Project II.3: MOLECULAR MATERIALS AS COMPONENTS OF ELECTRONIC DEVICES

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Research orientation:

- To investigate the potential of molecular materials to be used as active components in molecular devices e.g. as switching or memory elements.
- To evaluate elements of the class of organic crystals as components of organic FETs
- To develop techniques for thin film deposition and characterization of molecular materials.
- To use ab-initio electronic structure methods which are more appropriate to study semiconductor properties to be able to address different problems.
- To develop more semiempirical atomistic methods like tight-binding in order to describe optical properties.

Main results in 2005

The main results obtained in 2005 within the different tasks of the project are given below.

Task 1 Organic/inorganic composite materials as components of nano-devices

N. Glezos, A. M. Douvas, P. Argitis , D. Velessiotis and V. Ioannou-Sougleridis

A wide variety of organic molecules or metal nanoclusters have been proposed for molecular electronics applications in the past. Polyoxometalates (POMs) are inorganic metal-oxygen clusters that combine both the electron transport properties of the organic molecules with the charge confinement properties of the inorganic nanoclusters. POMs, especially the tungsten and molybdenum ones, have well-defined and stable structure consisted of clusters of coordination polyhedra MO_n that have a metal ion in their center and connect each other through common edges and apices. In previous work of our group, tungsten POMs were embedded into polymeric matrices using nano-distant planar electrodes, and conductivity peaks were evident even at room temperature conditions. During this year, the electric transport and charging properties of molecular monolayers consisted of POM anions and 1,12-diaminododecane (DD) cations, prepared with the layer-by-layer (LBL) self-assembly method were studied. It is shown that POM molecules act as electron traps and that tunneling dominates other transport mechanisms.

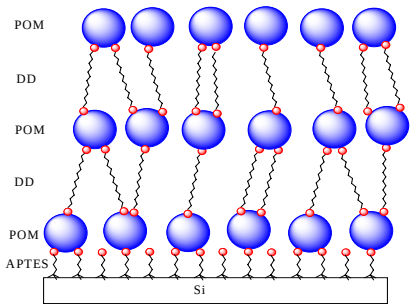

Fig. II.3.1: *Schematic diagram of APTES-(POM-DD)$_2$POM multilayer film (3-POM-layer film) prepared with LBL method on Si wafer.*

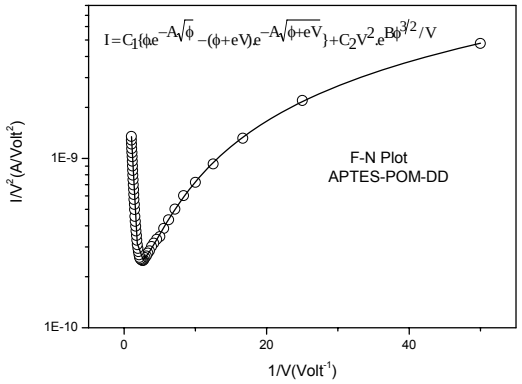

Fig. II.3.2: *Comparison of experimental results (symbols) with tunneling theory (solid line). This method allows the determination of the average film thickness and the potential step due to the film added on silicon.*

Multilayer films composed of successive monolayers of the polyoxometalate 12-phosphotungstic acid ($H_3PW_{12}O_{40}$) and 1,12-diaminododecane (DD, $H_2N(CH_2)_{12}NH_2$) have been prepared using the LBL method (fig. II.3.1) The preparation of the $(POM\text{-}DD)_n$ multilayer film was analyzed by UV-Visible spectroscopy following the characteristic POM spectrum, and specifically its characteristic 267nm-peak.

These films were electrically characterized in different ways: a) Capacitance and leackage current measurements of vertical structures (Al/POM layer/Si(p doped)/Al), b) Current voltage measurements of planar structures (Au electrodes 50nm apart), and c) STM measurements of vertical structures (STM probe/POM layer/Si(n++ doped)/Al). In the case of capacitance measurements the application of the standard MOS analysis in this region allowed the determination of the flat band voltage shift, which is caused by the charge accumulated in the molecular layer. Current measurements are discussed in terms of tunneling mechanisms (fig. II.3.2).

Task 2 Transport properties of Cyclodextrin/Au nanoparticle host/guest systems

N.Glezos, D. Maffeo,[1] K.Yannakopoulou[1] and I.M.Mavridis[1]
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The aim of this work is to fabricate nanodevices based on the transport properties of composite organic/Au nanoparticle systems. In this case, cyclodextrin derivatives bearing long aliphatic sulfide substituents were synthesized at the institute of Physical Chemistry. The derivatives feature (a) not-easily oxidizable sulfides (as opposed to thiol-groups which are prone to oxidation to sulfoxides or even sulfones), which offer seven points of attachment to the Au surface and (b) the -S- groups are connected to the cyclodextrin ring through a 10-carbon spacer, providing ample flexibility for structural organization during the deposition on the gold surface. Attachment of these molecules on Au surfaces was confirmed by RAIRS.

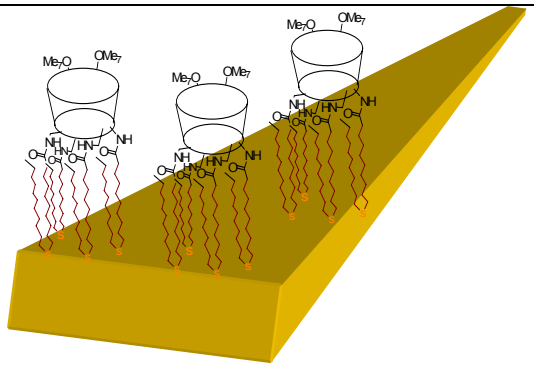

Fig II.3.3: *Cyclodextrin derivatives*

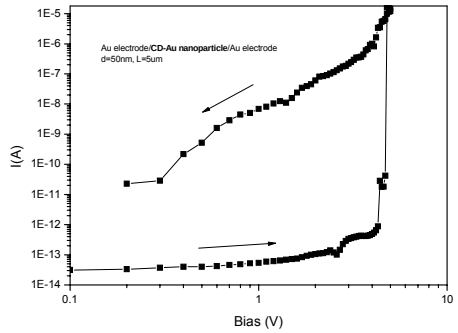

Fig II.3.4: *I-V characteristic of a composite Au nanoparticle (40nm) /CD system on Au nanoelectrodes.*

The resulting system consisted of the two nanoelectrodes (50nm) and an accumulation of Au nanoparticles bridged by the cyclodextrins. In the case of current measurements the Au nanoparticles act as donors/acceptors of electrons with different potential in each case. The system is reversibly charged/uncharged (fig. II.3.4) showing instability when the applied voltage is decreased. Further work will focus on the functionalisation of the nanoparrticles with selected organic guests for the cyclodextrin host.

Task 3 Evaluation of organic crystals for OTFT applications

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Organic thin film transistors (OTFTs) have already been used in diverse applications such as electronic paper, chemical sensors, radio frequency tags and memory devices. Pentacene and α-sexithiophene are the molecular materials with the highest reported field mobilities as p-channels in OTFTs. However both materials present processing difficulties due to their limited solubility. Metal phthalocyanines (MePc) is another class of compounds which has been investigated for the same purpose. Their advantages are their chemical and thermal stability (stable up to 400°C, easily vacuum evaporated). Their field mobilities in transistor structures are of order 0.01 $cm^2/V.s$ (for CuPc). Recently, the mobility value of 1 $cm^2/V.s$ for CuPc single crystals was reported. Sulfonated MePcs (Me = Co or Zn, Cobalt or Zinc phthalocyanine; mixtures of monosulfo and disulfo derivatives) were either synthesized by the Czech group, or purchased and purified.

Both spin coating and vacuum evaporation were used for the film preparation. The knowledge of the barrier heights at interfaces between the electrodes and the active organic layers is of great importance for understanding and improvement of organic semiconducting devices. The electronic structure of the metal phthalocyanines/ Au interface was investigated by X-ray and UV Photoelectron spectroscopies in the University of Patras. The band energy diagram of the interface was obtained in this way, from which the hole and electron injection barriers can be determined.

The transistor structures consist of source-drain Au electrodes on a Si (n++)/SiO_2 substrate with an Al backgate. Using interdigitated electrode geometries with gate lengths L = 2, 5, 10 and 30μm and channel width W in the millimeter range, ratios W/L ~10^3 were obtained.

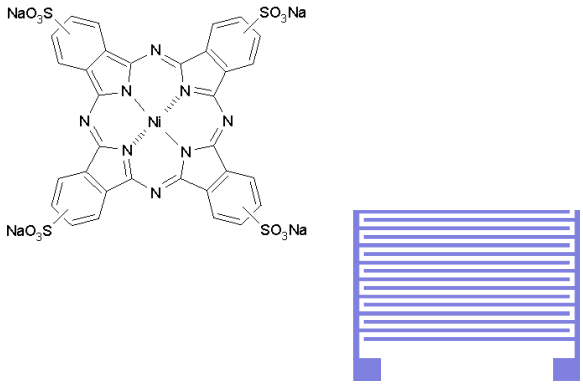

***Fig. II.3.5: (a)** Example of sulfonated Ni -PCs **(b)** Electrode geometry. Electrode size 1mm, interelectrode spacing 2-30μm.*

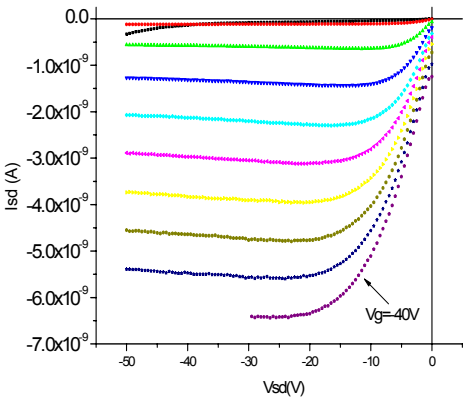

***Fig II.3.6:** Characteristics of an unsulfonated Ni –Pc, p type transistor prepared by sublimation. Film thickness 30nm and electrode distance 30μm.*

Task 4 Transport properties of nanostructures.

N.Papanikolaou , H. Ebert, I. Mertig

The last years witnessed an increased interest in investigating the spin-dependent transport between two ferromagnetic electrodes separated by either an insulator or a semiconductor, systems now commonly known as magnetic tunnel junctions MTJs. Generally a realistic geometry is required for theoretical investigations on the magnetoresistance to enable a sensible comparison between theory and experiment. Most of the theoretical investigations, however, treated the two spin subsystems participating in the conduction independently, two-current model, introducing this way a spin filter. The transport is treated either on the basis of the Kubo-Greenwood or on the Landauer-Büttiker formalisms. We have performed fully relativistic calculations and presented a detailed analysis on how spin-orbit coupling influences the conductance by mixing the different spin channels.

Another interesting field is electronic transport through atomic size constrictions. Small, few atom molecules are attached to metallic leads and the electronic conductance is calculated using the Bandauer formalism. The electronic structure of the molecule including the metallic lead are calculated using ab-inito calculations based on density functional theory. Our study is focused on the influence of the chemistry of the contact the bonding to the leads and the geometry of the contact to the transport properties

Task 5 Magnetic properties of II-VI dilute magnetic semiconductors.

N.Papanikolaou and K. Trohidou

Over the recent couple of years, Mn-doped III-V and II-VI diluted magnetic semiconductors (DMS) have become an important playground for developing our understanding of carrier-mediated magnetism in solids. To a large extent, this stems from the fact that in these systems the relevant interactions can be tuned by changing the carrier and magnetic ion densities as well as by imposing strain, confinement, electric field, or illumination. Monte Carlo simulations we employed to assess the influence of magnetization fluctuations, short-range antiferromagnetic interactions, disorder, magnetic polaron formation, and spin-Peierls instability on the carrier-mediated Ising ferromagnetism in two-dimensional electronic systems. The determined critical temperature and hysteresis are affected in a nontrivial way by the antiferromagnetic interactions. The findings explain striking experimental results for modulation-doped p-Cd1-xMnxTe quantum wells.

PROJECT OUTPUT in 2005

PUBLICATIONS in INTERNATIONAL JOURNALS

1. “Tungstate poloxometalates as active components of molecular devices”, D.Velessiotis, N.Glezos and V.Ioannou-Sogleridis, Journal of Applied Physics, 98 (8),084503 2005
2. “Monte Carlo Simulations of Ferromagnetism in p-Cd(1-x)Mn(x)Te Quantum Wells”, D. Kechrakos, N. Papanikolaou, K.N. Trohidou, and T. Dietl, Phys. Rev. Lett. 94, 127201 (2005)
3. “Influence of spin-orbit coupling on the transport properties of magnetic tunnel junctions”, V. Popescu, H. Ebert, N. Papanikolaou, R. Zeller, and P. H. Dederichs, Phys. Rev. B 72, 184427 (2005)
4. “Electronic transport through atomic size constrictions”, N. Papanikolaou A. Bagrets, I. Mertig, J. Phys. Conf. Ser. 10 109 (2005)

PRESENTATIONS in CONFERENCES

1. “Electronic transport properties of organic/inorganic composite materials in the nanoscale”, N.Glezos (Invited talk), Nanomeeting 2005, Minsk
2. “Electrical characterization of molecular monolayers containing tungsten polyoxometalates” , N.Glezos, Douvas A. M., Argitis P. , Saurenbach F., Chrost J., Livitsanos C., MNE Conference, Vienna