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.

MAIN RESULTS IN 2011

The main results obtained in 2011 within the different tasks of the project are given below.

1. Study of conduction mechanisms in molecular junctions made of tungsten-polyoxometalate self-assembled monolayers and bilayers

D. Velessiotis, A.M. Douvas, P. Dimitrakis, P. Argitis, N. Glezos

Polyoxometalates are inorganic salts or acids in which the anion is a complex oxide of transition metals. The anion is organized in a well-defined, closed-pack form, with a certain number of metal-oxygen polyedra surrounding one or more heteroatoms. They are highly reactive -yet stable- substnces, thus having a plethora of diverse applications. Due to this wealthy chemistry and photochemistry as well as their well-defined dimensions and their ability for electron storage and transfer without structural alteration, polyoxometalates have recently attracted attention as candidates for use in molecular electronic and photoelectronic applications.

In continuing our investigation concerning the electrical properties of 12-phosphotungstic acid (POM) self-assembled materials, a more thorough study of the molecular junctions based on POM monolayer or bilayer that started in 2010 was held during this year. Thus, by using the same configuration of Au electrodes and focusing in the parallel fingers junctions with 2μm overlap, we studied the influence of the number of POM layers and more importantly of the measurement temperature on the obtained current-voltage characteristics (IVs) in order to reveal the conduction mechanisms related to the POM materials.

POM anions can be considered as a group of regularly arranged semiconducting islands which -in the device under investigation- were placed between two electrodes. Under bias, charge can be stored in any of these anions and then move to the next one, consequently 'bridging' the gap between the electrodes. Obviously, the more anions between the electrodes, the more favorable is the situation about the junctions conductivity, thus junctions made by a bilayer material presented higher values of current under the same bias compared to monolayer-built junctions.

A number of different conduction mechanisms were tested by studying the temperature dependence of the obtained IVs in the monolayer junctions; namely, space charge limited current (SCLC), thermionic conduction, hopping and tunneling. For low bias, current was independent on temperature, so tunneling was the prevailing conduction mechanism. Taking into

account the junctions' dimensions (minimum distance 50nm), an indirect tunneling mechanism should be considered. The same mechanism applied also for high voltages and low temperatures (lower than 150K). A quantitative analysis of the tunneling regime was made using the Fowler-Nordheim (FN) representation ($\ln(I/V^2)=f(1/V)$) of the obtained IVs. Linear fitting in the FN regime (Fig 1) using the geometrical dimensions of the junction provided the tunneling barrier height φ. It was found that tunneling barrier was slightly decreasing with the rise of temperature, due to the variation of available electronic states in the metal electrodes (Fig 2) in agreement to a theoretical prediction made by Simmons. The intercepts (φ @ T=0K) of the fitting lines in Fig 2 were found to be approximately 0.5eV, which coincide with the Au Fermi level – POM LUMO energy difference, and independent on the electrodes distance. For temperatures higher than 150K, hopping arises as conduction mechanism and actually dominates when T≥200K as implied by the change in slope of the Arrhenius plots of Fig 3. Activation energies were found to be 82±1meV for the 50nm-distant junctions and 76.3±0.7meV for the 75nm distance. The lower value of activation energy obtained in the case of 100nm distance (43±2meV) was attributed to long range structural defects of the POM monolayer.

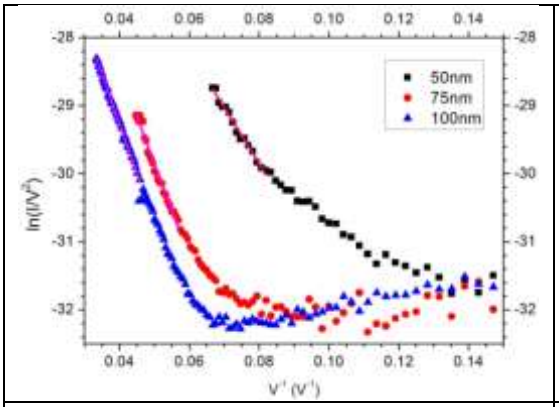

Fig. 1. *FN representation of the IVs in the case of 50, 75 and 100nm distance junctions and 120K measurement temperature. The solid magenta lines are fitting according to Simmons model for FN tunneling.*

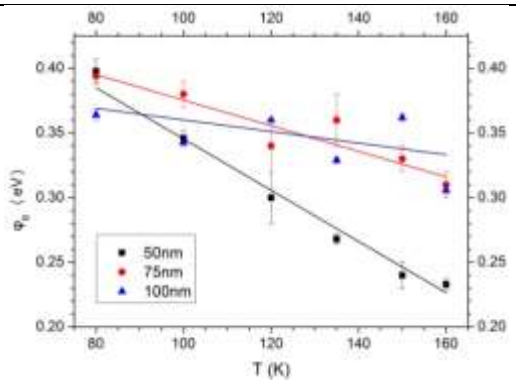

Fig. 2. *Obtained tunneling barriers for the POM monolayer junctions as a function of temperature.*

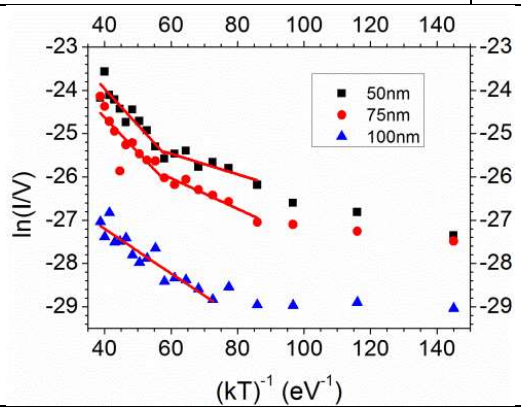

Fig. 3. *Arrhenius plots of conductance in the case of 50, 75 and 100nm distance junctions and 3MV/cm applied field.*

2. Study of the charging properties of molecular polyoxometalate capacitors

A. Balliou, A. Douvas, D. Velessiotis, V. Ioannou, P. Normand, P. Argitis, N. Glezos

The combination of molecular systems with semiconductors opens the road to hybrid systems with a potential for new applications such as sensors, switches, memories, or quantum devices based on discrete molecular levels. In this work we investigate the possibility of using inorganic tungsten polyoxometalate (POM) molecules as the charge trapping medium in future hybrid molecular/silicon memory devices. Capacitor devices containing molecular layers of a Keggin-structured polyoxometalate (POM: 12-tungstophosphoric acid) as trapping material and Isopentylamine (IPA: $C_5H_{13}N$) as cap dielectric on 3-aminopropyl triethoxysilane (APTES)-modified silicon surface, were fabricated via the layer-by-layer (LBL) self-assembly method (Fig.

1). Our intention is to isolate the molecular layer by means of two insulating layers, i.e the SiO_2 layer from below and the IPA on top, thus allowing charge retention within the molecular layer.

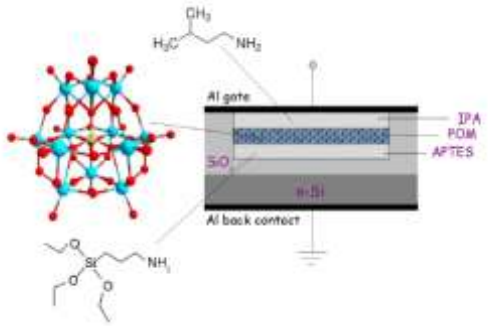

Fig. 1. *Planar MIS and incorporated functional layers.*

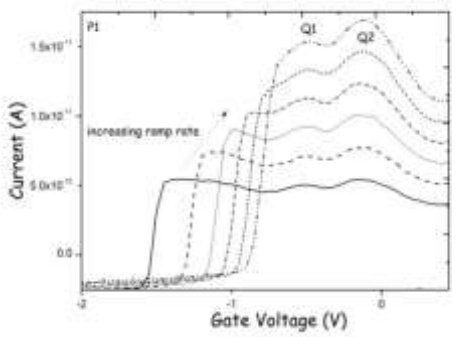

Fig. 2. *Ramp rate current-voltage characteristics at 140 K under gate injection. The emerging transient peaks (Q1, Q2) are manifestations of dynamic carrier exchange between the gate and the POM molecules.*

The fabrication process parameters as well as the effect of the precursor solution composition were monitored by means of UV reflection spectroscopy, Fourier-transform IR spectroscopy (FTIR) multi wavelength variable angle ellipsometry, AFM and SEM. The technique resulted in an average density of $5*10^{12}$ cm^{-2} active trap centers. The conduction and charging mechanisms in the composite MIS structures were elucidated by electrical characterization both of quasi-static, dynamic and transient type in a wide range of temperatures ([80->300] K) and the appropriate theoretical analysis. The special features rising in J-V characteristics yielded to the extraction of electrical parameters as well as to identification of the electronic structure of the functional molecules. More specifically, we determined the tunneling capacitance (C_t=$4.59*10^{-11}$ F) associated with the transfer process to the available POM states via determination of the displacement current under gate injection and assumption of linear dielectric medium. The two transient peaks (Q1 and Q2) observed in the experimental current versus voltage ramp rate curve (Fig. 2) are manifestations of POM molecular states and are attributed to the filling of the ground and first excited quantum states of POM molecules respectively.

The effective carrier confinement in the states of POM nanostructures and the relatively large separation of their molecular levels, allows for single-electron effects to be observed even at RT.

Transient capacitance measurements supply additional information, via a modified Zerbst equation, for the effective generation lifetimes in the molecular structures and the rate of change in the space charge region generated charge.

The mechanisms encountered are in reasonable correlation with the structural characteristics of the film. These are accompanied by hopping, coherent and incoherent tunneling in the low field regime. Each barrier dominates the current in a different bias and/or temperature regime. Moreover, the device exhibits discrete resistive states under gate injection possibly due to strong correlation effects originating from POM charging in that field region, indicating the potential of the POM molecules as sensitive resistive switches or memory elements.

PROJECT OUTPUT IN 2011

Publications in International Journals

1. "Molecular junctions made of tungsten-polyoxometalate self-assembled monolayers: Towards polyoxometalate-based molecular electronics devices", D.Velessiotis, A. M. Douvas, S. Athanasiou, B. Nilsson, G. Petersson, U. Södervall,G.Alestig,G., P. Argitis, N. Glezos, Microelectronic Engineering 88 (8) , pp. 2775-2777 (2011)

Conference Presentations

1. "Conduction mechanisms in tungsten-polyoxometalate self-assembled molecular junctions", D. Velessiotis, A. M. Douvas, P. Dimitrakis, P. Argitis, N. Glezos, MNE Conference, September, Berlin