Seminar: Semiconductor Physics and Nanoscience

Molecular Electronics

Daniel Pedone

June 7, 2005

Abstract

With this work I want to give a first insight into one alternative to the so called top-down approach, namely the bottom-up approach, in order to realize nanometer sized structures with certain functions.

Contents

1 Introduction - top-down vs. bottom-up

In 1965 the Intel founder Gordon Moore predicted that the number of transistors per integrated circuit will double every 18-24 months. This prediction is known as Moore's law, which proofed to be right up to now. By the increase of transistor density each transistor has to be smaller and smaller over the years. Today, transistors are fabricated with a size of 70nm by lithographic techniques. But this so called top-down approach will soon reach its limit because of the exponential growth of cost production and because of physical laws. In particular, at nanometer scale, the electronic properties of semiconductor structures fabricated via conventional lithographic processes are increasingly difficult to control, because any object of few nm in size shows discrete quantum energy levels and inorganic clusters will slightly differ in the number of atoms they consist of, which results in a scattering of quantum energy levels. This physical law cannot be overcome by any engineering technique. Thats why we need after about 2020 an alternative to todays top-down approach. One alternative is the bottom-up approach. In contrast to the top-down approach, small components are connected to produce larger objects. Nature efficiently builds nanostructures by assembling tiny molecular building blocks with a remarkable degree of structural control with defined shapes, properties and functions, for example cell membrane, enzymes or DNA. The goal of the bottom up approach is to mimick nature's building processes, which results in several advantages:

· Molecules are several orders of magnitude smaller than present feature size
· Organic molecules of a given compound are absolutely identical
· Great amount of different materials (i.e. molecules)

2 Electrodes and Contacts

Now we want to have a closer look on electrodes and contacts. In particular we want to know how we can connect the organic to the solid inorganic materials.

2.1 Self assembly

One example for this connection is self assembly. Here surface active molecules arrange themselves spontaneously into regular patterns without outside intervention. A Self Assemlbed Monolayer (SAM) film can be deposited on a substrate simply by exposing the surface to an environment containing surface active molecules for a certain period of time (solution or vapour phase deposition). During this time, the surface active anchoring group of the molecule chemically reacts with the substrate. A SAM requires a bonding with a good stability at room temperature which must be however loose enough so that the molecules can rearrange themselves in order to build up a self assembled monolayer. The best investigated bonding is the thiol(SH-group)-gold bonding. Rosa Di Felice described this bonding in the framework of density-functional theory (DFT) calculations for cystein (one of the 20 amino-acids) on a gold surface. The calculations results in an overlap of the gold d orbital with the Sulfur p orbital forming a chemical bond with the strength of about 1.8eV. (Covalent bond regime)

2.2 Langmuir-Blodgett (LB)-films

Another method to deposit molecules on solids is the Langmuir-Blodgett technique where amphiphilic molecules are used (with a hydrophobic tail and a hydrophobic headgroup). At the first step you spread an organic solution with the molecules in it onto water. After that, you have to evaporate the organic solvent and because the molecules do not go into solution you get disorganised molecules floating on the water surface. The molecular building blocks can be compressed into a monolayer with the aid of a moving barrier. The hydrophobic tails

align away from the aqueous phase. The monolayer prepared at the air/water interface can be transferred on the surface of a indium-tin oxide electrode due to Van der Waals interaction.

2.3 Electromigration Technique

In order to address not only a bulk of molecules or monolayers, but a single molecule, we need a tiny gap with the size of a single molecule. The use of high resolution lithography and shadow mask techniques allows the fabrication of metallic structures with a width in the order of 10 to 20 nm. These structures are still about one order of magnitude too large for single molecules. In order to get such tiny gaps you fabricate metallic wires with predetermined breaking points. Then you apply a certain voltage and due to electromigration of metal atoms the metal wire breaks up at the bottleneck. The resulting electrodes have a distance of about 1 to 3 nm, which can be estimated by the resistance or can be seen in this AFM image. All this happens in a solution with molecules which hopefully assemble themselves in between the tiny gap. In the best case just one molecule is trapped in the gap.

3 Functions of Single Molecules

Up to now we are able to contact molecules to electrodes. But in order to do electronics we do need to exploit several functions of the molecules for example . . .

3.1 Electron Transport Mechanism

We start with the question how to build up molecular wires . . .
An example for a molecular building block is the Benzene molecule. The Benzene consists of six Carbon atoms. Each Carbon atom is bond to two other C atoms and to an Hydrogen atom. In order to understand the bonding between the Carbon atoms we have to know something about hybridisation. The valence atomic orbitals of Carbon can be combined to form hybrid atomic orbitals, which are all energetically equivalent. In the case of Benzene only two p-orbitals hybridise with the s-orbital, which is called $sp^2 - Hybridisation$: three identical hybrid orbitals lying on a plane with an angle of 120 between them. In Benzene the three hybrid orbitals form a covalent bond to the neighbouring C atoms and to the Hydrogen atom. The molecule is therefor planar. The fourth electron sits on the remaining non hybridised p orbital, perpendicular to the molecular plane. Each of these p orbitals overlaps with the neighbouring ones. This overlap results in a so called π-bonding. The electrons involved in the π-bonds are not strongly tight to a specific atom and can be considered delocalized and in this way a negative cloud above and below the molecule is formed. The same type of delocalization is found on chains formed by interconnected benzene rings. These chains are called oligomers because they are synthesized by joining one molecular unit (for example benzene) to itself a few times. And they are called conjugated because the lowest energy π-orbital extends uniformly over the whole molecule. Such orbitals can provide channels that permit the transport of additional electrons from one side of the molecule to the other when a bias is applied. Such conductive structures are called Tour wires, from the name of the chemist that first synthesized them. The possibility to conduct currents remain also when other groups are inserted between the benzene rings, as long as the conjugation among the p-bonded components is maintained.

In solid state physics you get energy sub bands (bonding and antibonding) by adding atoms to one another in all three dimensions forming for example a crystal. Here, in the case of oligomers, it is very similar to solids. Every time an atom, for example a carbon atom, is added to the chain, the number of discrete energy sub bands is increased. The resulting energy gap, is the energy between the so called HOMO (Highest Occupied Molecular Orbital) and

the LUMO (Lowest Unoccupied Molecular Orbital) energy levels (about 3eV, Polyphenylene chain (Adv. Mater. 2003, 15, No.22)). According to this paper the Polyphenylene chain acts like a semiconductor. In comparison to semiconductor physics the conduction band is called LUMO and the valence band is called HOMO.

3.2 Electron Transport - Landauer approach

At this point it might be useful to give a physical description of the electron transport via molecules. The simplest case of description is the coherent electron motion on resonance
· coherent: Absence of dissipative effects (inelastic scattering)
· resonance: Metal Fermi level is resonant with an unoccupied molecular orbital
At the second step the Landauer Approach considers the molecule as a scatterer for the electron. The thiol breaks the electron conjugation, introducing a potential barrier between the metal contact and the delocalized electrons. This potential barrier acts as a contact resistance. From this assumptions Landauer derived its formula where the conductance:

$$g = \frac{e^2}{\pi \hbar} T(E_F) \tag{1}$$

is related to the transmission probability $T(E)$:

$$T(E) = \exp[-\frac{4\pi}{\hbar} \int [2m(V_B(x) - E_x)]^{\frac{1}{2}}] \tag{2}$$

3.3 Molecular Doping - Diodes

In order to get molecules with rectifying properties we are able to dope parts of them, analogue to semiconductors, so that we have pn-junctions:
· Donating substituent groups, which can easily be ionised and so you can call them donators (negativ doping)
· On the other hand electron withdrawing groups serve as p-dopants
When we now dope one Benzene ring positively and another negatively with a spacer in between (in the polyphenylene example) we get a molecule with rectifying properties, in other words a diode. Under equilibrium conditions, the different doped groups lead to an asymmetry in the energy level. Now we apply an bias over the pn-doped molecule neglecting band bending. Under the forward biased condition the metal fermi-level and the LUMO levels of the molecule are in resonance and current can flow. Applying the voltage into the opposite direction we get into the reversed biased case where it is not possible to get the LUMO levels of the molecule into resonance, so that approximately no current flows.

4 Molecular Electronic Devices

The long-term aim of molecular electronics, but still unattainable, is the parallel integration of single molecular structures as functional units in electronic circuits. Devices based on molecular films are much more promising for the near term displaying a variety of physical properties like rectifying, switchable memories or light Electroluminescence.
One of the very first examples of a device based on molecular films was the realization of the rectifying principle predicted in the seventies and demonstrated in the 1990s.

4.1 Switches and Storage Elements

Molecular films with switching properties - and so they can serve as storage elements - have also been realized in labs. Here a class of molecules is used which are stable in two different

states (bistable) and can be classified by:

· the stimulus that triggers the switch (light, pH value, electrical potential)

· property or function that is switched (structural feature, current transport)

In all cases, input stimulations reach the switch changing its physical state and producing a specific output. A system where such a switching behaviour has already been measured is the catenane in solution. Here two molecular rings are synthesized in that way, that they are interlocked. These interlocked rings rotate within each other by applying a certain voltage and thus changing their conductance. This rotation shows a hysteretic behaviour and so the states of the molecule can be regarded as memory bits which can be written and erased. Yong C. and co-workers introduced in 2003 a rotaxane (very similar switching behaviour like catenane) nanoscaled molecular-switch device, which can be fabricated by imprint lithography and works under dry conditions. In this paper the on/off switching events were repeatable. However, the on/of ratio of the resistance for this device decreased gradually after 40 switch cycles. Statistically, about three thirds of the 36 devices that were tested showed such reversible switching properties. (rest: shorted or open)

4.2 Single Molecule FET

Another molecular electronic device is the single molecule FET. This is a device where electrons hop on to, and off from, a single atom between two contacts. Mr. Park and co-workers fabricated and measured such a device based on an organometallic molecule. The molecule has one Co ion bonded within an approximately octahedral environment to two carbon chains with thiol end groups. This molecule was selected because its charge state of the Co ion can be changed from Co^{+2} to Co^{+3}. The Si-Substrate served as gate electrode, separated by a SiO_2 insulating layer. Gold wires are fabricated on the SiO_2 layer by e-bam lithography. Then the setup is placed in a solution of the molecules in order to form a self-assembled monolayer on the Au electrodes. The wires coated with molecules are then broken by electromigration while monitoring the current until only a tunnelling signal is presented. This produces a gap about 1-2nm wide, across which a molecule is often found. The measured behaviour is the signature of a single electron transistor, a device containing a small island which is attached to electrodes by tunnel barriers and whose charge state can be tuned using a gate voltage. If the charge of the central Co ion is fixed to either Co^{+2} or Co^{+3}, no current can flow at small bias voltage due to Coulomb blockade. If the gate is tuned such that Co^{+2} and Co^{+3} have the same energy, the ion can be continuously charged or uncharged: current can flow even at small bias voltages.

4.3 Organic Light Emitting Diode OLED

The last presented molecular device is the organic light emitting diode (OLED) which is based on amorphous films of molecules sandwiched between two electrodes (one has to be tranparent). For a wide range of modern applications including television and computer monitors, it would be useful to have inexpensive and efficient flat panel displays. The flat panel display market is currently dominated by liquid crystal displays (LCD) which can provide high intensity colour images at video rates. Advantages of OLEDs in comparison to LCDs are for example:

· do not require backlight or polarizers

· thin and can be deposited on flexible substrates

· Brighter and wider viewing angles

· Lower Power consumption

To a first approximation the working principle can be described by electrons and holes which are transported within the molecular film (electrons in the LUMO and holes in the HOMO level) where they recombine radiatively, this effect is called electroluminescence. In order to

inject electrons from one side and holes from the other, different metals (i.e. with different work function) are used for the two contacts. Injection of the electrons and holes occurs due to emission over the barrier or tunnelling across it. Because holes are much faster than electrons in organic materials, and the electrons also have to surmount a higher barrier, there is an imbalance in the current contribution in favour of the holes. This translates in poor efficiency. To overcome this problem one uses a metal for the electron injection contact with low workfunction and different organic layers for electrons and holes. By using two different molecular films one creates a barrier for holes due to the lower HOMO level of the electron transport layer. In the same way you get a barrier for the electrons. These barriers create an accumulation of electrons and holes at the heterostructure interface which results in a higher efficiency.

5 Outlook

In order to use the ultimate density of logic and memory functions of molecules, problems like their addressability, reproducibility and reliability have to be solved.
A lot of functions of molecules have only been measured in solution. In order to form a solid independent integrated circuit build up from a certain number of interconnected molecules it is necessary to adress single molecules, which is very difficult today. Even these interconnected molecules are not realized.
Furthermore the molecular solid interface is not that stable over the time in comparison to the interface of different solid semiconductors. That is why reliability and reproducibility is not guaranteed.
In my opinion molecular electronics for today is only for academical interest but in a few decades it might be an alternative to todays solid semiconductors.

6 Literature

General information:
· Nanoelectronics and Information Technology, Rainer Waser (Ed.), Wiley-VCH
· Handbook of Nanotechnology, Bhushan (Ed.), Springer
· Molecular Nanoelectronics, Mark A. Reed et al., ASP

Chemisorption:
· Mark H. Dishner et al., Langmuir, Vol. 13, 2318-2322, 1997
· Rosa Di Felice, J. Chem. Phys., Vol. 120, No. 10, 2004

Electronic Transport:
· Adi Salomon et al., Adv. Mater., Vol. 15, No.22, 2003
· Yoram Selzer et al., Nano Letters, Vol. 5, No.1, 61-65, 2005

SET:
· Jiwoong Park et al., Nature, Vol. 417, 13 June 2003

Molecular Switch:
· Yong Chen et al., Appl. Phys. Lett., Vol. 82, No.10, 2003

OLED:
· Molecular Nanoelectronics,Chapter 12, Mark A. Reed et al., ASP