

# STUDY OF HYBRID PORPHYRIN-BASED MONOLAYER / SILICON MEMORY DEVICES

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## Abstract

It is well recognized that in next decades, the device scaling process in traditional semiconductor technology will reach its limits. The latest conceived devices are already developed with a significant change in the basic structure. In Non-volatile memories, Single Electron Memory (SEM), like Nano-crystal memories, reduce the dimension of the device to few tenths of nanometers [1]. More recently, molecular electronics appear as a promising solution. They could offer significant advances in miniaturisation but also imply lower fabrication cost, thanks to a bottom-up manufacturing process.

In this context, our project aims to exploit molecules as charge storage media for a SEM based on a hybrid Molecule/Silicon structure. The charge storage effect can be obtained with a redox active molecule. We have chosen to use porphyrins such as H<sub>2</sub>TEPP, H<sub>2</sub>TAOPP and H<sub>2</sub>AB<sub>3</sub>P and their metal complexes (Fig. 1), which have several available redox states, either on the macrocycle or on the central metal, providing effective charge storage at the molecular level. These molecules are anchored as a monolayer on a silicon surface using combined hydrosilylation-cycloaddition reactions [2][3].

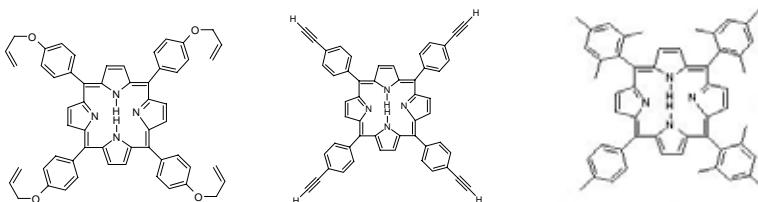
This work presents the electrical characterisation of different electronic devices. The objectives are 1- to control the redox behaviour of the various porphyrin monolayers by tuning the gate voltage, and 2- to test the charging effect of porphyrins on the device.

Furthermore, the same electrical characterization, on identical devices without porphyrin, allows us to make some comparisons.

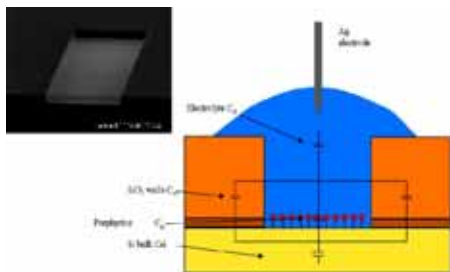
Firstly, we will present results obtained on electrochemical cells, similar works being already presented in the literature [4]. The cells, developed in our laboratory, correspond to wells

with a Si (100) base modified with a monolayer of molecules (base surfaces varying from 1 mm<sup>2</sup> to 576 μm<sup>2</sup>). The walls are made of 10.5μm-thick SiO<sub>2</sub> (Fig. 2) The well is then filled with electrolyte solution and C-V characterization is made.

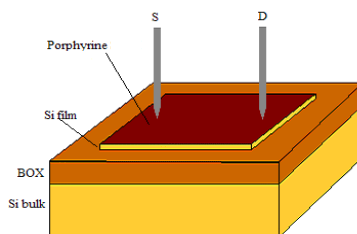
Tests on pseudo-MOS devices will also be presented (Fig. 3), where a monolayer of porphyrins lays on the Si film (thickness varying from 30 to 100 nm). The voltage is applied to the Si bulk while the current is measured by two tips, pressed on the top surface of the Si film, and between which a voltage difference is applied. This is an important device since it operates without an electrochemical process, hence it shows that interactions between porphyrins and a silicon device are possible and even controllable.



**Figure 1.** From left to right: free-base TAOPP, free-base TEPP, free-base AB<sub>3</sub>P. The central H atoms can be replaced with a metal such as Mn, Fe, Co or Zn.



**Figure 2:** Scheme of the electrochemical capacitor with porphyrin SAM. On the left corner: SEM image of a cell (300μm x 150μm).



**Figure 3:** Scheme of a pseudo-MOS device.

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 [3] G. Delapierre, Huang Kai, French Patent submitted N° 05 10987.  
 [4] Qiliang Li et al., Advanced Materials, Vol. 16, No. 2, p. 133, 2004.