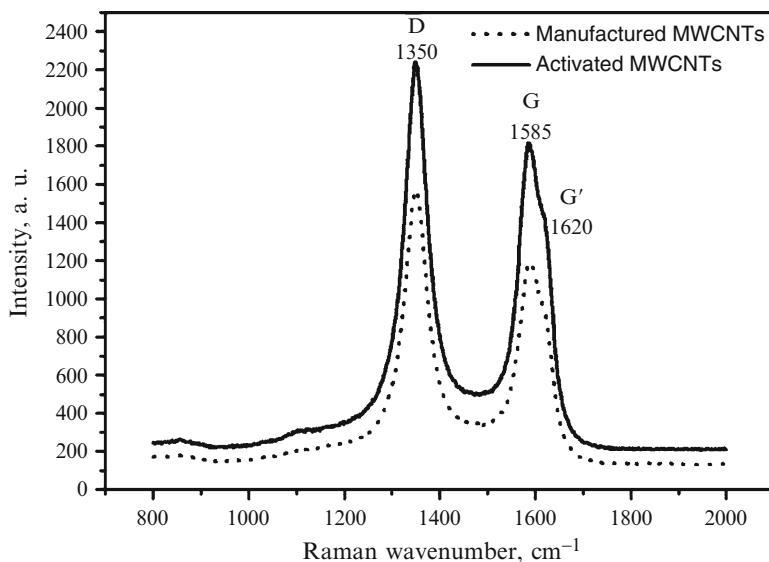


Fig. 58.8 Raman spectra of manufactured and activated MWCNTs

D'-peak indicates that these carbon nanotubes are multiwalled [47,48]. The ratio of the intensities of the characteristic peaks I_D/I_G indicates the extent of defects and impurities in the nanotubes.

After activation/purification of the MWCNTs the value of the I_D/I_G ratio decreases from 1.384 to 1.283 [43]. This means that the disordered (amorphous) carbonaceous phases are reduced. The relatively low decrease of the I_D/I_G ratio suggests that other disordered forms of carbon are formed. Namely, during the treatment with nitric acid, a shortening and thinning of the MWCNTs occurs, causing an increase of defect sites. The shortening of the MWCNTs can be seen well on the TEM images shown in Fig. 58.9.

As result of the shortening and opening of the MWCNTs during the activation process, the real surface area was increased as shown in Table 58.1. The intensity of the hypo-hyper d-interaction shown in Fig. 58.6 is equal for electrocatalysts deposited on both manufactured and activated MWCNTs. Therefore, the observed rise of the catalytic activity (see Fig. 58.7) is a result of the rise of the real surface area caused by shortening and opening of the MWCNTs by the treatment in HNO_3 solution. The overpotential for hydrogen evolution decreases from 235 for electrocatalysts deposited on manufactured MWCNTs to 215 mV for electrocatalysts deposited on activated MWCNTs at the reference current density of 60 mA cm^{-2} .

After applying support materials containing activated MWCNTs and TiO_2 , Co-based electrocatalysts approach or even exceed the electrocatalytic activity of the traditional Pt/Vulcan XC-72 electrocatalyst (see Fig. 58.7). So, an appropriate catalytic activity close to that of Pt-based electrocatalysts or even better

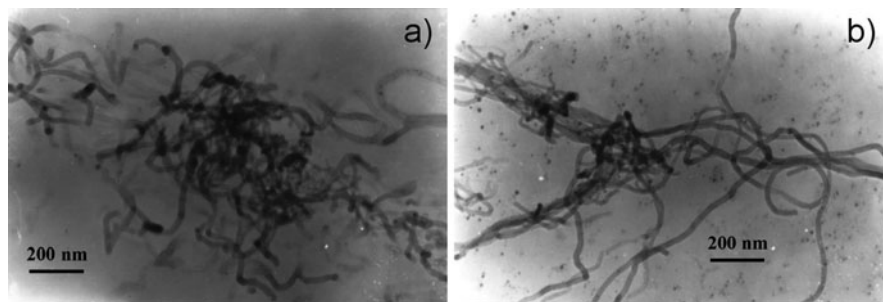


Fig. 58.9 TEM images of (a) manufactured and (b) activated MWCNTs

can be achieved by modification of the support material. The structural and surface changes of the support material affect the activity of the metallic catalytic phase.

Non-stoichiometric Oxides of Titania

Some of the transition metal oxides have the potential as possible electrode or support materials [49]. Recently, the so-called Magneli phases, i.e. nonstoichiometric titanium oxides with the general formula $\text{Ti}_n\text{O}_{2n-1}$ ($4 < n < 10$) have been considered as very promising support materials due to their high chemical stability and high electric conductivity. Especially, the first two suboxides of the series (Ti_4O_7 and Ti_5O_9) show the highest conductivity of $\approx 1,500 \text{ Scm}^{-1}$ (for single crystals) [50]. Structure, physical properties and the electrochemical behavior of the Magneli phases in various media and applications are given elsewhere [25]. They show a high overpotential for hydrogen and oxygen evolution as well as slow charge transfer kinetics. For this reason, they are more suitable as support than as electrode material [25,51].

As a support material, Magneli phases have a bifunctional role: as support (high conductivity dispersion) and for improvement of the intrinsic catalytic activity of the electrocatalyst as result of the hypo-hyper d -interaction with the metallic catalytic phase (SMSI). On the other side, they show a high chemical stability. But their main disadvantage is the low specific surface area [52]. The only commercial product known as Ebonex (Altraverda Inc., UK) is a micro-scaled material. In Jakšić's series of investigations [26,27,52] of oxygen reduction reactions, the maximal specific area of Ebonex achieved by mechanical treatment was $1.6 \text{ m}^2\text{g}^{-1}$. This low specific surface area can not provide a sufficient dispersion of the nano-scaled catalytic phase. "Top-down" methods for the reduction of the grain size of Ebonex and further appropriate impregnation methods for grafting of nano-scaled metallic phases on an Ebonex support (the boronhydride method [28] or ultrasonic blending of a Pt salt solution and previously mechanically treated Ebonex [26,27]) can give satisfactory results for oxygen reduction reactions. In comparison with

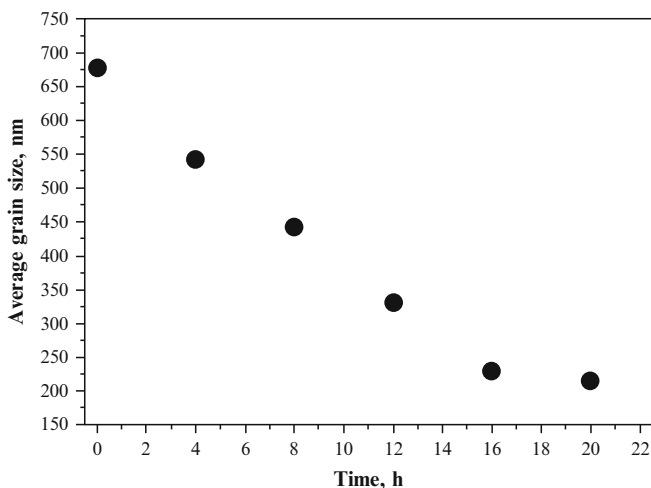


Fig. 58.10 Plot of the dependence of the average particle size of Magneli phases on the duration of mechanical treatment determined by TEM analysis

polycrystalline Pt, synthesized Pt/Ebonex catalysts have shown an enhancement of the catalytic activity for oxygen reduction reactions [26].

Co was grafted on Ebonex by sol–gel methods as in previous cases. Prior to that the macro-scaled Ebonex was mechanically treated to reduce the size of its particles. Dry ball milling was performed with a velocity of the balls of 200 rpm for different durations (4, 8, 12, 16 and 20 h).

The size of the Ebonex particles determined by TEM analysis decreases from 700 nm for untreated Magneli phases to 215 nm for samples with Magneli phases treated for 20 h (see Fig. 58.10). The samples treated for 16 and 20 h show very close values of the particle size, 230 and 215 nm respectively. This implies that further mechanical treatment can not reduce the particle size due to the increased surface energy during milling, making the treated material thermodynamically unstable. The mechanism by which the material can be moved to a thermodynamically stable state (reduction of the overall energy) is agglomeration of the grains. Therefore, the particle size achieved after 20 h mechanical treatment is the maximal reduction of the Ebonex particles possible.

Shown in Fig. 58.11 is a SEM image of a Co/Ebonex electrocatalyst in which the support material was mechanically treated for 20 h. Magneli phases mostly form micro-scaled and submicron aggregates, while the Co phase, i.e. the active catalytic centers are very small (≈ 2 nm) and uniformly dispersed over the support aggregates.

The electrocatalytic activity for this electrocatalyst is expressed by an overpotential of 365 mV at the reference current density of 60 mAcm^{-2} . This is a low activity and far from the activity of the traditional Pt/Vulcan XC-72 electrocatalyst. But this activity is slightly better than that of Co electrocatalysts deposited on pure Vulcan XC-72 (380 mV). Vulcan XC-72 affects the surface characteristics of the electrocatalyst, while Magneli phases significantly increase the intrinsic activity

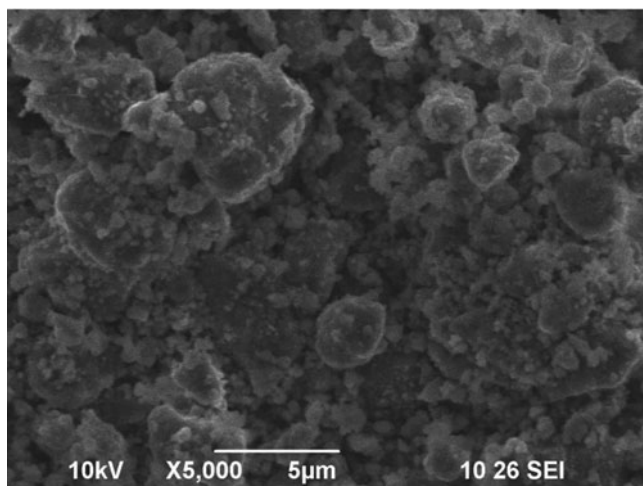


Fig. 58.11 SEM image of a Co/Ebonex electrocatalyst (Ebonex mechanically treated for 20 h)

of Co through hypo-hyper *d*-interactions. Comparing these two electrocatalysts, one can conclude that in this case the intrinsic effect is more pronounced than surface one.

It should be mentioned that the electrocatalytic activity of this catalyst for oxygen evolution reactions is very satisfactory, compared to other similar electrocatalysts for oxygen evolution, for example PtCo/Ebonex catalysts produced by boron-hydride reduction [28]. The good catalytic behaviour for oxygen evolution is connected to the formation of surface oxides and interaction between metallic phase (Co) and catalyst's support (Magneli phases). Metal-support interaction was clarified above. Electrode surface is composed of oxide support and Co which is in oxide state at potentials close to oxygen evolution region. In this case, Magneli phases behave not only as support material, but also, as an active oxide electrode.

Conclusion

The role of the support material for electrocatalysts is to provide sufficient electron conductivity for electron exchange with ions; to provide better surface characteristics of the electrocatalysts such as dispersion of the metallic catalytic phase over the surface and to avoid agglomerations of metallic particles; to have a satisfactory chemical stability, and to improve the intrinsic activity through strong-metal support interactions (SMSI).

The physical and chemical changes of the support material can influence the electrocatalytic activity of the metallic phase. Also, addition of a hypo *d*-phase (TiO₂) in the carbonaceous support material, improves considerably catalytic

activity of the electrocatalysts. Carbon nanotubes have been shown as the most perspective support material in electrocatalysis. Co-based electrocatalysts deposited on activated MWCNTs containing TiO_2 have shown the best performances for hydrogen evolution reactions. The activity of this electrocatalyst exceeds that of the traditional Pt/VulcanXC-72 electrocatalyst.

Acknowledgments The research presented in this study is result of perennial collaboration of the Faculty of Technology and Metallurgy Skopje, University “Sts. Cyril and Methodius” with the Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Science.

Special thank to Prof. Milan Jakšić, University of Belgrade and to Prof. Svetomir Hadži Jordanov, Faculty of Technology and Metallurgy, Skopje.

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Chapter 59

Materials for Photovoltaic Applications

Doriana Dimova-Malinovska

Abstract Energy priorities are changing nowadays. As mankind will probably have to face energy crisis, factors such as energy independence, energy security, stability of energy supply and the variety of energy sources become much more vital these days. Photovoltaics is exceptional compared to other renewable sources of energy due to its wide opportunity to gain energetic and environmental benefits. An overview of the present state of knowledge of the materials aspects of photovoltaic cells will be given, and new semiconductor materials, including nanomaterials, with potential for application in photovoltaic devices will be identified.

Keywords Photovoltaics · Solar cells · Nanomaterials

Introduction

Electricity from the sun (photovoltaics PV) is considered as one of the most prospective and environmental-friendly source of energy. Because of the universal availability of solar energy and the immense potential of direct conversion of solar radiation into electricity to use, it was predicted that photovoltaic will become a very serious alternative for fossil fuels in the nearest future. PV-generated electricity is totally environmental-friendly. This means that during its production no pollutants are release into the air and therefore PV constitutes the safest device for producing energy. Taking these factors into account it is obvious that photovoltaic is the most effective way to ensure a stable supply of clean energy in developed as well as in developing countries. That's why a huge number of present environmental programs is dedicated to PV applications both at international and local level. Not only the market development is crucial from the point of view of

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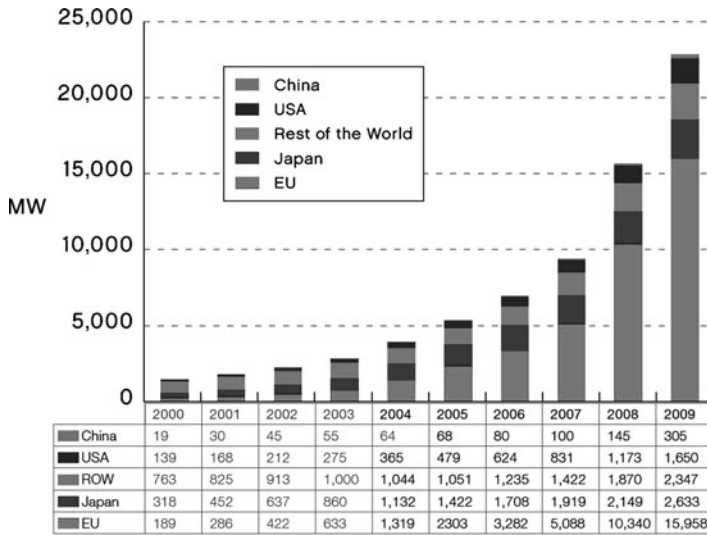


Fig. 59.1 Historical development of the world's cumulative PV power installed in main geographies [1]

these kind of programs. It is also necessary to lead research and development activity in photovoltaic area.

From the first space applications to the planned Gigawatt (GW) systems, more than 50 years have passed. The last decade has seen PV technology emerging as a potentially major technology for power generation in the world (Fig. 59.1). The robust and continuous growth experienced in the last 10 years is expected to continue in the coming years. By the end of 2008, the world's cumulative PV power installed was approaching 16 GW and today almost 23 GW are installed globally which produce about 25 TWh of electricity on a yearly basis. Europe is leading the way with almost 16 GW of installed capacity in 2009, representing about 70% of the world's cumulative PV power installed at the end of 2009 while Japan (2.6 GW) and the US (1.6 GW) are following behind. China makes its entry into the TOP ten of the world PV markets and is expected to become a major player in the coming years.

Solar Spectrum

Solar radiative energy has its origin in nuclear fusion reactions in the sun. The resulting energy is emitted mainly as electromagnetic radiation in the spectral range of 0.2–3 μm (Fig. 59.2). The intensity of solar radiation in free space at the average distance between the earth and the sun is called the solar constant and has a value of 1,353 W/m^2 . The spectral distribution of the solar radiation which reaches the earth can be approximated by that of a black body at a temperature of 5,800 K.

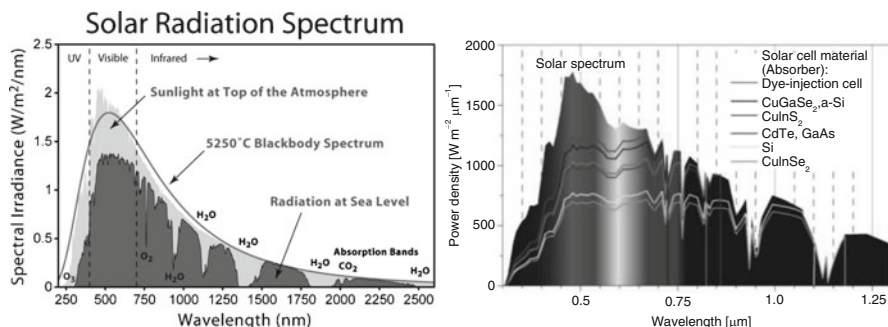


Fig. 59.2 Solar spectrum on the earth surface (*left*) and the sensitivity of different type solar cells (*right*) [2]

However, there are sufficient deviations from this idealized spectrum to make it desirable to use more exact data.

The sunlight is absorbed and scattered when it passes through the atmosphere on its way to the earth's surface. Basically, three sources of atmospheric absorption are important: atmospheric gases (O_2 , N_2 , etc.), water vapour, and dust. The degree of attenuation is defined as the air mass (AM).

AM0 describes the solar spectrum outside the earth's atmosphere, AM1 (925 W/m^2) describes the situation at the earth's surface when the sun is at its zenith, and AM1.5 that when the sun is 45° above the horizon. This spectrum (844 W/m^2) is used to characterize the solar energy for terrestrial conditions.

However, a standardized value of $1,000 \text{ W/m}^2$ is used for simplicity in the characterization of solar cells and modules. The solar spectrum under different conditions is shown in Fig. 59.2 (left) [2]. Figure 59.2 (right) illustrates the spectral sensitivity of different types of solar cells on the background of the solar spectrum at the earth surface. It can be seen that the different materials used for solar cell fabrication can transfer only a part of the sun spectrum into electricity.

Materials for Solar Cell Applications

Photovoltaic (PV) is a marriage of two words: “photo”, meaning light, and “voltaic” meaning electricity. Photovoltaic technologies are used to convert solar energy (light) into electricity. Photovoltaics can be used in many fields. Generally one distinguishes between on-grid and off-grid applications. On-grid applications are delivering either only the surplus energy (electricity not consumed by the producer) or all the produced electricity into the grid. Typical on-grid applications are roof top systems on private houses (average size 3 kW). Other on-grid applications are larger plants with capacities of several megawatt. Off-grid systems have no connection to an electricity grid. Off-grid systems are contributing to rural electrification in many developing countries. PV is also used for many industrial

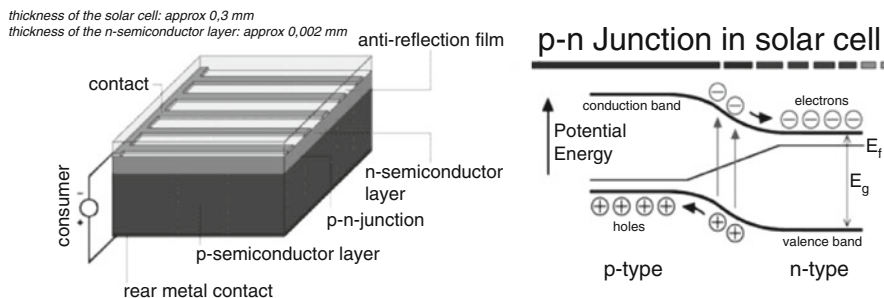


Fig. 59.3 Schemes of a solar cell and a p-n junction

applications where grid connection is not possible (e.g. telecommunication). Consumer goods are another application where PV can be used (e.g. pocket calculators).

Solar cells are in fact large area semiconductor diodes (Fig. 59.3). Due to photo-voltaic effect the energy of the light (the energy of the photons) converts into an electrical current. At the p-n junction, an electric field is built up which leads to the separation of the charge carriers (electrons and holes). On the incidence of a photon stream onto the semiconductor material, the electrons are released, if the photon energy is sufficient. The contact to a solar cell is realized by metal contacts. If the circuit is closed, i.e. an electrical load is connected, there is a direct current flow.

A number of properties are required for candidate PV materials and device structures. The most essential ones concern photonic and electrical conditions:

1. Strong light absorption over a large spectral range. This property implies that a tunable band gap is desirable. The peak of absorption should be at 1.4–1.5 eV for optimal efficiency.
2. Good collection properties for both minority and majority carriers, a low carrier recombination loss (in the bulk, at grain boundaries and at the front and back surfaces), and a large luminescence yield.
3. Low cost, so thin film structures are preferable.
4. Stability as functions of both time and illumination conditions (stable metal contacts, resistance to corrosion).
5. High abundance of the source materials (for large-scale production).
6. Environment friendly technology.

PV technologies can presently be divided into three categories:

1. Flat crystalline silicon plates (single crystal and multicrystalline silicon);
2. Si-based thin films (polycrystalline silicon, amorphous silicon and its tetrahedral alloys, protocrystalline and microcrystalline silicon) and polycrystalline films of CdTe, CuIn(Ga)Se₂;
3. GaAs and a multijunction approach using III–V alloy material combinations; a number of concentrator approaches (including Si, GaAs, GaAlAs).

The main technological goals are: (i) to increase the efficiency of solar cells via increasing the light absorption (applying antireflection coatings (ARC), a tunable

band gap E_g , tandem multilayer conception), decreasing of the recombination rate, applying of plasmonic effects (quantum dots), up- and down- conversion and (ii) to decrease the price (thin Si wafers (100 μm), thin films technology, non vacuum technology).

Crystalline (c-Si) and multicrystalline (mc-Si) silicon based technologies dominate today's PV production. Si is presently the most mature and best studied candidate for terrestrial PV applications. It offers several advantages over other PV materials, including abundance, an established technology base, high material quality and stability, and good surface passivation characteristics. The obvious disadvantages are the indirect band gap and the current high processing cost for silicon material and devices. Hence, research continues both in improving silicon and in studying and developing other Si-based technologies (e.g. thinner Si wafers of 100–50 μm).

Today, the most efficient c-Si solar cell is the “passivated emitter and rear locally diffused” (PERL) structure (Fig. 59.4), showing an efficiency of about 24.4% [3, 4]. The main features of this cell are: a front surface reflection loss reduced by inverted pyramids, a high quality emitter-diffusion profile, a high quality passivating thermal oxide on the front and back surfaces to reduce surface recombination losses, small front-contact fingers, and a p^+ diffusion layer localized at the back to reduce the contact contribution to total recombination losses. A similar approach has been applied for a multicrystalline silicon solar cell, where a “honeycomb” front surface texturing is utilized. As a result, multicrystalline Si solar cells with 19.8% efficiency have been produced [5].

Amorphous Silicon solar cells. a-Si:H is a non-crystalline solid, lacking long-range periodic ordering of its constituting atoms. However, it does have local order on an atomic scale. This short-range order is directly responsible for the observation of semiconductor properties such an optical absorption edge and a thermally activated

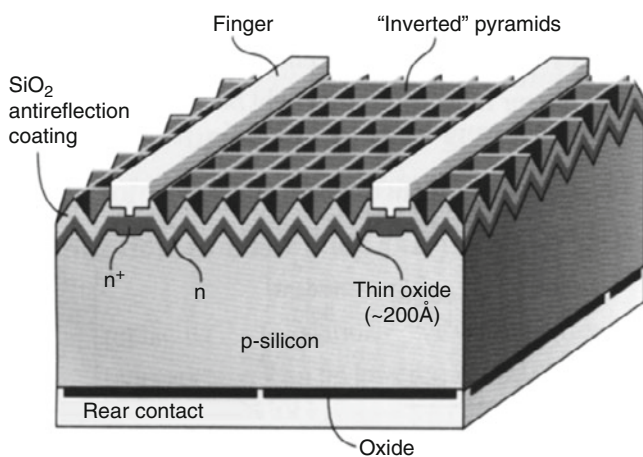


Fig. 59.4 Structure of PERL cells: (a) c-Si with a pyramidal textured surface [4]

Fig. 59.5 A typical amorphous silicon cell employs a p-i-n design, in which an intrinsic layer (i-layer) is sandwiched between a p-layer and an n-layer

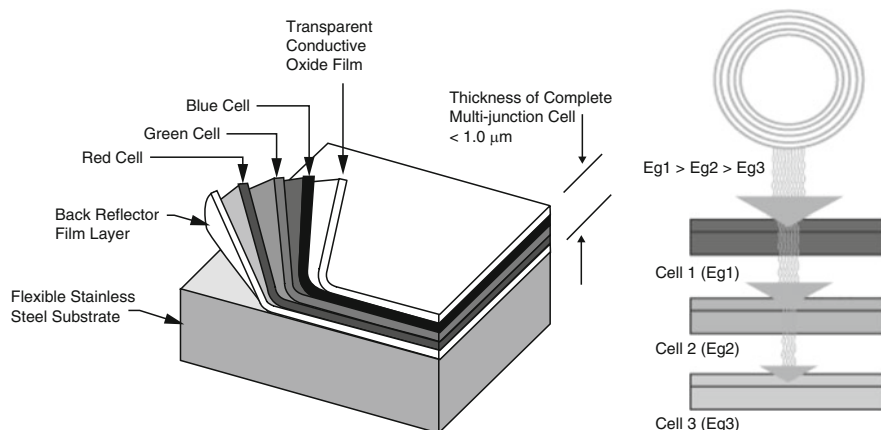
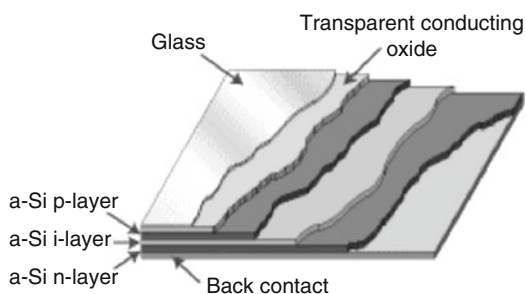


Fig. 59.6 A multijunction device is a stack of individual single-junction cells in descending order of the bandgap E_g

electrical conductivity. It lies on the borderline between amorphous and polycrystalline phases. A typical amorphous silicon cell employs a p-i-n design where an intrinsic layer (i-layer) is sandwiched between a p- and a n-layers (Fig. 59.5).

Flexible solar cells are based on a sophisticated multi-layer amorphous silicon thin-film solar cell stack. This spectrum-splitting cell, shown schematically in Fig. 59.6, is constructed of separate p-i-n type a-Si:H solar sub-cells, each with a different spectral response characteristic. This allows the cell to convert the different visible and near infrared wavelengths of sunlight with optimal efficiency. This increases the energy conversion efficiency of the multi-cell device and improves the performance stability. The multi-junction approach has resulted in world record efficiencies of 13% for this type of cells. Each of the nine thin film semiconductor layers that comprise the cell is sequentially deposited in separate plasma enhanced chemical vapour deposition (PECVD) chambers as the stainless steel substrate progresses through the machine.

Chalcopyrite solar cells (Fig. 59.7). Ternary chalcopyrite CuInSe_2 (CIS) and its modification Cu(In,Ga)Se (CIGS) were the first thin film materials to achieve

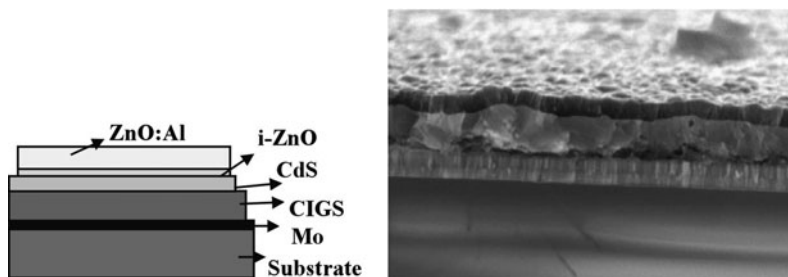
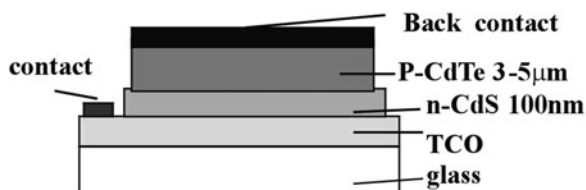


Fig. 59.7 Scheme of a typical CIS solar cell (*left*) and CIS cross section micrograph (*right*)

Fig. 59.8 Scheme of a typical CdTe-/CdS solar cell



solar cells with 10% efficiency. The device stability, together with improvements of the cell efficiency, has attracted the interest of researchers and industry in a CIS-based PV technology. The maximum efficiency reported to date is 19.19% for 50×50 mm test cells [6]. For modules on flexible Ti foil substrates, efficiencies of 17.9% [7] and 13.9% (for 90 cm^2) [8] were reported.

Cadmium telluride solar cells (Fig. 59.8). Many of the basic properties of CdTe make it an ideal material for thin film solar cells. For example:

- Its energy gap is direct; its value of 1.45 eV supports maximal conversion efficiency;
- It may be doped n- or p-type; the preparation of stoichiometric compounds can be achieved easily in the production process;
- CdTe thin films can be deposited at high rates by various methods: sublimation/condensation (S), close-spaced sublimation (CSS), chemical spraying (CS), electro-deposition (ED), screen printing (SP), chemical vapour deposition (CVD), and sputtering. A disadvantage of CdTe solar cells concerns environmental and safety problems, since the product contains Cd, a toxic element. It has been shown, however, that modules can be produced under normal industrial risk conditions, and suitable techniques for waste treatment and recycling of modules are available [9].

Recently, semiconductor nanowires grown by the vapour–liquid–solid (VLS) process have been shown to be a highly promising material system for photovoltaic devices [10–12]. Owing to their single-crystalline nature, they have the potential for high performance solar modules. The template-assisted VLS growth of

highly ordered, single-crystalline nanopillars on aluminium substrates has been demonstrated as a highly versatile approach for the fabrication of novel solar-cell modules. This approach could simplify the fabrication process of photovoltaics based on crystalline compound semiconductors while enabling the exploration of new device structures.

To explore the potential of the proposed strategy, highly ordered, single-crystalline n-CdS nanopillars have been synthesized [13] directly on an aluminium substrate; they are embedded in a thin p-CdTe film as the optical absorption material (Fig. 59.9). Conventional thin-film photovoltaics rely on the optical generation of electron–hole pairs (EHPs) and their separation by an internal electric field, as shown in Fig. 59.9 a. Among different factors, the absorption efficiency of the material and the minority carrier lifetime often determine the energy conversion efficiency [14].

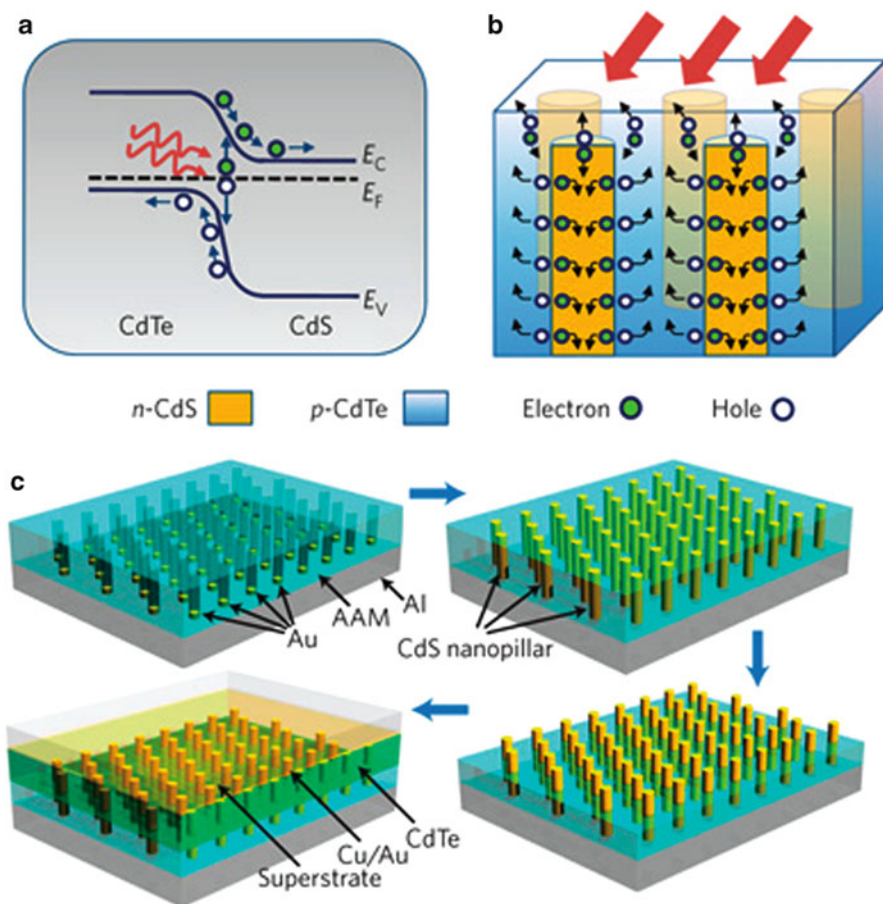


Fig. 59.9 CdS/CdTe solar cell with nanopillars: (a) energy band diagram of a CdTe/CdS heterojunction, (b) cross-sectional schematic diagram, illustrating the enhanced carrier collection efficiency, (c) fabrication process flow [13]

In this regard, simulation studies have previously shown the advantages of three-dimensional (3D) cell structures, such as those using coaxially doped vertical nanopillar arrays, in improving the photocarriers separation and their collection by orthogonalizing the direction of light absorption and electron–hole (EH) separation (Fig. 59.9 b). This type of structure is particularly advantageous when the thickness of the device is comparable to the optical absorption depth and the bulk minority carrier lifetime is relatively short. Under such circumstances, the optical generation of carriers is significant in the entire device volume; the 3D structure facilitates an efficient EH separation and collection [13].

Figure 59.10 (left) shows the I–V characteristics of a typical cell under different illumination intensities P ranging from 17 to 100 mW cm^{-2} (AM 1.5 G). Specifically, an efficiency $\eta = 6\%$ with an open circuit voltage $V_{oc} = 0.62 \text{ V}$, a short circuit current density $J_{sc} = 21 \text{ mA cm}^{-2}$ and a fill factor $FF = 0.43$ under AM1.5 G illumination is obtained. The dependency of the performance characteristics on the illumination intensity is shown in Fig. 59.10 (right). As expected, J_{sc} exhibits a near-linear dependency on the intensity because in this regime the photocurrent is proportional to the photon flux for a constant minority carrier lifetime. On the other hand, V_{oc} increases only slightly from 0.55 to 0.62 V with a linear increase of J_{sc} , which we attribute to a slight thermal heating of the device. As the efficiency of a solar cell is expressed as $\eta = V_{oc} J_{sc} FF / P$ and FF slightly decreases with light intensity, the efficiency is about 6% and shows a minimal dependence on the illumination intensity as shown in Fig. 59.10 (right). It should be noted that this modest efficiency is obtained without the use of an antireflective surface coating or concentrators.

For some years now silicon nanowire carpets receive growing interest for solar cell applications [15–17]. Independent of the nanowire preparation method two designs of nanowire solar cells are under consideration with the pn-junction either radial or axial (Fig. 59.11). In the radial case the p-n-junction covers the whole outer cylindrical surface of the nanowires. This is achieved either by gas doping [15, 17] or by CVD deposition of a shell doped oppositely to the wire [11, 18, 19].

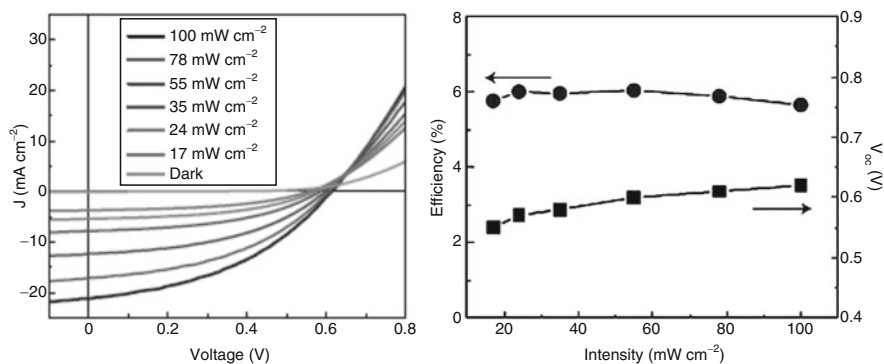


Fig. 59.10 *Left*: I–V characteristics and *right*: dependence of the efficiency and V_{oc} on the light intensity of a n-CdS/CdTe solar cell with CdS nanopillars [13]

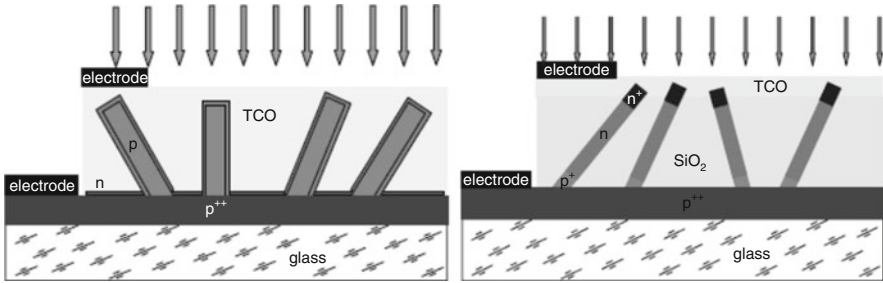


Fig. 59.11 Scheme of nanowire solar cells with radial (*left*) or axial (*right*) pn-junctions

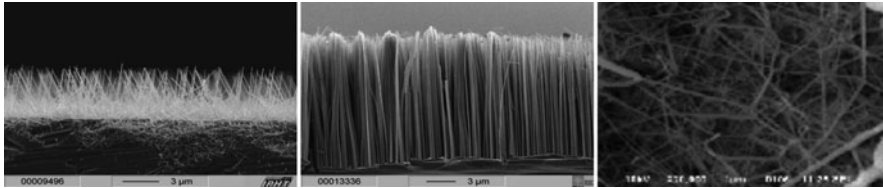
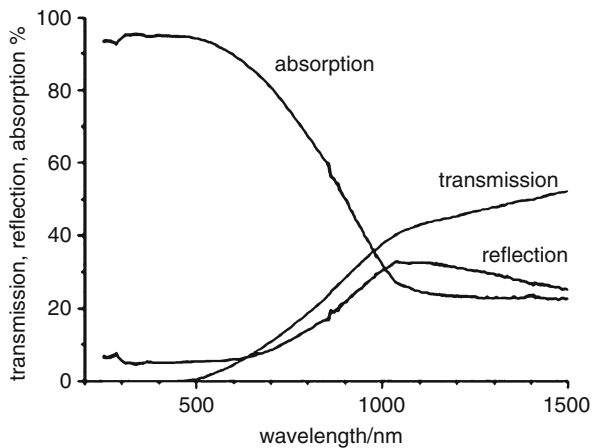


Fig. 59.12 SEM images of nanowire carpets grown on multicrystalline silicon layers on glass by the VLS method [20] (*left*), obtained by etching of a Si wafer [20] (*middle*) and by glow discharge processes [21] (*right*)

Fig. 59.13 Optical transmission, reflection, and absorption of a nanowire carpet etched into a 2.7 μm thick multicrystalline silicon film [20]

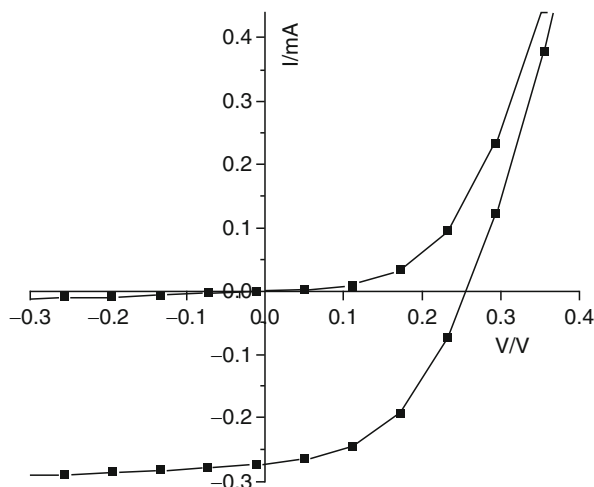


In the axial variant the p/n-junction cuts the nanowire in two cylindrical parts. Figure 59.12 demonstrates SEM images of the Si films with nanowires deposited by different methods [20, 21].

The optical reflection, transmission, and absorption of a 2.7 μm thick nanowire carpet etched into a laser crystallized Si layer are shown in Fig. 59.13.

Typical for these devices is the very low reflectivity of about 5% up to a wavelength of 800 nm. This demonstrates the perfect antireflection properties of

Fig. 59.14 I–V-curve dark (curve 1) and illuminated (curve 2) by AM1.5 of a cell consisting of n-doped nanowires grown by the VLS method onto a p-doped wafer [20]



the wire carpet. The transmission is low as well so that a 3 μm thick carpet absorbs nearly all the incident visible light. As a consequence, nanowire carpet acts as perfect light trapping structures. Figure 59.14 shows I–V-curves of a cell consisting of n-doped nanowires grown on a p-doped ($2 \cdot 10^{15} \text{ cm}^{-3} \text{ B}$) wafer. The open circuit voltage V_{oc} of 250 mV is rather low. Due to contacting by tips or transparent conductive foils the current and the fill factor is low. Open issues are the surface passivation of the nanowires, filling the space between the nanowires for stabilization purposes, and contacting.

Potential of Solar Cells and Modules

Table 59.1 gives data about the efficiency and cost potential of different types of solar modules. It can be seen that modules on the base of c-Si and mc-Si demonstrate the highest efficiency with comparable cost.

Although reliable PV systems are commercially available and widely deployed, further development of the PV technology is crucial to enabling PV to become a major source of electricity. The current price of PV systems is low for PV electricity to compete with the price of peak power grid-connected applications and with alternatives like diesel generators in stand-alone applications, but can not yet rival consumer or wholesale electricity prices. A major further reduction of turn-key system prices is therefore needed and fortunately possible. Further development is also required to enable the European PV industry to maintain and strengthen its position on the global market, which is highly competitive and characterized by rapid innovation.

Table 59.2 gives an indication of where PV was 30 years ago, where it stands today and what it could realistically achieve over the next 20–50 years.

Current turn-key system prices may vary from ~ 4 to ~ 8 €/W, depending on the type of system (roof-top, building-integrated, ground-based), size, country,

Table 59.1 Efficiency and cost potential of solar modules [22]

	c-Si	mc-Si	CdTe	CIS	a-Si:H	aSi:H/ μ c-Si
Efficiency achieved by industry, %	19.6	18.5	11.1	12	7	9
Efficiency achievable, %	>20	20	18	18	10	15
Manufacturing cost, €/W	2	1.5-2.0	0.67	2	1	1
Expected cost as from 2020, €/W	<0.5	<0.5	<0.3	<0.3	<0.3	<0.3

Table 59.2 Expected development of PV technology over the coming decades [22]

	1980	Today	2015	2030	Long term potential
Typical turn-key system price (2006 €/W _p , excl. VAT)	>30	5	2.5	1	0.5
Typical electricity generation costs southern Europe (2006 €/kWh)	>2	0.30	0.15 (competitive with retail electricity)	0.06 (competitive with wholesale electricity)	0.03
Typical commercial flat-plate module efficiencies	Up to 8%	Up to 15%	Up to 20%	Up to 25%	Up to 40%
Typical commercial concentrator module efficiencies	(~10%)	Up to 25%	Up to 30%	Up to 40%	Up to 60%
Typical system energy pay-back time southern Europe [years]	>10	2	1	0.5	0.25

and other factors. The figure of 5 €/W_p, however, is considered representative. Similarly, prices in 2015 may range between ~2 and ~4 €/W_p.

The overall aim of short-term research is to reduce the price of PV electricity to be comparable to the retail prices of electricity for small consumers in southern Europe by 2015. Continued price reduction after 2015 implies that this situation will apply to most of Europe by 2020. This state, where prices are comparable, is known as ‘grid parity’. Larger systems and ground-based PV power plants that are not connected directly to end-consumers will generally need to produce electricity at lower prices before they can be said to have reached ‘grid parity’.

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