Compound polymeric materials in molecular nanodevices:
Electrical behavior of zero-dimension semiconducting
inorganic molecules embedded in a polymer substrate

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Abstract. Several molecular materials are currently being investigated as candidates for
nanoelectronic devices with the hope to reduce critical device dimensions to the molecular
scale. Possible applications include switching circuits and multilevel memories based on the
excitation states of molecules. In this work, we present data about the electrical behavior of
two compound materials made by non-conductive poly (methyl methacrylate) (PMMA) or a
methacrylate copolymer (PHECIMA) and a certain tungsten polyoxometalate molecule
(PW12O40 – POM), which can be considered as a zero-dimension semiconductor. Certain
parameters are examined as variables of the experiments, such as the POM concentration,
the material of the electrodes (Al or Au), the inter-electrode separation or the conditions of the
preparation of the samples. Conductivity peaks depended on both the concentration of POM
and the inter-electrode distance are found at room temperature conditions. Using vertical
capacitor structures and thinner films, negative resistance effects are observed. These results
can be attributed to multiple tunnelling through a limited number of POM molecules and
shows that these systems are actually worth of further investigation.

1. Introduction
Molecular electronics may not be a completely new idea in the field of electronic devices [1], but it
was not until the late nineties that a lot of work was carried out in the field, mainly because of the
technological difficulties involved in tailoring such devices. The evolution of fabrication of traditional
MOS devices, which made tools needed for fabrication of molecular devices available, as well as the
future of MOS scaling (sub-10nm MOS devices in 2018) led to the consideration of non-traditional
approaches such as molecular electronics for future digital applications.

The usual approach in the field is to place one (mono-molecular electronics) or a few molecules
between two electrodes and examine the system’s electrical behaviour [2]. It is useful though to study
simpler systems, in order to determine the potential value of using a specific molecule in the more
sophisticated structures mentioned above. Such systems could be consisted of a compound polymeric
material -made by an inactive polymeric matrix containing the molecule concerned- between two
metallic electrodes. The latter approach was followed in this work. Planar Al or Au electrodes were
fabricated using a lift-off process, while vertical Al electrode structures were fabricated by sputtering
through a projection mask. The compound polymeric matrix was either PMMA or PHECIMA, and the
molecule studied was the well known, Keggin structured, phosphor-tungsten acid (H3PW12O40-POM)

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The material was applied to the electrodes by spinning and very good films of PMMA/POM or PHECIMA/POM were obtained [4].

2. Discussion
A complete study of the system mentioned above should take into account a lot of different parameters. There are three different types of parameters involved in our study, concerning:

- The POM itself (i.e. POM concentration).
- The electrodes (i.e. material of the electrodes and inter-electrode distance).
- The environment of measurements and sample preparation (i.e. baking of the film after spinning (PAB) and temperature in which the electrical measurements are performed).

2.1. POM concerning parameters
As seen in figure 1, a rise in POM concentration results in a rise of the measured current. This is expected, since larger POM concentration means larger number of molecules present in the film, which result in both smaller distances between the molecules and larger number of available paths between the electrodes.

![Figure 1. I-V measurements for different concentrations of POM relative to PMMA on Au electrodes. The 1 to 1 sample characteristic is suppressed as the sample produced currents on the 30pA range](image)

2.2. Electrode concerning parameters
2.2.1. Inter-electrode distance. The inter-electrode distance is a crucial parameter for our study. There are two distinct types of behavior depending on the scale of this distance for the horizontal structures described above:

- For sub-100nm distances the I-V characteristic can be separated into three regions [4]: In the small voltage region, the sample presents a behavior described by Simmons [5,6], then a Fowler-Nordheim tunneling region appears and in the large voltage region the sample follows either a Space Charge Limited (SCL) current flow law or even Ohm’s law.
- For larger distances the first two regions are suppressed and only the SCL law appears in the I-V (see figure 2).
It must be noted here, that the same behavior is found in sample made by PHECIMA and POM, as shown elsewhere [4]. Vertical structures with inter-electrode distances of about 10nm were also fabricated. In these devices quantum behavior was even more prominent and negative resistance phenomena were observed [4].

Figure 2. Electrode distance dependence of I-V characteristic for a 1 to 5 PMMA to POM concentration sample spinned on Al electrodes (Semi-log graph). The plateaus in the small voltage region (shown with the arrows), that are present for 50 and 100nm electrode distance, but not for the 1µm distance, indicate quantum behavior.

2.2.2. Electrode material. The electrode material affects mainly in a quantitative way the I-V characteristics. Samples prepared on Au electrodes produced far more current than similar samples on Al electrodes [4]. This could be directly attributed to the presence of the natural aluminum oxide on Al electrodes as well as band alignment between electrodes and molecular levels. However, band alignment is not vital for the structures we study here.

More specifically, it is known that Al Fermi level is approximately 0.5eV above Lowest Unoccupied Molecular Orbit (LUMO) of POM, while Fermi level of Au is 0.4eV below LUMO [7]. In the symmetrical Metal-Insulator-Metal device, that we study here, though, the effect should be similar due to symmetry.

2.3. Environmental and sample preparation parameters
2.3.1. Post Apply Bake (PAB) conditions. Usual lithographic conditions for PMMA include a PAB in 160°C for 1h. Measurements shown till now were performed on specimens baked at 120°C for 2min. A comparison on otherwise similar samples was carried out showing that more aggressive PAB conditions result in lower currents (see figure 3).

2.3.2. Measurement temperature effects. I-V measurements were carried out in temperatures for both below or above room temperature. In the case of low temperatures a dramatic reduction of current flow was observed. However, it was possible to deduce a value of conductance for the Ohmic region of the I-V for the 1 to 5 PMMA to POM case. An Arrhenius law was followed with activation energy $E_0=(0.12±0.01)eV$.

For temperatures higher than room temperature a gradual moderate reduction of current was observed, as the temperature was raised. However, subsequent reduction of the temperature to its previous value or even room temperature didn’t mean that current value was also return to the former
values indicating that apart from the direct temperature effect on the I-V, an accelerated film aging is induced.

![I-V dependence on the PAB conditions](image)

**Figure 3.** I-V dependence on the PAB conditions

3. **Conclusions**
Taking into account the transport characteristics presented in this work, we support the idea of using POM in purely molecular systems in addition to further investigation POM based compound polymeric materials. However, in doing the latter, a more strict environmental control is desirable in order to avoid aging phenomena that appeared in the devices mentioned.

We have to emphasize the fact that Au electrodes are preferable than the Al ones, because of the absence of a natural oxide (such as Al₂O₃) enclosing the electrodes. The qualitative characteristics of the measurements do not depend on the electrode material though, but only on the compound polymeric material that lies between the electrodes.

Yet, PMMA lithographic conditions (especially PAB) proved to be extreme and were altered in order to achieve better transport quality for the compound material.

4. **References**
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