Project II.3:MOLECULAR MATERIALS as COMPONENTS of ELECTRONIC DEVICES

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Projects Running:

- Greek - Czech Cooperation project (GSRT)
- EU RTD project Uninanocups

Goals

- To investigate the potential of molecular materials in the class of polyoxometalates to be used as active components in molecular devices e.g. as switching or memory elements.
- To evaluate elements of the class of metal phthalocyanines as components of organic FETs
- To investigate electronic transport in the atomic limit

Main results:

a) Molecular nanodevices containing polyoxometalates

D. Velessiotis, N.Glezos, V. Ioannou-Sougleridis and G. Chaidogiannos

Molecular materials are being extensively investigated as components of electronic devices hoping to deminish device dimensions to the atomic scale. Polyoxometalates (POMs) are a class of welldefined metal oxygen clusters that can be envisioned as soluble molecular semiconductors. These compounds for reasons of cationic radius size and oxygen pπ bonding capabilities can be formed having as basis only 5 elements of the periodic table (V, Nb, Ta, Mo, W) but the most stable and well characterized elements that offer substantial chemical handling capability and property tunability are those based on WO_4^{2-} and MoO_4^{2-}, primarily $H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$, $H_3SiMo_{12}O_{40}$ and $H_3SiW_{12}O_{40}$.

The work of this group on tungstate POMs has been motivated by the comparison of the electronic properties of these molecules to metallic and conducting nanoclusters. POMs are stable inorganic oxides of size ~1nm that do not suffer from the limitations of size and process reproducibility. Their charging energies are in the range of 0.1-4.0 eV therefore the resolution of discrete electronic levels at room temperature conditions is expected. The search for a suitable polymer matrix resulted in poly (methyl methacrylate) PMMA, although other systems have also been tested. The host material should not react with the embedded molecules, thus altering their transport properties, and at the same time the composite material should preferably behave as a lithographic resist with nanometer resolution for nanofabriation process simplification reasons. PMMA meets both demands. The electrical transport properties of polymer/POM blends were tested using planar and vertical devices with nanometer distant electrodes. Aluminum or gold planar electrodes distant 20-500nm apart were fabricated on silicon dioxide using a standard PMMA lift-off process and electron beam lithography. Two different electrode configurations have been used a) in the shape of opposing fingers with a nanometer distance and b) in the shape of parallel lines with nanometer interspacing.

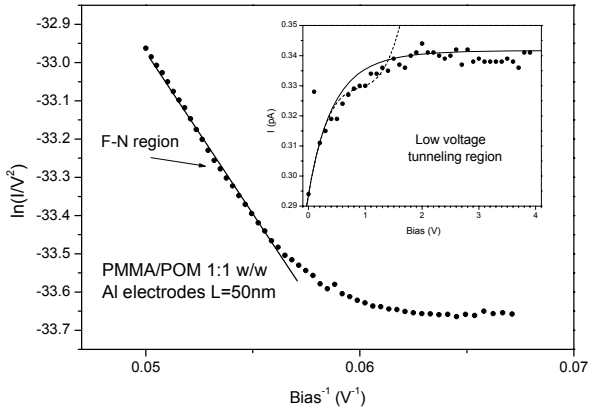

Fig. II.3.1: *Analysis of the tunneling regimes in the case of a 50nm Al contact. The low voltage region is shown in the inset. The experimental curve is fitted using both the low power extrapolation model and the model of Simmons.*

In order to study the transport characteristics and single out the tunneling effects of these composite systems, the electrode distance, the electrode material and the molecular concentration were treated as variable parameters. In the case of inter-electrode distances larger than 50 nm the behavior is approximately Ohmic with the exception of a small non linear region for voltages lower than 1V. This Ohmic behaviour is due to hopping conductivity through tungstate molecules which in our case are distant 2.25nm apart. Since the molecular size is 1-1.5 nm the net distance between molecules is estimated to be 0.75-1.25nm in this concentration. In the case of small interelectrode distance for L=50nm, a nonlinear plateau appears. The plateau suggests a saturation effect i.e. the transition from the barrier limited conduction to the bulk limited conduction dominated by hoping transport. In order to investigate this effect and distinguish the part that is due to the insulating PMMA matrix, structures with Au electrodes were also tested. The conductivity plateau still appears and this is evidence of the fact that it is mainly dependent on the material, rather than the electrode. Comparing the results in the case of Al and Au electrodes it is deduced that the barrier appears for smaller electrode distances in both cases. Effects are less dramatic in the case of Al electrodes due to the presence of the natural oxide which has a high contribution in the case of lower voltages. We have checked electrode distances as low as 10nm obtaining qualitatively the same results. In the case of such small distances only a few molecules are aligned in the direction of the electric field. For example, in the case of a 1:1 w/w concentration and 10 nm electrode distance, the mean distance between molecules is <d>=3nm resulting in 3-4 molecules along the field. The electrons reach the molecules through the PMMA insulating barrier undergoing multiple tunneling.

b) Evaluation of sulfonated metal phthalocyanines 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^{o}C, easily vacuum evaporated). Their field mobilities in transistor structures are of order 0.01 cm^2/V.s (for CuPc).

We investigate the class of metal phthalocyanine sulfonate sodium salts ($MePcS_x$) as candidates for p-type channels in organic transistors. These materials were selected because of their enhanced solubility compared to their unsulfonated counterparts. Sulfonated MePcs have been either synthesized (Me = Co or Zn, Cobalt or Zinc phthalocyanine; mixtures of monosulfo and disulfo derivatives), or purchased from Aldrich Co (Me=Cu, Copper phthalocyanine-3, 4', 4", 4"'-tetrasulfonic acid tetrasodium salt, 85% dye content). $CoPcS_{1-2}$ and $ZnPcS_{1-2}$ were prepared from Co or Zn phthalocyanine, respectively, dissolved in 10 % fuming sulphuric acid and subsequently heated (85^{o}C, 6 h). The reaction mixture was pured into the mixture of water and ice, filtered and washed. The filter cake was dispersed in water and pH adjusted with NaOH to the value of about 11. Metal phthalocyaninesulfonate was changed into dark blue water soluble sodium salt, which was isolated by evaporation of water by using a water bath. Preliminary tests for Al (OH) PcS_x based transistors have given promising results.

Both spin coating and vacuum evaporation are used for the film preparation. After the spin coating, the samples are sequentially stored in room temperature for 4 h., dried in vacuum (0,1 atm) for 1.5 h and dried in the same vacuum at elevated temperature (60 ^{o}C) for 4 h. Thin films of MePcs up to 10nm were evaporated in Ultra High Vacuum (UHV) conditions (P ~ 1x 10^{-9} mbar) from an effusion cell kept at ~ 420°C.

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. Representative results are shown in *figures II.3.2* and *II.3.3*.

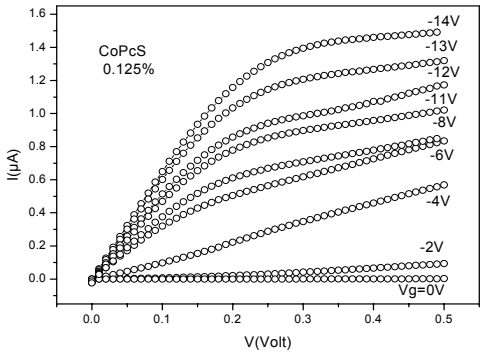

Fig. II.3.2: *Characteristics of a sulfonated cobalt Pc p-type transistor prepared by spin coating. The gate oxide is 82nm and the gate length L=10μm. The mobility resulting from conventional analysis is 0.005 $cm^2/V.s$*

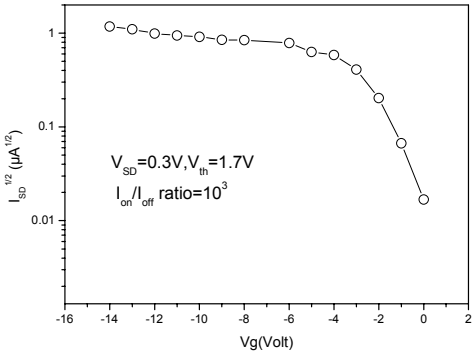

Fig. II.3.3: *Square root of source-drain current vs gate voltage at the onset of saturation. The current on/off ratio is ~10^3 and the threshold voltage is 1.7Volts.*

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. The band energy diagram of the interface was obtained, from which the hole and electron injection barriers were determined.

c) Electronic transport in the atomic limit.

N. Papanikolaou

Manufacturing electronic devices using molecules and individual atoms is probably the ultimate limit of integration. Despite the fact that molecular electronic devices have been demonstrated over the last few years, many questions remain towards the realization of molecular electronic circuits. In the atomic limit, the usual laws of electronics like Ohms law are no longer valid. Instead, electronic transport is ballistic and coherent electron waves obey the laws of quantum mechanics. We study theoretically the electronic transport through single-atom contacts connected to two leads using ab-initio electronic structure calculations, without any adjustable parameters. The local density approximation to the density functional theory is used to map the many interacting electron problem to a single electron approximation. Ballistic transport is described within the Landauer approach. We are interested in the influence of the leads to the transport properties, as well as the effect of geometrical structure of the nanocontact and study electronic transport through different atoms.

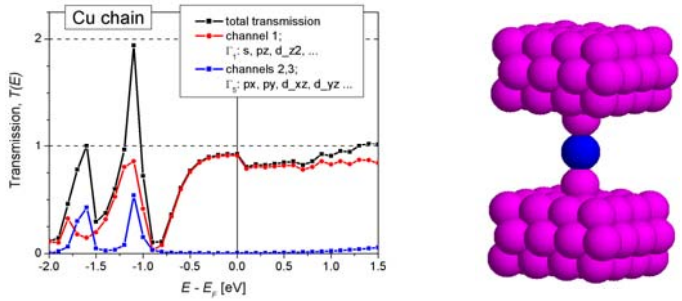

Fig. II.3.4: *Calculated transmission coefficient though a Cu nanojunction. The atomic geometry of the constriction is shown on the right.*

PUBLICATIONS in INTERNATIONAL JOURNALS

1. "Tunneling and negative resistance effects for composite materials containing polyoxometalate molecules", G. Chaidogiannos, D. Velessiotis, P. Argitis, P. Koutsolelos, C. D. Diakoumakos, D. Tsamakis and N. Glezos, *Microel. Eng.* 73-74, 746 (2004)
2. "Magnetoresistance of atomic-sized contacts: An ab initio study", A. Bagrets, N. Papanikolaou and I. Mertig, *Phys. Rev.* B 70 064410, (2004)

3. “Korringa-Kohn-Rostoker Green-function formalism for ballistic transport”, P. Mavropoulos, N. Papanikolaou and Ph. Dederichs*, Phys. Rev. B* 69 125104 (2004)
4. “Spin-dependent transport in ferromagnet/semiconductor/ferromagnet junctions: a fully relativistic approach”, V. Popescu, H. Eberrt, N. Papanikolaou, R. Zeller and Ph. Dederichs, *J. Phys: Condens. Mat.* 16 (48) p. S5579-S5586 (2004)

PUBLICATIONS in CONFERENCE PROCEEDINGS

1. “Poly [(ethylenedioxy) thiophene] conductive films”, M. Biler, L. T. D. Dvorakova, S. Nespurek and N. Glezos, World Polymer Conference, 40th Symposium on Macromolecules, Paris 2004
2. “Quantum effects in molecular nanodevices based on tungsten polyoxometalates”, D. Velessiotis, G. Chaidogiannos, N. Glezos and P. Argitis, *European Microelectronics and Packaging Symposium, Prague* 2004

PARTICIPATION in CONFERENCES

1. “Compound polymeric materials in molecular nanodevices: Electrical behavior of zero-dimension semiconducting inorganic molecules embedded in a polymer substrate”, D Velessiotis, V Ioannou-Sougleridis, G Chaidogiannos and N. Glezos, MMN Conference, Athens 2004

DIPLOMA THESIS

“Electronic structure properties of Si nanosructures”, P. Xidi, Completed in September 2004, presented at the University of Athens, Physics Department.