

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 develop consistent evaluation methods based on the electronic transport properties at the nano- level for the characterization of single layered and few-layered systems.
- to produce physical parameters (film thickness, surface molecular density, contact potential) that could be cross-checked with other surface characterization methods
- 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.

RESEARCH RESULTS

A. Organic/inorganic composite materials as components of nano-devices

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a₁ Synthesis and electrical characterisation of polyoxometallate layers

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.

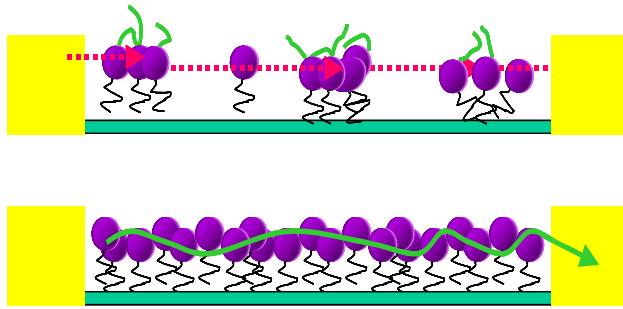


Fig. II.3.1. Schematic diagram of APTES-POM films. The presence of diamine molecules on the top of the POM layer (purple spheres) results in creating clusters (top figure).

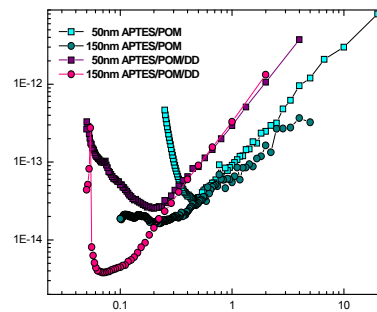


Fig. II.3.2. I-V characterization and extraction of parameters from the F-N plots in the case of the various films. The transition point is affected by the presence of the diamine layer.

During this year we studied the electronic transport properties of POM monolayers in planar structures using Au or Al electrodes on a silicon surface. Transport is dominated by tunneling through the molecular layer. The presence of diamines result in a change of the film morphology which is detected as a change in the tunneling characteristic (figure II.3.2)

a₂ C-MOS capacitor devices containing molecular monolayers

Novel structures using C-MS compatible processes were fabricated. These structures contain patterned molecular layers. The aim is to selectively charge the molecular layer and thus create a molecular memory module. These structures were extensively studied using I-V and CV spectroscopy. The gate / substrate properties are under investigation. It is desirable to charge the system only from one side (substrate).

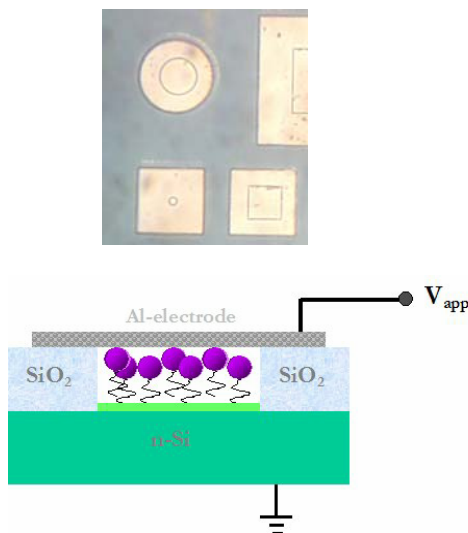


Fig. II.3.3: Schematic of the fabricated capacitors which encapsulate the molecular layer.

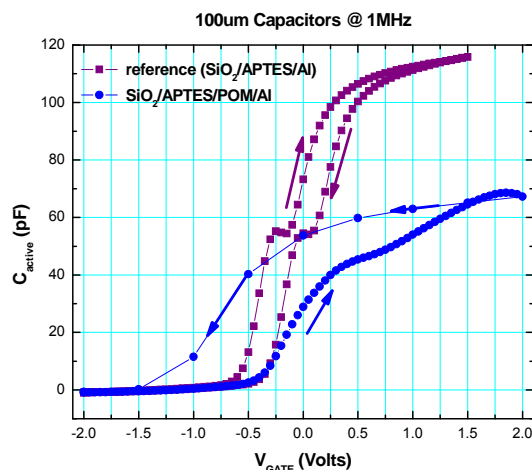


Fig. II.3.4: CV behaviour of the molecular films.

B. Transport properties of Cyclodextrin/Au nanoparticle host/guest systems

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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.

The resulting system consisted of the two nanoelectrodes (50nm distance 5 μ m length) and an accumulation of Au nanoparticles bridged by the cyclodextrins properly functionalised for attachment on gold nanoelectrodes. 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.3.6) showing instability when the applied voltage is decreased. In the optimised case only one pair of molecules are coupled to one gold nanoparticle and the nanoelectrodes.

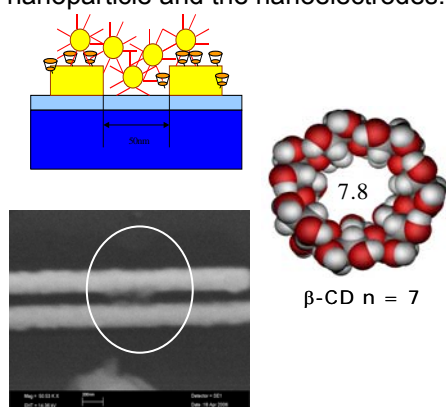


Fig. II.3.5: Cyclodextrin nanodevice. The cyclodextrins are accumulated in the electrode gap.

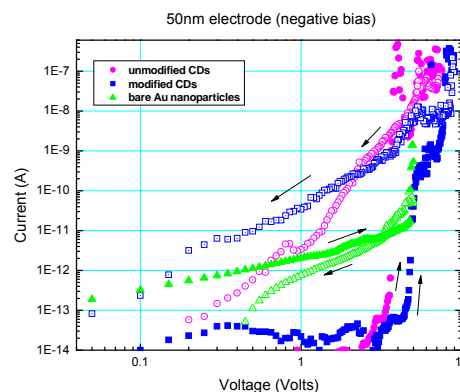


Fig. II.3.6: Memory effect (blue line) resulting from tunnelling through modified cyclodextrines

The cyclodextrine functionalised gold surfaces were also studied using STM imaging and I-V spectroscopy. The morphology of the film was demonstrated. Small clusters of very few atoms are created on the surface. These clusters are organised in larger stripes. The tunnelling barrier height decreases due to the presence of the molecular layer.

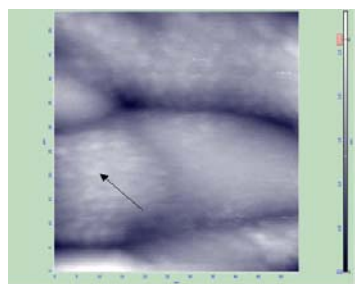


Fig. II.3.7: Cyclodextrine arrangement on a gold surface using STM. The nanometer size spots correspond to the accumulation of a small number of molecules.

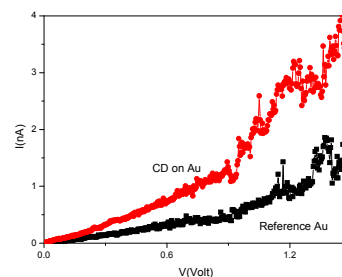


Fig. II.3.8: STM spectroscopy of cyclodextrines on gold.

C. Evaluation of organic crystals for OTFT applications

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We investigate the class of metal phthalocyanine salts (MePCs) and metal phthalocyanine sulfonate sodium salts (MeS_xPCs) as candidates for p-type channels in organic transistors. Both kinds have the advantage of chemical and thermal stability (stable up to 400°C, easily evaporated). The field mobilities of MePCs in transistor structures are in the range of 0.02 cm²/V.s (for CuPC). Recently, a mobility value of 1 cm²/V.s in the case of CuPC single crystals was reported. Furthermore, MePCs are interesting for electronic applications such as chemical sensors and solar cells]. MeS_xPCs are selected because of their enhanced solubility compared to their non-sulfonated counterparts, and were either synthesized (Me=Ni, Co, Zn or Al) by the Czech partner, or purchased by Aldrich Co (Me=Cu).

The comparison between the MePCs studied was based on their electric behavior depending on a) the method of deposition, b) the type of metal and c) the presence of pendant groups. The objective is to select the type of material and the film preparation process with the optimal performance. Preliminary tests for Al(OH)PC(SO₃Na)_x based transistors have given promising results.

On the other hand, metal phthalocyanine sulfonate sodium salts, are innovative materials, which can be used to construct OTFTs with much less effort. The processes are much simpler and the mobilities obtained are much higher. In that case the active layer is prepared by spin coating at room temperature, using the MeS_xPC solutions. Afterwards, the samples are dried at elevated temperature (50°C) for 20 minutes.

The first system studied was NiPC as a reference. Fig. II.3.9(a) shows a typical set of characteristics for a device with a 50nm active layer. The field effect mobility is 10⁻⁵ cm²/V.sec, a value that agrees with previously published results and is acceptable for the applications to which those materials address.

Higher mobility values are obtained in the case of metal phthalocyanine sulfonate sodium salts. The drain source conductivity increases with negative gate bias indicating typical p-type conductivity. OFETs with MeS_xPCs as the active channel cannot be fabricated by evaporation, since the material tends to burn out before it evaporates. Results for the whole class has been investigated.

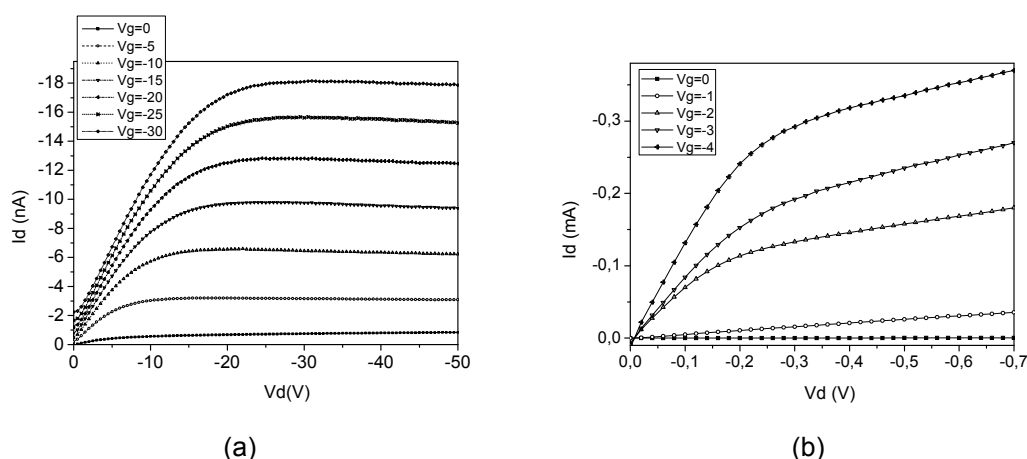


Fig.II.3.9: Dependence of drain current on the drain voltage of an OFET with 50nm organic layer, W/L ratio of 23275 and 82nm thick SiO₂ oxide dielectric: (a) NiPC deposited at a substrate temperature 100°C. The calculated field effect mobility is 10⁻⁵ cm²/V.sec. (b) NiS_{2.4}PC layer, deposited by spin-coating and annealed at 50°C. The calculated field effect mobility is 1.08 cm²/V.sec. All device characteristics are measured in room ambient.

PROJECT OUTPUT in 2006

Publications in International Journals

1. "Electrical characterization of molecular monolayers containing tungsten polyoxometalates", Glezos N, Douvas AM, Argitis P, et al., *Microelectron. Eng.* 83 (4-9): 1757-1760 Apr-Sep. 2006
2. "Electron-beam lithography simulation for the fabrication of EUV masks", Patsis, G.P., Tsirikas, N., Raptis, I., Glezos, N., *Microelectronic Engineering* 83 (4-9 SPEC. ISS.), pp. 1148-1151 (2006)

Papers in Conference Proceedings

1. "Single-Component Nickel-1,2-Dithiolene Complexes, Candidate Semiconductors For Field-Effect Transistors", G.C.Papavassiliou, G.C.Anyfantis, B.R.Steele, A.Terzis, C.P.Raptopoulou, G.Tatakis, G.Chaidogiannos, N.Glezos, Y.F.Weng, H.Yoshino, and K.Murata, *International Conference on Science and Technology of Synthetic Metals (2006)*, Dublin, Ireland
2. "Organic transistors using metal phthalocyanines", G.Chaidogiannos, F.Petraki, N.Glezos, S.Kennou, S.NešpùrekXXII Greek Solid State and Material Science Conference (2006), Patras, Greece

PhD Thesis

1. D.Velessiotis, *Microelectronic nanostructures and nanodevices based on polyoxometalates*, Information Faculty, University of Athens, December 2006

Diploma Theses

1. M.Kalonakis, *Molecular Transistors using organic crystals*, SEMFE, NTUA, November 2006
2. C.Livitatsanos, *Electrical properties of molecular devices based on organic/inorganic materials*, SEMFE, NTUA, November 2006