



# Organic Electronics

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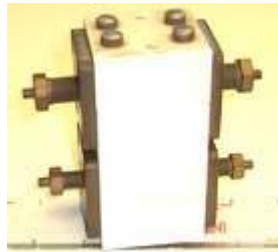
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## Introduction



Melanin voltage-controlled switch, an "active" organic polymer electronic device from 1974.

**Organic electronics, plastic electronics or polymer electronics**, is a branch of electronics that deals with conductive polymers, plastics, or small molecules. It is called 'organic' electronics because the polymers and small molecules are carbon-based, like the molecules of living things. This is as opposed to traditional electronics (or metal electronics) which relies on inorganic conductors such as copper or silicon.

Polymer electronics are laminar electronics, a category that also includes transparent electronic package and paper based electronics.

In addition to organic charge transfer complexes, technically, electrically conductive polymers are mostly derivatives of polyacetylene black (the "simplest melanin"). Examples include polyacetylene (PA; more specifically iodine-doped trans-polyacetylene); polyaniline (PANI), when doped with a protonic acid; and poly(dioctyl-bithiophene) (PDOT).

## History

In 1862, Henry Letheby obtained a partly conductive material by anodic oxidation of aniline in sulfuric acid. The material was probably polyaniline. In the 1950s, it was discovered that polycyclic aromatic compounds formed semi-conducting charge-transfer complex salts with halogens. This finding indicated that organic compounds could carry current. High conductivity of 1 S/cm in linear backbone polymers (in an iodine-"doped" and oxidized polypyrrole black) was reported in 1963. Likewise, an actual organic-polymer electronic device was reported in the journal *Science* in 1974. This device is

now in the "Smithsonian Chips" collection of the American Museum of History (see figure).

However, Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa are often credited for the "discovery and development" of conductive polymers and were jointly awarded the Nobel Prize in Chemistry in 2000 for their 1977 report of similarly-oxidized and iodine-doped polyacetylene.

Conduction mechanisms in such materials involve resonance stabilization and delocalization of pi electrons along entire polymer backbones, as well as mobility gaps, tunneling, and phonon-assisted hopping.

Technology for plastic electronics on thin and flexible plastic substrates was developed at Cambridge University's Cavendish Laboratory in the 1990s. In 2000, Plastic Logic was spun out of Cavendish Laboratory to develop a broad range of products using the plastic electronics technology.

## **Features**

Conductive polymers are lighter, more flexible, and less expensive than inorganic conductors. This makes them a desirable alternative in many applications. It also creates the possibility of new applications that would be impossible using copper or silicon.

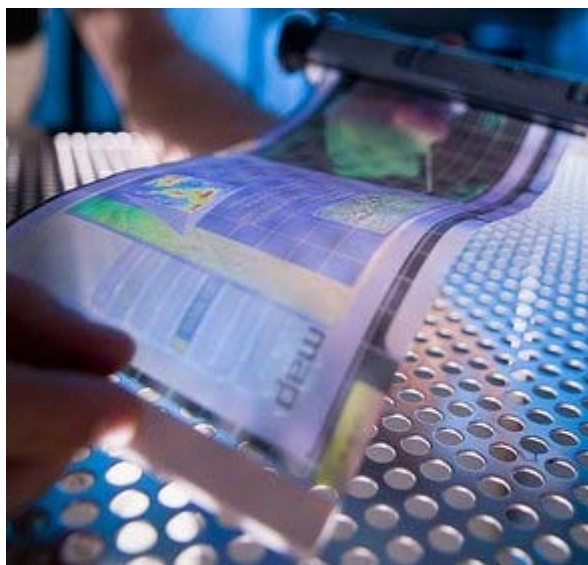
Organic electronics not only includes organic semiconductors, but also organic dielectrics, conductors and light emitters.

New applications include smart windows and electronic paper. Conductive polymers are expected to play an important role in the emerging science of molecular computers.

In general organic conductive polymers have a higher resistance and therefore conduct electricity poorly and inefficiently, as compared to inorganic conductors. Researchers currently are exploring ways of "doping" organic semiconductors, like melanin, with relatively small amounts of conductive metals to boost conductivity. However, for many applications, inorganic conductors will remain the only viable option.

Organic electronics can be printed.

## **Organic electronic devices**



### Organics-based flexible display

A 1972 paper in the journal *Science* proposed a model for electronic conduction in the melanins. Historically, melanin is another name for the various oxidized polyacetylene, polyaniline, and Polypyrrole "blacks" and their mixed copolymers, all commonly-used in present day organic electronic devices. For example, some fungal melanins are pure polyacetylene. This model drew upon the theories of Neville Mott and others on conduction in disordered materials. Subsequently, in 1974, the same workers at the Physics Department of The University of Texas M. D. Anderson Cancer Center reported an organic electronic device, a voltage-controlled switch.

Their material also incidentally demonstrated "negative differential resistance", now a hall-mark of such materials. A contemporary news article in the journal *Nature* noted this materials "strikingly high conductivity". These researchers further patented batteries, etc. using organic semiconductive materials. Their original "gadget" is now in the Smithsonian's collection of early electronic devices.

This work, like that of the decade-earlier report of high-conductivity in a polypyrrole, was "too early" and went unrecognized outside of pigment cell research until recently. At the time, few except cancer researchers were interested in the electronic properties of conductive polymers, in theory applicable to the treatment of melanoma.

## Plastic solar cells

Organic solar cells could cut the cost of solar power by making use of inexpensive organic polymers rather than the expensive crystalline silicon used in most solar cells. What's more, the polymers can be processed using low-cost equipment such as ink-jet printers or coating equipment employed to make photographic film, which reduces both capital and manufacturing costs compared with conventional solar-cell manufacturing.

Silicon thin film solar cells on flexible substrates allow a significant cost reduction of large-area photovoltaics for several reasons :

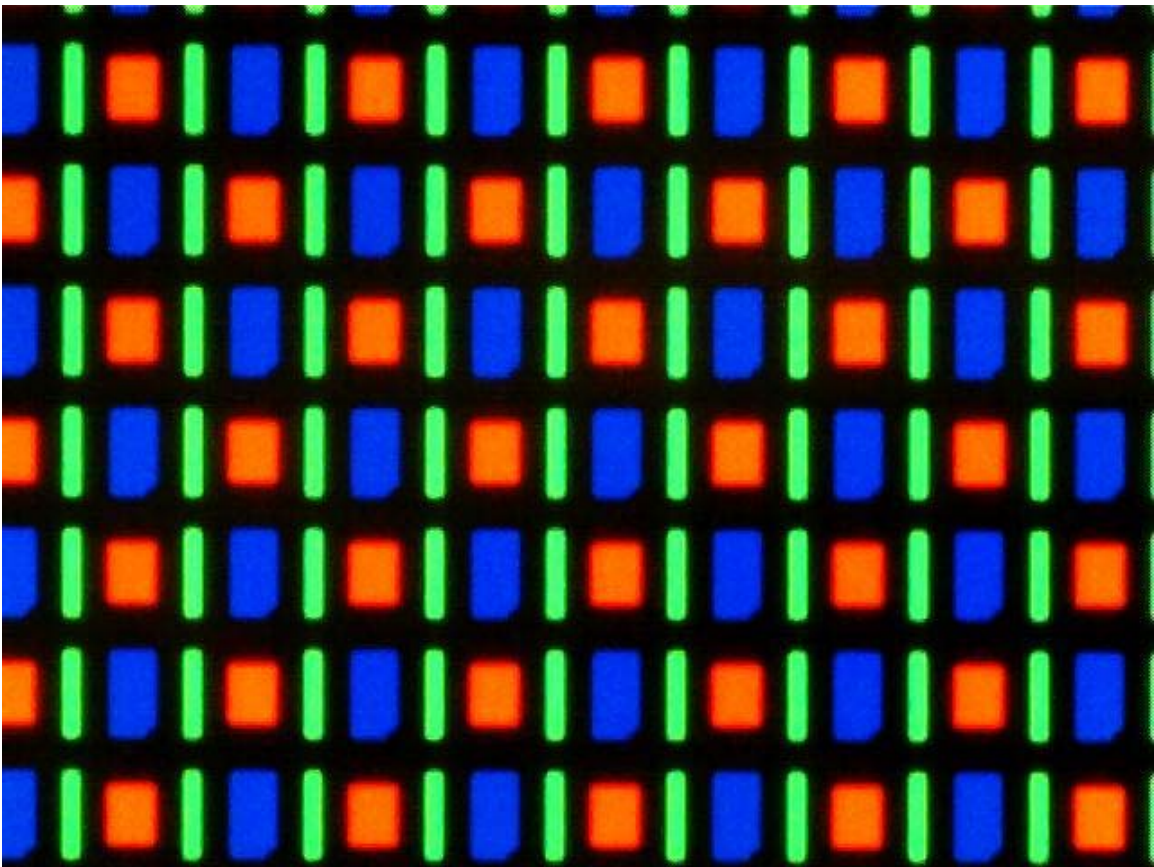
1. The so-called 'roll-to-roll'-deposition on flexible sheets is much easier to realize in terms of technological effort than deposition on fragile and heavy glass sheets.
2. Transport and installation of lightweight flexible solar cells also saves cost as compared to cells on glass.

Inexpensive polymeric substrates like polyethylene terephthalate (PET) or polycarbonate (PC) have the potential for further cost reduction in photovoltaics. Protomorphous solar cells prove to be a promising concept for efficient and low-cost photovoltaics on cheap and flexible substrates for large-area production as well as small and mobile applications.

One advantage of printed electronics is that different electrical and electronic components can be printed on top of each other, saving space and increasing reliability and sometimes they are all transparent. One ink must not damage another, and low temperature annealing is vital if low-cost flexible materials such as paper and plastic film are to be used. There is much sophisticated engineering and chemistry involved here, with iTi, Pixdro, Asahi Kasei, Merck, BASF, HC Starck, Hitachi Chemical and Frontier Carbon Corporation among the leaders.

## Chapter- 1

### Active-Matrix OLED



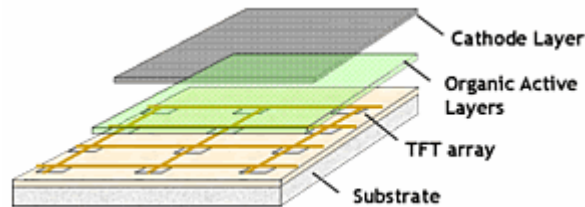
Magnified image of the AMOLED screen on the Google Nexus One smartphone using the RGBG system of the PenTile Matrix Family.

**Active-matrix OLED (Active-matrix organic light-emitting diode or AMOLED)** is a display technology for use in mobile devices and televisions. OLED describes a specific type of thin film display technology in which organic compounds form the electroluminescent material, and active matrix refers to the technology behind the addressing of pixels. AMOLED technology is currently used in mobile phone and media



players and continues to make progress towards low power, low cost and large size (for example 40 inch) for applications such as televisions.

## Technical



Schematic of an active matrix OLED display

An active matrix OLED display consists of a matrix of OLED pixels that generate light upon electrical activation that have been deposited or integrated onto a thin film transistor (TFT) array, which functions as a series of switches to control the current flowing to each individual pixel.

Typically, this continuous current flow is controlled by at least two TFTs at each pixel, one to start and stop the charging of a storage capacitor and the second to provide a voltage source at the level needed to create a constant current to the pixel and eliminating need for the very high currents required for passive matrix OLED operation.

TFT backplane technology is crucial in the fabrication of AMOLED displays. Two primary TFT backplane technologies, namely polycrystalline silicon (poly-Si) and amorphous silicon (a-Si), are used today in AMOLEDs. These technologies offer the potential for fabricating the active matrix backplanes at low temperatures (below 150°C) directly onto flexible plastic substrates for producing flexible AMOLED displays.

### AMOLED In-Cell Touch Panels

Manufacturers have developed in-cell touch panels, integrating the production of capacitive sensor arrays in the AMOLED module fabrication process. In-cell sensor AMOLED fabricators include AU Optronics and Samsung. Samsung has marketed their version of this technology as Super AMOLED.

## Advantages

- **Lower cost in the future:** OLEDs can be printed onto any suitable substrate by an inkjet printer or even by screen printing, theoretically making them cheaper to produce than LCD or plasma displays. However, fabrication of the OLED substrate is more costly than that of a TFT LCD, until mass production methods lower cost through scaleability.

- **Light weight & flexible plastic substrates:** OLED displays can be fabricated on flexible plastic substrates leading to the possibility of Organic light-emitting diode roll-up display being fabricated or other new applications such as roll-up displays embedded in fabrics or clothing. As the substrate used can be flexible such as PET. , the displays may be produced inexpensively.
- **Wider viewing angles & improved brightness:** OLEDs can enable a greater artificial contrast ratio (both dynamic range and static, measured in purely dark conditions) and viewing angle compared to LCDs because OLED pixels directly emit light. OLED pixel colours appear correct and unshifted, even as the viewing angle approaches 90 degrees from normal.
- **Better power efficiency:** LCDs filter the light emitted from a backlight, allowing a small fraction of light through so they cannot show true black, while an inactive OLED element does not produce light or consume power.
- **Response time:** OLEDs can also have a faster response time than standard LCD screens. Whereas LCD displays are capable of a 1 ms response time or less offering a frame rate of 1,000 Hz or higher, an OLED can theoretically have less than 0.01 ms response time enabling 100,000 Hz refresh rates.

Active-matrix OLED displays provide higher refresh rates than their passive-matrix OLED counterparts, and they consume significantly less power. This advantage makes active-matrix OLEDs well suited for portable electronics, where power consumption is critical to battery life.

The amount of power the display consumes varies significantly depending on the color and brightness shown. As an example, one commercial QVGA OLED display consumes 3 watts while showing black text on a white background, but only 0.7 watts showing white text on a black background.

## Disadvantages

- **Lifespan:** The biggest technical problem for OLEDs was the limited lifetime of the organic materials. In particular, blue OLEDs historically have had a lifetime of around 14,000 hours to half original brightness (five years at 8 hours a day) when used for flat-panel displays. This is lower than the typical lifetime of LCD, LED or PDP technology—each currently rated for about 60,000 hours to half brightness, depending on manufacturer and model. However, some manufacturers' displays aim to increase the lifespan of OLED displays, pushing their expected life past that of LCD displays by improving light outcoupling, thus achieving the same brightness at a lower drive current. In 2007, experimental OLEDs were created which can sustain  $400 \text{ cd/m}^2$  of luminance for over 198,000 hours for green OLEDs and 62,000 hours for blue OLEDs.



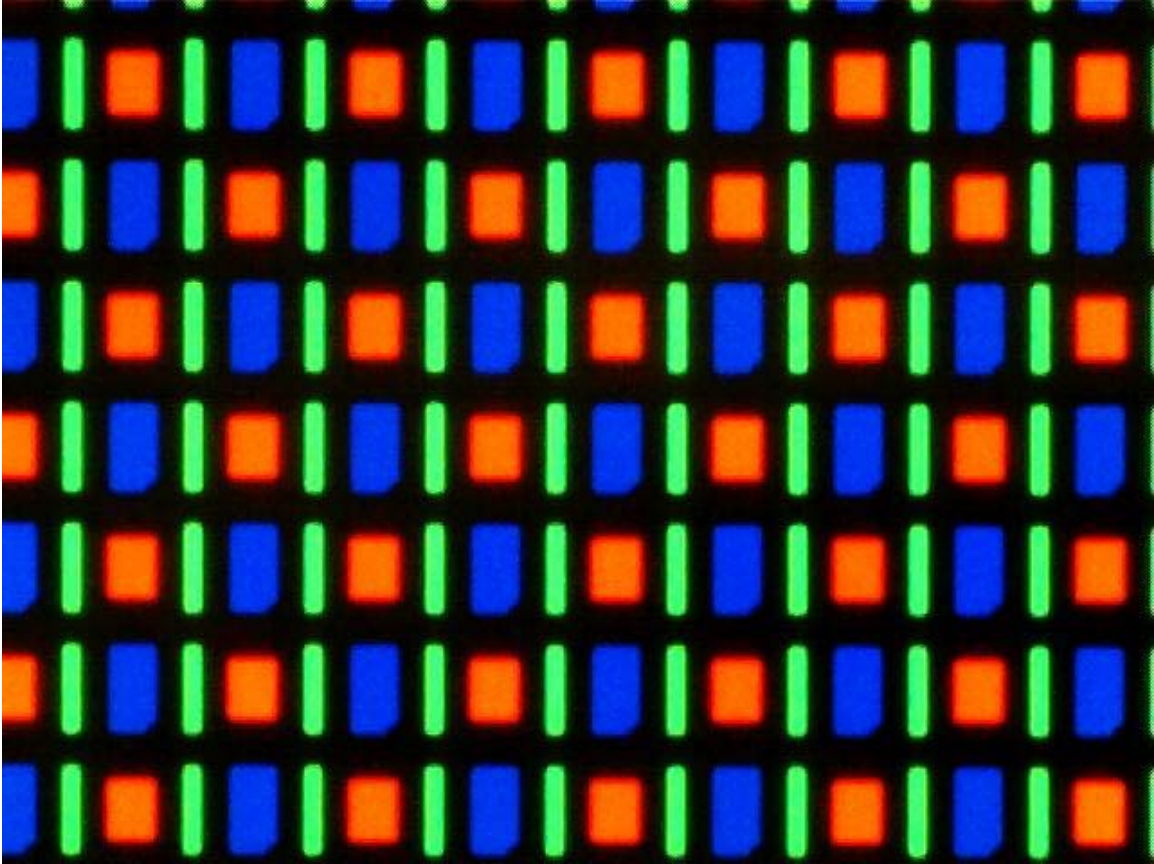
LEP display showing partial failure

- **Color balance issues:** Additionally, as the OLED material used to produce blue light degrades significantly more rapidly than the materials that produce other colors, blue light output will decrease relative to the other colors of light. This differential color output change will change the color balance of the display and is much more noticeable than a decrease in overall luminance. This can be partially avoided by adjusting colour balance but this may require advanced control circuits and interaction with the user, which is unacceptable for some users. In order to delay the problem, manufacturers bias the colour balance towards blue so that the display initially has an artificially blue tint, leading to complaints of artificial-looking, over-saturated colors. More commonly, though, manufacturers optimize the size of the R, G and B subpixels to reduce the current density through the subpixel in order to equalize lifetime at full luminance. For example, a blue subpixel may be 100% larger than the green subpixel. The red subpixel may be 10% smaller than the green.



An old OLED display showing wear

- **Efficiency of blue OLEDs:** Improvements to the efficiency and lifetime of blue OLED's is vital to the success of OLED's as replacements for LCD technology. Considerable research has been invested in developing blue OLEDs with high external quantum efficiency as well as a deeper blue color. External quantum efficiency values of 20% and 19% have been reported for red (625 nm) and green (530 nm) diodes, respectively. However, blue diodes (430 nm) have only been able to achieve maximum external quantum efficiencies in the range between 4% to 6%. By calculating the band gap ( $E_g = hc/\lambda$ ), it is clear that the shorter wavelength of the blue OLED results in a larger band gap at 2.9 eV. This leads to higher barriers, causing lower efficiency.
- **Water damage:** Water can damage the organic materials of the displays. Therefore, improved sealing processes are important for practical manufacturing. Water damage may especially limit the longevity of more flexible displays.



Magnified image of the AMOLED screen on the Google Nexus One smartphone using the RGBG system of the PenTile Matrix Family.

- **Outdoor performance:** As an emissive display technology, OLEDs rely completely upon converting electricity to light, unlike most LCDs which are to some extent reflective; e-ink leads the way in efficiency with  $\sim 33\%$  ambient light reflectivity, enabling the display to be used without any internal light source. The metallic cathode in an OLED acts as a mirror, with reflectance approaching 80%, leading to poor readability in bright ambient light such as outdoors. However, with the proper application of a circular polarizer and anti-reflective coatings, the diffuse reflectance can be reduced to less than 0.1%. With 10,000 fc incident illumination (typical test condition for simulating outdoor illumination), that yields an approximate photopic contrast of 5:1.
- **Power consumption:** While an OLED will consume around 40% of the power of an LCD displaying an image which is primarily black, for the majority of images it will consume 60–80% of the power of an LCD - however it can use over three times as much power to display an image with a white background such as a document or website. This can lead to disappointing real-world battery life in mobile devices. Websites and tools exist to help disappointed mobile phone users display a black background in places where it would normally be white. For

example, the mobile Google search engine can now be used in black to save battery power by using a custom version called Black Google Mobile.

- **Screen burn-in:** Unlike displays with a common light source, the brightness of each OLED pixel fades depending on the content displayed. The varied lifespan of the organic dyes can cause a discrepancy between red, green, and blue intensity. This leads to image persistence, also known as burn-in.

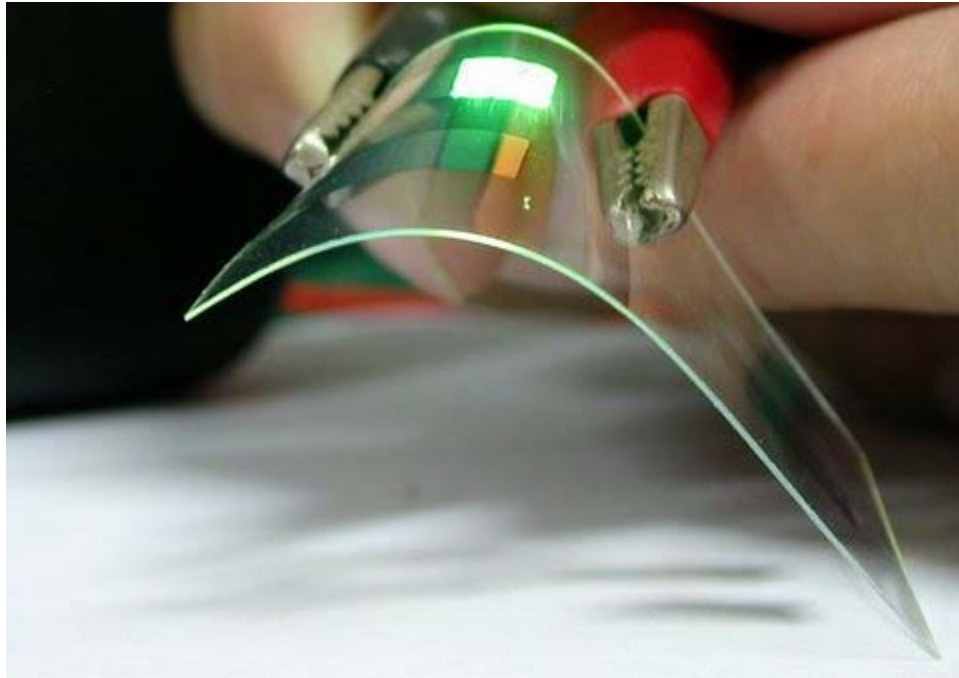
AMOLED displays may be difficult to view in direct sunlight compared to LCD displays. Samsung's Super AMOLED technology addresses this issue by reducing the size of gaps between layers of the screen.

The organic materials used in AMOLED displays are prone to degradation over a period of time. However, technology has been developed to compensate for material degradation.

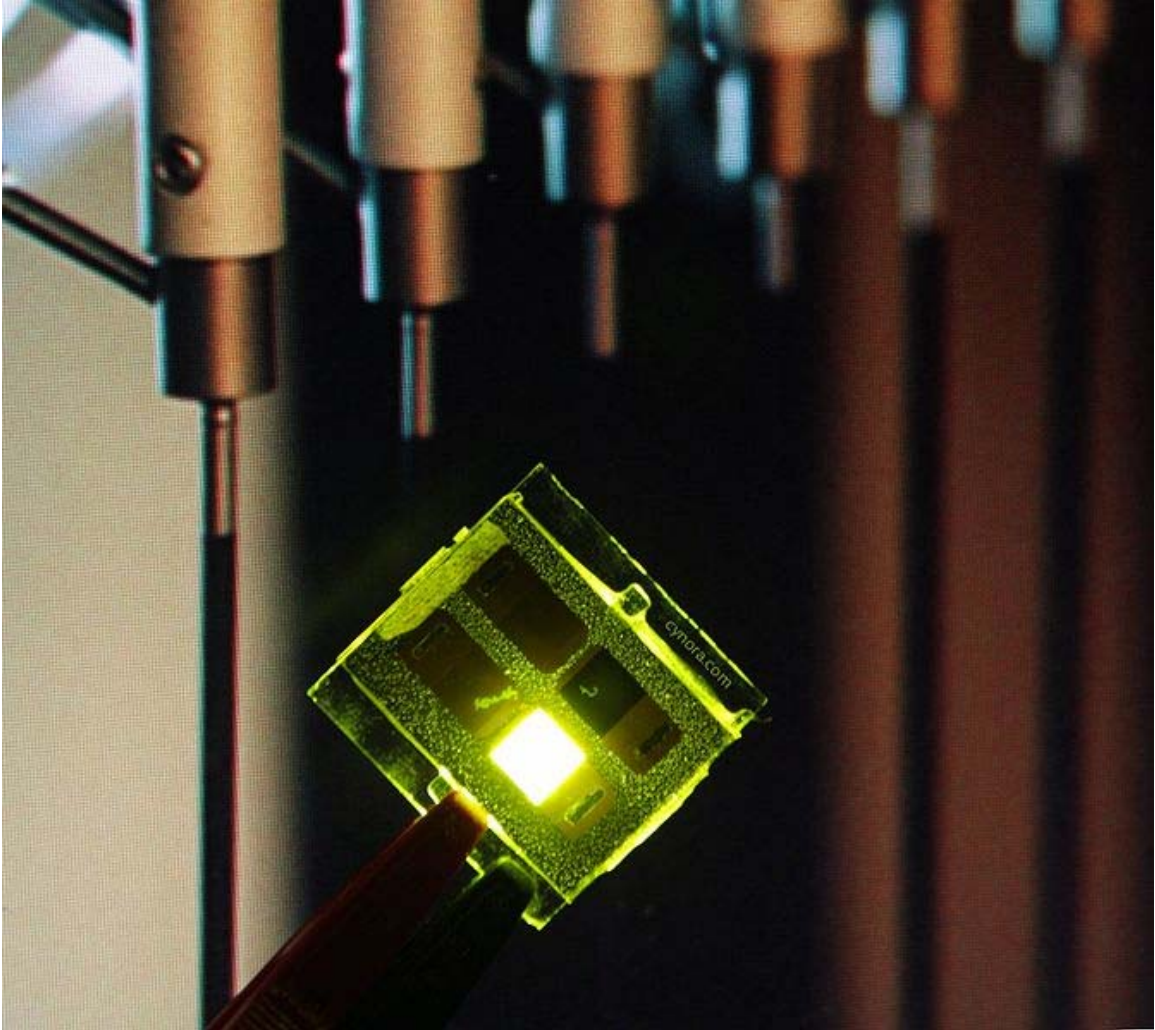
The current demand for AMOLED screens is high but production rate is slow until new factories are established and begin more production in 2011. Thus many smartphone models such as those from HTC and even some of Samsung's own cannot keep up with the high demand in AMOLED screens for long and turns to Sony's Super LCD technology.

Chapter- 2

## Organic Light-Emitting Diode



Demonstration of a flexible OLED device



A green emitting OLED device





Sony XEL-1, the world's first OLED TV.

An **organic light emitting diode (OLED)** is a light-emitting diode (LED) in which the emissive electroluminescent layer is a film of organic compounds which emit light in response to an electric current. This layer of organic semiconductor material is situated between two electrodes. Generally, at least one of these electrodes is transparent.

OLEDs are used in television screens, computer monitors, small, portable system screens such as mobile phones and PDAs, watches, advertising, information and indication. OLEDs are also used in light sources for general space illumination and in large-area light-emitting elements. Due to their comparatively early stage of development, they typically emit less light per unit area than inorganic solid-state based LED point-light sources.

An OLED display functions without a backlight. Thus, it can display deep black levels and can also be thinner and lighter than established liquid crystal displays. Similarly, in low ambient light conditions such as dark rooms, an OLED screen can achieve a higher contrast ratio than an LCD screen using either cold cathode fluorescent lamps or the more recently developed LED backlight.

There are two main families of OLEDs: those based upon small molecules and those employing polymers. Adding mobile ions to an OLED creates a Light-emitting Electrochemical Cell or LEC, which has a slightly different mode of operation.

OLED displays can use either passive-matrix (PMOLED) or active-matrix addressing schemes. Active-matrix OLEDs (AMOLED) require a thin-film transistor backplane to switch each individual pixel on or off, and can make higher resolution and larger size displays possible.

## History

The first observations of electroluminescence in organic materials were in the early 1950s by A. Bernanose and co-workers at the Nancy-Université, France. They applied high-voltage alternating current (AC) fields in air to materials such as acridine orange, either deposited on or dissolved in cellulose or cellophane thin films. The proposed mechanism was either direct excitation of the dye molecules or excitation of electrons.

In 1960, Martin Pope and co-workers at New York University developed ohmic dark-injecting electrode contacts to organic crystals. They further described the necessary energetic requirements (work functions) for hole and electron injecting electrode contacts. These contacts are the basis of charge injection in all modern OLED devices. Pope's group also first observed direct current (DC) electroluminescence under vacuum on a pure single crystal of anthracene and on anthracene crystals doped with tetracene in 1963 using a small area silver electrode at 400V. The proposed mechanism was field-accelerated electron excitation of molecular fluorescence.

Pope's group reported in 1965 that in the absence of an external electric field, the electroluminescence in anthracene crystals is caused by the recombination of a thermalized electron and hole, and that the conducting level of anthracene is higher in energy than the exciton energy level. Also in 1965, W. Helfrich and W. G. Schneider of the National Research Council in Canada produced double injection recombination electroluminescence for the first time in an anthracene single crystal using hole and electron injecting electrodes, the forerunner of modern double injection devices. In the same year, Dow Chemical researchers patented a method of preparing electroluminescent cells using high voltage (500–1500 V) AC-driven (100–3000 Hz) electrically-insulated one millimetre thin layers of a melted phosphor consisting of ground anthracene powder, tetracene, and graphite powder. Their proposed mechanism involved electronic excitation at the contacts between the graphite particles and the anthracene molecules.

Device performance was limited by the poor electrical conductivity of contemporary organic materials. However this was overcome by the discovery and development of highly conductive polymers.

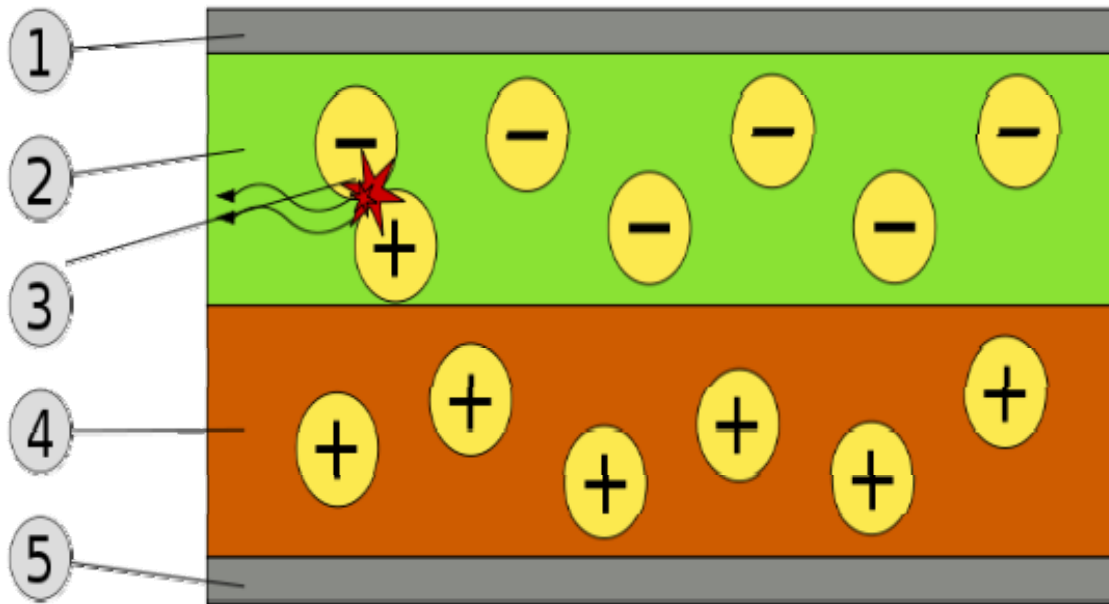
Electroluminescence from polymer films was first observed by Roger Partridge at the National Physical Laboratory in the United Kingdom. The device consisted of a film of

poly(n-vinylcarbazole) up to 2.2 micrometres thick located between two charge injecting electrodes. The results of the project were patented in 1975 and published in 1983.

The first diode device was reported at Eastman Kodak by Ching W. Tang and Steven Van Slyke in 1987. This device used a novel two-layer structure with separate hole transporting and electron transporting layers such that recombination and light emission occurred in the middle of the organic layer. This resulted in a reduction in operating voltage and improvements in efficiency and led to the current era of OLED research and device production.

Research into polymer electroluminescence culminated in 1990 with J. H. Burroughes *et al.* at the Cavendish Laboratory in Cambridge reporting a high efficiency green light-emitting polymer based device using 100 nm thick films of poly(p-phenylene vinylene).

## Working principle



Schematic of a bilayer OLED: 1. Cathode (-), 2. Emissive Layer, 3. Emission of radiation, 4. Conductive Layer, 5. Anode (+)

A typical OLED is composed of a layer of organic materials situated between two electrodes, the anode and cathode, all deposited on a substrate. The organic molecules are electrically conductive as a result of delocalization of pi electrons caused by conjugation over all or part of the molecule. These materials have conductivity levels ranging from insulators to conductors, and therefore are considered organic semiconductors. The highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of organic semiconductors are analogous to the valence and conduction bands of inorganic semiconductors.

Originally, the most basic polymer OLEDs consisted of a single organic layer. One example was the first light-emitting device synthesised by J. H. Burroughes *et al.*, which involved a single layer of poly(p-phenylene vinylene). However multilayer OLEDs can be fabricated with two or more layers in order to improve device efficiency. As well as conductive properties, different materials may be chosen to aid charge injection at electrodes by providing a more gradual electronic profile, or block a charge from reaching the opposite electrode and being wasted. Many modern OLEDs incorporate a simple bilayer structure, consisting of a conductive layer and an emissive layer.

During operation, a voltage is applied across the OLED such that the anode is positive with respect to the cathode. A current of electrons flows through the device from cathode to anode, as electrons are injected into the LUMO of the organic layer at the cathode and withdrawn from the HOMO at the anode. This latter process may also be described as the injection of electron holes into the HOMO. Electrostatic forces bring the electrons and the holes towards each other and they recombine forming an exciton, a bound state of the electron and hole. This happens closer to the emissive layer, because in organic semiconductors holes are generally more mobile than electrons. The decay of this excited state results in a relaxation of the energy levels of the electron, accompanied by emission of radiation whose frequency is in the visible region. The frequency of this radiation depends on the band gap of the material, in this case the difference in energy between the HOMO and LUMO.

As electrons and holes are fermions with half integer spin, an exciton may either be in a singlet state or a triplet state depending on how the spins of the electron and hole have been combined. Statistically three triplet excitons will be formed for each singlet exciton. Decay from triplet states (phosphorescence) is spin forbidden, increasing the timescale of the transition and limiting the internal efficiency of fluorescent devices. Phosphorescent organic light-emitting diodes make use of spin-orbit interactions to facilitate intersystem crossing between singlet and triplet states, thus obtaining emission from both singlet and triplet states and improving the internal efficiency.

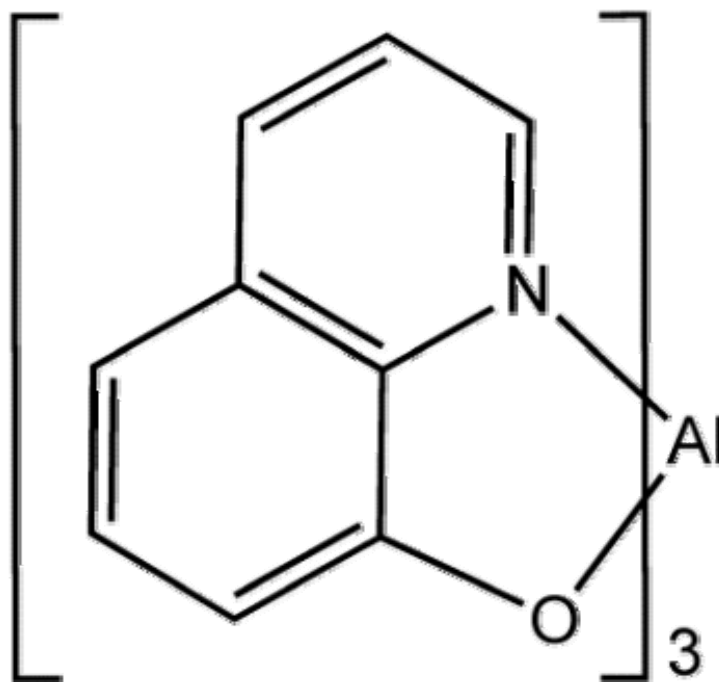
Indium tin oxide (ITO) is commonly used as the anode material. It is transparent to visible light and has a high work function which promotes injection of holes into the HOMO level of the organic layer. A typical conductive layer may consist of PEDOT:PSS as the HOMO level of this material generally lies between the workfunction of ITO and the HOMO of other commonly used polymers, reducing the energy barriers for hole injection. Metals such as barium and calcium are often used for the cathode as they have low work functions which promote injection of electrons into the LUMO of the organic layer. Such metals are reactive, so require a capping layer of aluminium to avoid degradation.

Single carrier devices are typically used to study the kinetics and charge transport mechanisms of an organic material and can be useful when trying to study energy transfer processes. As current through the device is composed of only one type of charge carrier, either electrons or holes, recombination does not occur and no light is emitted. For example, electron only devices can be obtained by replacing ITO with a lower work

function metal which increases the energy barrier of hole injection. Similarly, hole only devices can be made by using a cathode comprised solely of aluminium, resulting in an energy barrier too large for efficient electron injection.

## Material technologies

### Small molecules



Alq<sub>3</sub>, commonly used in small molecule OLEDs.

Efficient OLEDs using small molecules were first developed by Dr. Ching W. Tang *et al.* at Eastman Kodak. The term OLED traditionally refers specifically to this type of device, though the term SM-OLED is also in use.

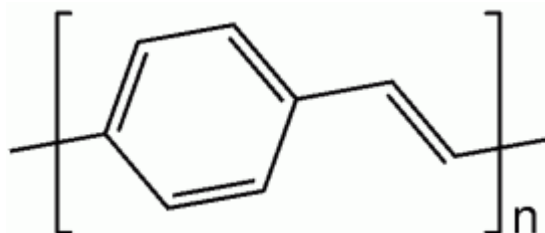
Molecules commonly used in OLEDs include organometallic chelates (for example Alq<sub>3</sub>, used in the organic light-emitting device reported by Tang *et al.*), fluorescent and phosphorescent dyes and conjugated dendrimers. A number of materials are used for their charge transport properties, for example triphenylamine and derivatives are commonly used as materials for hole transport layers. Fluorescent dyes can be chosen to obtain light emission at different wavelengths, and compounds such as perylene, rubrene and quinacridone derivatives are often used. Alq<sub>3</sub> has been used as a green emitter, electron transport material and as a host for yellow and red emitting dyes.

The production of small molecule devices and displays usually involves thermal evaporation in a vacuum. This makes the production process more expensive and of limited use for large-area devices than other processing techniques. However, contrary to

polymer-based devices, the vacuum deposition process enables the formation of well controlled, homogeneous films, and the construction of very complex multi-layer structures. This high flexibility in layer design, enabling distinct charge transport and charge blocking layers to be formed, is the main reason for the high efficiencies of the small molecule OLEDs.

Coherent emission from a laser dye-doped tandem SM-OLED device, excited in the pulsed regime, has been demonstrated. The emission is nearly diffraction limited with a spectral width similar to that of broadband dye lasers.

### Polymer light-emitting diodes



poly(*p*-phenylene vinylene), used in the first PLED.

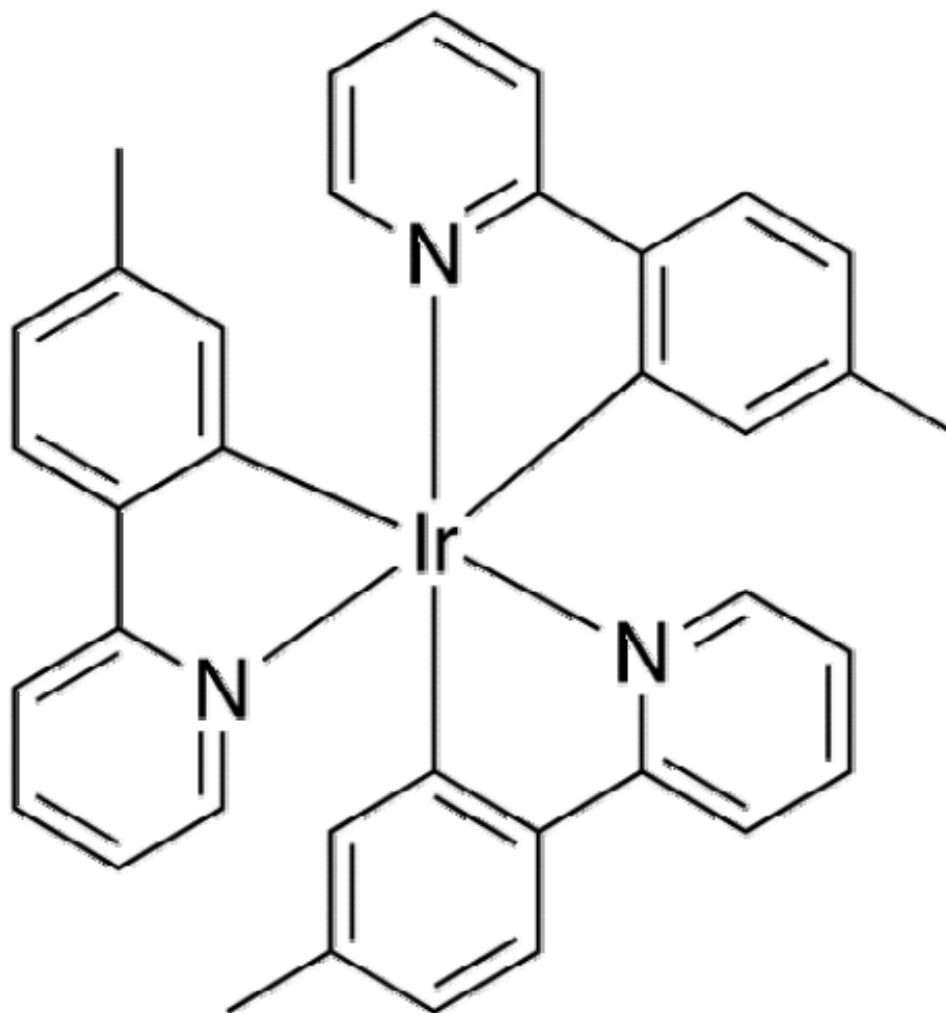
Polymer light-emitting diodes (PLED), also light-emitting polymers (LEP), involve an electroluminescent conductive polymer that emits light when connected to an external voltage. They are used as a thin film for full-spectrum colour displays. Polymer OLEDs are quite efficient and require a relatively small amount of power for the amount of light produced.

Vacuum deposition is not a suitable method for forming thin films of polymers. However, polymers can be processed in solution, and spin coating is a common method of depositing thin polymer films. This method is more suited to forming large-area films than thermal evaporation. No vacuum is required, and the emissive materials can also be applied on the substrate by a technique derived from commercial inkjet printing. However, as the application of subsequent layers tends to dissolve those already present, formation of multilayer structures is difficult with these methods. The metal cathode may still need to be deposited by thermal evaporation in vacuum.

Typical polymers used in PLED displays include derivatives of poly(*p*-phenylene vinylene) and polyfluorene. Substitution of side chains onto the polymer backbone may determine the colour of emitted light or the stability and solubility of the polymer for performance and ease of processing.

While unsubstituted poly(*p*-phenylene vinylene) (PPV) is typically insoluble, a number of PPVs and related poly(naphthalene vinylene)s (PNVs) that are soluble in organic solvents or water have been prepared via ring opening metathesis polymerization.

## Phosphorescent materials



$\text{Ir}(\text{mppy})_3$ , a phosphorescent dopant which emits green light.

Phosphorescent organic light emitting diodes use the principle of electrophosphorescence to convert electrical energy in an OLED into light in a highly efficient manner, with the internal quantum efficiencies of such devices approaching 100%.

Typically, a polymer such as poly(*n*-vinylcarbazole) is used as a host material to which an organometallic complex is added as a dopant. Iridium complexes such as  $\text{Ir}(\text{mppy})_3$  are currently the focus of research, although complexes based on other heavy metals such as platinum have also been used.

The heavy metal atom at the centre of these complexes exhibits strong spin-orbit coupling, facilitating intersystem crossing between singlet and triplet states. By using these phosphorescent materials, both singlet and triplet excitons will be able to decay radiatively, hence improving the internal quantum efficiency of the device compared to a standard PLED where only the singlet states will contribute to emission of light.

Applications of OLEDs in solid state lighting require the achievement of high brightness with good CIE coordinates (for white emission). The use of macromolecular species like polyhedral oligomeric silsesquioxanes (POSS) in conjunction with the use of phosphorescent species such as Ir for printed OLEDs have exhibited brightnesses as high as 10,000 cd/m<sup>2</sup>.

## Device Architectures

### Structure

- **Bottom or top emission:** Bottom emission devices use a transparent or semi-transparent bottom electrode to get the light through a transparent substrate. Top emission devices use a transparent or semi-transparent top electrode emitting light directly. Top-emitting OLEDs are better suited for active-matrix applications as they can be more easily integrated with a non-transparent transistor backplane.
- **Transparent OLEDs** use transparent or semi-transparent contacts on both sides of the device to create displays that can be made to be both top and bottom emitting (transparent). TOLEDs can greatly improve contrast, making it much easier to view displays in bright sunlight. This technology can be used in Head-up displays, smart windows or augmented reality applications. Novaled's OLED panel presented in Finetech Japan 2010, boasts a transparency of 60-70%.
- **Stacked OLEDs** use a pixel architecture that stacks the red, green, and blue subpixels on top of one another instead of next to one another, leading to substantial increase in gamut and color depth, and greatly reducing pixel gap. Currently, other display technologies have the RGB (and RGBW) pixels mapped next to each other decreasing potential resolution.
- **Inverted OLED:** In contrast to a conventional OLED, in which the anode is placed on the substrate, an Inverted OLED uses a bottom cathode that can be connected to the drain end of an n-channel TFT especially for the low cost amorphous silicon TFT backplane useful in the manufacturing of AMOLED displays.

### Patterning technologies

Patternable organic light-emitting devices use a light or heat activated electroactive layer. A latent material (PEDOT-TMA) is included in this layer that, upon activation, becomes highly efficient as a hole injection layer. Using this process, light-emitting devices with arbitrary patterns can be prepared.

Colour patterning can be accomplished by means of laser, such as radiation-induced sublimation transfer (RIST).



Organic vapour jet printing (OVJP) uses an inert carrier gas, such as argon or nitrogen, to transport evaporated organic molecules (as in Organic Vapor Phase Deposition). The gas is expelled through a micron sized nozzle or nozzle array close to the substrate as it is being translated. This allows printing arbitrary multilayer patterns without the use of solvents.

Conventional OLED displays are formed by vapor thermal evaporation (VTE) and are patterned by shadow-mask. A mechanical mask has openings allowing the vapor to pass only on the desired location.

## Backplane technologies

For a high resolution display like a TV, a TFT backplane is necessary to drive the pixels correctly. Currently, Low Temperature Polycrystalline silicon LTPS-TFT is used for commercial AMOLED displays. LTPS-TFT has variation of the performance in a display, so various compensation circuits have been reported. Due to the size limitation of the excimer laser used for LTPS, the AMOLED size was limited. To cope with the hurdle related to the panel size, amorphous-silicon/microcrystalline-silicon backplanes have been reported with large display prototype demonstrations.

## Advantages



Demonstration of a 4.1" prototype flexible display from Sony

The different manufacturing process of OLEDs lends itself to several advantages over flat-panel displays made with LCD technology.

- **Lower cost in the future:** OLEDs can be printed onto any suitable substrate by an inkjet printer or even by screen printing, theoretically making them cheaper to produce than LCD or plasma displays. However, fabrication of the OLED substrate is more costly than that of a TFT LCD, until mass production methods lower cost through scalability.
- **Light weight & flexible plastic substrates:** OLED displays can be fabricated on flexible plastic substrates leading to the possibility of Organic light-emitting diode roll-up display being fabricated or other new applications such as roll-up displays

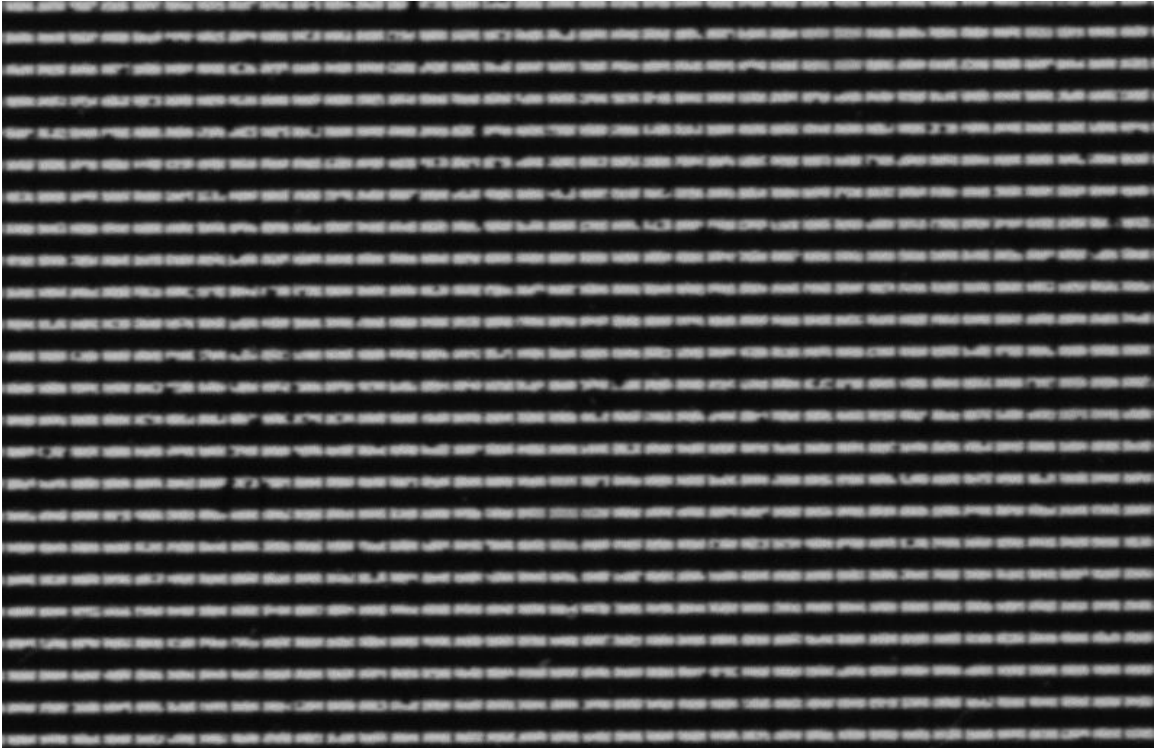
embedded in fabrics or clothing. As the substrate used can be flexible such as PET. , the displays may be produced inexpensively.

- **Wider viewing angles & improved brightness:** OLEDs can enable a greater artificial contrast ratio (both dynamic range and static, measured in purely dark conditions) and viewing angle compared to LCDs because OLED pixels directly emit light. OLED pixel colours appear correct and unshifted, even as the viewing angle approaches 90 degrees from normal.
- **Better power efficiency:** LCDs filter the light emitted from a backlight, allowing a small fraction of light through so they cannot show true black, while an inactive OLED element does not produce light or consume power.
- **Response time:** OLEDs can also have a faster response time than standard LCD screens. Whereas LCD displays are capable of a 1 ms response time or less offering a frame rate of 1,000 Hz or higher, an OLED can theoretically have less than 0.01 ms response time enabling 100,000 Hz refresh rates.

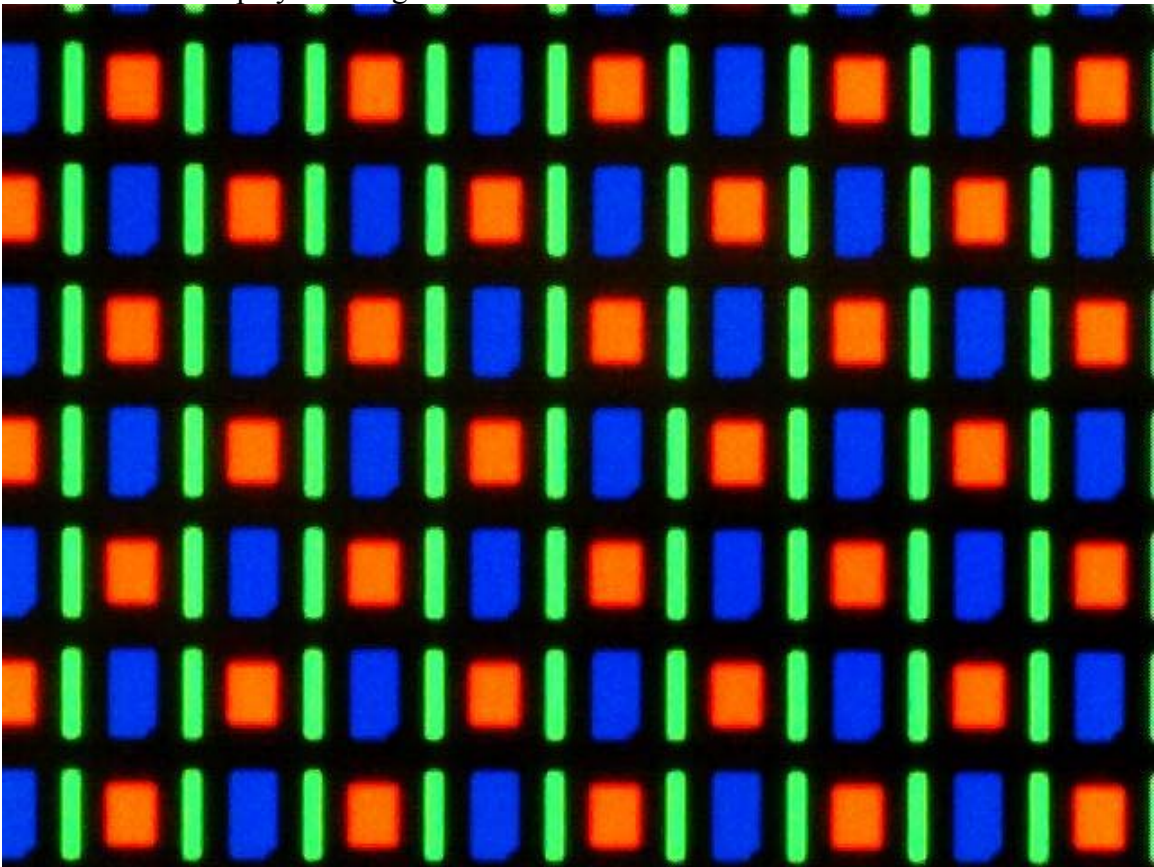
## **Disadvantages**



LEP display showing partial failure



An old OLED display showing wear



Magnified image of the AMOLED screen on the Google Nexus One smartphone using the RGBG system of the PenTile Matrix Family.

- Lifespan:** The biggest technical problem for OLEDs was the limited lifetime of the organic materials. In particular, blue OLEDs historically have had a lifetime of around 14,000 hours to half original brightness (five years at 8 hours a day) when used for flat-panel displays. This is lower than the typical lifetime of LCD, LED or PDP technology—each currently rated for about 60,000 hours to half brightness, depending on manufacturer and model. However, some manufacturers' displays aim to increase the lifespan of OLED displays, pushing their expected life past that of LCD displays by improving light outcoupling, thus achieving the same brightness at a lower drive current. In 2007, experimental OLEDs were created which can sustain  $400 \text{ cd/m}^2$  of luminance for over 198,000 hours for green OLEDs and 62,000 hours for blue OLEDs.
- Color balance issues:** Additionally, as the OLED material used to produce blue light degrades significantly more rapidly than the materials that produce other colors, blue light output will decrease relative to the other colors of light. This differential color output change will change the color balance of the display and is much more noticeable than a decrease in overall luminance. This can be partially avoided by adjusting colour balance but this may require advanced control circuits and interaction with the user, which is unacceptable for some users. In order to delay the problem, manufacturers bias the colour balance towards blue so that the display initially has an artificially blue tint, leading to complaints of artificial-looking, over-saturated colors. More commonly, though, manufacturers optimize the size of the R, G and B subpixels to reduce the current density through the subpixel in order to equalize lifetime at full luminance. For example, a blue subpixel may be 100% larger than the green subpixel. The red subpixel may be 10% smaller than the green.
- Efficiency of blue OLEDs:** Improvements to the efficiency and lifetime of blue OLED's is vital to the success of OLED's as replacements for LCD technology. Considerable research has been invested in developing blue OLEDs with high external quantum efficiency as well as a deeper blue color. External quantum efficiency values of 20% and 19% have been reported for red (625 nm) and green (530 nm) diodes, respectively. However, blue diodes (430 nm) have only been able to achieve maximum external quantum efficiencies in the range between 4% to 6%. By calculating the band gap ( $E_g = hc/\lambda$ ), it is clear that the shorter wavelength of the blue OLED results in a larger band gap at 2.9 eV. This leads to higher barriers, causing lower efficiency.
- Water damage:** Water can damage the organic materials of the displays. Therefore, improved sealing processes are important for practical manufacturing. Water damage may especially limit the longevity of more flexible displays.
- Outdoor performance:** As an emissive display technology, OLEDs rely completely upon converting electricity to light, unlike most LCDs which are to some extent reflective; e-ink leads the way in efficiency with  $\sim 33\%$  ambient light reflectivity, enabling the display to be used without any internal light source. The

metallic cathode in an OLED acts as a mirror, with reflectance approaching 80%, leading to poor readability in bright ambient light such as outdoors. However, with the proper application of a circular polarizer and anti-reflective coatings, the diffuse reflectance can be reduced to less than 0.1%. With 10,000 fc incident illumination (typical test condition for simulating outdoor illumination), that yields an approximate photopic contrast of 5:1.

- **Power consumption:** While an OLED will consume around 40% of the power of an LCD displaying an image which is primarily black, for the majority of images it will consume 60–80% of the power of an LCD - however it can use over three times as much power to display an image with a white background such as a document or website. This can lead to disappointing real-world battery life in mobile devices. Websites and tools exist to help disappointed mobile phone users display a black background in places where it would normally be white. For example, the mobile Google search engine can now be used in black to save battery power by using a custom version called Black Google Mobile.
- **Screen burn-in:** Unlike displays with a common light source, the brightness of each OLED pixel fades depending on the content displayed. The varied lifespan of the organic dyes can cause a discrepancy between red, green, and blue intensity. This leads to image persistence, also known as burn-in.

## **Manufacturers and Commercial Uses**



A 3.8 cm (1.5 in) OLED display from a Creative ZEN V media player

OLED technology is used in commercial applications such as displays for mobile phones and portable digital media players, car radios and digital cameras among others. Such portable applications favor the high light output of OLEDs for readability in sunlight and their low power drain. Portable displays are also used intermittently, so the lower lifespan of organic displays is less of an issue. Prototypes have been made of flexible and rollable displays which use OLEDs' unique characteristics. Applications in flexible signs and lighting are also being developed. Philips Lighting have made OLED lighting samples under the brand name 'Lumiblade' available online.

OLEDs have been used in most Motorola and Samsung colour cell phones, as well as some HTC, LG and Sony Ericsson models. Nokia has also recently introduced some OLED products including the N85 and the N86 8MP, both of which feature an AMOLED display. OLED technology can also be found in digital media players such as the Creative ZEN V, the iriver clix, the Zune HD and the Sony Walkman X Series.

The Google and HTC Nexus One smartphone includes an AMOLED screen, as does HTC's own Desire and Legend phones. However due to supply shortages of the Samsung-produced displays, certain HTC models will use Sony's SLCD displays in the future.

The Google and Samsung Nexus S smartphone includes a Super AMOLED screen, as does Samsung's own Galaxy S phone. However due to supply shortages of the Samsung-produced displays certain countries, such as Russia, will have Nexus S models that use "Super Clear LCD" instead; the same display used by Samsung for its new Wave II S8530.

Other manufacturers of OLED panels include Anwell Technologies Limited, Chi Mei Corporation, LG, and others.

DuPont stated in a press release in May 2010 that they can produce a 50-inch OLED TV in two minutes with a new printing technology. If this can be scaled up in terms of manufacturing, then the total cost of OLED TVs would be greatly reduced. Dupont also states that OLED TVs made with this less expensive technology can last up to 15 years if left on for a normal eight hour day.

Handheld computer manufacturer OQO introduced the smallest Windows netbook computer, including an OLED display, in 2009.

The use of OLEDs may be subject to patents held by Eastman Kodak, DuPont, General Electric, Royal Philips Electronics, numerous universities and others. There are by now literally thousands of patents associated with OLEDs, both from larger corporations and smaller technology companies .

## **Samsung applications**

By 2004 Samsung, South Korea's largest conglomerate, was the world's largest OLED manufacturer, producing 40% of the OLED displays made in the world, and as of 2010 has a 98% share of the global AMOLED market. The company is leading the world OLED industry, generating \$100.2 million out of the total \$475 million revenues in the global OLED market in 2006. As of 2006, it held more than 600 American patents and more than 2800 international patents, making it the largest owner of AMOLED technology patents.

Samsung SDI announced in 2005 the world's largest OLED TV at the time, at 21 inches (53 cm). This OLED featured the highest resolution at the time, of 6.22 million pixels. In addition, the company adopted active matrix based technology for its low power consumption and high-resolution qualities. This was exceeded in January 2008, when Samsung showcased the world's largest and thinnest OLED TV at the time, at 31 inches and 4.3 mm.

In May 2008, Samsung unveiled an ultra-thin 12.1 inch laptop OLED display concept, with a 1,280×768 resolution with infinite contrast ratio. According to Woo Jong Lee, Vice President of the Mobile Display Marketing Team at Samsung SDI, the company expected OLED displays to be used in notebook PCs as soon as 2010.



In October 2008, Samsung showcased the world's thinnest OLED display, also the first to be 'flappable' and bendable. It measures just 0.05 mm (thinner than paper), yet a Samsung staff member said that it is "technically possible to make the panel thinner". To achieve this thickness, Samsung etched an OLED panel that uses a normal glass substrate. The drive circuit was formed by low-temperature polysilicon TFTs. Also, low-molecular organic EL materials were employed. The pixel count of the display is  $480 \times 272$ . The contrast ratio is 100,000:1, and the luminance is  $200 \text{ cd/m}^2$ . The colour reproduction range is 100% of the NTSC standard.

In the same month, Samsung unveiled what was then the world's largest OLED Television at 40-inch with a Full HD resolution of  $1920 \times 1080$  pixel. In the FPD International, Samsung stated that its 40-inch OLED Panel is the largest size currently possible. The panel has a contrast ratio of 1,000,000:1, a colour gamut of 107% NTSC, and a luminance of  $200 \text{ cd/m}^2$  (peak luminance of  $600 \text{ cd/m}^2$ ).

At the Consumer Electronics Show (CES) in January 2010, Samsung demonstrated a laptop computer with a large, transparent OLED display featuring up to 40% transparency and an animated OLED display in a photo ID card.

Samsung's latest AMOLED smartphones use their Super AMOLED trademark, with the Samsung Wave S8500 and Samsung i9000 Galaxy S being launched in June 2010.

### **Sony applications**



Sony XEL-1, the world's first OLED TV. (front)



Sony XEL-1 (side)

The Sony CLIÉ PEG-VZ90 was released in 2004, being the first PDA to feature an OLED screen. Other Sony products to feature OLED screens include the MZ-RH1 portable minidisc recorder, released in 2006 and the Walkman X Series.

At the Las Vegas CES 2007, Sony showcased 11-inch (28 cm, resolution 960×540) and 27-inch (68.5 cm, full HD resolution at 1920×1080) OLED TV models. Both claimed 1,000,000:1 contrast ratios and total thicknesses (including bezels) of 5 mm. In April 2007, Sony announced it would manufacture 1000 11-inch OLED TVs per month for market testing purposes. On October 1, 2007, Sony announced that the 11-inch model, now called the XEL-1, would be released commercially; the XEL-1 was first released in Japan in December 2007.

In May 2007, Sony publicly unveiled a video of a 2.5-inch flexible OLED screen which is only 0.3 millimeters thick. At the Display 2008 exhibition, Sony demonstrated a 0.2 mm thick 3.5 inch display with a resolution of 320×200 pixels and a 0.3 mm thick 11 inch display with 960×540 pixels resolution, one-tenth the thickness of the XEL-1.

In July 2008, a Japanese government body said it would fund a joint project of leading firms, which is to develop a key technology to produce large, energy-saving organic displays. The project involves one laboratory and 10 companies including Sony Corp. NEDO said the project was aimed at developing a core technology to mass-produce 40 inch or larger OLED displays in the late 2010s.

In October 2008, Sony published results of research it carried out with the Max Planck Institute over the possibility of mass-market bending displays, which could replace rigid LCDs and plasma screens. Eventually, bendable, transparent OLED screens could be stacked to produce 3D images with much greater contrast ratios and viewing angles than existing products.

Sony exhibited a 24.5" prototype OLED 3D television during the Consumer Electronics Show in January 2010.

## **LG applications**

Since 2010 LG sells one 15" OLED TV, the 15EL9500 and has announced a 31" OLED 3D TV for March 2011.

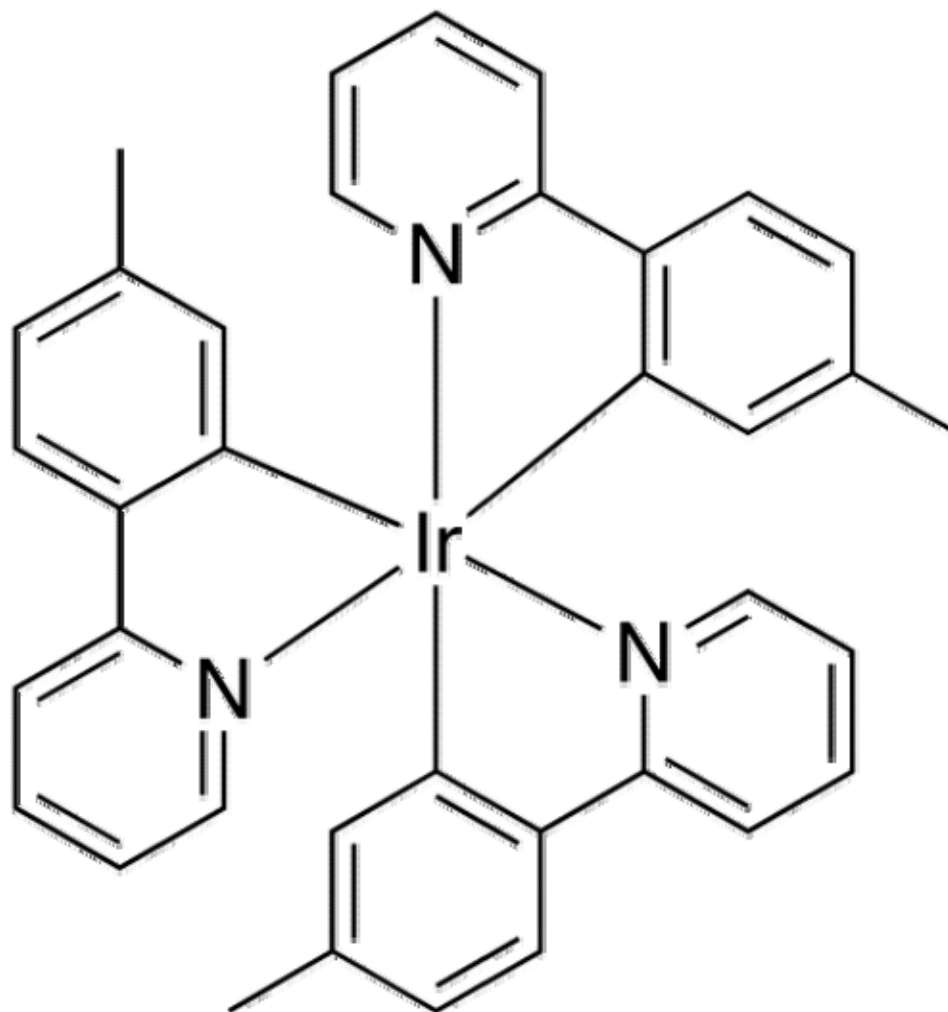
## **Range of OLED screens sizes in production products**

- Media Player - 2.2" to 3.3" - various
- Mobile Phone - 2.6" to 4.1" - various
- Tablet - none
- Laptop - none
- PC monitor - none
- TV - 11" to 15" - Sony XEL-1 and LG 15EL9500

## **Phosphorescent organic light-emitting diode**

**Phosphorescent organic light-emitting diodes (PHOLED)** are a type of organic light-emitting diode (OLED) that use the principle of phosphorescence to obtain higher internal efficiencies than fluorescent OLEDs. This technology is currently under development by many industrial and academic research groups.

## **Method of operation**



$\text{Ir}(\text{mppy})_3$ , an example of a phosphorescent dopant which emits green light.

Like all types of OLED, phosphorescent OLEDs emit light due to the electroluminescence of an organic semiconductor layer in an electric current. Electrons and holes are injected into the organic layer at the electrodes and form excitons, a bound state of the electron and hole.

Electrons and holes are both fermions with half integer spin. An exciton formed by the recombination of two such particles may either be in a singlet state or a triplet state, depending on how the spins have been combined. Statistically, there is a 25% probability of forming a singlet state and 75% probability of forming a triplet state. Decay of the excitons results in the production of light through spontaneous emission.

In OLEDs using fluorescent organic molecules only, the decay of triplet excitons is quantum mechanically forbidden by selection rules, meaning that the lifetime of triplet excitons is long and phosphorescence is not readily observed. Hence it would be expected that in fluorescent OLEDs only the formation of singlet excitons results in the emission

of useful radiation, placing a theoretical limit on the internal quantum efficiency (the percentage of excitons formed that result in emission of a photon) of 25%.

However, phosphorescent OLEDs generate light from both triplet and singlet excitons, allowing the internal quantum efficiency of such devices to reach nearly 100%.

This is commonly achieved by doping a host polymer with an organometallic complex. These contain a heavy metal atom at the centre of the molecule, for example platinum or iridium, of which the green emitting complex Ir(mppy)<sub>3</sub> is just one of many examples. The large spin-orbit interaction experienced by the molecule due to this heavy metal atom facilitates intersystem crossing, a process which mixes the singlet and triplet character of excited states. This reduces the lifetime of the triplet state, therefore phosphorescence is readily observed.

## **Applications**

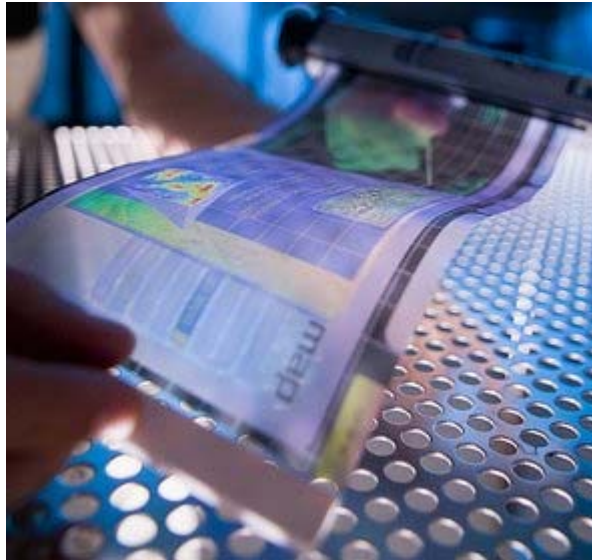
Due to their potentially high level of energy efficiency, even when compared to other OLEDs, PHOLEDs are being studied for potential use in large-screen displays such as computer monitors or television screens, as well as general lighting needs. One potential use of PHOLEDs as lighting devices is to cover walls with large area PHOLED displays. This would allow entire rooms to glow uniformly, rather than require the use of light bulbs which distribute light unequally throughout a room. The United States Department of Energy has recognized the potential for massive energy savings via the use of this technology and therefore has awarded 200 000 US\$ in contracts to develop PHOLED products for general lighting applications.

## **Challenges**

One problem that currently hampers the widespread adoption of this highly energy efficient technology is that the average lifetimes of red and green PHOLEDs are often tens of thousands of hours longer than those of blue PHOLEDs. This may cause displays to become visually distorted much sooner than would be acceptable for a commercially viable device.

## Chapter- 3

# Organic Field-Effect Transistor



OFET-based flexible display

An **organic field-effect transistor (OFET)** is a field effect transistor using an organic semiconductor in its channel. OFETs can be prepared either by vacuum evaporation of small molecules, by solution-casting of polymers or small molecules, or by mechanical transfer of a peeled single-crystalline organic layer onto a substrate. These devices have been developed to realize low-cost, large-area electronic products. OFETs have been fabricated with various device geometries. The most commonly used device geometry is bottom gate with top drain- and source electrodes, because this geometry is similar to the thin-film silicon transistor (TFT) using thermally grown Si/SiO<sub>2</sub> oxide as gate dielectric. Organic polymers, such as poly(methyl-methacrylate) (PMMA), can be used as dielectric, too.

In May 2007, Sony reported the first full-color, video-rate, flexible, all plastic display, in which both the thin film transistors and the light emitting pixels were made of organic materials.

## History of OFETs

The field-effect transistor (FET) was first proposed by J.E. Lilienfeld, who received a patent for his idea in 1930. He proposed that a field-effect transistor behaves as a capacitor with a conducting channel between a source and a drain electrode. Applied voltage on the gate electrode controls the amount of charge carriers flowing through the system.

The first field-effect transistor was designed and prepared in 1960 by Kahng and Atalla using a metal-oxide-semiconductor. However, rising costs of materials and manufacturing, as well as public interest in more environmentally friendly electronics materials have supported development of organic based electronics in more recent years. In 1987, Koezuka and co-workers reported the first organic field-effect transistor based on a polymer of thiophene molecules. The thiophene polymer is a type of conjugated polymer that is able to conduct charge, eliminating the need to use expensive metal oxide semiconductors. Additionally, other conjugated polymers have been shown to have semi-conducting properties. OFET design has also improved in the past few decades. Many OFETs are now designed based on the thin-film transistor (TFT) model, which allows the devices to use less conductive materials in their design. Improvement on these models in the past few years have been made to field-effect mobility and on-off current ratios.

## Materials

One common feature of OFET materials is the inclusion of an aromatic or otherwise conjugated  $\pi$ -electron system, facilitating the delocalization of orbital wavefunctions. Electron withdrawing groups or donating groups can be attached that facilitate hole or electron transport.

OFETs employing many aromatic and conjugated materials as the active semiconducting layer have been reported, including small molecules such as rubrene, tetracene, pentacene, diindenoperylene, perylenediimides, tetracyanoquinodimethane (TCNQ), and polymers such as polythiophenes (especially poly 3-hexylthiophene (P3HT)), polyfluorene, polydiacetylene, poly 2,5-thienylene vinylene, poly p-phenylene vinylene (PPV).

The field is very active, with newly synthesized and tested compounds reported weekly in prominent research journals. Many review articles exist documenting the development of these materials.

Rubrene-based OFETs show the highest carrier mobility 20–40  $\text{cm}^2/(\text{V}\cdot\text{s})$ . Another popular OFET material is pentacene, which has been used since 1980s, but resulted in about 10 times lower mobilities than rubrene. The major problem with pentacene, as well as many other organic conductors, is its rapid oxidation in air to form pentacene-quinone. However if the pentacene is preoxidized, and the thus formed pentacene-quinone is used

as the gate insulator, then the mobility can approach the rubrene values. This pentacene oxidation technique is akin to the silicon oxidation used in the silicon electronics.

Polycrystalline tetrathiafulvalene and its analogues result in mobilities in the range 0.1–1.4  $\text{cm}^2/(\text{V}\cdot\text{s})$ . However, the mobility exceeds 10  $\text{cm}^2/(\text{V}\cdot\text{s})$  in solution-grown or vapor-transport-grown single crystalline hexamethylene-tetrathiafulvalene (HMTTF). The ON/OFF voltage is different for devices grown by those two techniques, presumably due to the higher processing temperatures using in the vapor transport grows.

All the above-mentioned devices are based on p-type conductivity. N-type organic OFETs are yet poorly developed. They are usually based on perylenediimides or fullerenes or their derivatives, and show electron mobilities below 2  $\text{cm}^2/(\text{V}\cdot\text{s})$ .

## **Device design of organic field-effect transistors**

Three essential components of field-effect transistors are the source, the drain and the gate. Field-effect transistors usually operate as a capacitor. They are composed of two plates. One plate works as a conducting channel between two ohmic contacts, which are called the source and the drain contacts. The other plate works to control the charge induced into the channel, and it is called the gate. The direction of the movement of the carriers in the channel is from the source to the drain. Hence the relationship between these three components is that the gate controls the carrier movement from the source to the drain.

When this capacitor concept is applied to the device design, various devices can be built up based on the difference in the controller-the gate. This can be the gate material, the location of the gate with respect to the channel, how the gate is isolated from the channel, and what type of carrier is induced by the gate voltage into channel (such as electrons in an n-channel device, holes in a p-channel device, and both electrons and holes in a double injection device).



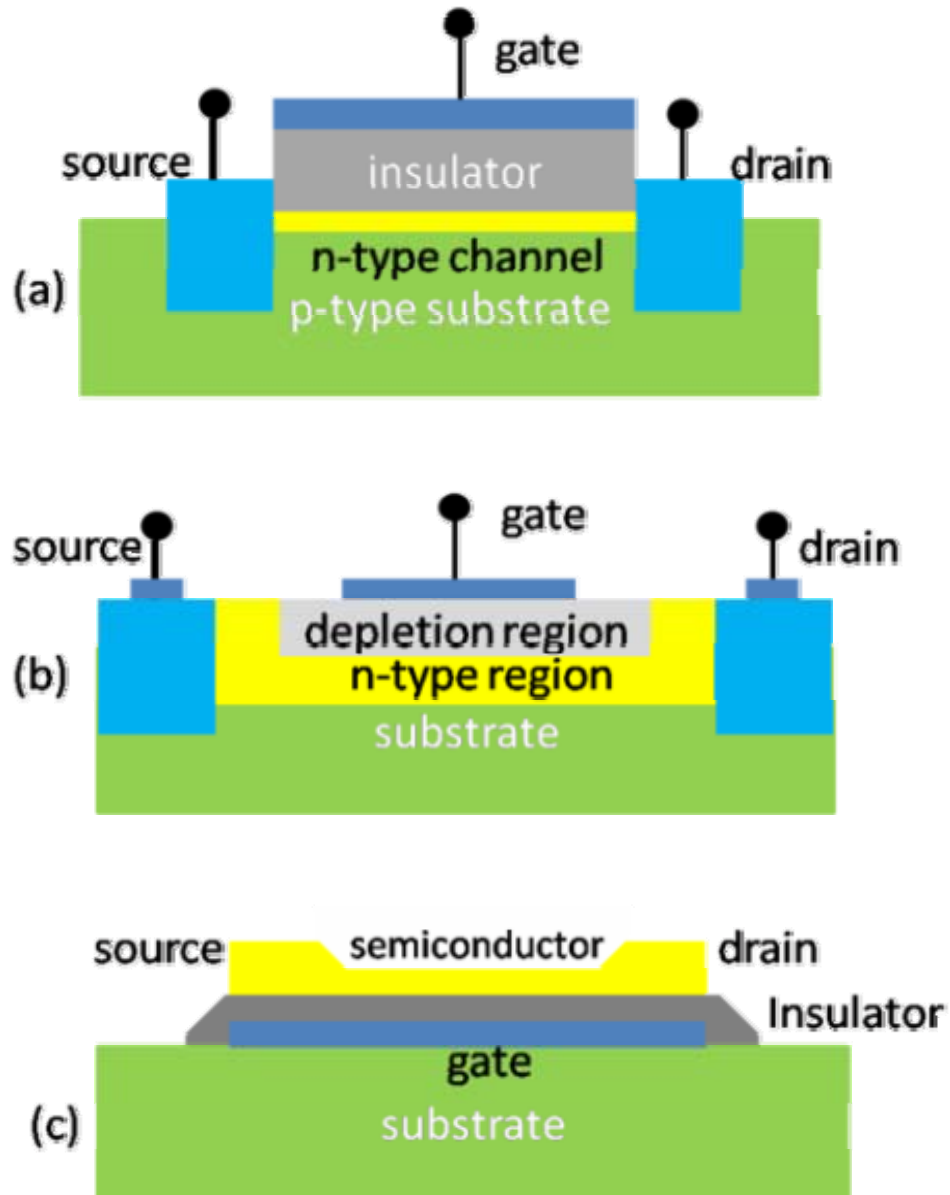


Figure 1 Schematic graphs of three different kinds of Field-Effect Transistor (FET): (a) the metal- insulator -semiconductor FET( MISFET); (b) the metal-semiconductor FET (MESFET); (c) the thin-film transistor (TFT).

Classified by the properties of the carrier, three types of FETs are shown schematically in Figure 1. They are MOSFET (Metal Oxide Semiconductor Field-Effect Transistor), MESFET (MEtal Semiconductor Field-Effect Transistor) and TFT (Thin Film Transistor).

### **MISFET**

The most prominent and widely used FET in modern microelectronics is the MOSFET. There are different kinds in this category, such as MISFET (Metal Insulator

Semiconductor Field-Effect Transistor), and IGFET (Insulator Gate Field-Effect Transistor). The scheme of a MISFET is shown in Figure 1a. The source and the drain are connected by a semiconductor and the gate is separated from the channel by a layer of insulator. If there is no bias (potential difference) applied on the gate, the band bending is induced due to the energy difference of metal conducting band and the semiconductor Fermi-level. Therefore a higher concentration of holes is formed on the interface of the semiconductor and the insulator. When an enough positive bias is applied on the gate contact, the bended band becomes flat. If a larger positive bias is applied, the band bending in the opposite direction occurs and the region close to the insulator-semiconductor interface becomes depleted of holes. Then the depleted region is formed. At an even larger positive bias, the band bending becomes so large that the Fermi-level at the interface of the semiconductor and the insulator becomes closer to the bottom of the conduction band than to the top of the valence band, therefore, it forms an inversion layer of electrons, providing the conducting channel. Finally, it turns the device on.

## **MESFET**

The second type of device is described in Fig.1b. The only difference of this one from the MISFET is that the n-type source and drain are connected by an n-type region. In this case, the depletion region extends all over the n-type channel at zero gate voltage in a normally “off” device (it is similar to the larger positive bias in MISFET case). In the normally “on” device, a portion of the channel is not depleted, and thus leads to passage of a current at zero gate voltage.

## **TFT**

The concept of TFT was first proposed by Paul Weimer in 1962. This is illustrated in Fig. 1c. Here the source and drain electrodes are directly deposited onto the conducting channel (a thin layer of semiconductor) then a thin film of insulator is deposited between the semiconductor and the metal gate contact. This structure suggests that there is no depletion region to separate the device from the substrate. If there is zero bias, the electrons are expelled from the surface due to the Fermi-level energy difference of the semiconductor and the metal. This leads to band bending of semiconductor. In this case, there is no carrier movement between the source and drain. When the positive charge is applied, the accumulation of electrons on the interface leads to the bending of the semiconductor in an opposite way and leads to the lowering of the conduction band with regards to the Fermi-level of the semiconductor. Then a highly conductive channel forms at the interface (shown in Figure 2).

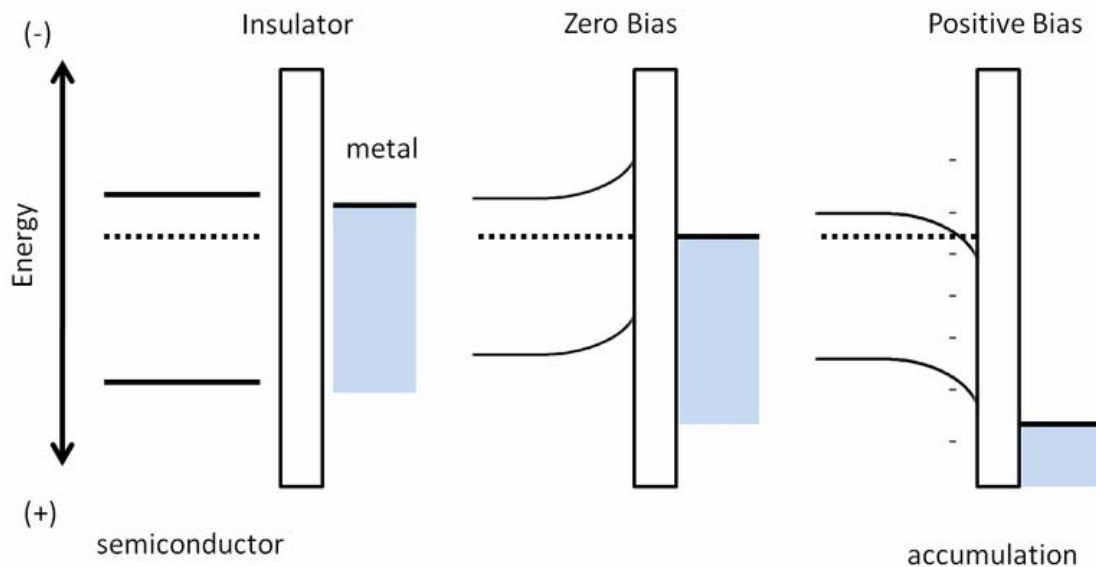
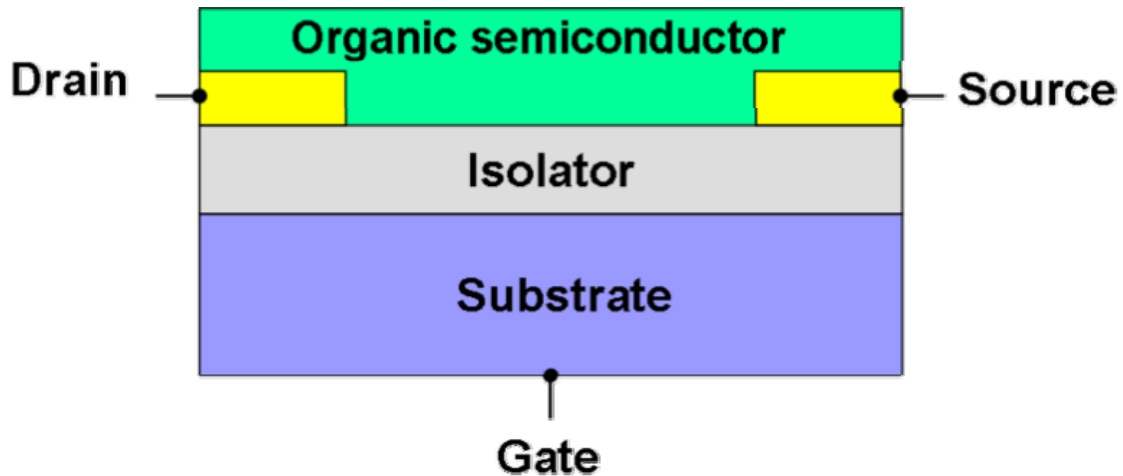


Figure 2: Schematic graphs of band-bending in the TFT device model.

## OFET

OFETs adopt the architecture of TFT. With the development of the conducting polymer, the semiconducting properties of small conjugated molecules have been recognized. The interest in OFETs has grown enormously in the past ten years. The reasons for this surge of interest are manifold. The performance of OFETs, which can compete with that of amorphous silicon (a-Si) TFTs with field-effect mobilities of  $0.5^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and ON/OFF current ratios (which indicate the ability of the device to shut down) of 106–108, has improved significantly. Currently, thin-film OFET mobility values of  $5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  in the case of vacuum-deposited small molecules and  $0.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for solution-processed polymers have been reported. As a result, there is now a greater industrial interest in using OFETs for applications that are currently incompatible with the use of a-Si or other inorganic transistor technologies. One of their main technological attractions is that all the layers of an OFET can be deposited and patterned at room temperature by a combination of low-cost solution-processing and direct-write printing, which makes them ideally suited for realization of low-cost, large-area electronic functions on flexible substrates.

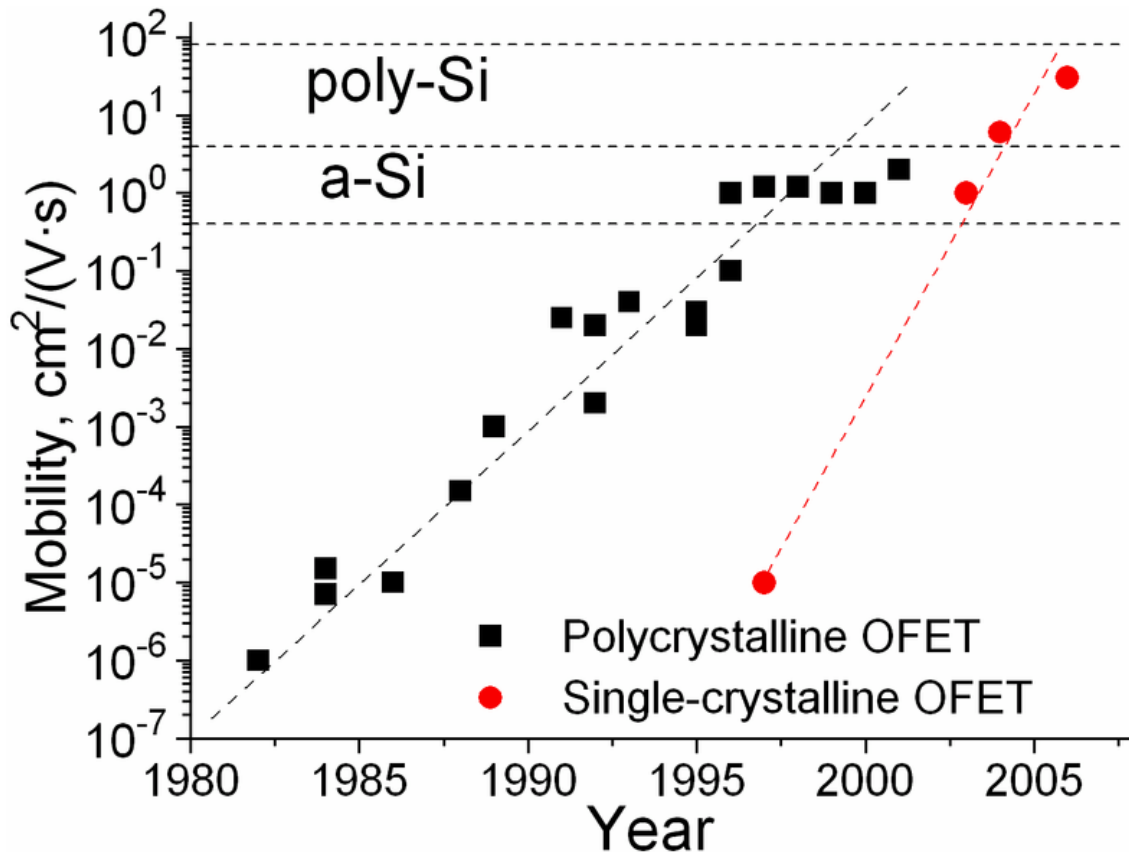
## Device preparation



OFET schematic

Thermally oxidized silicon is a traditional substrate for OFETs where the silicon dioxide serves as the gate insulator. The active FET layer is usually deposited onto this substrate using either (i) thermal evaporation, (ii) coating from organic solution, or (iii) electrostatic lamination. The first two techniques result in polycrystalline active layers; they are much easier to produce, but result in relatively poor transistor performance. Numerous variations of the solution coating technique (ii) are known, including dip-coating, spin-coating, inkjet printing and screen printing. The electrostatic lamination technique is based on manual peeling of a thin layer off a single organic crystal; it results in a superior single-crystalline active layer, yet it is more tedious. The thickness of the gate oxide and the active layer is below one micrometer.

## Carrier transport



Evolution of carrier mobility in organic field-effect transistor.

The carrier transport in OFET is specific for two-dimensional (2D) carrier propagation through the device. Various experimental techniques were used for this study, such as Haynes - Shockley experiment on the transit times of injected carriers, time-of-flight (TOF) experiment for the determination of carrier mobility, pressure-wave propagation experiment for probing electric-field distribution in insulators, organic monolayer experiment for probing orientational dipolar changes, optical time-resolved second harmonic generation (TRM-SHG), etc. Whereas carriers propagate through polycrystalline OFETs in a diffusion-like (trap-limited) manner, they move through the conduction band in the best single-crystalline OFETs.

The most important parameter of OFET carrier transport is carrier mobility. Its evolution over the years of OFET research is shown in the graph for polycrystalline and single crystalline OFETs. The horizontal lines indicate the comparison guides to the main OFET competitors – amorphous (a-Si) and polycrystalline silicon. The graph reveals that the mobility in polycrystalline OFETs is comparable to that of a-Si whereas mobility in rubrene-based OFETs (20–40 cm<sup>2</sup>/(V·s)) approaches that of best poly-silicon devices.

## Light-emitting OFETs

Because an electric current flows through such a transistor, it can be used as a light-emitting device, thus integrating current modulation and light emission. In 2003, a German group reported the first organic light-emitting field-effect transistor (OLET). The device structure comprises interdigitated gold source- and drain electrodes and a polycrystalline tetracene thin film. Both, positive charges (holes) as well as negative charges (electrons) are injected from the gold contacts into this layer leading to electroluminescence from the tetracene.

## Chapter- 4

# Organic Solar Cell

An organic photovoltaic cell (OPVC) is a photovoltaic cell that uses organic electronics-- a branch of electronics that deals with conductive organic polymers or small organic molecules for light absorption and charge transport.

The plastic itself has low production costs in high volumes. Combined with the flexibility of organic molecules, this makes it potentially lucrative for photovoltaic applications. Molecular engineering (e.g. changing the length and functional group of polymers) can change the energy gap, which allows chemical change in these materials. The optical absorption coefficient of organic molecules is high, so a large amount of light can be absorbed with a small amount of materials. The main disadvantages associated with organic photovoltaic cells are low efficiency, low stability and low strength compared to inorganic photovoltaic cells.

## Organic photovoltaic materials

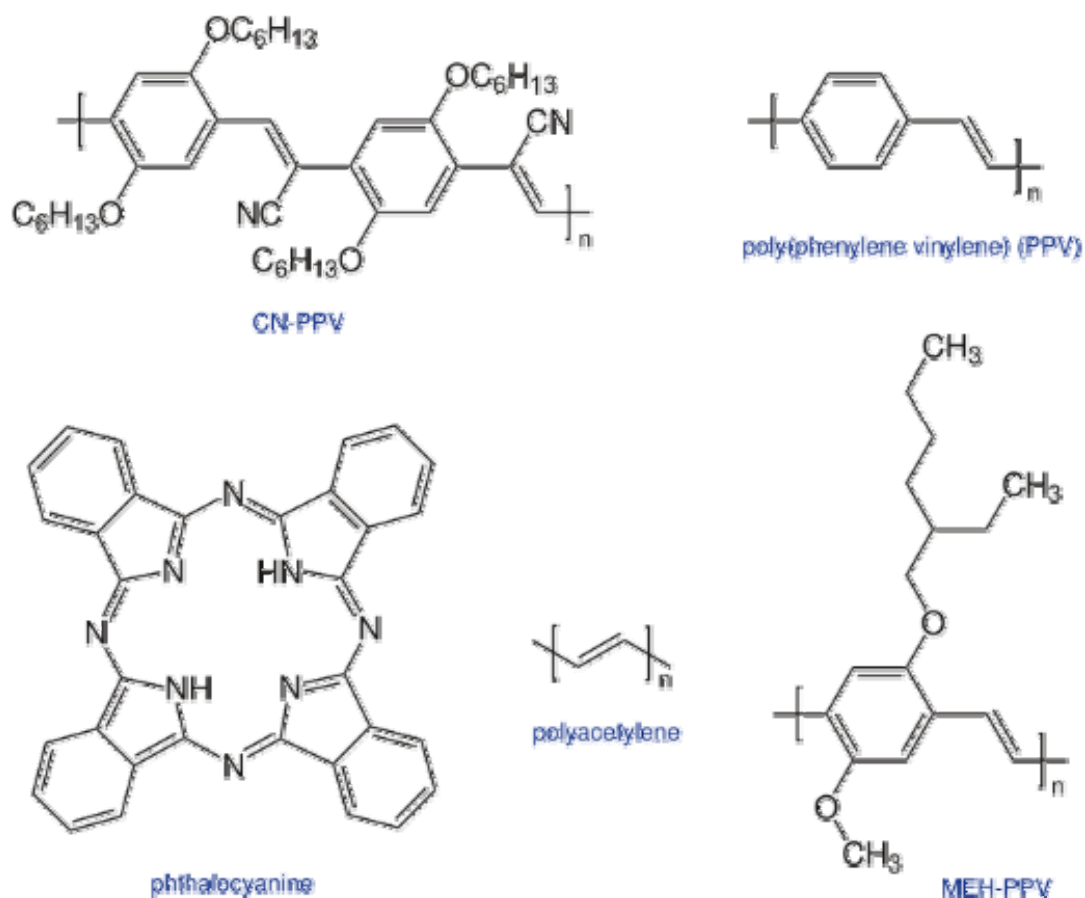


Fig 1: Examples of organic photovoltaic materials

A photovoltaic cell is a specialized semiconductor diode that converts visible light into direct current (DC) electricity. Some photovoltaic cells can also convert infrared (IR) or ultraviolet (UV) radiation into DC. A common characteristic of both the small molecules and polymers (Fig 1) used in photovoltaic is that they all have large conjugated systems. A conjugated system is formed where carbon atoms covalently bond with alternating single and double bonds, in other words these are chemical reactions of hydrocarbons. These hydrocarbons electrons pz orbitals delocalize and form a delocalized bonding  $\pi$  orbital with a  $\pi^*$  antibonding orbital. The delocalized  $\pi$  orbital is the highest occupied molecular orbital (HOMO), and the  $\pi^*$  orbital is the lowest unoccupied molecular orbital (LUMO). The separation between HOMO and LUMO is considered as the band gap of organic electronic materials. The band gap is typically in the range of 1-4 eV.

When these materials absorb a photon, an excited state is created and confined to a molecule or a region of a polymer chain. The excited state can be regarded as an electron hole pair bound together by electrostatic interactions. In photovoltaic cells, excitons are broken up into free electrons-hole pairs by effective fields. The effective field are set up by creating a heterjunction between two dissimilar materials. Effective fields break up excitons by causing the electron to fall from the conduction band of the absorber to the



conduction band of the acceptor molecule. It is necessary that the acceptor material has a conduction band edge that is lower than that of the absorber material.

## Types of junctions for OPVC

### Single layer organic photovoltaic cell

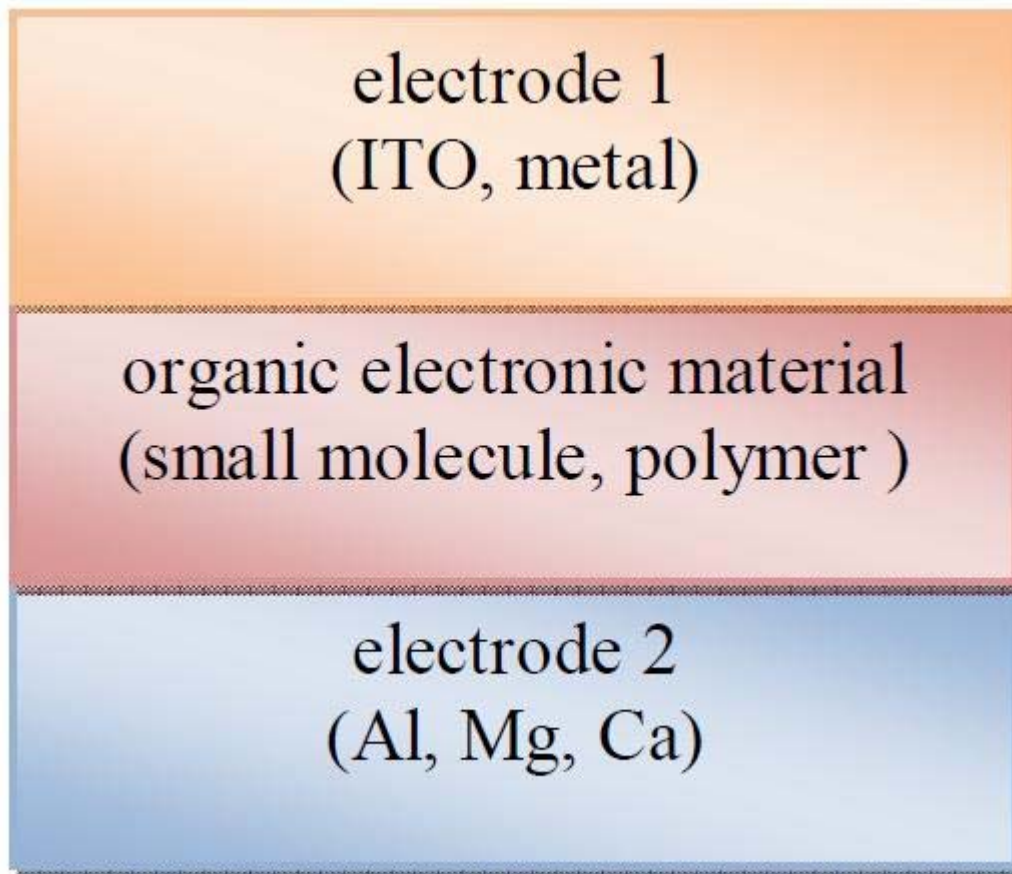


Fig 2: Sketch of a single layer organic photovoltaic cell

Single layer organic photovoltaic cells are the simplest form among various organic photovoltaic cells. These cells are made by sandwiching a layer of organic electronic materials between two metallic conductors, typically a layer of indium tin oxide (ITO) with high work function and a layer of low work function metal such as Al, Mg and Ca. The basic structure of such a cell is illustrated in Fig 2.

The difference of work function between the two conductors sets up an electric field in the organic layer. When the organic layer absorbs light, electrons will be excited to Lowest Unoccupied Molecular Orbital (LUMO) and leave holes in the Highest Occupied Molecular Orbital (HOMO) forming excitons. The potential created by the different work functions helps to separate the exciton pairs, pulling electrons to the positive electrode

(an electrical conductor used to make contact with a nonmetallic part of a circuit) and holes to the negative electrode. The current and voltage resulting from this process can be used to do work. Using electric fields is not the best way to break up excitons, heterojunction based cells which rely on effective fields are more effective.

## **Examples**

Cells with phthalocyanine (Fig 1) as organic layer were investigated at the early stage. As early as 1958, Kearns et al. reported the photovoltaic effect the creation of voltage of a cell based on magnesium phthalocyanine a macrocyclic compound having an alternating nitrogen atom-carbon atom ring structure (MgPh), which had a photovoltage of 200mV. Ghosh et al. investigated the Al/MgPh/Ag cell, and obtained photovoltaic efficiency of 0.01% under illumination at 690 nm.

Conjugated polymers were also used in this type of photovoltaic cell. Weinberger et al. used polyacetylene (Fig 1) as the organic layer, Al and graphite as electrodes to fabricate a cell, which had an open circuit voltage of 0.3 V and a charge collection efficiency of 0.3%. Glenis et al. reported a Al/poly(3-nethyl-thiophene)/Pt cell had an external quantum yield of 0.17%, an open circuit voltage of 0.4V and a fill factor of 0.3. Karg et al. fabricated an ITO/PPV/Al cell, showing an open circuit voltage of 1V and a power conversion efficiency of 0.1% under white-light illumination.

## **Problems**

In practice, single layer organic photovoltaic cells of this type do not work well. They have low quantum efficiencies (<1%) and low power conversion efficiencies (<0.1%). A major problem with them is the electric field resulting from the difference between the two conductive electrodes is seldom sufficient to break up the photogenerated excitons. Often the electrons recombine with the holes rather than reach the electrode. To deal with this problem, the multilayer organic photovoltaic cells were developed.

### Bilayer organic photovoltaic cells

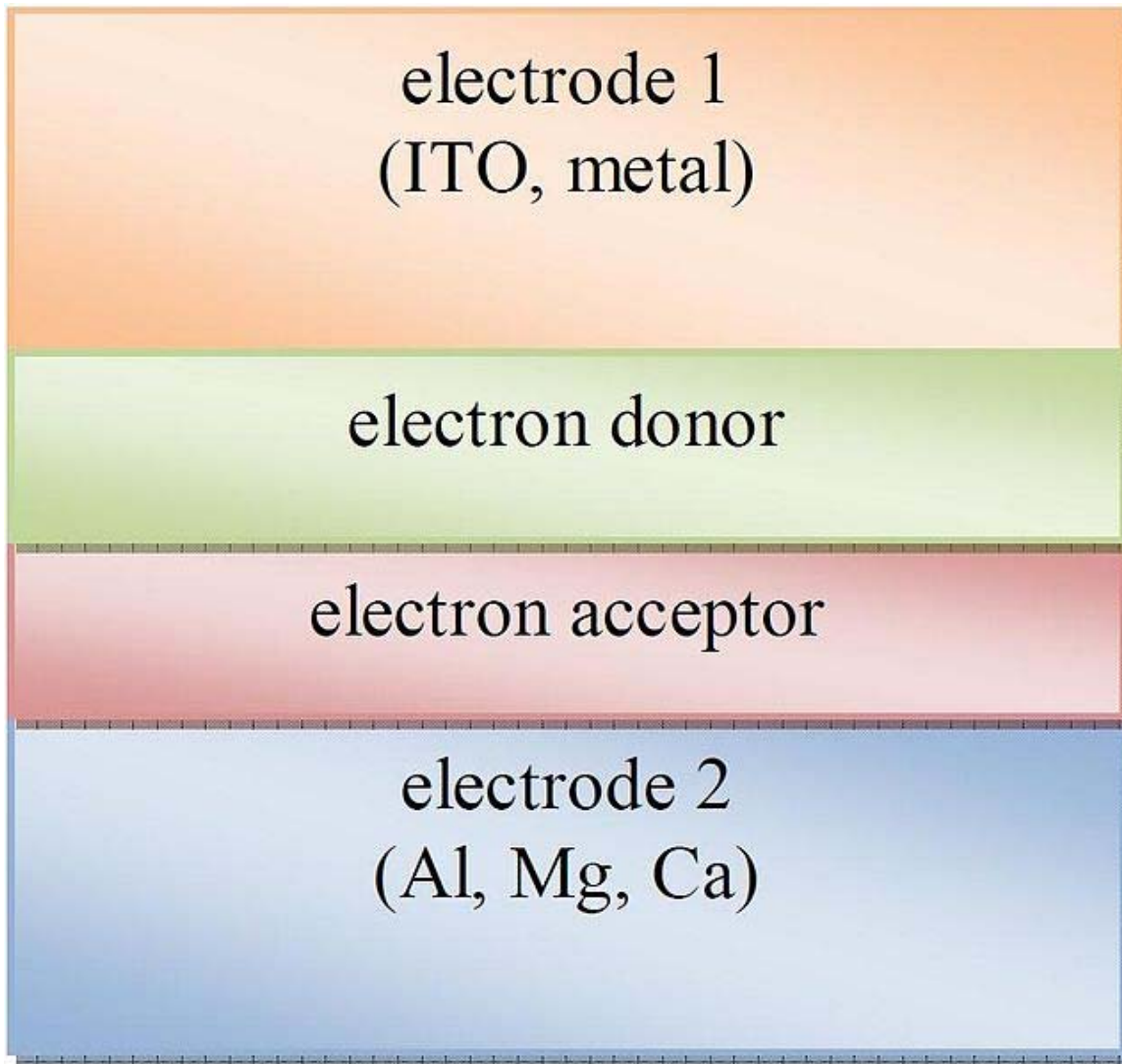


Fig 3: Sketch of a multilayer organic photovoltaic cell.

This type of organic photovoltaic cell contains two different layers in between the conductive electrodes (Fig 3). These two layers of materials have differences in electron affinity and ionization energy, therefore electrostatic forces are generated at the interface between the two layers. The materials are chosen properly to make the differences large enough, so these local electric fields are strong, which may break up the excitons much more efficiently than the single layer photovoltaic cells do. The layer with higher electron affinity and ionization potential is the electron acceptor, and the other layer is the electron donor. This structure is also called planar donor-acceptor heterojunctions.

## Examples

C<sub>60</sub> has high electron affinity, making it a good material as electron acceptor in photovoltaic cells of this type. Sariciftci et al. fabricated a C<sub>60</sub>/MEH-PPV double layer cell, which had a relatively high fill factor of 0.48 and a power conversion efficiency of 0.04% under monochromatic illumination. For PPV/C<sub>60</sub> cells, Halls et al. reported a monochromatic external quantum efficiency of 9%, a power conversion efficiency of 1% and a fill factor of 0.48.

Perylene derivatives are a group of organic molecules with high electron affinity and chemical stability. Ching W. Tang deposited a layer of copper phthalocyanine as electron donor and perylene tetracarboxylic derivative as electron acceptor, fabricating a cell with a fill factor as high as 0.65 and a power conversion efficiency of 1% under simulated AM2 illumination. Halls et al. fabricated a cell with a layer of bis(phenethylimido) perylene over a layer of PPV as the electron donor. This cell had peak external quantum efficiency of 6% and power conversion efficiency of 1% under monochromatic illumination, and the fill factor is up to 0.6.

## Problems

The diffusion length of excitons in organic electronic materials is typically on the order of 10 nm. In order for most excitons to diffuse to the interface of layers and break up into carriers, the layer thickness should also be in the same range with the diffusion length. However, typically a polymer layer needs a thickness of at least 100 nm to absorb enough light. At such a large thickness, only a small fraction of the excitons can reach the heterojunction interface. To address this problem, a new type of heterojunction photovoltaic cells is designed, which is the dispersed heterojunction photovoltaic cells.

## Bulk heterojunction photovoltaic cells

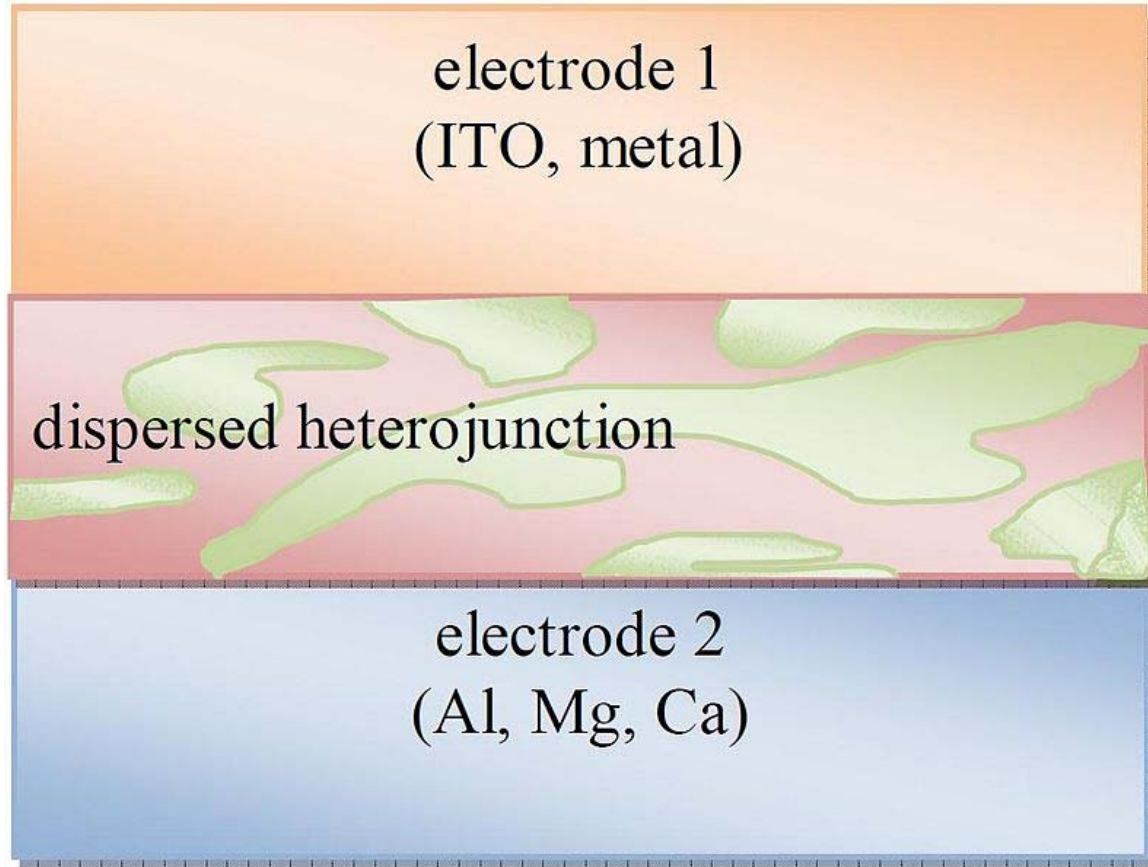


Fig 4: Sketch of a dispersed junction photovoltaic cell

In this type of photovoltaic cell, the electron donor and acceptor are mixed together, forming a polymer blend (Fig 4). If the length scale of the blend is similar with the exciton diffusion length, most of the excitons generated in either material may reach the interface, where excitons break efficiently. Electrons move to the acceptor domains then were carried through the device and collected by one electrode, and holes were pulled in the opposite direction and collected at the other side.

### Examples

$C_{60}$  and its derivatives are also used as electron acceptor in the dispersed heterojunction photovoltaic cells. Yu et al. fabricated a cell with the blend of MEH-PPV and a methano-functionalized  $C_{60}$  derivative as the heterojunction, ITO and Ca as the electrodes. This cell showed a quantum efficiency of 29% and a power conversion efficiency of 2.9% under monochromatic illumination. Later they replaced MEH-PPV with P3OT, which obtained a cell with a quantum yield of 45% under a 10V reverse bias.

Polymer/polymer blends are also used in dispersed heterojunction photovoltaic cells. Halls et al. used a blend of CN-PPV and MEH-PPV, fabricated a cell with Al and ITO as

the electrodes, whose peak monochromatic power conversion efficiency is 1% and fill factor is 0.38.

Dye sensitized photovoltaic cells can also be considered as important ones of this type.

## Current challenges and recent progress

Difficulties associated with organic photovoltaic cells include their low quantum efficiency (~3%) in comparison with inorganic photovoltaic devices; due largely to the large band gap of organic materials. Instabilities against oxidation and reduction, recrystallization and temperature variations can also lead to device degradation and decreased performance over time. This occurs to different extents for devices with different compositions, and is an area into which active research is taking place.

Other important factors include the exciton diffusion length; charge separation and charge collection; and charge transport and mobility, which are affected by the presence of impurities.

### Effect of film morphology

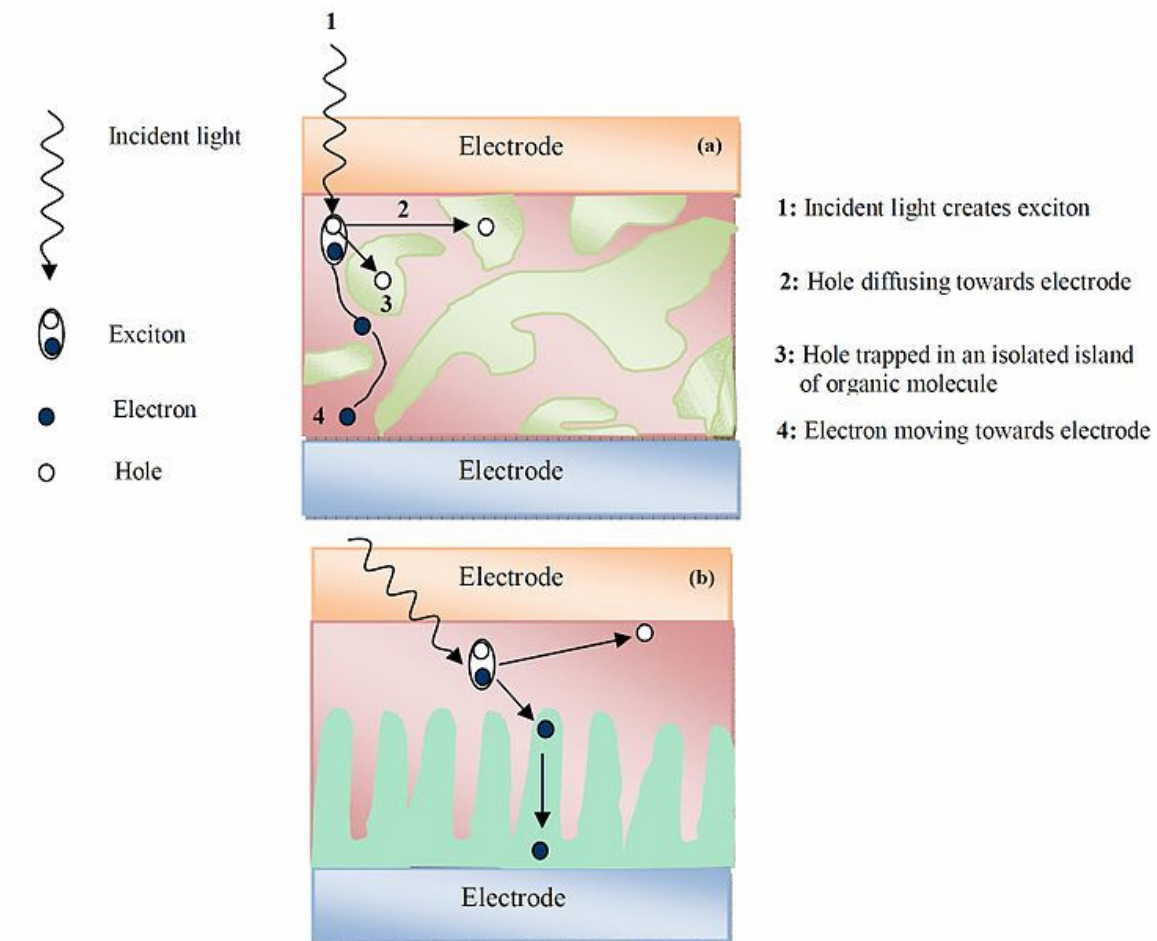


Fig 5a: Highly folded Hetero-junction; 5b: Hetero-junction with controlled growth

As described in section 2.3, dispersed heterojunction of donor-acceptor organic materials have high quantum efficiency compared to the planar hetero-junction, because it is more likely for an exciton to find an interface within its diffusion length. Film morphology can also have a drastic effect on the quantum efficiency of the device. Rough surfaces and presence of voids can increase the series resistance and also the chance of short circuiting. Film morphology and as a result quantum efficiency can be improved by annealing of a device after covering it by  $\sim 1000\text{\AA}$  thick metal cathode. Metal film on top of the organic film applies stresses on the organic film, which helps to prevent the morphological relaxation in the organic film. This gives more densely packed films while at the same time allows the formation of phase-separated interpenetrating donor-acceptor interface inside the bulk of organic thin film.

### **Controlled growth heterojunction**

Charge separation occurs at the donor acceptor interface. Whilst traveling to the electrode, a charge can become trapped and/or recombine in a disordered interpenetrating organic material, resulting in decreased device efficiency. Controlled growth of the heterojunction provides better control over positions of the donor-acceptor materials, resulting in much greater power efficiency (ratio of output power to input power) than that of planar and highly disoriented hetero-junctions (as shown in Fig 5(a), (b)). Thus, the choice of suitable processing parameters in order to better control the structure and film morphology is highly desirable.

### **Progress in growth techniques**

Mostly organic films for photovoltaic applications are deposited by spin coating and vapor-phase deposition. However each method has certain draw backs, spin coating technique can coat larger surface areas with high speed but the use of solvent for one layer can degrade the already existing polymer layer. Another problem is related with the patterning of the substrate for device as spin-coating results in coating the entire substrate with a single material.

## Vacuum thermal evaporation

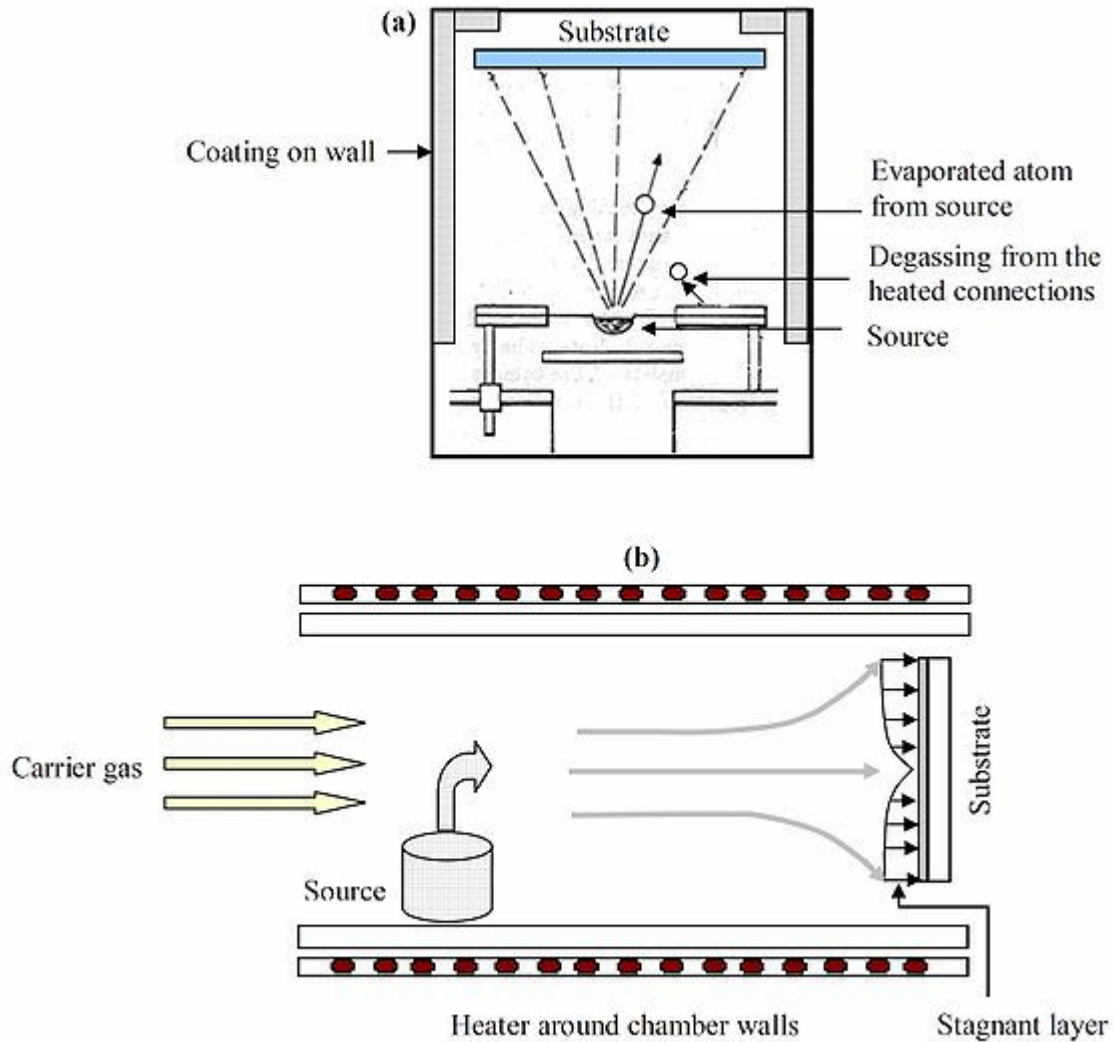


Fig.6 (a) Vapor thermal Evaporation , (b) Organic vapor phase deposition

Fig 6a: Vapor thermal evaporation

Another deposition technique is "Vacuum thermal evaporation" (VTE) which involves the heating of an organic material in vacuum. The substrate is placed several centimeters away from the source so that evaporated material may be directly deposited onto the substrate, as shown in Fig 6(a). This method is useful for depositing many layers of different materials without chemical interaction between different layers. However, there are sometimes problems with film-thickness uniformity and uniform doping over large-area substrates. In addition, the materials that deposit on the wall of the chamber can contaminate later depositions. This is "line of sight" technique also can create holes in the film due to shadowing, which causes an increase in the device series-resistance and short circuit.



## **Organic vapor phase deposition**

Organic thin film grown from "Organic vapor phase deposition" (OVPD) is proven to give better control on the structure and morphology of the film than vacuum thermal evaporation. The process involves evaporation of the organic material over a substrate in the presence of an inert carrier gas. Resulting film morphology can be changed by changing the gas flow rate and the source temperature. Uniform film can be grown by reducing the carrier gas pressure, which will increase the velocity and mean free path of the gas, and as a result boundary layer thickness decreases. Cells produced by OVPD do not have issues related with contaminations from the flakes coming out of the walls of the chamber, as the walls are warm and do not allow molecules to stick to and produce a film upon them.

Another advantage over VTE is the uniformity in evaporation rate. This occurs because the carrier gas becomes saturated with the vapors of the organic material coming out of the source and then moves towards the cooled substrate, Fig6(b). Depending on the growth parameters (temperature of the source, base pressure and flux of the carrier gas) the deposited film can be crystalline or amorphous in nature. Devices fabricated using OVPD show a higher short-circuit current density than that of devices made using VTE. An extra layer of donor-acceptor hetero-junction at the top of the cell may block excitons, whilst allowing conduction of electron; resulting in improved cell efficiency.

## **Organic solar ink**

Plextronics Plexcore PV 2000 organic solar ink is able to deliver higher performance in fluorescent lighting conditions in comparison to amorphous silicon solar cells. The Plexcore PV 2000 is said to have a 30% to 40% increase in indoor power density in comparison to the standard organic solar technology.

Plextronics has also developed a breakthrough manufacturing method that allows for low-temperature processing of OPV. While previous industry standard techniques required a glass substrate to be annealed at temperatures at or above 110° C, the method developed at Plextronics enables annealing at less than 65° C. This new method is expected to reduce manufacturing costs by enabling the use of less expensive substrates, especially once the process is transferred to flexible substrates such as plastic.

## Chapter- 5

# Hybrid Solar Cell

**Hybrid solar cells** combine advantages of both organic and inorganic semiconductors. Hybrid photovoltaics have organic materials that consist of conjugated polymers that absorb light as the donor and transport holes. Inorganic materials in hybrid cell are used as the acceptor and electron transporter in the structure. The hybrid photovoltaic devices have a significant potential for not only low-cost by roll-to-roll processing but also scalable solar power conversion.

## Theory

### Solar cell

Solar cells are devices that convert sunlight directly into electricity by the photovoltaic effect. Electrons in a solar cell absorb photon energy in sunlight, resulting in jumping to a conduction band from a valence band. This process generates a hole-electron pair, which is separated by a potential barrier (such as p-n junction), and induces a current flow.

### Organic solar cell

Organic solar cells use organic materials in the active layer of the devices. Molecular, polymer, and hybrid organic photovoltaics are the main kinds of organic photovoltaic devices that are currently studied.

## Hybrid solar cell

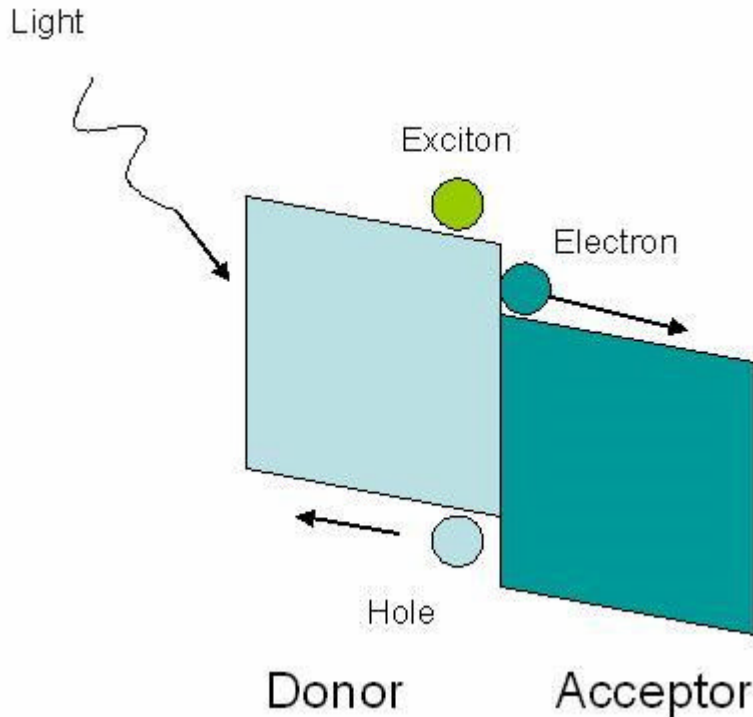


Figure 1. Energy diagram of the donor and acceptor. The conduction band of the acceptor is lower than the LUMO of the polymer, allowing for transfer of the electron.

In hybrid solar cells, an organic material is mixed with a high electron transport material to form the photoactive layer. The two materials are assembled together in a heterojunction type photoactive layer. By placing one material into contact with each other, the power conversion efficiency can be greater than a single material.

One of the materials acts as the photon absorber and exciton donor, and the other facilitates exciton dissociation at the junction by charge transfer.

The steps for the charge transfer are:

1. Excitation on donor
2. Excitation delocalized on a donor-acceptor complex
3. Charge-transfer initiated.
4. Charge separation.

The acceptor material needs a suitable energy offset to the binding energy of the exciton to the absorber. Charge transfer is favorable if the following condition is satisfied:

$$E_A^A - E_A^D > U_D$$

Where  $E_A$  is the electron affinity and  $U$  is the coulombic binding energy of the exciton on the donor, and superscript A refers to the acceptor and superscript D refers to the donor. An energy diagram of the interface is shown in figure 1. In commonly used photovoltaic polymers such as MEH-PPV, the exciton binding energy ranges from 0.3 eV to 1.4 eV.

The energy required to separate the exciton is provided by the energy offset between the LUMOs or conduction band of the donor and acceptor. After dissociation, the carriers are transported to the respective electrodes through a percolation network.

The average distance an exciton can diffuse through a material before annihilation by recombination happens is the exciton diffusion length. This is short in polymers, on the order of 5-10 nanometers. The time scale for radiative and non-radiative decay is from 1 picosecond to 1 nanosecond. Excitons generated within this length close to an acceptor would contribute to the photo current.

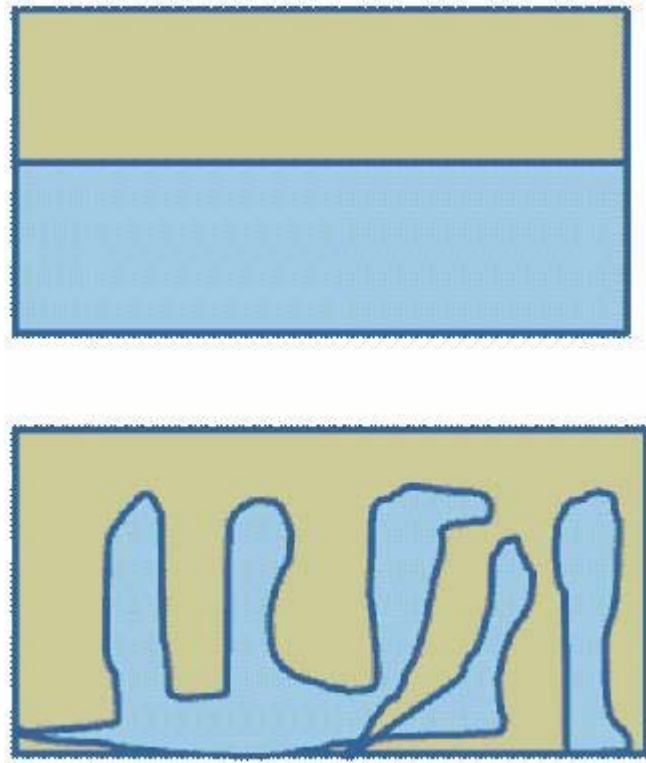


Figure 2. Two different structures of heterojunctions, a) phase separated bi-layer and b) bulk heterojunction. The bulk heterojunction allows for more interfacial contact between the two phases, which is beneficial for the nanoparticle-polymer compound as it provides more surface area for charge transfer.

To deal with the problem of the short exciton diffusion length, rather than a phase-separated bilayer, a bulk heterojunction structure is used. Dispersing the particles throughout the polymer matrix creates a larger interfacial area for charge transfer to occur. Figure 2 displays the difference between a bilayer and a bulk heterojunction.

## **Fundamental challenge factors**

In order to start large-scale manufacturing, the efficiency must be higher. There are three factors that must be considered: 1) bandgap, 2) interfaces, and 3) charge transport.

### **Bandgap**

Current organic photovoltaics have shown 70% of quantum efficiency for blue photons. However, the bandgap should be reduced to absorb red photons, which contains a significant fraction of the energy in the solar spectrum.

### **Interfaces**

Contact resistance between each layer in the device should be minimized to offer higher fill factor and power conversion efficiency.

### **Charge transport**

Higher charge carrier mobility allows the photovoltaics to have thicker active layers while photovoltaics minimize carrier recombination and keep the series resistance of the device low.

## **Types of hybrid solar cells**

### **Polymer–nanoparticle composite**

Nanoparticles are a class of semiconductor materials whose size in at least one dimension ranges from 1 to 100 nanometers, on the order of exciton wavelengths. This size control creates quantum confinement and allows for the tuning of optoelectronic properties, such as band gap and electron affinity. Nanoparticles also have a large surface area to volume ratio, which presents more area for charge transfer to occur.

The photoactive layer can be created by mixing nanoparticles into a polymer matrix.

## Structure and processing

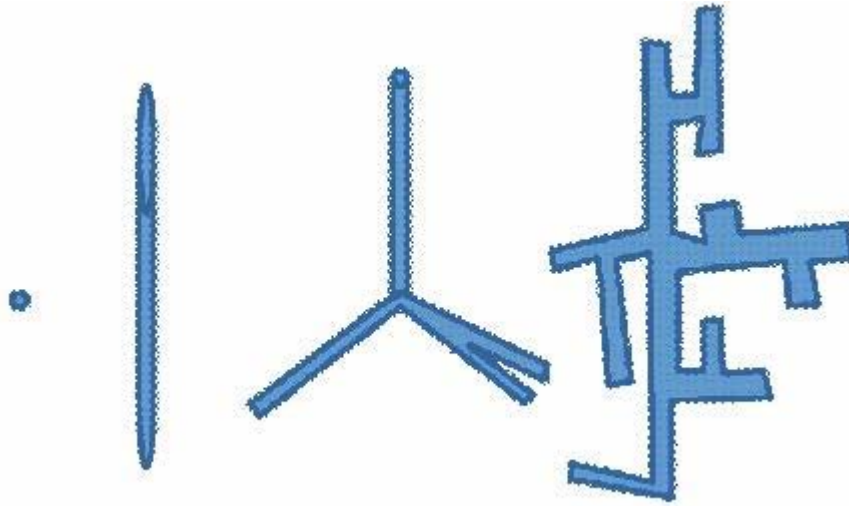


Figure 3. Four different structures of nanoparticles, which have at least 1 dimension in the 1-100 nm range, retaining quantum confinement. Left is a nanocrystal, next to it is nanorod, third is tetrapod, and right is hyperbranched.

For polymers used in this device, the hole mobilities are greater than electron mobilities, so the polymer phase is used to transport holes. The nanoparticles transport electrons to the electrode.

The interfacial area between the polymer phase and the nanoparticles needs to be large and this is achieved by dispersing the particles throughout the polymer matrix. However, the nanoparticles need to be interconnected to form percolation networks for electron transport, which occurs by hopping events.

Aspect ratio, geometry, and volume fraction of the nanoparticles are factors in their efficiency. The structure of the nanoparticles can take a shape of a nanocrystal, nanorods, hyperbranched, and others. Figure 3 contains a picture of each structure. Implementing different structures changes the conversion efficiency in terms of nanoparticle dispersion in the polymer and providing pathways for electron transport.

The nanoparticle phase is required to provide a pathway for the electrons to reach the electrode. By using nanorods instead of nanocrystals, the hopping event from one crystal to another can be avoided.

Fabrication methods include mixing the two in a solution and spin-coating onto a substrate, and solvent evaporation (sol-gel). Most of these polymer fabrication methods do not involve high temperature processing. Annealing increases order in the polymer phase, increasing conductivity. However, annealing for too long would cause the polymer domain size to increase, eventually becoming larger than the exciton diffusion length, and

possibly allowing some of the metal from the contact to diffuse into the photoactive layer, reducing the efficiency of the device.

## **Materials**

Inorganic semiconductor nanoparticles used in hybrid cells include CdSe (size ranges from 6-20 nm), ZnO, TiO, and PbS. Common polymers used as photo materials have extensive conjugation and also happen to be hydrophobic. Their efficiency as a photo material is affected by the HOMO level position and the ionization potential, which directly affects the open circuit voltage and the stability in air. The most common polymers used are P3HT (poly (3-hexylthiophene)), and M3H-PPV (poly[2-methoxy, 5-(2'-ethyl-hexyloxy)-p-phenylenevinylene]). P3HT has a bandgap of 2.1 eV and M3H-PPV has a bandgap of around 2.4 eV. These values mesh with the bandgap of CdSe, which is 2.10 eV. The electron affinity of CdSe ranges from 4.4 to 4.7 eV. If the polymer used was MEH-PPV which has an electron affinity of 3.0 eV, the difference between the two is large enough to drive electron transfer from the CdSe to the polymer. CdSe also has a high electron mobility of  $600 \text{ cm}^2/(\text{V}\cdot\text{s})$ .

## **Performance values**

Values demonstrated for a cell with a PPV derivate as the polymer and CdSe tetropods as the nanoparticle phase has an open circuit voltage of 0.76 V, a short circuit current of  $6.42 \text{ mA/cm}^2$ , a fill factor of 0.44, and a power conversion efficiency of 2.4%.

## **Challenges**

These structures need increased efficiency values and good stability over time before commercialization is feasible. Silicon photodevices has power conversion efficiencies greater than 20%, much greater than the 2.4% of the CdSe-PPV system.

Problems include controlling the amount of nanoparticle aggregation as the photolayer forms. The particles need to be dispersed in order to maximize interface area, but need to aggregate to form networks for electron transport. The network formation is sensitive to the fabrication conditions. Dead end pathways can impede flow. A possible solution is implementing ordered heterojunctions, where the structure is well controlled.

The structures can undergo morphological changes over time, namely phase separation. Eventually, the polymer domain size will be greater than the carrier diffusion length, which lowers performance.

Even though the nanoparticle bandgap can be tuned, it needs to be matched with the corresponding polymer. The 2.0 eV bandgap of CdSe is larger than an ideal bandgap of 1.4 for absorbance of light.

Compared to bulk silicon semiconductors, the properties of these structures are lacking. The carrier mobilities are much smaller than that of silicon. Electron in silicon is 1000

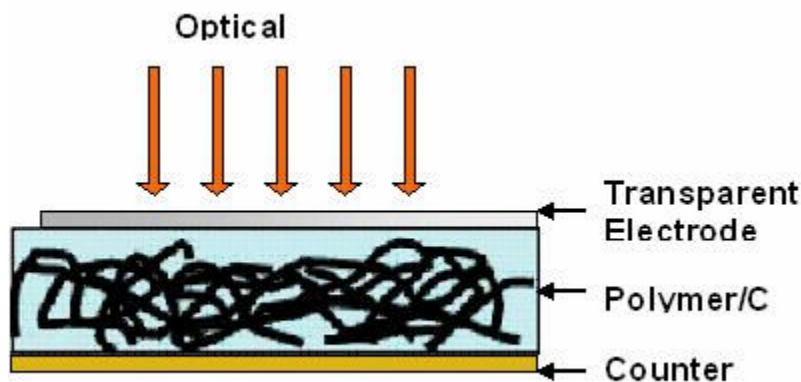
$\text{cm}^2/(\text{V}\cdot\text{s})$  while in CdSe it's  $600 \text{ cm}^2/(\text{V}\cdot\text{s})$ , and other quantum dot materials is less than  $10 \text{ cm}^2/(\text{V}\cdot\text{s})$ . Hole mobility in MEH-PPV is  $0.1 \text{ cm}^2/(\text{V}\cdot\text{s})$ , while in silicon it is  $450 \text{ cm}^2/(\text{V}\cdot\text{s})$ .

## Carbon nanotubes

Carbon nanotubes (CNTs) have high electron conductivity, high thermal conductivity, robustness, and are flexible by nature. Field emission displays (FED), strain sensors, field effect transistor (FET) have been demonstrated. Each application shows the potential of CNT for nanoscale devices and for flexible electronics applications. Photovoltaic applications have also been explored for this novel material.

Mainly, CNT have been utilized as either the photo-induced exciton carrier transport medium impurity within a polymer-based photovoltaic layer or as the photoactive (photon-electron conversion) layer. The metallic CNT is preferred for the former application, while semiconducting CNT is preferred for the later.

### Efficient carrier transport medium



Device diagram for CNT as efficient carrier transport medium.

To increase the photovoltaic efficiency, electron accepting impurities must be added within the photoactive region. Thus, by incorporating CNT within the polymer, dissociation of the exciton pair can be accomplished by the CNT matrix. The high surface area ( $\sim 1600 \text{ m}^2/\text{g}$ ) of CNT offers a tremendous opportunity for exciton dissociation. The separated carriers within the polymer-CNT matrix are transported by the percolation pathways of adjacent CNTs, providing the means for high carrier mobility and efficient charge transfer. The factors of performance of CNT-polymer hybrid photovoltaic are low compared to inorganic photovoltaic. SWNT in P3OT semiconductor polymer demonstrated open circuit voltage ( $V_{oc}$ ) is under  $0.94 \text{ V}$ , with short circuit current ( $I_{sc}$ ) of  $0.12 \text{ mA}/\text{cm}^2$ .

Metal nanoparticles may be applied to the exterior of CNT to increase the exciton separation efficiency. The metal provides a higher electric field at the CNT-polymer



interface, hence accelerating the exciton carriers to be more effectively transferred to the CNT matrix. In this case,  $V_{oc}$  is 0.3396 V, with  $I_{sc}$  to be 5.88 mA/cm<sup>2</sup>. The fill factor is 0.3876%, with the white light conversion factor being 0.775%.

## **Photoactive matrix layer**

CNT may be used as a photovoltaic device not only as an add-in material to increase carrier transport, but also as the photoactive layer itself. The semiconducting single walled CNT (SWCNT) is a potentially attractive material for photovoltaic applications for the unique structural and electrical properties. SWCNT has high electric conductivity (100 times that of copper) and show ballistic carrier transport, greatly decreasing carrier recombination. Bandgap of the SWCNT is inversely proportional to the tube diameter. Hence this single material may show multiple direct bandgaps matching the solar spectrum.

A strong built-in electric field in SWNT for efficient photogenerated electron-hole pair separation has been demonstrated by using two asymmetrical metal electrodes with high and low work functions. The open circuit voltage ( $V_{oc}$ ) is 0.28 V, with short circuit current ( $I_{sc}$ ) of 1.12 nA/cm<sup>2</sup>, with an incident light source of 8.8 W/cm<sup>2</sup>. The resulting white light conversion factor is 0.8%.

## **Challenges**

Several challenges must be addressed for CNT to be used in photovoltaic applications. CNT degrades overtime in oxygen rich environment. The passivation layer required to prevent CNT oxidation may reduce the optical transparency of the electrode region, hence lowering the photovoltaic efficiency.

### **Challenges as efficient carrier transport medium**

Additional challenges involve the dispersion of CNT within the polymer photoactive layer. The CNT is required to be well dispersed within the polymer matrix to form efficient pathways between the occurrence of the excitons and the electrode. Failure to do so will result in inefficient charge transfer.

**Challenges as photoactive matrix layer** Challenges of CNT for the photoactive layer include the lack of capability to form a p-n junction. The latter results in an internal built-in potential, providing pathway for efficient carrier separation within the photovoltaic. It is extremely difficult to dope certain segments of a CNT, hence the formation of PN junction has not been demonstrated thus far. To overcome this difficulty, energy band bending has been done by the use of two electrodes having different work functions. A strong built-in electric field covering the whole SWNT channel is formed for high-efficiency carrier separation. Also, oxidation issue of CNT is more critical for this application. Oxidized CNT have a tendency to become more metallic, losing merit as a photovoltaic material.

## Dye-sensitized

Dye-sensitized solar cells consists of a photo-sensitized anode, an electrolyte, and a photo-electrochemical system. Hybrid solar cells based on dye-sensitized solar cells are formed with inorganic materials ( $\text{TiO}_2$ ) and organic materials.

## Materials

Hybrid solar cells based on dye-sensitized solar cells are fabricated by dye-absorbed inorganic materials and organic materials.  $\text{TiO}_2$  is the preferred inorganic material since this material is easy to synthesize and acts as a n-type semiconductor due to the donor-like oxygen vacancies. However, titania only absorbs a small fraction of the UV spectrum. Molecular sensitizers (dye molecules) attached to the semiconductor surface are used to collect a greater portion of the spectrum. In the case of titania dye-sensitized solar cells, a photon absorbed by a dye-sensitizer molecule layer induces electron injection into the conduction band of titania, resulting in current flow. However, short diffusion length (diffusivity,  $D_n \leq 10^{-4} \text{cm}^2/\text{s}$ ) in titania dye-sensitized solar cells decrease the solar-to-energy conversion efficiency. To enhance diffusion length (or carrier lifetime), a variety of organic materials are attached to the titania.

## Fabrication scheme

### *Dye-sensitized photoelectrochemical cell (Grätzel cell)*

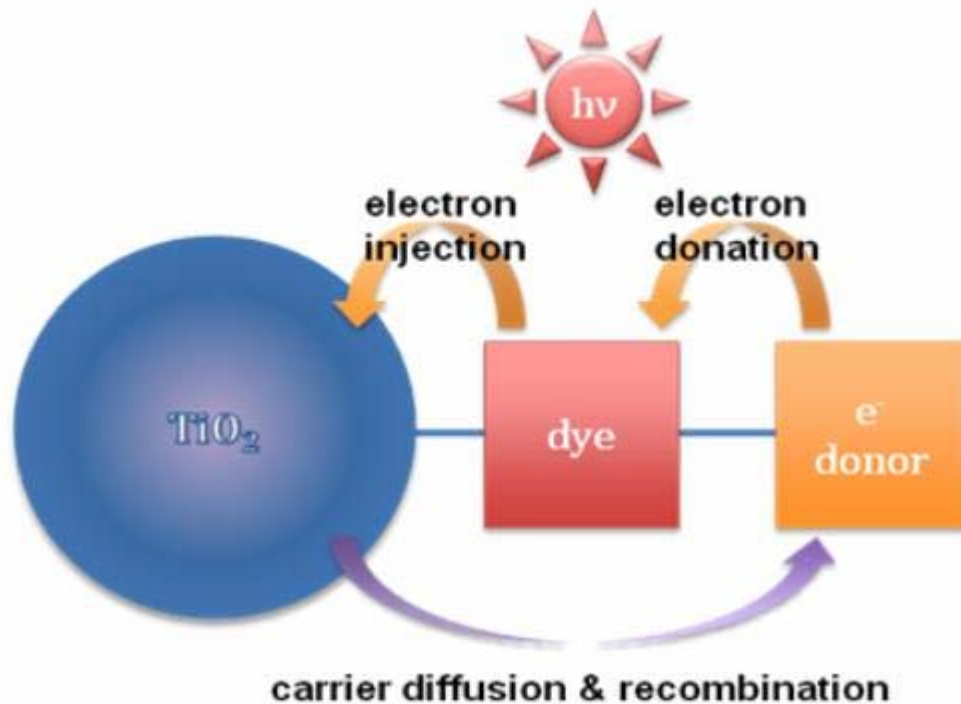


Fig. 5. Schematic representation of electron-hole generation and recombination

TiO<sub>2</sub> nanoparticles are synthesized in several tens of nanometer scales (~100 nm). In order to make a photovoltaic cell, molecular sensitizers (dye molecules) are attached to the titania surface. The dye-absorbed titania is finally enclosed by a liquid electrolyte. This type of dye-sensitized solar cell is also known as a Grätzel cell. Dye-sensitized solar cell has a disadvantage of a short diffusion length. Recently, supermolecular or multifunctional sensitizers have been investigated so as to enhance carrier diffusion length. For example, a dye chromophore has been modified by the addition of secondary electron donors. Minority carriers (holes in this case) diffuse to the attached electron donors to recombine. Therefore, electron-hole recombination is retarded by the physical separation between the dye-cation moiety and the TiO<sub>2</sub> surface, as shown in Fig. 5. Finally, this process raises the carrier diffusion length, resulting in the increase of carrier lifetime.

### ***Solid-state dye sensitized solar cell***

Mesoporous materials contain pores with diameters between 2 and 50 nm. A dye-sensitized mesoporous film of TiO<sub>2</sub> can be used for making photovoltaic cells and this solar cell is called a 'solid-state dye sensitized solar cell'. The pores in mesoporous TiO<sub>2</sub> thin film are filled with a solid hole-conducting material such as p-type semiconductors or organic hole conducting material. Replacing the liquid electrolyte in Grätzel's cells with a solid charge-transport material can be beneficial. The process of electron-hole generation and recombination is the same as Grätzel cells. Electrons are injected from photoexcited dye into the conduction band of titania and holes are transported by a solid charge transport electrolyte to an electrode. Many organic materials have been tested to obtain a high solar-to-energy conversion efficiency in dye synthesized solar cells based on mesoporous titania thin film.

### **Efficiency factors**

Efficiency factors demonstrated for dye-sensitized solar cells are

<b>Cell type</b>	<b>Grätzel cell</b>	<b>Solid-state dye sensitized solar cell</b>
<b>Efficiency</b>	~ 10-11%	~ 4%
<b>V<sub>oc</sub></b>	~ 0.7 V	~ 0.40 V
<b>J<sub>sc</sub></b>	~ 20 mA/cm <sup>2</sup>	~ 9.10 mA/cm <sup>2</sup>
<b>Fill factor</b>	~ 0.67	~ 0.6

### **Challenges**

Liquid organic electrolytes contain highly corrosive iodine, leading to problems of leakage, sealing, handling, dye desorption, and maintenance. Therefore, much effort are now involved in the electrolyte to overcome the above problems.

For solid-state dye sensitized solar cells, first challenge originates from disordered titania mesoporous structures. Mesoporous titania structures should be fabricated with well-ordered titania structures in uniform size (~ 10 nm). Second challenge comes from solid electrolyte. To develop the solid electrolyte, several requirements should be considered. The solid electrolyte is required to have special properties:

1. The electrolyte should be transparent to the visible spectrum (wide band gap)
2. Fabrication should be possible for depositing the solid electrolyte without degrading the dye molecule layer on titania.
3. LUMO level of dye molecule should be higher than the conduction band of titania.
4. Several p-type semiconductors tend to crystallize inside the mesoporous titania films, destroying the dye molecule-titania contact. Therefore, the solid electrolyte needs to be stable during operation.

### **Nanostructured inorganic–small molecules**

Recently, scientists have been able to achieve a nanostructured lamellar structure that provides an ideal design for bulk heterojunction solar cells. The observed structure is composed of ZnO and small, conducting organic molecules, which co-assemble into alternating layers of organic and inorganic components. This highly organized structure, which is stabilized by  $\pi$ - $\pi$  stacking between the organic molecules, enables the presence of conducting pathways in both the organic and inorganic layers. The thickness of each layer (about 1-3 nm) are well within the exciton diffusion length, which ideally minimizes recombination among charge carriers. This structure also maximizes the interface between the inorganic ZnO and the organic molecules, which enables a high chromophore loading density within the structure. In addition, due to the choice of materials, this system is non-toxic and environmentally friendly, unlike many other systems which use lead or cadmium.

Although this system has not yet been incorporated into a photovoltaic device, preliminary photoconductivity measurements have shown that this system exhibits among the highest values measured for organic, hybrid, and amorphous silicon photoconductors, and so, offers promise in creating efficient hybrid photovoltaic devices.

## Applications of Organic Electronics

### Smart glass

**Smart glass**, **EGlass**, or **switchable glass**, also called **smart windows** or **switchable windows** in its application to windows or skylights, refers to electrically switchable glass or glazing which changes light transmission properties when voltage is applied.

Certain types of smart glass can allow users to control the amount of light and heat passing through: with the press of a button, it changes from transparent to translucent, partially blocking light while maintaining a clear view of what lies behind the window. Another type of smart glass can provide privacy at the turn of a switch.

Smart glass technologies include electrochromic devices, suspended particle devices, Micro-Blinds and liquid crystal devices.

The use of smart glass can save costs for heating, air-conditioning and lighting and avoid the cost of installing and maintaining motorized light screens or blinds or curtains. When opaque, liquid crystal or electrochromic smart glass blocks most UV, thereby reducing fabric fading; for SPD-type smart glass, this is achieved when used in conjunction with low-e low emissivity coatings.

Critical aspects of smart glass include installation costs, the use of electricity, durability, as well as functional features such as the speed of control, possibilities for dimming, and the degree of transparency of the glass.



Soundproof smart glass "on"



Soundproof smart glass "off"

# Electrically switchable smart glass

## Electrochromic devices

Electrochromic devices change light transmission properties in response to voltage and thus allow to control the amount of light and heat passing through. In electrochromic windows, the electrochromic material changes its opacity: it changes between a colored, translucent state (usually blue) and a transparent state. A burst of electricity is required for changing its opacity, but once the change has been effected, no electricity is needed for maintaining the particular shade which has been reached. Darkening occurs from the edges, moving inward, and is a slow process, ranging from many seconds to several minutes depending on window size. Electrochromic glass provides visibility even in the darkened state and thus preserves visible contact with the outside environment. It has been used in small-scale applications such as rearview mirrors. Electrochromic technology also finds use in indoor applications, for example, for protection of objects under the glass of museum display cases and picture frame glass from the damaging effects of the UV and visible wavelengths of artificial light.

Recent advances in electrochromic materials pertaining to transition-metal hydride electrochromics have led to the development of reflective hydrides, which become reflective rather than absorbing, and thus switch states between transparent and mirror-like.

Recent advancements in modified porous nano-crystalline films have enabled the creation of electrochromic display. The single substrate display structure consists of several stacked porous layers printed on top of each other on a substrate modified with a transparent conductor (such as ITO or PEDOT:PSS). Each printed layer has a specific set of functions. A working electrode consists of a positive porous semiconductor (say Titanium Dioxide,  $\text{TiO}_2$ ) with adsorbed chromogens (different chromogens for different colors). These chromogens change color by reduction or oxidation. A passivator is used as the negative of the image to improve electrical performance. The insulator layer serves the purpose of increasing the contrast ratio and separating the working electrode electrically from the counter electrode. The counter electrode provides a high capacitance to counterbalances the charge inserted/extracted on the SEG electrode (and maintain overall device charge neutrality). Carbon is an example of charge reservoir film. A conducting carbon layer is typically used as the conductive back contact for the counter electrode. In the last printing step, the porous monolith structure is overprinted with a liquid or polymer-gel electrolyte, dried, and then may be incorporated into various encapsulation or enclosures, depending on the application requirements. Displays are very thin, typically 30 micrometer, or about 1/3 of a human hair. The device can be switched on by applying a electrical potential to the transparent conducting substrate relative to the conductive carbon layer. This causes a reduction of viologen molecules (coloration) to occur inside the working electrode. By reversing the applied potential or providing a discharge path, the device bleaches. A unique feature of the electrochromic monolith is the relatively low voltage (around 1 Volt) needed to color or bleach the

viologens. This can be explained by the small over- potentials needed to drive the electrochemical reduction of the surface adsorbed viologens/chromogens.

## **Suspended particle devices**

In suspended particle devices (SPDs), a thin film laminate of rod-like particles suspended in a fluid is placed between two glass or plastic layers, or attached to one layer. When no voltage is applied, the suspended particles are arranged in random orientations and tend to absorb light, so that the glass panel looks dark (or opaque), blue or, in more recent developments, grey or black colour. When voltage is applied, the suspended particles align and let light pass. SPDs can be dimmed, and allow instant control of the amount of light and heat passing through. A small but constant potential difference is required for keeping the SPD smart window in its transparent state.

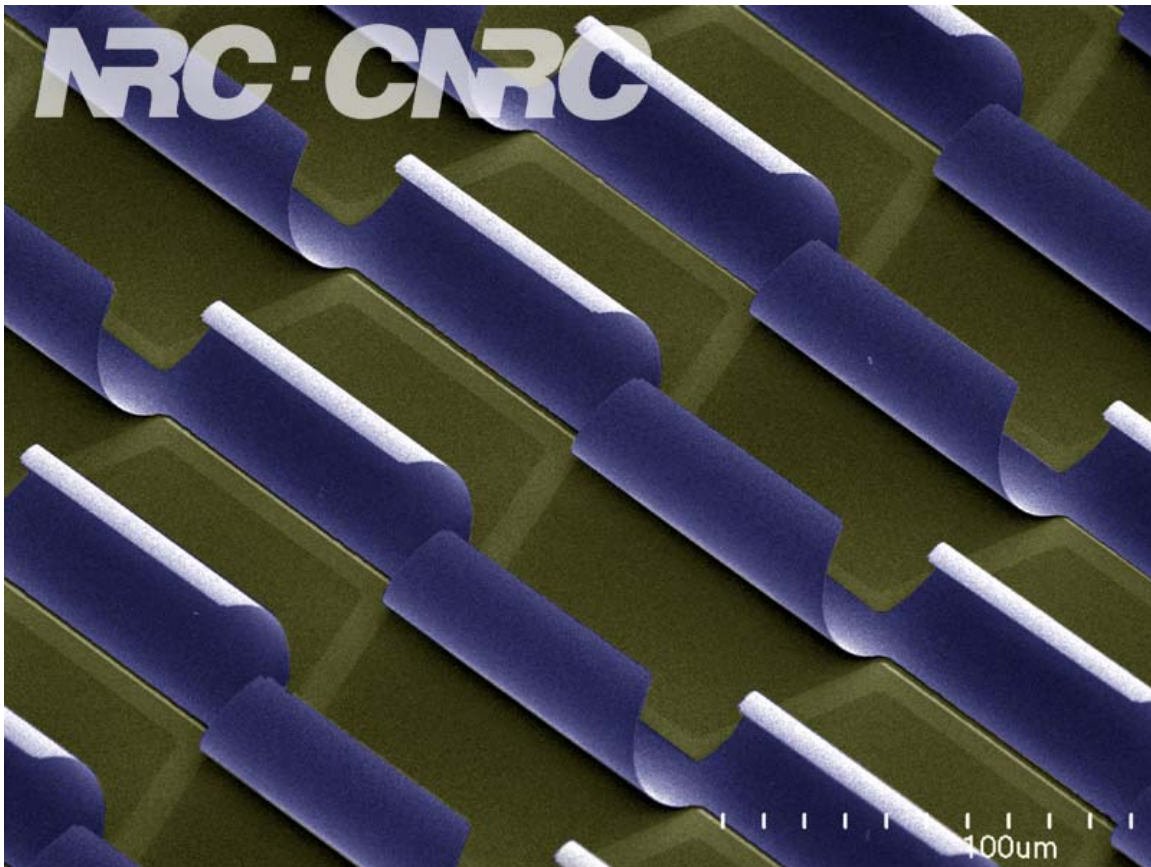
## **Polymer dispersed liquid crystal devices**

In polymer dispersed liquid crystal devices (PDLCs), liquid crystals are dissolved or dispersed into a liquid polymer followed by solidification or curing of the polymer. During the change of the polymer from a liquid to solid, the liquid crystals become incompatible with the solid polymer and form droplets throughout the solid polymer. The curing conditions affect the size of the droplets that in turn affect the final operating properties of the "smart window". Typically, the liquid mix of polymer and liquid crystals is placed between two layers of glass or plastic that include a thin layer of a transparent, conductive material followed by curing of the polymer, thereby forming the basic sandwich structure of the smart window. This structure is in effect a capacitor.

Electrodes from a power supply are attached to the transparent electrodes. With no applied voltage, the liquid crystals are randomly arranged in the droplets, resulting in scattering of light as it passes through the smart window assembly. This results in the translucent, "milky white" appearance. When a voltage is applied to the electrodes, the electric field formed between the two transparent electrodes on the glass causes the liquid crystals to align, allowing light to pass through the droplets with very little scattering and resulting in a transparent state. The degree of transparency can be controlled by the applied voltage. This is possible because at lower voltages, only a few of the liquid crystals align completely in the electric field, so only a small portion of the light passes through while most of the light is scattered. As the voltage is increased, fewer liquid crystals remain out of alignment, resulting in less light being scattered. It is also possible to control the amount of light and heat passing through, when tints and special inner layers are used. It is also possible to create fire-rated and anti X-Ray versions for use in special applications. Most of the devices offered today operate in on or off states only, even though the technology to provide for variable levels of transparency is easily applied. This technology has been used in interior and exterior settings for privacy control (for example conference rooms, intensive-care areas, bathroom/shower doors) and as a temporary projection screen.



## Micro-Blinds



Scanning Electron Microscope (SEM) image of Micro-blinds

Micro-blinds control the amount of light passing through in response to applied voltage. The micro-blinds are composed of rolled thin metal blinds on glass. They are very small and thus practically invisible to the eye. The metal layer is deposited by magnetron sputtering and patterned by laser or lithography process. The glass substrate includes a thin layer of a transparent conductive oxide (TCO) layer. A thin insulator is deposited between the rolled metal layer and the TCO layer for electrical disconnection. With no applied voltage, the micro-blinds are rolled and let light pass through. When there is a potential difference between the rolled metal layer and the transparent conductive layer, the electric field formed between the two electrodes causes the rolled micro-blinds to stretch out and thus block light. The micro-blinds have several advantages including switching speed (milliseconds), UV durability, customized appearance and transmission. The micro-blinds are under development at the National Research Council (Canada). One of the novelties is their simple and cost-efficient fabrication scheme.

## Related areas of technology

The expression **smart glass** can be interpreted in a wider sense to include also glazings that change light transmission properties in response to an environmental signal such as light or temperature.

- Different types of glazing can show a variety of chromic phenomena, that is, based on photochemical effects the glazing changes its light transmission properties in response to an environmental signal such as light (photochromism), temperature (thermochromism), or voltage (electrochromism).
- Liquid crystals, when they are in a thermotropic state, can change light transmission properties in response to temperature.
- Recent advancements in electrochromic materials have led to the discovery that transition metal hydride electrochromics that create a reflective face instead of an absorbent. These materials have the same idea but go about the problem in a different way by switching between a transparent state when they are off to a reflective state when a voltage is applied. Switchable mirrors were originally developed by Tom Richardson and Jonathon Slack of Berkeley Lab's Environmental Energy Technologies Division. They used rare earth metals and created the first metal-hydride switchable mirrors. Low emittance coatings reject unwanted thermal heat due to solar infrared<sup>21</sup>. These mirrors have become common place in cars' rearview mirrors in order to block the glare of following vehicles. An optically absorbing electrochromic color reduces the reflection intensity. These mirrors must be fully transformed to a reflective state as muted reflection must persist in the darkened state. Originally a metal, they are converted into a transparent hydride by injecting hydrogen in a gas or liquid phase. It then switches to a reflective state.
- Various metals have been looked into. Thin Ni-Mg films have low visible transmittance and are reflective. When they are exposed to H<sub>2</sub> gas or reduced by an alkaline electrolyte, they become transparent. This transition is attributed to the formation of nickel magnesium hydride, Mg<sub>2</sub>NiH<sub>4</sub>. Films were created by cosputtering from separate targets of Ni and Mg to facilitate variations in composition. Single-target d.c. magnetron sputtering could be used eventually which would be relatively simple compared to deposition of electrochromic oxides, making them more affordable. Lawrence Berkeley National Laboratory determined that new transition metals were cheaper and less reactive but contained the same qualities further reducing the cost.
- Tungsten doped Vanadium dioxide VO<sub>2</sub> coating reflects infrared light when the temperature rises over 29 degrees Celsius, to block out sunlight transmission through windows at high ambient temperatures.

These types of glazing cannot be controlled manually. In contrast, all electrically switched smart windows can be made to automatically adapt their light transmission properties in response to temperature or brightness by integration with a thermometer or photosensor, respectively.

The topic of **smart windows** in a wider sense also includes also self-cleaning glass and the automatic opening or closing of windows for ventilation purposes, for example according to a timer or in response to a rain sensor.

The topic of **smart windows** in a further sense includes LED Embedded Films which may be switched on at reduced light intensity. The process of laminating these LED embedded films between glass will allow the production of Transparent LED embedded glasses. As most glass companies are not skilled in mounting LEDs (Light Emitting Diodes) onto metallized glass, the LEDs are located on a separate transparent conductive polymeric interlayer that may be laminated by any glass lamination unit.

### **Examples of use**

Smart Glass using one of the aforementioned technologies has been seen in a number of high profile applications. Large scale installations were completed at the Guinness Storehouse in Dublin where over 800,000 people per year can see LC SmartGlass being used in interactive displays and privacy windows. LC SmartGlass was used to launch the Nissan Micra CC in London using a four-sided glass box made up of 150 switchable glass panels which switched in sequence to create a striking outdoor display. The main use for LC SmartGlass is in internal partitions where many companies now enjoy the ability to switch screens and doors from clear to private.



Polyvision Smart Glass, clear mode



Polyvision Smart Glass, projection mode

One of the most popular Smart Glass applications is as projection screens.

A new generation 3G Switchable Film/Glass is widely used at World Expo 2010 Shanghai, with projection showrooms at 24 major airports in China. 3G Switchable Film/Glass is used in giant projection screens, sunrooms, glass walls of buildings, and on luxury cruise ships.

Another example of use is the installation of PDLC-based smart glass , in *the EDGE*, a glass cube which protrudes out from the 88th floor skydeck of the world's highest residential tower, Eureka Towers, located in Melbourne. The cube can hold 13 people. When it extends out of the building by 3 metres, the glass is made transparent, giving the cube's occupants views of Melbourne from a height of 275 metres. The same type of smart glass has also been proposed for use in hospital settings to controllably provide patients with privacy as needed.

PDLC technology was used in a display to unveil the Nissan GTR at the Canadian International Auto Show in Toronto.

In the media, the updated set for the Seven Network's *Sunrise* program features a Smart Glass background that uses liquid crystal switchable glass (AGP UMU Glass) supplied by Architectural Glass Projects. The technology is especially suited to this purpose, as the set was originally open to a public place, meaning that people could do obscene things

behind the presenters. The new set with Smart Glass allows the street scene to be visible at times, or replaced with either opaque or transparent blue colouring, masking the view.

Bloomberg Television features Smart Glass backgrounds in the studios in New York City, London and Hong Kong.

The new Boeing 787 Dreamliner features electrochromic windows which replace the pull down window shades on existing aircraft. NASA is looking into using electrochromics to manage the thermal environment experienced by the newly developed Orion and Altair space vehicles.

Smart glass has been used in some small-production cars. The Ferrari 575 M Superamerica had an electrochromic roof as standard, and the Maybach has a PDLC roof as option. Some Polyvision Privacy Glass has been applied in the Maybach 62 car for privacy protection purposes.

A Hong Kong office uses 130 square meters of Polyvision Privacy Glass, which is available in sizes up to 1,500 x 3,200 mm.

MagicGlas(tm) Smart Glass from GlasNovations has been used in a number of projects around the world.

ICE 3 high speed trains use electrochromatic glass panels between the passenger compartment and the driver's cabin. The standard mode is clear/lucent and can be switched by the driver to frosted/translucent mainly to keep passengers off "unwanted sights" for example in case of (human) obstacles.

The elevators in the Washington Monument use smart glass in their design; it is essential in order for passengers to view the commemorative stones inside the monument.

## **Electronic paper**



iLiad e-book reader equipped with an electronic paper display. E-ink displays can be read even under bright sunlight since it has no backlighting.

**Electronic paper, e-paper or electronic ink display** is a display technology designed to mimic the appearance of ordinary ink on paper. Unlike a conventional flat panel display, which uses a backlight to illuminate its pixels, electronic paper reflects light like ordinary paper. It is capable of holding text and images indefinitely without drawing electricity, while allowing the image to be changed later. This is created via several different technologies, some using plastic substrate and electronics so that the display is flexible.

E-paper has the potential to be more comfortable to read than conventional displays. This is due to the stable image, which does not need to be refreshed constantly, the wider viewing angle, and the fact that it reflects ambient light rather than emitting its own light. An e-paper display can be read in direct sunlight without the image appearing to fade. The contrast ratio in available displays as of 2008 might be described as similar to that of newspaper, though newly-developed implementations are slightly better. There is ongoing competition among manufacturers to provide full-color capability.

Applications include electronic pricing labels in retail shops, and general signage, time tables at bus stations, electronic billboards, mobile phone displays, and e-Readers capable of displaying digital versions of books and e-paper magazines. Electronic paper

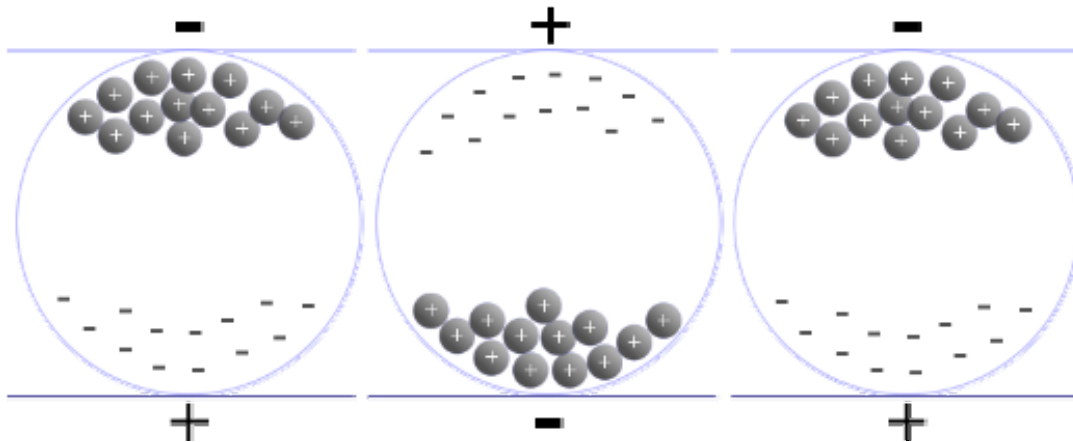
should not be confused with digital paper, which is a pad to create handwritten digital documents with a digital pen.

## Technology

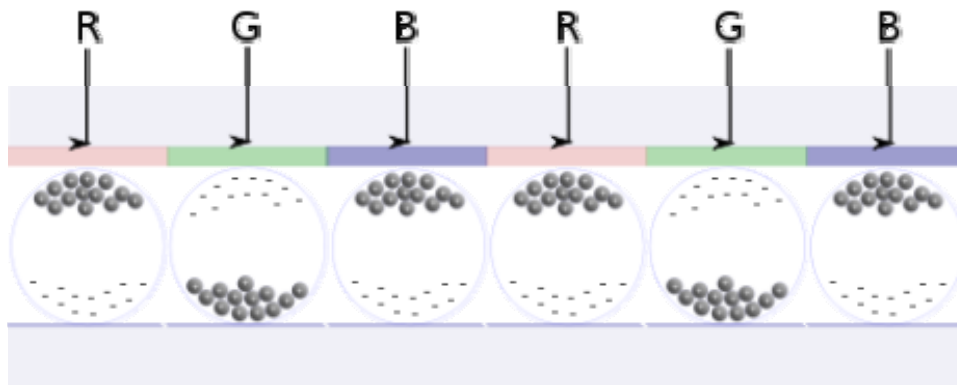
### Gyricon

Electronic paper was first developed in the 1970s by Nick Sheridan at Xerox's Palo Alto Research Center. The first electronic paper, called Gyricon, consisted of polyethylene spheres between 75 and 106 micrometres across. Each sphere is a janus particle composed of negatively charged black plastic on one side and positively charged white plastic on the other (each bead is thus a dipole). The spheres are embedded in a transparent silicone sheet, with each sphere suspended in a bubble of oil so that they can rotate freely. The polarity of the voltage applied to each pair of electrodes then determines whether the white or black side is face-up, thus giving the pixel a white or black appearance. At the FPD 2008 exhibition, Japanese company Soken has demonstrated a wall with electronic wall-paper using this technology.

### Electrophoretic



Scheme of an electrophoretic display.



Scheme of an electrophoretic display using color filters.

An **electrophoretic display** forms visible images by rearranging charged pigment particles using an applied electric field.

In the simplest implementation of an electrophoretic display, titanium dioxide particles approximately one micrometer in diameter are dispersed in a hydrocarbon oil. A dark-colored dye is also added to the oil, along with surfactants and charging agents that cause the particles to take on an electric charge. This mixture is placed between two parallel, conductive plates separated by a gap of 10 to 100 micrometres. When a voltage is applied across the two plates, the particles will migrate electrophoretically to the plate bearing the opposite charge from that on the particles. When the particles are located at the front (viewing) side of the display, it appears white, because light is scattered back to the viewer by the high-index titania particles. When the particles are located at the rear side of the display, it appears dark, because the incident light is absorbed by the colored dye. If the rear electrode is divided into a number of small picture elements (pixels), then an image can be formed by applying the appropriate voltage to each region of the display to create a pattern of reflecting and absorbing regions.

Electrophoretic displays are considered prime examples of the electronic paper category, because of their paper-like appearance and low power consumption.

Examples of commercial electrophoretic displays include the high-resolution active matrix displays used in the Amazon Kindle, Barnes & Noble Nook, Sony Librie, Sony Reader, and iRex iLiad e-readers. These displays are constructed from an electrophoretic imaging film manufactured by E Ink Corporation. Also the technology has been developed by Sipix Microcup and Bridgestone Quick Response Liquid Powder Display (QR-LPD). The Motorola MOTO F3 was the first mobile phone to use the technology, in an effort to help eliminate glare from direct sunlight during outdoor use.

Electrophoretic displays can be manufactured using the Electronics on Plastic by Laser Release (EPLaR) process developed by Philips Research to enable existing AM-LCD manufacturing plants to create flexible plastic displays.



## Development

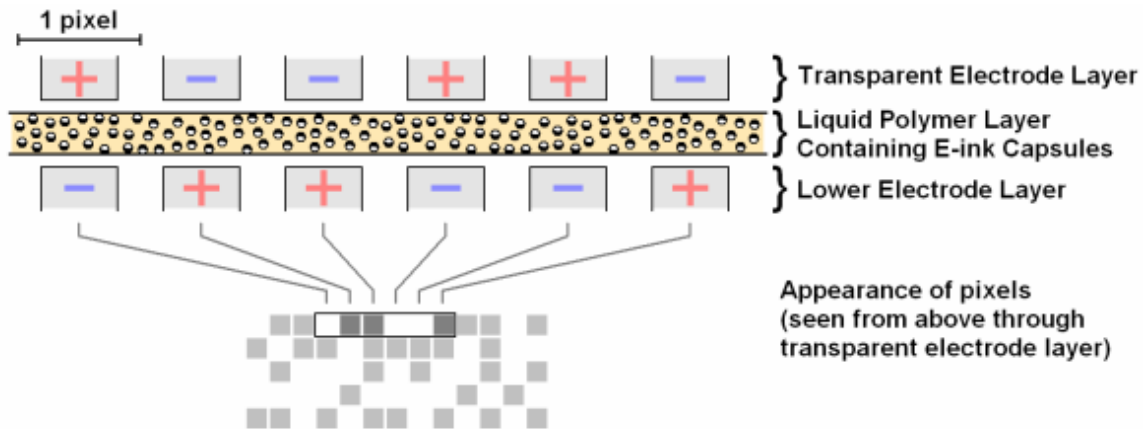


Macro photograph of Kindle 3 screen; microcapsules are evident at full size

In the 1990s another type of electronic paper was invented by Joseph Jacobson, who later co-founded the E Ink Corporation which formed a partnership with Philips Components two years later to develop and market the technology. In 2005, Philips sold the electronic paper business as well as its related patents to Prime View International. This used tiny microcapsules filled with electrically charged white particles suspended in a colored oil. In early versions, the underlying circuitry controlled whether the white particles were at the top of the capsule (so it looked white to the viewer) or at the bottom of the capsule (so the viewer saw the color of the oil). This was essentially a reintroduction of the well-known electrophoretic display technology, but the use of microcapsules allowed the display to be used on flexible plastic sheets instead of glass.

One early version of electronic paper consists of a sheet of very small transparent capsules, each about 40 micrometres across. Each capsule contains an oily solution containing black dye (the electronic ink), with numerous white titanium dioxide particles suspended within. The particles are slightly negatively charged, and each one is naturally white.

The microcapsules are held in a layer of liquid polymer, sandwiched between two arrays of electrodes, the upper of which is made transparent. The two arrays are aligned so that the sheet is divided into pixels, which each pixel corresponding to a pair of electrodes situated either side of the sheet. The sheet is laminated with transparent plastic for protection, resulting in an overall thickness of 80 micrometres, or twice that of ordinary paper.



### Appearance of pixels

The network of electrodes is connected to display circuitry, which turns the electronic ink 'on' and 'off' at specific pixels by applying a voltage to specific pairs of electrodes. Applying a negative charge to the surface electrode repels the particles to the bottom of local capsules, forcing the black dye to the surface and giving the pixel a black appearance. Reversing the voltage has the opposite effect - the particles are forced from the surface, giving the pixel a white appearance. A more recent incarnation of this concept requires only one layer of electrodes beneath the microcapsules.

### Electrowetting

Electro-wetting display (EWD) is based on controlling the shape of a confined water/oil interface by an applied voltage. With no voltage applied, the (coloured) oil forms a flat film between the water and a hydrophobic (water-repellent), insulating coating of an electrode, resulting in a coloured pixel.

When a voltage is applied between the electrode and the water, the interfacial tension between the water and the coating changes. As a result the stacked state is no longer stable, causing the water to move the oil aside.

This results in a partly transparent pixel, or, in case a reflective white surface is used under the switchable element, a white pixel. Because of the small size of the pixel, the user only experiences the average reflection, which means that a high-brightness, high-contrast switchable element is obtained, which forms the basis of the reflective display.

Displays based on electro-wetting have several attractive features. The switching between white and coloured reflection is fast enough to display video content.

It is a low-power and low-voltage technology, and displays based on the effect can be made flat and thin. The reflectivity and contrast are better than or equal to those of other reflective display types and are approaching those of paper.

In addition, the technology offers a unique path toward high-brightness full-colour displays, leading to displays that are four times brighter than reflective LCDs and twice as bright as other emerging technologies.

Instead of using red, green and blue (RGB) filters or alternating segments of the three primary colours, which effectively result in only one third of the display reflecting light in the desired colour, electro-wetting allows for a system in which one sub-pixel is able to switch two different colours independently.

This results in the availability of two thirds of the display area to reflect light in any desired colour. This is achieved by building up a pixel with a stack of two independently controllable coloured oil films plus a colour filter.

The colours used are cyan, magenta and yellow, which is a so-called subtractive system, comparable to the principle used in inkjet printing for example. Compared to LCD another factor two in brightness is gained because no polarisers are required.

Examples of commercial electrowetting displays include Liquavista, ITRI, PVI and ADT.

## **Electrofluidic**

Electrofluidic displays are a variation of an electrowetting display. Electrofluidic displays place an aqueous pigment dispersion inside a tiny reservoir. The reservoir comprises <5-10% of the viewable pixel area and therefore the pigment is substantially hidden from view. Voltage is used to electromechanically pull the pigment out of the reservoir and spread it as a film directly behind the viewing substrate. As a result, the display takes on color and brightness similar to that of conventional pigments printed on paper. When voltage is removed liquid surface tension causes the pigment dispersion to rapidly recoil into the reservoir. As reported in the May 2009 Issue of Nature Photonics, the technology can potentially provide >85% white state reflectance for electronic paper.

The core technology was invented at the Novel Devices Laboratory at the University of Cincinnati. The technology is currently being commercialized by Gamma Dynamics.

## **Interferometric modulator**

### **Other bistable displays**

- Kent Displays, manufacturer of cholesteric liquid crystal display (ChLCD).
- Nemoptic, Nematic materials
- TRED

### **Other technologies**

Other research efforts into e-paper have involved using organic transistors embedded into flexible substrates, including attempts to build them into conventional paper. Simple color e-paper consists of a thin colored optical filter added to the monochrome technology described above. The array of pixels is divided into triads, typically consisting of the standard cyan, magenta and yellow, in the same way as CRT monitors (although using subtractive primary colors as opposed to additive primary colors). The display is then controlled like any other electronic color display.

Examples of electrochromic displays include Acreo, Ajjer, Aveso and Ntera.

## **Disadvantages**

Electronic paper technologies have a very low refresh rate comparing with other low-power display technologies, such as LCD. This prevents producers from implementing sophisticated interactive applications (using fast moving menus, mouse pointers or scrolling) like those which are possible on handheld computers. An example of this limitation is that a document cannot be smoothly zoomed without either extreme blurring during the transition or a very slow zoom.



An e-ink screen showing the "ghost" of a previous image

Another limitation is that an imprint of an image may be visible after refreshing parts of the screen. Those imprints are known as "ghost images", and the effect is known as "ghosting". This effect is reminiscent of screen burn-in but, unlike it, is solved after the screen is refreshed several times. Turning every pixel white, then black, then white, helps normalize the contrast of the pixels. This is why several devices with this technology "flash" the entire screen white and black when loading a new image.

## **Applications**

Several companies are simultaneously developing electronic paper and ink. While the technologies used by each company provide many of the same features, each has its own distinct technological advantages. All electronic paper technologies face the following general challenges:

- A method for encapsulation
- An ink or active material to fill the encapsulation
- Electronics to activate the ink

Electronic ink can be applied to both flexible and rigid materials. In the case of flexible displays, the base requires a thin, flexible material tough enough to withstand considerable wear, such as extremely thin plastic. The method of how the inks are encapsulated and then applied to the substrate is what distinguishes each company from

each other. These processes are complex and are carefully guarded industry secrets. The manufacture of electronic paper promises to be less complicated and less costly than traditional LCD manufacture.

There are many approaches to electronic paper, with many companies developing technology in this area. Other technologies being applied to electronic paper include modifications of liquid crystal displays, electrochromic displays, and the electronic equivalent of an Etch A Sketch at Kyushu University. Advantages of electronic paper includes low power usage (power is only drawn when the display is updated), flexibility and better readability than most displays. Electronic ink can be printed on any surface, including walls, billboards, product labels and T-shirts. The ink's flexibility would also make it possible to develop rollable displays for electronic devices. The ideal electronic paper product is a digital book that can typeset itself and could be read as if it were made of regular paper, yet programmed to download and display the text from any book. Another possible use is in the distribution of an electronic version of a daily paper.

### **Commercial applications**



The Motorola F3 uses an e-paper display instead of an LCD.

## **Education: digital schoolbooks**

- In January 2007, the Dutch specialist in e-Paper edupaper.nl started a pilot project in a secondary school in Maastricht, using e-Paper as digital schoolbooks to reduce costs and students' daily burden of books.

## **Wristwatches**

- In December 2005 Seiko released their Spectrum SVRD001 wristwatch, which has a flexible electrophoretic display and in March 2010 Seiko released a second generation of this famous e-ink watch with an active matrix display.
- Phosphor of Hong Kong have launched 3 series of watches using flexible electrophoretic display using eink technology.

## **e-Books**

- In 2004 Sony released Librie EBR-1000EP in Japan, the first e-book reader with an electronic paper display. In September 2006 Sony released the PRS-500 Sony Reader e-book reader in the USA. On October 2, 2007, Sony announced the PRS-505, an updated version of the Reader. In November 2008, Sony released the PRS-700BC which incorporated a backlight and a touchscreen.
- In November 2006, the iRex iLiad was ready for the consumer market. Consumers could initially read e-Books in PDF and HTML formats, and in July 2007 support for the popular Mobipocket PRC format was added, but price was still a problem. With the introduction of the competing Cybook, prices have decreased almost 50%.
- In late 2007, Amazon began producing and marketing the Amazon Kindle, an e-book reader with an e-paper display. In February 2009, Amazon released the Kindle 2 and in May 2009 the larger Kindle DX was announced. In July 2010 the third generation Kindle was announced.
- In November 2009 Barnes and Noble launched the Barnes & Noble Nook, based on the Android operating system. It differs from other big name readers in that it has a replaceable battery and a separate touch-screen below the main reading screen.

## **Newspapers**

- In February 2006, the Flemish daily *De Tijd* distributed an electronic version of the paper to select subscribers in a limited marketing study, using a pre-release version of the iRex iLiad. This was the first recorded application of electronic ink to newspaper publishing.

- In September 2007, the French daily *Les Échos* announced the official launch of an electronic version of the paper on a subscription basis. Two offers are available, combining a one year subscription and a reading device. One interesting point of the offer is the choice of a light (176g) reading device (adapted for Les Echos by Ganaxa) or the iRex iLiad. Two different processing platforms are used to deliver readable information of the daily, one based on the newly developed GPP electronic ink platform from *Ganaxa*, and the other one developed internally by Les Echos.
- Since January 2008, the Dutch daily *NRC Handelsblad* is distributed for the iRex iLiad reader.

### **Displays embedded in smart cards**

- Flexible display cards enable financial payment cardholders to generate a one-time password to reduce online banking and transaction fraud. Electronic paper could offer a flat and thin alternative to existing key fob tokens for data security.

### **Status displays**

- Some devices, like USB flash drives, have used electronic paper to display status information, such as available storage space.

### **Mobile phones**

- Motorola's low-cost mobile phone, the Motorola F3, also uses an alphanumeric black/white electrophoretic display.
- The Samsung Alias 2 mobile phone incorporates electronic ink from E Ink into the keypad, which allows the keypad to change character sets and orientation while in different display modes.

### **Other applications**

Other proposed applications include digital photo frames and information boards.