Lecture notes: Organic Electronics

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Contents

1 Advantages and limitations of organic electronics

1.1 Consequences of physical cohesion

Organic media mostly are poor electronic conductors because they are held together by physical interactions. (Graphite is an exception.[1]) Even highly crosslinked plastics ("duromers") are poor electronic conductors. There is no quasi-free electron gas. In principle, one might hope for efficient electronic transport along polymer chains. These are covalently linked. However, there are no 1D-metals because of the Peierls transition (section 2.4).

Another problem with organic-electronics is poor chemical stability. Electron transport in these materials comes close to redox processes. Oxidizing agents can easily attack the sites where electrons reside.

Physical cohesion has the advantage of good processability. Small molecules and polymers can be dissolved in liquids. They can be printed, where printing is easier for polymers than for small molecules because polymer solutions become highly viscous when the solvent evaporates. Small molecules can be deposited by evaporation. The process is called physical vapor deposition, PVD.[2] Films made from organic materials may or may not contain small crystals. Conductivity can be improved by crystallinity. Grain boundaries, on the other hand, entail complications, both for electronic processes and mechanical properties. Flat, transparent films are most easily produced from amorphous materials. Amorphous silicon (a-Si) and amorphous oxide semiconductors, AOSs can be sputtered.[3]

Another advantage of organic materials can be flexibility and stretchability. Electronic circuits can be realized on soft substrates (like PET foils), textiles, or even the human skin. Amorphous oxide semiconductors, AOSs, have moderate conductivity, moderate mobility, and can also be flexible enough for application on PET films (Box 2.1).

At this point, it is worthwhile to compare organic electronics with silicon-based electronics. Disadvantages of silicon are:

- Single crystals cannot be coated onto a substrate. They would have to be cut into small pieces, which all would have to be handled individually.
- Silicon is not transparent.
- Silicon does not have a direct band gap.[4] LEDs are not easily produced from Si. GaAs has such a direct bandgap and finds use in LEDs for that reason.
- Silicon is rigid.

When it comes to cables, extrinsically conducting polymers often are the materials of choice. Fillers can be silver, carbon black, graphite, carbon nanotubes, graphene oxide, metallic fibers, or metallic oxides.[5] Extrinsically conducting polymers are widespread. They have lower density than metals and can be formulated to be durable, strong, and easily processable. Applications include batteries, sensors, drug delivery, solar cells, smart textiles, antistatic coatings, and corrosion inhibition.

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[1] Graphite is unique in many ways. It is not only conductive, but also is inert a high temperatures, which makes it a suitable electrode when electric arcs are involved. It is also used in electrochemistry and is an additive in the electrodes of batteries.

[2] There also is "chemical vapor deposition”, CVD. CVD makes use of precursors. The material to be coated is given a shell of groups which facilitate evaporation without decomposition. Later, these groups are removed from the film by heating.

[3] Sputtering is different from evaporation in that the atoms are transferred to the substrate by subjecting the base material to a high-energy electron beam. The atoms and ions have high kinetic energy when they hit the target, which helps in the formation of compact films

[4] When the bandgap is indirect, the highest point in the valence band and the lowest point in the conduction band occur at different k-vectors.

[5] Fillers can have functions other than conductivity. Examples are the „actives“ in the electrodes of lithium ion batteries.

The molecules for organic electronics at some points were advertised has components of what was called "molecular electronics". The promise were electronic devices on the molecular scale. Molecular-scale transistors and diodes have been demonstrated, but integration was difficult. Interestingly, the feature width in conventional electronics meanwhile has come down to the nanometer range, as well. Conventional electronics has reached the size range which was previously associated with molecules.

Remember:

- Organic materials often are poor electronic conductors because they held together by physical cohesion.
- Small molecules can be deposited as films by evaporation.
- Polymers can be printed.
- Amorphous films are advantageous for flatness and transparency.
- Flexibility and stretchability are advantages of polymer electronics.
- Nanocrystallinity can improve electronic transport.
- Extrinsic polymer conductors carry current and share some of the advantages of organic electronics (such as printability and flexibility).

Box 1.2
Differences between electronic conduction and conduction of ions in electrolytes

- Typical electrolytes have a conductivity below 1 S/cm.
- For water, the conductivity is a measure of purity. For ultrapure water, $\rho = 1/\kappa \geq 18$ MΩ cm.
- Signal transport with the speed of light, as known from electric cables, is not possible in electrolytes, because of mobile counter ions. In metals, the ionic lattice is immobile and the movement of charge leads to an electric field. This fields carries the signal and it does so at almost the speed of light.
- The counter-ion cloud forms an electric double layer at electrodes. As long as there is no electrochemistry at the electrodes, static fields do not penetrate into electrolytes. (Electrophoresis requires such chemical process at the electrode in order to maintain the field.)
- Electrons carry functions in electroluminescence, photovoltaics, and photo-conductivity. Ions in electrolytes do not have such functions.

Box 1.1
RFID tags

- RFID stands for Radio-Frequency Identification. RFID systems consist of a tag that is attached to the object and a reader that reads the tag's information wirelessly. The tag contains an antenna and a chip.
- Active RFID tags contain batteries.
- Applications are the tracking of goods in warehouses and during transport, identifying authorized personnel for entering secure areas, and contactless payments using credit cards or mobile phones.
- Advantages are non-contact readability, flexibility with regard to environments, the possibility to read multiple tags at once, and a larger information storage capability compared to bar codes.
- Disadvantages are cost and privacy concerns.

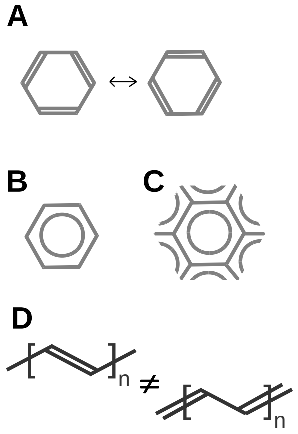
1.2 Functions in organic electronics other than the transport of charge

Again, organic materials have problematic electronic properties. Because of the limited conductivity, polymers will not replace metallic wires or silicon-based semiconductor components in the foreseeable future. In this context, it must be borne in mind that the transport of charge (as in metallic wires) is by no means the only function of electronic materials. Other functions are:

- Antistatic activity
- Photoconductivity (xerography, section 5)

- Signal transport, for example in RFID tags (Box 1.1)
- Signal amplification and signal processing, e.g. with transistors
  The target here is the organic field-effect transistor, OFET, section 8.2.
  Printed organic-electronic circuits are discussed for the "back-planes" of displays (LCDs, OLEDs, electrophoretic displays). The back-planes contain thin-film transistors (TFTs). Electrophoretic displays ("e-paper", "e-ink") are less demanding than OLEDs because of their low switching rates.
- Electroluminescence
  Applications include large-area lighting and OLEDs (section 7).

Box 1.4
Mesomeric and tautomeric states
Mesomeric states are usually explained using benzene as the example. The electrons are everywhere on the ring at the same time. The structure at the bottom is not a mesomeric state. The double bands can move, but at any one given time, they are localized.
Mesomerism and tautomerism differ by how frequently the position of the electrons is “measured”. Measurement is linked to decoherence and localization.
Mesomerism is typically linked to electrons being delocalized. Protons tunnel, but still are localized at room temperature. That can be different at very low temperature, where the interaction with phonons decreases in rate because there are fewer photons.
Protons tunnel in ice, which gives rise to the Grotthuß effect. The conductivity is low, though (10^{-9} S/cm). There is no "protonic" analog of electronic conduction.



Box 1.3
Remarks on electrical conductivity
The unit of conductivity κ is S/cm = mho/cm. S stands for "Siemens", mho stands for 1/ohm. More rarely, the meter is used instead of the cm (mostly in Europe, where the SI system is more common than the cgs system). Values of conductivity range from ~10^{-23} S/cm (Teflon) to ~10^{6} S/cm (silver).
Moderate conductivity (~1 S/cm, give and take two decades) is interesting if the distances are short and if there is additional functionality. The materials for organic electronics and the AOSs (Box 2.1) have moderate conductivity of that kind. κ then strongly depends on preparation conditions, defect density, and doping.

- Photovoltaics
  Although organic photovoltaics (OPV) has been the subject of much research, it is not currently considered competitive due to its low efficiency. There may be niche markets. OPV is not covered here, although there are a number of interesting materials aspects.
- Information storage
  At this point, the flash memory (Fig. 1.1) is the dominant technology. There are no organic flash memories.
- Transparent electrodes (e.g. for displays), transparent anti-static films
- Chemically modulated conductivity (chemical sensors)
- Anti-corrosion coatings (several potential mechanisms)

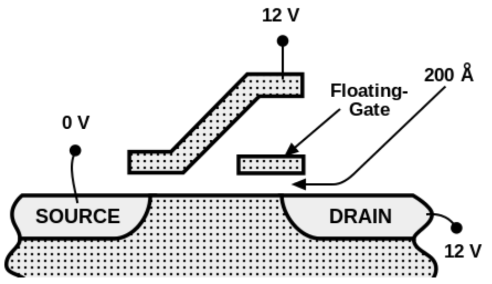


Fig. 1.1
The flash memory consists of a field effect transistor (Fig.8.2), where the gate is switched between an uncharged and a charged state.
en.wikipedia.org/wiki/flash-memory

Remember:
- Organic electronics is driven by functions other than simple conduction of electric charge.

2 Mechanisms of electronic conduction in organic media

2.1 Double-well potentials, the transfer integral

Key to the electron mobility is tunneling. In the following, we work our way forward to the "transfer integral". Tunneling is a process leading from one wave function to another wavefunction with altered expectation values for position. There is some care required here with regard to terminology. It is sometimes argued that electrons in delocalized systems tunnel back and forth between the different locations in the system. Using this terminology, the electrons in benzene would "tunnel back and forth" between the different double bonds. That is not the meaning of tunneling adopted here. Tunneling here is a transition between two separate states. For instance, the α-particle is inside the heavy nucleus before the α-decay, while it is outside after the decay.

For any given barrier, the tunneling rate is proportional to $m^{-1/2}$ with m the mass of the particle. That is why tunneling mostly occurs with electrons. (It does occur with heavier particles as well.[6])

The charge-transfer integral is best explained using tetrathiofulvalene (TTF) molecule as the example (Fig. 2.1). After an “interaction”[7] the electron is located either on the left ring or on the right ring. Call those states ϕ_L and ϕ_R. These are the "interaction states". The interaction states are not the energy eigenstates. These are $\phi_L + \phi_R$ and $\phi_L - \phi_R$ (the symmetric and the antisymmetric state, normalization omitted).

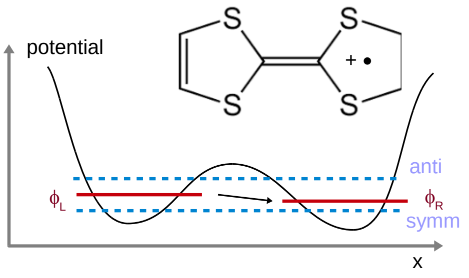


Fig. 2.1
In the double-well potential, the interaction states differ from the energy-eigenstates. The height and the width of the barrier determine both the degree of the level splitting and the tunneling rates between the two interaction states. The double well potential was drawn with a tilt to indicate the external electric field.

The symmetric and the antisymmetric energy eigenstate differ in energy. For the sake of this argument, we calculate the energy as the expectation value (as opposed to the eigenvalue). The expectation value of the symmetric state is

Glg. 2.1

$$E_{symm} = \frac{\int (\phi_L + \phi_R)\hat{H}(\phi_L + \phi_R)\,\mathrm{d}x}{\int (\phi_L + \phi_R)(\phi_L + \phi_R)\,\mathrm{d}x} = \frac{\langle L+R|H|L+R\rangle}{\langle L+R|L+R\rangle} =$$

$$= \frac{\langle L|H|L\rangle + \langle L|H|R\rangle + \langle R|H|L\rangle + \langle R|H|R\rangle}{\langle L|L\rangle + \langle L|R\rangle + \langle R|L\rangle + \langle R|R\rangle} = \frac{H_{LL} + H_{LR} + H_{RL} + H_{RR}}{1 + S + S + 1}$$

Bracket notation was used in step 2. In step 4, variables were renamed. Because normalization was ignored when defining "symm" as $\phi_L + \phi_R$, it now must be included in the denominator. $S = \int \phi_L \phi_R dx$ is the overlap integral. We approximate S as zero here. Because ϕ_L and ϕ_R were assumed to be normalized ($\langle L|L\rangle = \langle R|R\rangle = 1$), the denominator turns into 2.

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[6] Protons tunnel between the two potential wells of the hydrogen bond in the Grotthuß mechanism. Helium nuclei tunnel in the α-decay. Nitrogen atoms tunnel in pyramidal inversion of the ammonia molecule.

[7] “Interaction” here is synonymous to a measurement, which changes the phase in unpredictable ways. That decoherence in quantum mechanics usually leads to localization. This is of fundamental importance in the transition from quantum mechanics to classical mechanics.

For the numerator, we exploit symmetry: $H_{LL} = H_{RR}$ and $H_{LR} = \mathrm{H}_{RL}$. H_{LL} is the energy of the solution to the single-well potential. Inserting these approximations leads to

Glg. 2.2

$$E_{symm} \approx H_{LL} + H_{LR}$$

Doing the same calculation for the antisymmetric state leads to

Glg. 2.3

$$E_{anti} \approx H_{LL} - H_{LR}$$

Assume that the molecule initially is in the state $\phi_L = (\psi_{symm}+\psi_{anti})/2$. The wavefunction evolves in time following

Glg. 2.4

$$\begin{aligned}\psi(x,t) &= \frac{1}{2}\left(\psi_{symm}(t)+\psi_{anti}(t)\right)\\ &= \frac{1}{2}\left((\phi_L+\phi_R)\exp\left(-\mathrm{i}\omega_{symm}t\right)+(\phi_L-\phi_R)\exp\left(-\mathrm{i}\omega_{anti}t\right)\right)\end{aligned}$$

After at time of $\Delta t = \pi(\Delta\omega)^{-1} = \pi(\omega_{anti} - \omega_{symm})^{-1}$, the second term has reversed sign relative to the first term.

Glg. 2.5

$$\begin{aligned}\psi(x,\Delta t) &= \frac{1}{2}\left(\psi_{symm}(t)+\psi_{anti}(t)\right)\\ &= \exp\left(-\mathrm{i}\omega_{symm}t\right)\frac{1}{2}\left((\phi_L+\phi_R)-(\phi_L-\phi_R)\right)\\ &= \exp\left(-\mathrm{i}\omega_{symm}t\right)\phi_R\end{aligned}$$

The electron atom has moved to the right-hand side. The rate for this transition is proportional to $\Delta\omega$, which in turn is proportional to the "transfer integral" $H_{LR} = \int\phi_L\hat{H}\phi_R dx$. The transfer integral governs both the energy splitting and the tunneling rate. That is a general rule for couplings of all kind.

A single electron was considered in Fig. 2.1. There was an unoccupied state, into which the electron could transition. Similarly, fully occupied bands will not allow for conduction in section 2.2.

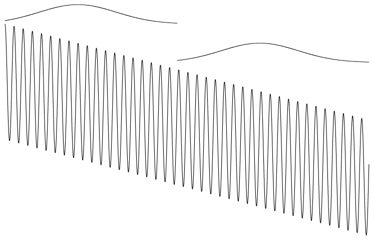

Fig. 2.2
A multi-well potential with a superimposed electric field. The top shows delocalized electrons, the coherence length of which is large, but still not infinite. These are not energy eigenstates. They occur because interactions between electrons and phonons leads to some (limited) localization.

Remember:

– The transfer integral governs the level splitting, the width of the bands, and the rate of transport by tunneling.

2.2 Band conduction

Expanding on the previous section, the double well potential can be turned into a multi-well potential. A few things happen:

– The number of energy states doubles, whenever a new well is added. The number of levels exponentially depends on the number of wells. The levels are so numerous that they cannot be recognized, individually. They form bands.

- If the wells form a periodic structure, the Bloch theorem applies. All solutions to the Schrödinger equation can be written as

Glg. 2.6

$$\psi\left(x\right) = u(k,x)\exp\left(-\mathrm{i}kx\right)$$

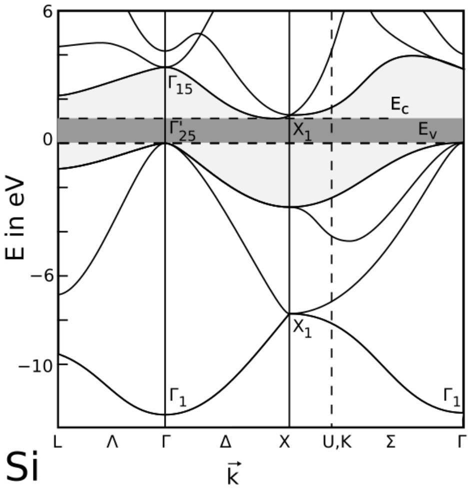

Fig. 2.3
The bands of silicon
en.wikipedia.org/wiki/File:Band_structure_Si_schematic.svg

The wave vector, k, is between the 0 and $2\pi/\Lambda$ with Λ the repeat length of the periodic structure. $u(k,x)$ is periodic with the period of the potential. There are a few such function, giving rise to the different bands (Fig. 2.3).

- Similar to how tunneling in the double-well potential is only possible as long as there is an unoccupied state into which the electron can transition, band conduction does not happen if a band is fully occupied. The Fermi level must be inside a band. Otherwise, the material is a semiconductor.
- If a band is almost filled, it helps to think of unfilled levels as "holes". Holes are largely equivalent to electrons with an effective positive charge.
- The electrons in the band are delocalized. The coherence length is much larger than the periodicity of the potential (Fig. 2.2). The coherence length is not infinite, though. There is a limit degree of localization.
- Semiconductors with a large band gap in effect are insulators.
- There is an analogy to diffusion in gases and diffusion in solids. Diffusion in gases takes place via a free flight interrupted by collisions. Electrons in metals move freely over many interatomic distances before they are scattered by phonons of impurities. The mean free path of electrons in metals is tens of nanometers.

The curvature of the dispersion relation close to its minimum is related to the electron mobility. It the curvature is large, the effective mass is small, following the relation

Glg. 2.7

$$\omega = \frac{E}{\hbar} = \frac{1}{\hbar}\frac{p^2}{2m_{eff}} = \frac{\hbar k^2}{2m_{eff}}$$

Small effective mass implies high mobility.

Remember:

- The transfer integral governs the level splitting, the width of the bands, and the rate of transport by tunneling.

2.3 Hopping conduction

Electronic conduction in organic materials differs from band conduction in a few regards:

- Because the barriers between the wells are high, the transfer integral is small. The splitting between levels is small and the bands – if they form in a periodic structure – are rather narrow. In photoelectron spectroscopy, they are hardly distinguished from the lines, which correspond to the localized orbitals.
- The small transfer integral causes the mobility of the charges to be small.
- Because of the small mobility, the charges do not travel far before experiencing a decoherence. followed by localization. The charges mostly are localized to a single well. In amorphous materials, band conduction does not happen altogether. There is a random distribution of wells with different heights. Should there be an external field, the energy landscape is tilted (similar to what is shown in Fig. 2.2).
- What follows from these considerations is called "hopping conduction". "Hopping" is tunneling between potential wells – as opposed to a thermally activated transition across the top of the barrier.
- Even though hopping amounts to tunneling, the hopping conductivity improves with increasing temperature, following $\sigma = \sigma_0 \exp(-(T_0/T)^\beta)$. β is smaller than unity (often $\beta \approx 1/4$). The dependence on temperature is rooted in thermally activated fluctuations of the potential energy landscape.

Remember:

- Hopping denotes a tunneling process between two adjacent potential wells.
- The barriers are rather high and the tunneling rates are corresponding low.
- The electronic states are localized to the wells.
- There is a dependence on temperature, mediated by fluctuations of the energy landscape.
- There are no bands because of the amorphous structure.

Box 2.1

Amorphous oxide semiconductors (AOSs)

Amorphous oxide semiconductors compete with organic compounds for some electronic applications. Importantly, they can be sputtered, forming flat, transparent films. Conductivity and mobility are comparable to what is achieved with organic materials. They are not usually luminescent. At this point, they dominate the market for the transparent field effect transistors (section 6), but not for LEDs.

For a while, amorphous silicon (a-Si) was the main inorganic material to be used for transparent transistors. The single electrons at the dangling bonds are the charge carriers. The conductivity of a-Si depends on the degree of doping. The mobility is around 1 $cm^2/(Vs)$.

Since then, metals have been added as electron donors. These materials are called amorphous oxide semiconductors (AOSs). A wide-spread material is indium-gallium-zinc-oxide (IGZO). Note that indium is contained in this substances, similar to indium-tin-oxide (ITO, section 6.) Indium donates three electrons from its valence shell. Two of these are s-electrons, which is advantageous because the s-orbitals are spherical with no preferred direction. Indium has just the right size to make tunneling of electrons easy. Indium is expensive, but there is no convenient replacement. (The same problems exist for transparent electrodes made of ITO.) The conductivity of IGZO can be as high as 200 S/cm. The mobility can be up to 160 $cm^2/(Vs)$. (The mobility in ITO is less.) IGZO is more chemically inert than the polymers. At this point, the organic field effect transistor (OFET= is not used for thin film transistors (TFTs) in the back plane of displays. AOSs are flexible enough to be deposited onto PET substrates, to be used in moderately flexible displays. They are not flexible enough to be deposited on textiles or on human skin.

2.4 *The Peierls transition*

One might think that band conduction was possible in linear polymer chains because these have periodic structure and low barriers across the bonds between segments. However, bands do not exist in 1D- systems.[8] This is the consequence of the Peierls transition.[9]

In the Peierls transition, a lowered energy of electronic states drives a lattice distortion. A similar phenomenon is known from the coordination bond and from the Jahn-Teller effect. Both involve half-filled d-shells as found in transition metals. The d-shells are 10-fold degenerate in isotropic environments. Ligands (in coordination chemistry) break isotropy and lift the degeneracy. Because the d-shell is partially filled, the electrons preferentially occupy the orbitals with lowered energy. The electron system thereby gains energy. The Jahn-Teller effect occurs in inorganic solids. It amounts to a lattice distortion, driven by the splitting of energies in the d-shells. The Jahn-Teller effects mostly amounts to a second-order phase transition. The distorted state can be ferro-electric. Among the important materials is $BaTiO_3$.[10]

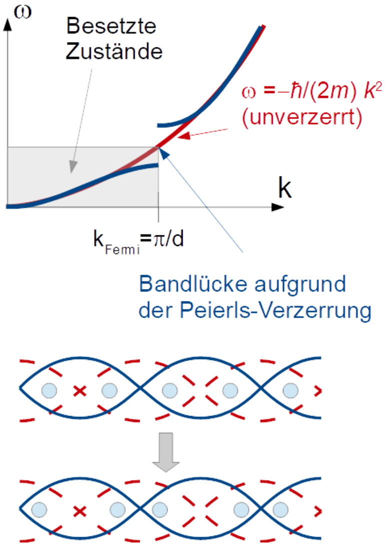

Fig. 2.4
The Peierls distortion lowers the energy of the waves with the antinodes at the double bonds (red dashed wave).

The mechanism leading to the Peierls distortion is sketched in Fig. 2.4. The upper part shows the frequency (the energy divided by $\hbar$, following $E = \hbar\omega$) of standing waves in a hypothetical band as a function of the wave number k. In this simple argument, $E = 1/2\ mv^2 = p^2/(2m) = \hbar^2k^2/(2m)$. However, this "band" is only half filled (gray rectangle in Fig. 2.4). At the Fermi edge, the antinode of a standing wave therefore extends over two ions (instead of one, which is situation and the edge of the Brillouin zone). If two ions move closer together, this lowers the energy of those standing waves, whose antinode extends over these two ions (dashed red line in Fig. 2.4). The distortion causes the energy of the other wave to increase (blue solid line in Fig. 2.4). Because these waves are located at the Fermi edge, the favorable states are occupied and the unfavorable ones remain unoccupied (similar to what happens with the d-electrons in coordination chemistry). This reduces the electronic energy.[11] Again: The Peierls distortion turns a 1D metal into a 1D semiconductor (with a Fermi edge in a band gap).

The consequences of the Peierls distortion are best illustrated using the example of trans-polyacetylene (Fig. 2.7). The two compounds shown on the bottom right in Box 1.4 are non-mesomeric structures. The chain is either in one state or in the other. This is only the case for linear chains. For graphene (a two-dimensional system), Lewis structures with single bonds and double bonds are mesomeric states.[12]

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[8] Carbon nanotubes do not count as 1D-systems here. Depending on the tilt of the hexagons with respect to the symmetry axis, the conductivity can be high. Carbon nanotubes can be molecular-scale wires. Problems are sorting and forming electrical contacts at the ends.

[9] The Peierls transition is discussed in a footnote in Peierls' book on quantum mechanics. He considered it irrelevant because he thought that there were no 1D crystals.

[10] There is much talk about ferroelectric memories. A small, switchable dot of a ferroelectric material might replace the floating gate in Fig. 1.1.

[11] A similar effect is also known from the anti-aromatics. If a chain of alternating single bonds and double bonds runs in a circle and if the number of double bonds is even (as for cyclobutadiene), aromaticity does not occur.

[12] The electronic properties of graphene continue to draw interest. Twisted bilayer graphene it particularly intriguing.

Remember:

- The Peierls transition turns 1D metals into 1D semiconductors.

2.5 *Organic electronics usually requires doping*

Most organic molecules do not contain single electrons, which might undergo charge transfer. Single electrons mostly are created by doping. Dopants often are small molecules, which extract an electron from a polymer chain. Dopants for polyacetylene (Fig. 2.7) can be Br_2, I_2, or AsF_5. These are p-type dopants. Dopants more often extract electrons from a chain than they inject extra electrons. The reason is that n-doped chains are susceptible to attack by oxidizing agents. For that reason, the electrons transport layers (ETLs) in OLEDs and organic solar cells (OSCs) are more difficult to produce than the hole transport layers (HTLs). In the case of the ETLs, electrons often hop between dopant molecules, not actually being injected into the polymer chain. Even then, oxidation of the dopants in air remains a problem.[13]

That electronic conductivity requires a dopant is among the mechanisms underlying conductometric sensing employing conducting polymers. The dopant in these cases is the analyte. A similar process underlies the electrochemically induced release of drugs from conducting polymer films (Fig. 2.5). The polymer in the oxidized state fixes the drug by way of electroneutrality. Once the polymer is reduced by a cathodic charge transfer from the electrode, the dopant (the drug) is released.

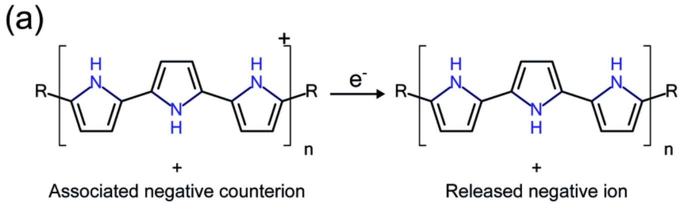

Fig. 2.5
Electrochemically controlled drug release
www.researchgate.net/figure/a-Polypyrrole-reduction-and-associated-counterion-release-half-cell-reaction-b_fig1_362769893

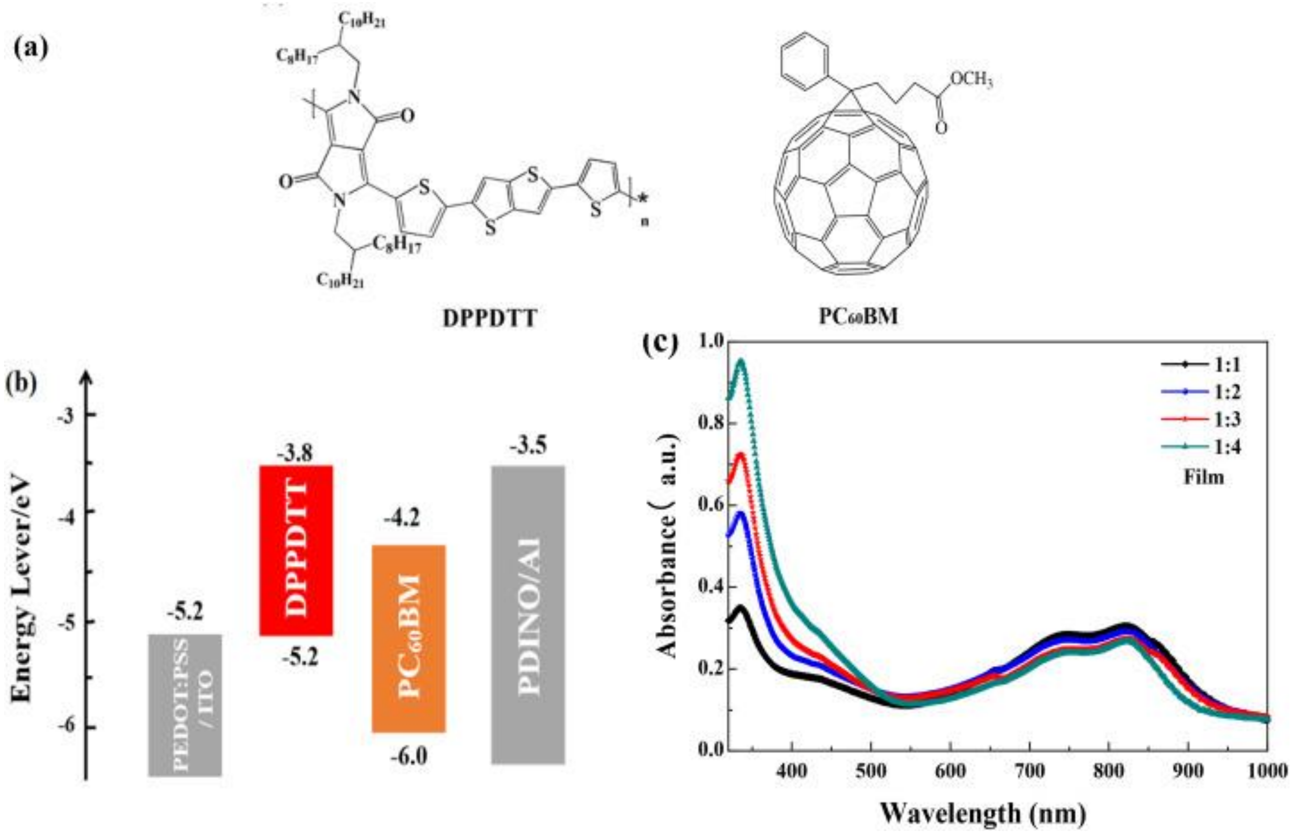

Fig. 2.6
(a) Molecular structures of DPPDTT and PC60BM. (b) Molecular energy levels. (c) Thin film optical absorption of DPPDTT and PC60BM at different mixture ratio (by weight) blend on quartz.
Sun, Y et al. *Materials and Solar Cells* 215 **2020**: 110684.

Remember:

- Electric conductivity in organic materials usually requires doping.
- n-doping is more difficult than p-doping because the high-lying electronic orbitals are easily attacked by oxidizing agents.
- The need of doping can be the base for conductometric sensing using conducting polymers.

2.6 Polaronic effects

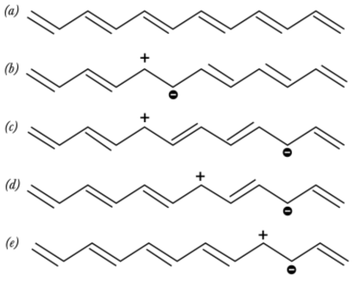

Fig. 2.7
Doped trans-polyacetylene. The figure also shows a bipolaron.
www.nobelprize.org/nobel_prizes/chemistry/laureates/2000/advanced-chemistryprize2000.pdf

In the Peierls transition, electrons induce a lattice distortion. Such couplings are called polaronic effects. A polaron is a quasi-particle consisting of a charge and a lattice distortion. The lattice distortions are particularly strong in organic materials because they then involve double bonds turning into single bonds and vice versa. In polyacetylene, there often are “bipolarons”, which reverse the sequence of single bonds and double bonds in a stretch of limited length (Fig. 2.7). Fig. 2.8 shows a bipolaron in polythiophene.

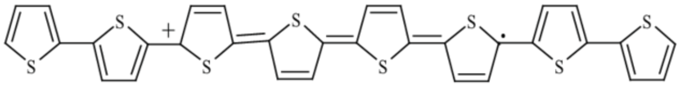

Fig. 2.8
A bipolaron in polythiophene
www.researchgate.net/figure/Simplified-neutral-a-polaron-b-and-bipolaronic-c-structures_fig4_268374402

Polaronic effects can give rise to superconductivity. They can couple two electrons with opposite spin, resulting in a quasi-particle with zero spin (a “Cooper pair”). Some charge transfer salts where indeed found to be superconductive. Given the strong polaronic effects, it was hoped that these salts might be high-temperature superconductors. So far, that has not come true.

Remember:

- The motion of charge is coupled to bipolarons in many conduction polymers.

2.7 Electronic circuits need insulating materials for separation

It is sometimes overlooked that electron-carrying units need to be separate from each other, which requires insulators. These often are polymers, even in conventional electrical engineering.[14] (Inorganic materials like porous SiO_2 are also used.)

- If fast signal propagation is needed, the dielectric constant should be low ("low-k dielectrics"). Porosity can help.
- When the dielectric is part of a capacitor, a high dielectric constant us needed because of $C = \varepsilon\varepsilon_o A/d$ with ε the dielectric constant ("high-k dielectrics.").
- A high break-through voltage may be required. This holds for insulators inside narrow gaps. It also hold for power electronics (e-mobility). It holds for high-voltage DC transmission lines. Interestingly, the insulating material in these lines is not Teflon (which is one the best insulators), but rather slightly cross-linked polyethylene.

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[14] Most cables are coated with a polymer. An extrusion press that accomplished that, was a key innovation of the up-and-coming company Siemens and Halske in 1847.

2.8 High-barrier materials prevent oxidation

High-barrier materials are important for many kinds of packaging. They should be a barrier against oxygen and water vapor.

As far polymers as concerned, polyvinylidene chlorid (PVDC) is the best material. Sometimes, films are coated with thin aluminum layers. (Polymers usually are permeable to vapors.)

For OLEDs, demands are much too high to be met with PVDC. For these, in-situ polymerized parylene, blended with inorganic platelets, are used.

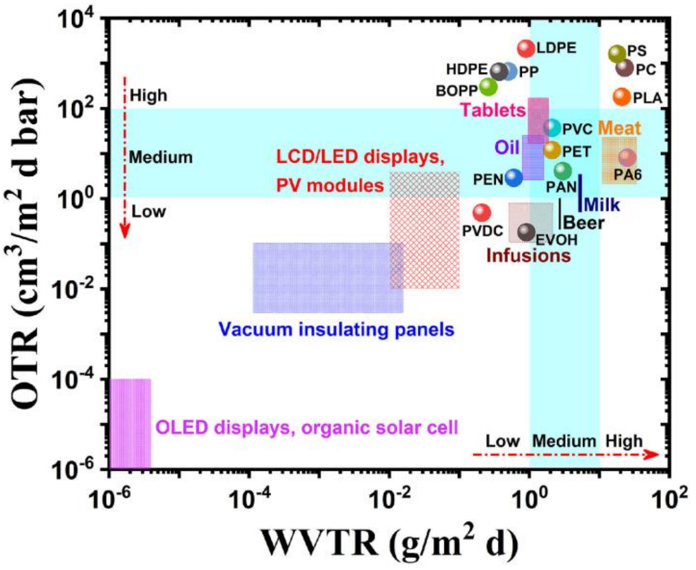

Fig. 2.9
Applications of high-barrier materials, high-barrier polymers
Huang, Hua-Dong et al. *Progress in Polymer Science* 144 **2023**: 101722

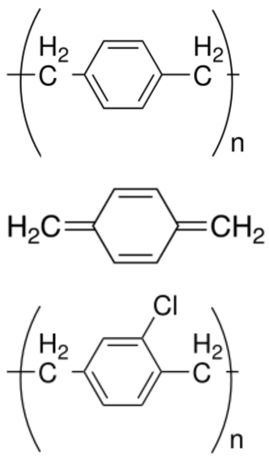

Fig. 2.10
The barrier films for OLEDs often contain parylenes, prepared by chemical vapor deposition. Often they are organic-inorganic composites, where inorganic nanoplatelets improve the barrier properties.
https://en.wikipedia.org/wiki/Parylene

3 Materials for organic electronics

This section discusses representative materials. Other materials are discussed in the context of their applications.

3.1 Historical remarks

Conductivity in polymers was systematically studied for the first time by Bolto and Weiss in 1963 on (doped) polypyrrole (Fig. 3.2).[15] The conductivity was $\kappa \sim 1$ S/cm. Polypyrrole can be prepared from the pyrrole monomer by adding an oxidizing agent. It can also be electropolymerized anodically. The latter process amounts to an in-situ polymerization. In-situ polymerization is the only feasible synthesis route if the polymer can hardly be processed (e.g. due to poor solubility). This is often the case with conductive polymers.

The conductivity of organic materials composed of small molecules was investigated in the 1970s using charge-transfer salts. An example (TTF:TCNQ) is shown in Fig. 3.6. Historically, TTF:TCNQ attracted much attention because it exhibits superconductivity. This proves that the movement of the electrons is coupled to a movement of the ions. This coupled movement is characteristic of all organic conductors.

The field of organic electronics took off when trans-polyacetylene in doped form (Fig. 2.7) was found to have a conductivity slightly below that of silver ($\kappa \approx 10^5$ S/cm, silver and copper: $\kappa \approx 10^6$ S/cm). Doped polyacetylene looks shiny. (Polypyrrole is not shiny. It is black when conductive.) The high conductivity of trans-polyacetylene is surprising because one would expect polaron conduction to be inefficient compared to band conduction. Normally it is. Polyacetylene is an exception (for reasons see the source from footnote 16). Polyacetylene is not stable in air. This is not surprising insofar as the charge transport is linked to redox processes. It is plausible that oxidation may interfere with these redox processes. Therefore, a common opinion was: "Conductive polymers are not technically relevant." That turned out to be a misconception.

Conductive organic materials became known to the general public when the Nobel Prize was awarded to this field in 2000 (Heeger, McDiarmid and Shirakawa). Of particular importance were electroluminescent polymers such as poly(*p-phenylene-vinylene*) (PPV, Fig. 3.1). In the meantime, there have been sobering results, but "organic electronics" has nevertheless established itself as a field of knowledge and technology.

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[15] There is earlier evidence from the 19th century. In 1862, Letheby used electro-oxidation to produce "a blue substance" from aniline, which was conductive. Today, this material is called polyaniline (Fig. 3.3).

[16] www.nobelprize.org/nobel_prizes/chemistry/laureates/2000/advanced-chemistryprize2000.pdf

3.2 *Examples*

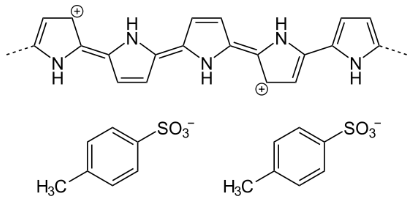

Fig. 3.2
Polypyrrole, doped with p-toluene sulfonic acid.
en.wikipedia.org/wiki/Polypyrrole

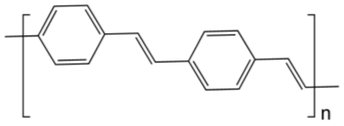

Fig. 3.1
Poly(*p-phenylene-vinylene*), PPV
en.wikipedia.org/wiki/Poly(p-phenylene-vinylene)

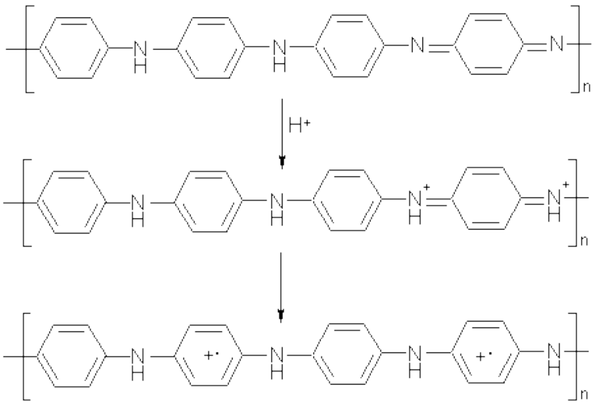

Fig. 3.3
Doped polyaniline. Among the applications are printed circuit boards (PCBs).
www.chemgapedia.de/vsengine/vlu/vsc/de/ch/9/mac/neu/leit-poly/leitpoly.vlu/Page/vsc/de/ch/9/mac/neu/leit-poly/pani.vscml.html

3.3 *The special case of PEDOT:PSS*

A particularly successful intrinsically conducting polymer is PEDOT:PSS. It also goes by the name Baytron. PEDOT:PSS (Fig. 3.4) is a remarkable material in two respects:

- The oxygen in the side group increases the oxidation stability (Fig. 3.5).
- The dopant (polystyrene sulphonate) itself is a polymer.

Baytron is transparent. It is available in a variety of forms and grades. That includes polymer dispersions, to be coated and dried similar to conventional paints. Its conductivity can be up to 4600 S/cm.

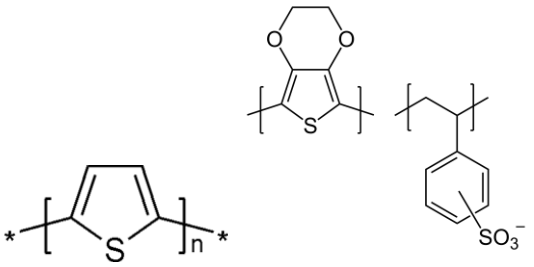

Fig. 3.4
Left: Polythiophene.
n.wikipedia.org/wiki/Polythiophene
Right PEDOT:PSS. Here the dopant (PSS) is a polymer, as well.
Right: http://www.tda.com/eMatls/icp.htm

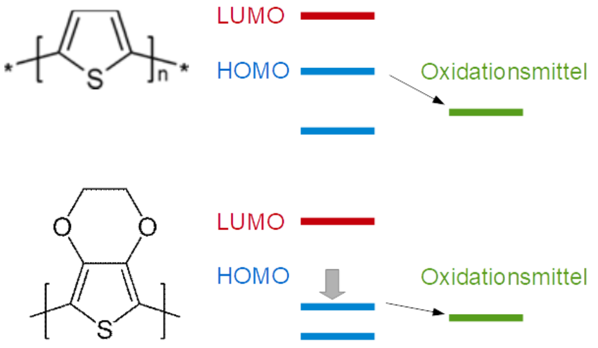

Fig. 3.5
The oxygen in the side groups of the thiophene lowers the energy of the HOMO and thus increases the oxidation stability.

3.4 Charge transfer salts

In charge-transfer salts the mobile charges are generated by internal doping. They contain donors and acceptors (**Fehler! Verweisquelle konnte nicht gefunden werden.**).

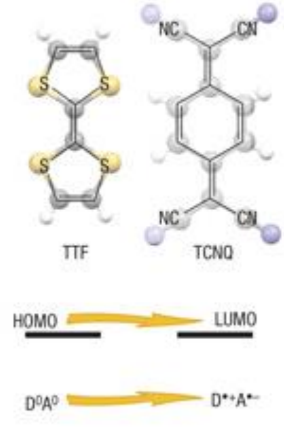

Fig. 3.6
Charge transfer in the TTF–TCNQ system *https://www.researchgate.net/figure/Charge-transfer-in-the-TTF-TCNQ-systemab-The-TTF-and-TCNQ-molecules-a-are-well-known_fig5_5303772*

4 Printed electronics

Among the outstanding properties of polymers is their ability to *form films*. Drying processes always involve a shrinkage. The substrate constrains the shrinkage to be non-affine, which leads to a tensile in-plane stress and – in case the stress cannot relax – cracks. Polymers relax the stress by internal reorganization.[17] This also applies to polymers close to the glass temperature, which do not flow. The ability to relax stress is also favorable for electronics on flexible substrates including textiles.

Note: Film formation of polymers is also exploited in the “extrinsic” conductors. The best-known example is silver conductive varnish. The (electronic or other) function is brought about by embedded particles (“pigments”). The polymer only acts as a binder. Polymeric binders are widely used. For example, PVDF is the binder in the electrodes of lithium-ion batteries. Interior paints contain more than 50% pigments, held together by polymers. Inks oftan contain polymeric binders. When evaluating printed organic electronics in terms of performance, printed inorganic electronics must always be kept in mind as a competing technology.

"Inks" of all kinds have grown enormously in importance since printing machines have made a leap in speed and precision. That includes "2-1/2-D-printing", which refers to multilayered printed products with functions that go beyond color (electrical circuits, sensors, piezo elements, light-emitting diodes, photodiodes).

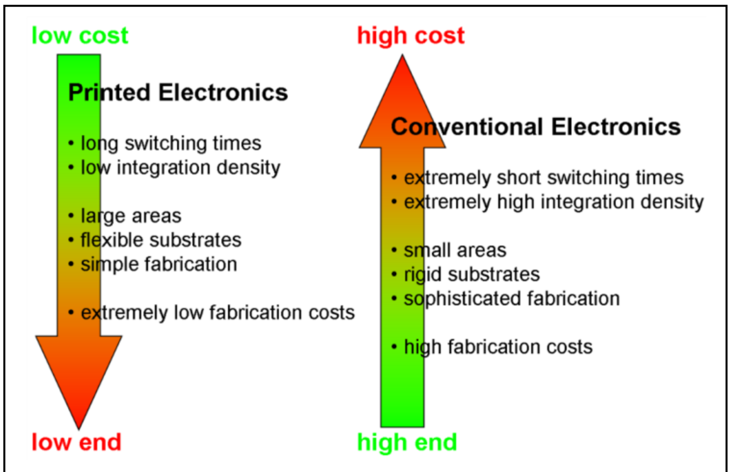

Fig. 4.1
Advantages and disadvantages of printed electronics
en.wikipedia.org/wiki/Printed_electronics

The advantages and disadvantages of printed electronics are summarized in Fig. 4.1. Again: Crystalline inorganic semiconductors cannot be printed, sputtered, or vapor-deposited.

A few more comments on printed electronics:

- Only polymers can be printed. Small molecules must be vapor-deposited. Small molecules hardly be printed because the solutions does not turn viscous when solvent evaporates. One might use polymers as thickeners, but these stand in the way of crystallization and the latter is important for electron transport. Vacuum is required for vapor deposition. In addition, high temperatures can lead to decomposition.
- For cost reasons, it is attractive to use either vacuum processes (physical vapor deposition PVD, chemical vapor deposition CVD[2]), or wet technologies (printing, spraying, ...).
- If multi-layer systems are to be printed successively, the solvent of the next layer must not dissolve the previously applied substance. "Orthogonal solvents" are needed. It is not trivial to produce multilayer systems.
- There is a large variety of printing technologies. Roll-to-roll printing can be very cheap. Inkjet printing is very flexible, but slow. Screen printing is flexible and easy but does not achieve good resolution.

---

[17] The central step towards the blue (inorganic) light-emitting diode was to control the mechanical stresses in the GaN layers produced by hetero-epitaxy. No polymers are involved here. Shuji Nakamura was awarded the Nobel Prize in 2014 for controlling the mechanical stresses.

- The spatial resolution achieved in printing (~ 10 µm) stays behind what can be achieved in evaporation with masks and with photolithography. It is difficult to produce droplets smaller than 10 µm because of the large associated capillary pressure. (E-jet printing can go lower in resolution.)
- There is research on processes of sintering and curing after printing.

Remember:

- Polymers can be printed because they allow stresses to relax.
- Small molecules can be vapor-deposited (PVD or CVD).

5 The xerography process

The xerography process (used in copiers and printers) is as old as it is successful. The images Fig.5.1 and Fig.5.2 show the principle and some photoconductors. It can be seen that TPD could induce photoconductivity. First – like many dyes – TPD contains a large delocalized π electron systems that pulls the absorption into the visible range. Secondly, the large π σψστεμ acts as an antenna. There is a similarity to the light-harvesting complex in biology.

Do not confuse photoconduction with photovoltaics. In the xerography process, there is a strong external field in which the electrons migrate. In photovoltaics, both the electrons and the holes have to move to the electrodes while consuming as little energy as possible. From a materials science perspective, the xerography process is less demanding than photovoltaics. One is free to optimize the polymers in many respects (price, mechanical strength, ...).

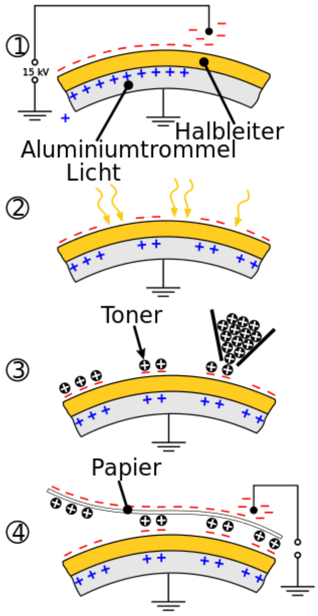

Fig.5.1
Xerography
en.wikipedia.org/wiki/Electrophotography

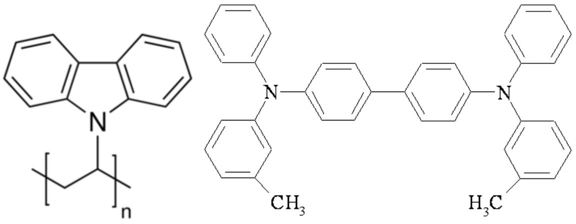

Fig.5.2
Left: An important photoconductor is polyvinylcarbazole.
www.sigmaaldrich.com/catalog/product/aldrich/182605?lang=de&region=DE
Right: TPD (*N*, *N*′-diphenyl-*N*, *N*′-bis(3-methylphenyl)-[1, 1′-biphenyl]-4, 4′-diamine (TPD)bottom) is a common dopant. The commercially used photoconductors are more complex.
photonicswiki.org/index.php?title=File:Triphenyldiamine.png

6 Transparent electrodes

Transparent electrodes are needed for large-scale displays – both LCDs and OLEDs. In the following, we elaborate on why electrical conductivity may lead to silvery appearance.

The dominant material at present is indium tin oxide (ITO). Indium tin oxide (ITO) is conductive but not silvery because the concentration of charge carriers is just such that the plasma frequency is just below the frequencies of visible light. Metals reflect light because the quasi-free electron gas is excited to oscillate by the light. Specifically, the electrons oscillate *against* the light. This is explained below in the context of Fig.6.1.

There is a maximum frequency for this oscillation, the so-called plasma frequency ω_{pe}. The plasma frequency follows the relation[18]

Eq. 3.4.1

$$\omega_{\mathrm{pe}} = \sqrt{\frac{n_{\mathrm{e}} e^2}{m^* \varepsilon_0}}$$

n_e is the number density of electrons; m^* is an "effective mass" (of the order of the electron mass). All metals have such a plasma frequency and all metals therefore become transparent in the somewhere in the UV range. For silver, the plasma frequency is 2.17×10^{15} Hz, corresponding to a wavelength of 138 nm. In terms of the conductivity mechanism, ITO is close to the metals. The charge carrier density is such that the cutoff wavelength for transparency is slightly larger than 1 µm.

The conductivity of ITO is $\kappa > 10^4$ S/cm. The calls of substances class also goes by the name of "transparent conductive oxides", TCOs. Despite intense efforts, it has not been possible to find better and cheaper TCOs than ITO. PEDOT:PSS (Baytron, Fig. 3.4) is a competitor. Its conductivity can be up to 4600 S/cm (meaning: less than the conductivity of ITO).

Fig.6.1 explains why the dielectric constant of metals in the visible is negative. In this case, the wave number becomes imaginary:

Eq. 3.4.2

$$k = n\frac{\omega}{c} = \sqrt{\varepsilon}\,\frac{\omega}{c} = \mathrm{i}n''\frac{\omega}{c} \quad \text{because of } \varepsilon < 0$$

c is the speed of light in vacuum. The imaginary wave number results in an exponentially decaying wave in the metal:

Eq. 3.4.3

$$\frac{E(x)}{E_0} = \exp(\mathrm{ik}x) = \exp(\mathrm{ii}k''x) = \exp(-k''x)$$

---

[18] https://en.wikipedia.org/wiki/Plasma_oscillation

Note: Metals are shiny, similar to a how the base of prism is shiny when looked at under total internal reflection. In both cases, the wave beyond the interface is of the form $\exp(-\alpha z)$. Those wave are also called “evanescent”. The mechanisms leading to an evanescent wave differ between reflection at a metal surface and total internal reflection. In the case of black substances (good absorbers) the wave behind the interface is of the form $\exp(-\alpha(1-i)z)$. The dielectric constant is almost purely imaginary and the refractive index therefore has real and imaginary parts of equal magnitude.

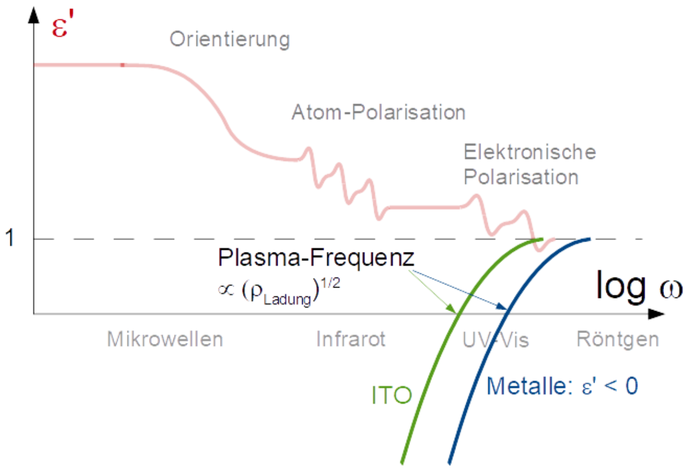

Fig.6.1
The dielectric constant of metals is negative due to the extraordinarily high polarizability in the visible range. This leads to a silvery sheen. With ITO, the charge carrier density is reduced to such an extent that the "plasma frequency" is in the near IR. ITO is therefore conductive, but transparent in the visible range.

7 Organic LEDs

The light emitting diode (LED) is one of the most important technical light sources. It is normally made from inorganic semiconductors. Electrons and holes recombine at a pn junction and emit radiation (Fig.7.1). However, this technology is neither suitable for large surfaces (large-area lighting) nor for a large number of pixels (displays).

For displays, LEDs have the advantage over liquid crystal displays of lower energy consumption. The LCD is based on light-valve technology and therefore consumes power even when the color black is displayed. For the same reason, it is easier to display a deep black with OLEDs. (At this point, consider the logarithmic sensitivity scale of the eye).

There are basically two different manufacturing processes that can be used for large-area lighting and displays: *printing* and *vapor deposition*. Polymers are somewhat more suitable for printing, while only small molecules can be vapor-deposited. Organic LEDs have been commercially implemented as displays (OLEDs, also known as AMOLEDs for "active matrix OLEDs"), including those manufactured by Samsung for mobile phones. Polymer LEDs (PolyLEDs) have been researched by Philips (and others) for some time, but have not yet led to a product. PolyLEDs would be suitable for large-area lighting.

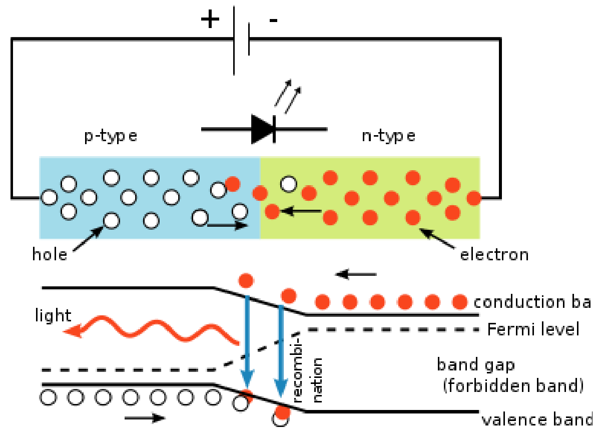

Fig.7.1
The light-emitting diode
www.licht-im-terrarium.de/led/start

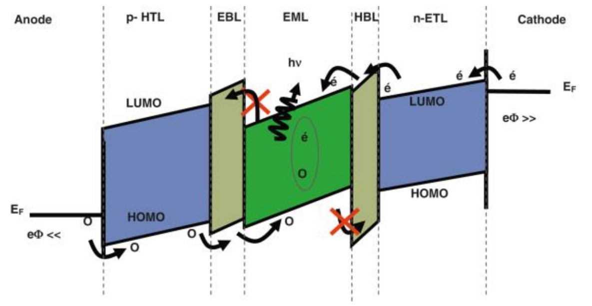

Fig.7.2
A multi-layer OLED
photonicsforenergy.spiedigitallibrary.org/data/Journals/PHOTOE/23506/011015_1_5.png

Fig.7.2 shows the structure of a multilayer OLED. Some remarks:

- The anode (left) requires a material with a low Fermi level, i.e. a high work function. Indium tin oxide (ITO) is often used. An ITO-coated glass is then the substrate for the subsequent process.
- A metal with a small work function (e.g. calcium) is normally used as the cathode. This material does not need to be transparent. Because metals cannot be printed, vacuum is needed I the preparation of OLEDs.
- The energy levels are inclined because of the external field and the low conductivity. (Levels are hardly inclined in inorganic LEDs because of the better conductivity.
- Electrons and holes can tunnel through barriers to some extent.

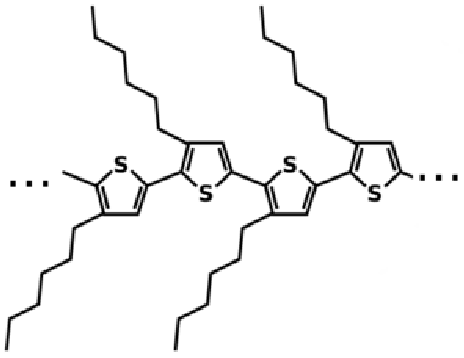

Fig.7.3
Structure of poly(3-hexylthiophene) (P3HT). The side groups cause processability and crystallization. In particular, crystallization leads to lamellae in which the aromatic rings are in contact.
It is important to control crystallization - also through suitable preparation.
gisaxs.com/index.php/Material:P3HT

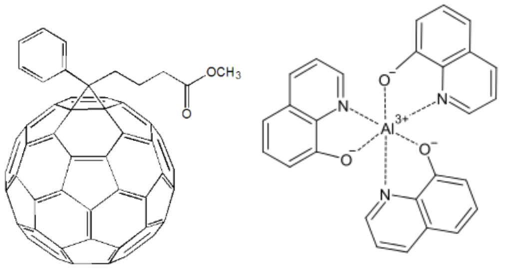

Fig.7.4
Two dopants for electron conduction
Left: PCBM ((phenyl-C61-butyric acid methyl ester**).**
en.wikipedia.org/wiki/Phenyl-C61-butyric_acid_methyl_ester
Right: Alq3 (aluminum tris(8-hydroxyquinoline)
en.wikipedia.org/wiki/Aluminum-tris(8-hydroxyquinoline)

- Band-level engineering can be carried out with electron-pulling or electron-pushing side groups. These primarily shift the band gap up and down. The width remains unchanged. Band-level engineering (not to be confused with doping) does not occur in this form with inorganic semiconductors.[19]
- To the left and right are hole-transport layers and electron-transport layers (HTLs and ETLs). Most conductive polymers are hole conductors (p-type). Fig.7.3 shows P3HT, an important hole conductor. P3HT is easily processed due to its flexible side groups. It also crystallizes well. (Why this is so is not quickly explained.) Good crystallinity is a prerequisite for good intermolecular charge transport (hopping between the chains). For electron conduction (in the ETLs), a polymer is loaded with PCBM or Alq3 (Fig.7.4). The molecules must be small because the polymers are all hole conductors.
- The escape of electrons to the anode and of holes to the cathode is prevented by electron-blocking layers and hole-blocking layers (EBLs, HBLs).
- The light emission takes place in "emission layer" in the center. This is where electrons (injected from the right) and holes (injected from the left) meet. Electrons and holes first form Coulomb-bonded pairs (excitons), which can diffuse over a certain distance before they annihilate (radiatively or non- radiatively).
- Among the electroluminescent groups, fluorene plays a special role (Fig.7.5).
- Crystallinity is unfavorable for luminescence because it leads to self-quenching. For this reason, the polymers used for electroluminescence tend to have be amorphous. The five-membered ring limits aromaticity and thus the delocalization of electrons. PPV (Fig. 3.1) used to play a major role as an electroluminescent polymer. .
- For entirely statistical reasons, 3 out of 4 excitons are in a triplet state. Because of the long phosphorescence lifetime, non-radiative excitation mechanisms compete efficiently with the emission of light. To reduce the phosphorescence lifetime, spin-orbit coupling (which enables phosphorescence) must be promoted. This is done by inserting heavy elements. The “phosphorescence emitters” contain such heavy

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[19] There are exceptions. With AlGaAs, the width of the band gap can be adjusted by the relative ratio of Al and Ga.

elements (iridium in Fig.7.5).
Triplet states are not a problem for inorganic light-emitting diodes because the singlet-triplet splitting is smaller than $k_B T$. The excitons can transition to the singlet state by thermal activation..

- The color is adjusted by molecular design on the emitter. There is a difference here compared to inorganic LEDs. With these, the primary light source is usually blue. The color is adjusted by (mostly inorganic) coatings that absorb the blue light and re-emit it in a different color.

Problems with OLEDs are:

- Insufficient durability of the blue dyes ($t_{1/2} < 14000$ hr, corresponding to 5 years times 8 hours)
  Color distortion due to fading occurs at times significantly shorter than $t_{1/2}$.
- Problems in sunlight because the brightness of the display cannot compete with the sun. Reflective displays are superior in this regard (“E-ink”).
- Lack of stability in humid environments.

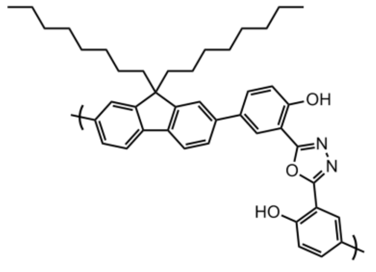


Fig.7.5
An electroluminescent polymer. The structure at the top left is a *fluorene*.

Remember:

- LEDs use the recombination of electrons and holes (of pairs of these two, "excitons") at a pn junction.
- OLEDs are currently made from small molecules.
- Modern OLEDs are multi-layer structures.
- The PolyLED would be useful for large-area lighting.

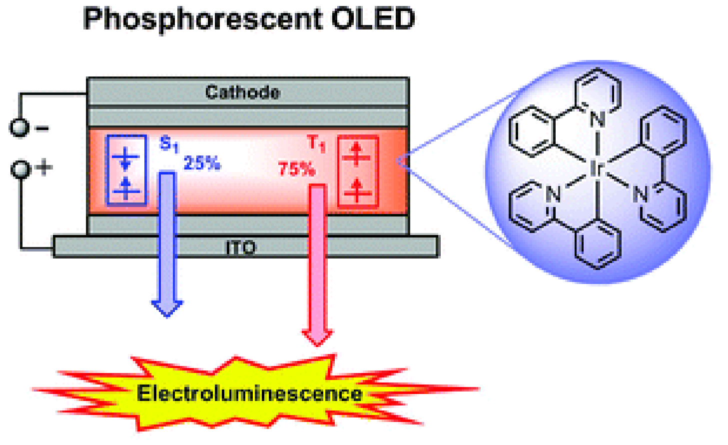


Fig.7.6
A phosphorescence emitter. It is characterized by the incorporation of a heavy element (here: iridium).
https://pubs.rsc.org/en/content/articlelanding/2014/cp/c3cp53806k#! divAbstract

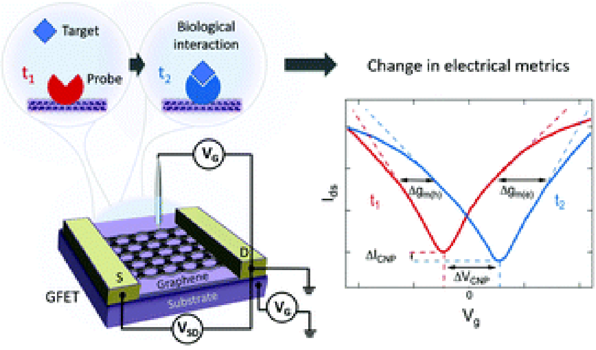
Box 7.1
Graphene transistors

The graphene field-effect transistor (GFET) utilize graphene as the channel material between source and drain. GFETs are similar to conventional FETs, the difference being the smallness and exceptional electron mobility.

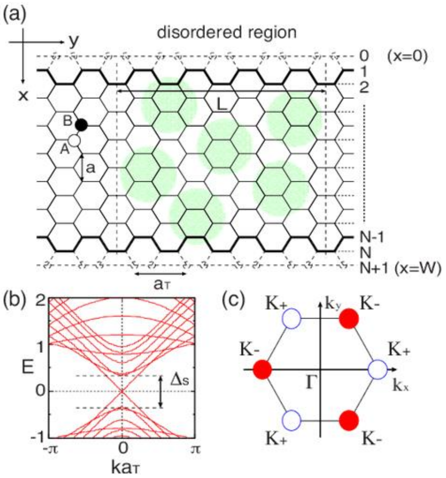
The mobility of electrons in graphene is high because the curvature of the dispersion relation close to $k = 0$ is almost infinite. It is infinite at the "Dirac point" in graphene, when the sheet has infinite lateral extension. This sheet then has no band gap at the same time. A band gap is needed for transistors. Graphene nanoribbons produce a band gap while still having a large curvature of the dispersion relation close the minimum.

The problems with the graphene transistor are twofold. Firstly, the lagers have to be prepared in-situ by a process similar to PVD or CVD. Also, they have to be structured. Graphene nanoribbons can also be prepared by organic synthesis, but these then still need to be arranged suitably on the substrates. A second problem is contacting graphene from the outside. The contact resistance tends to be high. Because the electrons stabilize the 2D structure efficiently, they do not readily tunnel to the outside of this structure into a contacting wire.

There is a steady flow of results on twisted bilayer graphene. Of course, these structures are even more difficult to handle.



https://pubs.rsc.org/en/content/articlelanding/2021/an/d0an01661f



https://www.researchgate.net/figure/Color-online-a-Structure-of-graphene-armchair-nanoribbon-The-area-with-the-length-L_fig1_230731125

8 Organic field-effect transistors

8.1 *Mobility and the rate of switching*

The conductivity, κ, basically is close to the product of the charge carrier density, ρ, and the mobility, μ[20] κ can depend on ρ, but the dependence usually is weak. In electronics, a high mobility is usually a good mobility.

In semiconductors, the charge carrier density can be modulated externally. The functionality of the transistor is based on that mechanism. Electronic amplifiers and digital logic components are based on the transistor.[21] In the following, we discuss the field-effect transistor (FET, Fig.8.2), to be distinguished from the bipolar transistor (with npn or pnp doping)[22] . The FET shown in Fig.8.2 is based of silicon. The struc-

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[20] This is known from the conductivity of electrolytes. There, the mobility is called u and is given by Stokes' law as $u = -ez/(6\pi\eta r_H)$. Also remember the relations $\kappa = \Lambda_m c$, $\Lambda_m = \Lambda_m^0 - Kc^{1/2}$, $\Lambda_m^0 = \nu_+\lambda_+ + \nu_-\lambda_-$ and $\lambda = Fuz$. Also remember that the salt content can be determined simply by measuring conductivity – if the mobility is known.
The mobility can depend on the charge carrier concentration in electrolytes (Kohlrausch's square root law, see the term $Kc^{1/2}$ above).

[21] In the transistor, current flows through the drain, when the source *and* the gate have the correct voltage.

[22] The bipolar transistor is based on the fact that there are space charge zones at pn junctions. Electrons and holes jump into the neighboring zone and thus create a dipole layer. In the dipole layers, the mobile charge carriers are depleted,

ture at the gate is MOS structure (for "metal-oxide-semiconductor"). The abbreviation CMOS (C for "compensated") is derived from the MOS structure. In the FET, a channel with the same charge carriers as in the source and drain is created under the gate when the opposite potential is applied to the gate. This channel then conducts electricity. An FET can be produced as a printed circuit.

In FETs used as TFTs for displays, the *mobility* of the charge carriers in the channel (instead of the conductivity of the material, which depends on the charge carrier density and is modulated externally) is the key performance parameter.[23] The mobility limits the maximum current and thus the brightness of the pixel (Fig.8.3). Table 1 shows numerical values of mobilities.

Some comments on mobility*:*

- The best mobilities are a few 1000 cm^2/(Vs). Extremely high values quoted for graphene should be interpreted with caution when measured on single molecules rather than bulk materials.
- The mobility, μ, and the effective mass, m^*, are related as $\mu = e\tau_c/m^*$. τ_c is the collision time. The effective mass is related to the band structure by the relation
  $E(k) = E_0 + \hbar^2 k^2/(2m^*)$
- The mobility of charge carriers in organic materials is lower than the mobility in metals and semiconductors.
- For K^+ in water, the mobility is 10^{-4} cm^2/(Vs). Electrons and holes in solids are much more mobile than ions in water, even in moderately conductive media.
- Even in crystalline quartz, the mobility of electrons and holes is comparable to that of Si. Quartz is an insulator because the band gap is large and the charge carrier density is correspondingly low.
- Mobility strongly depends on impurities, crystal defects, and temperature.
- There are various ways to measure κ, leading to different results. The "field-effect mobility" is important here.
- GaAs has a better mobility than Si. This is why GaAs is used for some fast logic components. (These are bipolar transistors, not FETs).

	μ [cm^2/(Vs)]
Si, undoped	1 400
GaAs	9 000
Organic semiconductors	< 10 rubrene: 40
a-Si	0.5 – 1
IGZO	10 – 50
Common metals	50
Electrolytes	10^{-4}

Table 1

8.2 The organic field-effect transistor (OFET)

Printed FETs could replace the thin-film transistors (TFTs) used in TFT displays.[24] In a TFT display (also known as an "active matrix display", abbreviated as AM), there is a small logic unit behind each individual pixel, which is addressed via two intersecting lines and which switches the relevant pixel to the desired brightness for one cycle (Fig.8.3).

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which hinders conductivity. In the transistor, there are two such dipole layers in series, whose charge densities can be manipulated via the voltage at the base ("base" equivalent to "gate" in the FET).

The thickness of the space charge zones scales like $n_0^{-1/2}$ with n_0 the charge carrier density. Compare with the thickness of the double layer in electrolytes (given as the Debye length, proportional to $I^{-1/2}$ with I the ionic strength). Because the charge carrier density in organic electronics is small, the space charge zones for bipolar transistors are impractically wide. For this reason, the field-effect transistor is mainly used in organic electronics.

In conventional electronics, bipolar transistors are faster than FETs. However, they consume more power.

[23] With other transistors, the mobility limits the *switching time*.

[24] Sirringhaus, H., 25th Anniversary Article: Organic Field-Effect Transistors: The Path Beyond Amorphous Silicon. *Advanced Materials* **2014,** 26, (9), 1319-1335.

Aspects for the design of polymers for OFETs are:

- Crystalline packing is favorable for *intermolecular* charge transfer. There is then a low "reorganization energy" during charge transfer. The term "reorganization energy" is part of Marcus theory. It refers to changes in the positions of the atoms that must take place before charge transfer can occur.
- Charge-transfer groups are favorable (section 2.3).
- π stacking is favorable, preferably in the "brick-wall morphology" (i.e. with overlap).
- Flexible side groups are used for processability (solubility).
- As always in electronics, purity is favorable. Impurities are often traps on which the charges remain localized.
- Strong bonds reduce the thermal oscillations. This is favorable.

The numerous technical constraints and conflicting targets make materials development expensive.

Remember:

- Conductivity is the product of charge carrier density and mobility.
- In electronics, you want high mobility.
- Electronic logic is largely based on the external modulation of charge carrier density.
- The FET switches the charge carrier density in the channel via a voltage at the gate.
- The polymers of high mobility and high conductivity are semi-crystalline charge-transfer polymers.
- A potential application for OFETs are the TFTs in active matrix displays.
- Another application are the backplanes in electrophoretic displays (Fig.8.1). These have lower switching rates and lower power consumption.

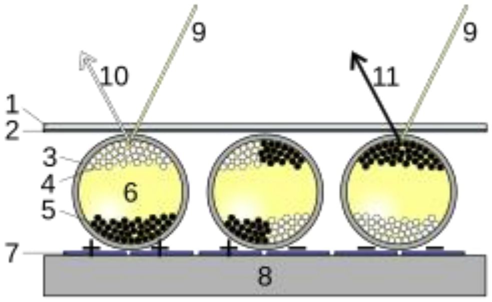

Fig.8.1
An electrophoretic display (EPD)
en.wikipedia.org/wiki/E_Ink

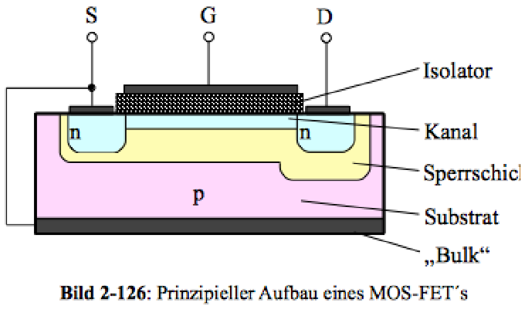

Fig.8.2
The field-effect transistor
elektronik-kurs.net/elektronik/mosfet-mos-field-effect-transistor

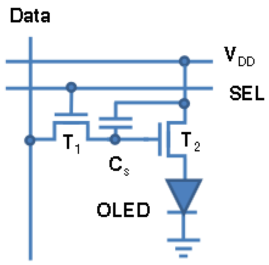

Fig.8.3
The thin-film transistor (TFT) in the back-plane of active matrix displays
onlinelibrary.wiley.com/ doi /10.1002/adma. 201304346/pdf

9 PEDOT:PSS based bioelectronics

The following paragraph is adapted from *https://www.sigmaaldrich.com/DE/de/technical-documents/technical-article/materials-science-and-engineering/bioelectronics/applications-of-conducting-polymer-devices-in-life-sciences?srsltid=AfmBOoor-NeX90YzZAQkRu9dWgaPgG6Evzi74bX0jQUyeoOK7x2Wj2KO0*

The application of conducting polymers at the interface with biology is an exciting new trend in organic electronics research. The nascent field of organic bioelectronics involves the coupling of organic electronic devices (such as electrodes and transistors) with biological systems, in an effort to bridge the biotic/abiotic interface. There are a number of unique characteristics of conducting polymers that make them well suited for integration with living systems:

- Mixed conduction of both electronic and ionic charge carriers is a major advantage for communication with biological systems, which rely heavily on ionic fluxes.
- Conducting polymers form ideal interfaces with electrolyte solutions that lack native oxides and dangling bonds.
- These van-der-Waals bonded solids have “soft” mechanical properties that better match those of the majority of biological tissues, leading to a lower mechanical mismatch in implanted devices.
- As in other applications for conducting polymers, solution processing of these materials facilitates easy fabrication and unique form factors.

Solution-processability becomes especially important when designing flexible devices or inexpensive single-use sensors. These characteristics combine to provide a new toolbox for interfacing electronics with biology, and more importantly, solving problems related to biodiagnostics and treatment of biological dysfunction.

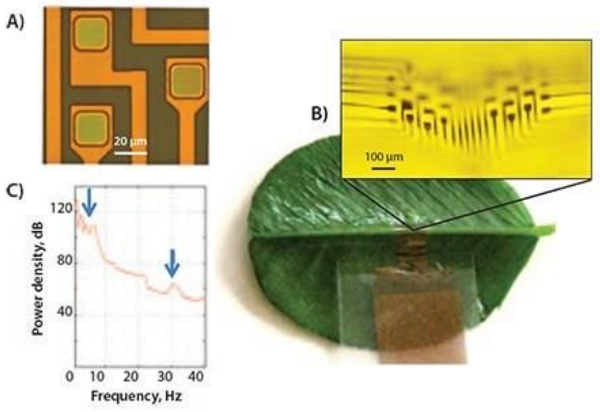

Fig.9.1
A) Micrograph of the array showing a detailed view of three electrodes.
B) An electrode array is shown to conform to the mid-rib of a small leaf.
C) Power spectrum of representative recording with a PEDOT:PSS electrode.

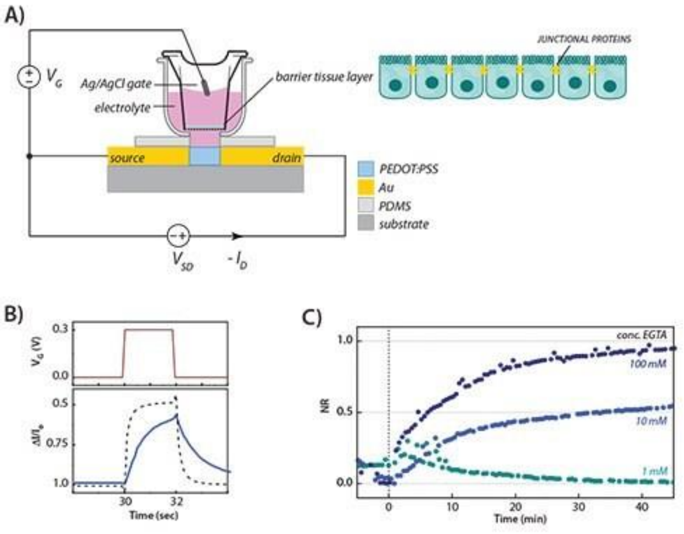

Fig.9.2
Architecture of an OECT integrated with barrier tissue layer; tissue is supported on a permeable membrane. The illustration on the right shows tightly packed epithelial cells with junctional proteins that regulate transport. **B**) OECT characteristics, showing a VG pulse (top) and normalized drain current, ΔI/Io (bottom), when healthy cells are present (solid blue) and when no cells are present (dashed black). A reduction in ionic flux caused by the presence of a barrier tissue layer slows device response time (VG = 0.3 V). **C**) Normalized Response (NR) calculated from OECT modulation on addition of varying concentrations of ethylene glycol-bis(2-aminoethyl ether)-N,N,N’,N’-tetraacetic acid (EGTA), as shown. EGTA was added at time=0. NR=0 refers to observed modulation when a healthy barrier layer is present, and NR=1 refers to observed modulation when barrier properties are destroyed: progression from 0 to 1 indicates barrier tissue disruption.