

# Electrical Characteristics of Metal-insulator-semiconductor Diodes and Transistors with Space Charge Electret Insulators: Towards Nonvolatile Organic Memories

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## ABSTRACT

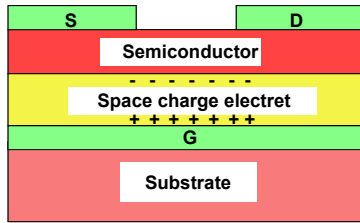
Organic field-effect transistors (OFETs) consist of a gate dielectric and an organic semiconductor film. The performance of organic electronic devices substantially depends on the dielectric properties of the insulating gate layer. Only a few key parameters, primarily the dielectric constant and the resulting device capacitance, have been regarded to be of central importance. Many insulating layers are however not simple dielectrics, an example are space charge gate electrets with internally trapped charges. Space charge gate electrets affect the electrical characteristics of diodes and transistors in a much more sophisticated manner, they are for example the key element in flash memories. We present impedance measurements of an organic metal-insulator-semiconductor (MIS) diode and corresponding measurements of a related organic field effect transistor. Both devices have a comparable design, with polyvinylalcohol as gate electret and the methanofullerene PCBM as organic semiconductor. Pronounced electret effects of charge injection and trapping are observed by impedance measurements of the MIS structure and these effects are found equally expressed in the electrical characteristics of the OFET configuration, reflecting first steps towards organic flash memories.

Index Terms — OFET, electret, space charges, gate dielectrics, organic semiconductors, hysteresis.

## 1 INTRODUCTION

SINCE the beginning of modern electret research, approximately 50 years ago [1], major discoveries have been reported in every decade since then [2], such as the observation of the excellent charge stability of polytetrafluoroethylene and its copolymers, the proof of strong piezo-, pyro- and ferroelectricity in polyvinylidene fluoride, the introduction of amorphous dipole polymer electrets with large nonlinear optical effects, of photorefractive polymers, a combination of dipole and space charge electrets and of internally charged cellular polymers, with strong piezoelectric responses. Most recently, the application range of electrets extended further, by combining them with organic semiconductors in functional organic field effect transistors [3-10].

Organic semiconductors are under scrutiny for more than twenty years and the following research on organic diodes and organic field effect transistors (OFETs) initiated world wide efforts in academia and industry thereby defining a new field of research [11]. Organic field effect transistors do not work without a properly chosen dielectric. To our surprise, the crucial role of the dielectric and the dielectric/semiconductor-interface between the active organic semiconductor device and the gate dielectric has not yet been fully explored. Trapped space charges, as well as molecular dipoles have a strong impact on device performance as has already been pointed out in 2002 [3]. Since then the important role of gate dielectrics became more and more obvious [4-10]. It seems that the use of electrets as gate dielectrics in “**electret-field effect-transistors**” (EFET’s) is ideal for the production of functional OFET’s, like non-volatile memories and various kinds of transducers. A schematic sketch of a space-charge EFET is shown in Figure 1.



**Figure 1.** Schematic sketch of a space-charge electret field effect transistor. The external field of the charged electret alters the conductance of the semiconductor channel between the source and the drain electrode, enabling applications in nonvolatile memories and sensors. In an organic flash memory cell, an additional floating gate electrode is employed within the charge electret, in order to define the spatial position of the trapped charges.

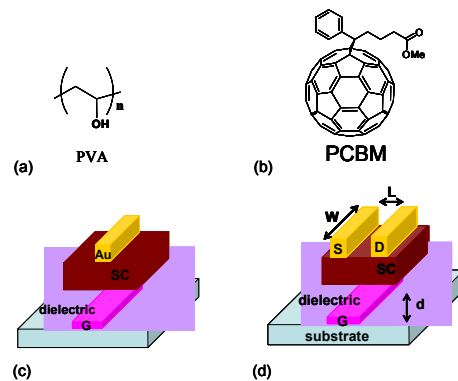
Here we show results obtained on a polymeric metal-insulator-semiconductor diode (MIS) and a corresponding OFET, based on the gate electret polyvinylalcohol and the organic methanofullerene semiconductor PCBM. Impedance measurements on the MIS structure in the small signal regime, performed by employing a dc-bias voltage together with a small ac-voltage revealed a large metastable hysteresis in the capacitance when the dc voltage is cycled from negative to positive values and vice versa. The hysteresis is assumed to be caused either by the storage of charges within the bulk of the gate dielectric and/or at the interface between the insulating gate electret and the organic semiconductor. The closely related OFET revealed a similar hysteresis in the source-drain current versus gate voltage, which suggests usage in nonvolatile memories. Our work is also a preliminary step towards organic flash memories, where charges are trapped in an additional floating gate electrode within the gate electret [12].

## 2 MIS AND CORRESPONDING OFET STRUCTURE

Figure 2 shows the chemical formulas of the polyvinylalcohol gate dielectric and the methanofullerene organic semiconductor employed in the MIS and corresponding OFET structure.

As also revealed in Figure 2, both the MIS and OFET structure consist of a dielectric layer and an organic semiconductor in close contact to the dielectric. Whereas the MIS structure is a two terminal device with only two electrodes on the dielectric and on the semiconductor, the OFET is a three terminal structure with the so called gate electrode on the dielectric layer and two source and drain electrodes on the semiconductor. Both structures were prepared on an indium tin oxide (ITO) coated glass substrate by spin-coating. The poly(vinylalcohol) (PVA) gate electret is sandwiched between the ITO electrode and the semiconductive methanofullerene [6,6]-phenyl C<sub>61</sub>-butyric acid methyl ester (PCBM). The ITO gate electrode of the MIS and OFETs is etched with a diluted HCl solution. After cleaning the substrates in an ultrasonic bath, PVA is spin coated onto the cleaned substrate. PVA with a molecular

weight of 100,000 was used as received from Fluka Chemicals. The PVA employed was dissolved in distilled water and filtered using 0.2  $\mu\text{m}$  filters and lyophilized and re-dissolved again in distilled water. With a 10 % wt. ratio of a highly viscous PVA solution a film thickness of 0.6 to 1.5  $\mu\text{m}$  is achieved by spin coating at 1500 rpm. A 150 nm thick PCBM semiconductor layer is spin coated on top of the PVA film from a chlorobenzene solution (3% wt.) in argon atmosphere inside a glove box. Cr top electrodes are evaporated under vacuum ( $3 \times 10^{-6}$  mbar) on the MIS structure. By using a shadow mask, source and drain contacts are evaporated under the same conditions on the MIS layer structure to form the OFET.



**Figure 2.** Chemical structure of (a) polyvinyl alcohol (PVA) (b) methanofullerene [6, 6]-phenyl C<sub>61</sub>-butyric acid methyl ester (PCBM). (c) Metal-Insulator-Semiconductor (MIS) and (d) corresponding staggered mode nonvolatile memory organic electret field effect transistor (EFET).

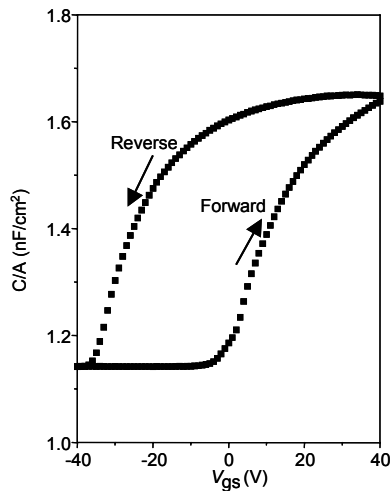
The electrical characterisation of the MIS and OFETs is carried out under an inert argon environment inside a glove box. Impedance measurements on the MIS systems were recorded with a HP 4284A LCR meter. For the steady state current-voltage measurements of the transistors Keithley 236 and Keithley 2400 instruments were used. The surface morphology and the thickness of the PVA and PCBM films has been determined with a Digital Instrument 3100 atomic force microscope (AFM) and a Dektak surface profilometer. The channel length  $L$  of the OFET is 65  $\mu\text{m}$  and the channel width is  $W = 1.4$  mm. The  $W/L$  ratio of  $\approx 0.02$  is an acceptable value for the OFET which does not cause screening of the gate field by the source drain contacts. For the PVA gate dielectric a dielectric constant of  $\epsilon_{pva} = 5$  was measured.

## 3 ELECTRICAL CHARACTERIZATION

### 3.1 Impedance measurements of the MIS structure

The impedance of the MIS-structure is measured with a small test signal of 50 mV at a frequency of 112 Hz superimposed on a dc bias voltage, which is cycled between  $\pm 40$  volts at a linear rate of approximately 0.2 V/s. The data are represented in terms of an equivalent capacitance model, where the respective values of the measured capacity are shown in Figure 3. At -40 V the MIS device is entirely depleted and the capacitance reflects the geometric

capacitance of a double layered dielectric system. During the course of measurement with increasing bias voltage up to a level of approximately -7 V the capacitance of the system is practically constant. By further increasing the bias voltage level, the capacitance starts to increase progressively up to a forward voltage of about 5 V since the semiconducting PCBM layer acts as a field dependent resistor, becoming more and more conductive. At higher forward voltages beginning saturation is observed. However, even at +40 V full saturation is not reached. In the reverse bias voltage sweep, with a descending bias voltage the capacitance of the MIS system drops at a much smaller rate in comparison to the previous run with an increasing bias voltage.



**Figure 3.** Capacitance-per-unit-area voltage scan for forward and reverse bias cycles, showing a pronounced hysteresis in the capacity of the MIS structure shown in Figure 2 left. The capacitance was obtained at a measurement frequency of 112 Hz.

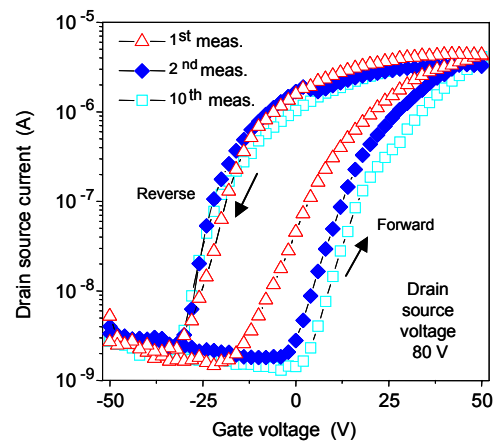
The evolving significant hysteresis in the capacitance is explained by assuming injection of static charges into the PVA gate electret. Charge trapping and charge based hysteresis effects in PVA capacitors were already reported in [13]. Thus, PVA significantly influences the internal electric field across the active semiconductor. It is immediately evident that the drastic hysteresis in the capacitance of the MIS structure should also be reflected in the corresponding OFET. Therefore it seems ideal to perform a first quick characterization of a new material combination in a MIS structure, since capacitance measurements can be easily performed. In a second step, when the results from the impedance measurements look promising, it is worth to also investigate the main characteristics of the corresponding OFET structure.

### 3.2 Output characteristics of the OFET structure

Figure 4 demonstrates that the hysteresis reflected in the capacitance of the MIS structure, as depicted in Figure 3 is also prominent in the output characteristics of the corresponding OFET. The hysteresis obtained by employing a space charge electret appears to be quite similar to hysteresis loops obtained on other EFET's with ferroelectric-like and ferroelectric polymer electrets. In Figure 4 the drain-source current  $I_{ds}$  of the three terminal OFET is shown versus the

gate-source voltage  $V_{gs}$  at a constant drain-source voltage of  $V_{ds}=80$  V, where the gate-source voltage is cycled at the same rate of 0.2 V/s as in the capacitance measurements shown in Fig. 2. The same cycling rate is chosen to have comparable time scales for the hysteresis in both measurements. As reported earlier, the electron mobility  $\mu$  in PCBM is around  $0.1 \text{ cm}^2/\text{Vs}$ , quite high in comparison to other PCBM based devices. The improved mobility here is ascribed to result from a smooth and homogeneous film formation on top of the PVA electret.

The magnitude of the source-drain current  $I_{ds}$  increases with an amplification of up to  $10^4$  at a gate voltage of  $V_g \approx 50$  V with respect to the initial "off" state with  $V_g = 0$  V. The saturated drain source currents  $I_{ds}$  remain at high values even when  $V_g$  is reduced back to  $V_g = 0$  V (hysteresis). In order to completely deplete  $I_{ds}$  one needs to apply a reverse voltage of  $V_g \approx -30$  V. A large shift in the threshold voltage  $V_t$  by 14 V is observed when measured the second time in comparison to the initial cycle. After that, there is practically no more shift in  $V_t$ . The 10<sup>th</sup> cycle showed no significant shift in  $V_t$  in comparison to the 2<sup>nd</sup> cycle. Each measurement has been performed with a long integration time of 1 s.

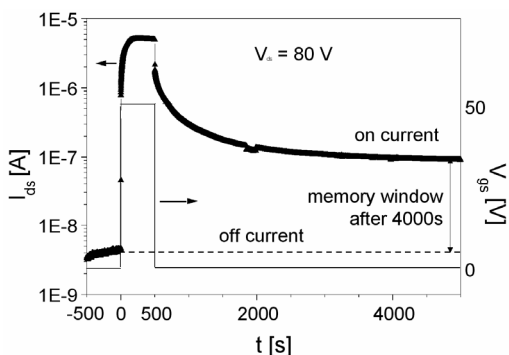


**Figure 4.** Output characteristics of the corresponding OFET shown in Figure 2 right, demonstrating the memory (hysteresis) in the drain-source current versus gate voltage for a fixed drain source voltage of 80 V. The similarity between the results obtained on the MIS and OFET structure is remarkable.

It is evident from Figure 4 that the device acts as a nonvolatile memory element. As in the capacitance measurements, the results cannot be explained by dipole polarization of the electret, since no metastable or frozen polarization is observed. Similar to the impedance measurement results, trapping of injected charges or of mobile ionic charges present in PVA is proposed to explain the hysteresis effect in the device characteristics. Measurements of the temperature dependent transfer characteristics  $I_{ds}(V_g)$  are also in favor of a charge trapping mechanism [6].

To estimate the retention time of the stored charges remaining in the electret (*i.e.* storage time of the memory element), a time resolved measurement was performed, as revealed in Figure 5. The device was biased with  $V_{ds}=80$  V and then kept at a floating gate of 0 V. At time  $t = 0$  s, a gate voltage of  $V_g = 50$  V is applied until a stable current is obtained. After a time of  $t = 500$  s the device is at a gate

voltage of 0 V.  $I_{ds}$  remains high (memory “on” state) for more than 15 hours. This implies that once the electret is charged fully, the relaxation of the charges is a slow process as expected for charged electrets.<sup>23</sup>



**Figure 5.** Drain-source current  $I_{ds}$  vs. time ( $t$ ) at a constant  $V_{ds}=80$  V for floating gate (denoted by  $V_g=0$  V), during a gate voltage of  $V_g=50$  V (write) and 0 V showing the decrease in the on-current. The data were taken each 250 ms and every 2 data point is plotted. After more than 4000s of operation, a memory window (ratio between on and off current) of more than 1 order of magnitude is still observed.

Our studies reflect first steps towards organic flash memory elements. Flash memories are based on space charge electrets, where the spatial location of trapped charges is defined by introducing a second floating gate electrode into the charge electret material. Given the enormous applications of inorganic flash memories today, for instance in USB sticks, portable MP3 players etc., there is huge prospect for the development of the organic flash counterpart.

## 4 DISCUSSION AND CONCLUSION

In conclusion we have shown that the electret field effect transistor is potentially interesting for applications in nonvolatile memories. In order to characterize devices, we have shown that a wealth of information can be gained from simple impedance measurements of a corresponding MIS structure. Hysteresis effects in the capacitance of the MIS device are reflected in a similar manner in the output characteristics of the OFET. Therefore it seems viable to first prepare and characterize the simpler MIS device, before a full transistor structure is developed and employed.

Further there is potential in combining electrets and organic semiconductors, or more general electrets and flexible electronics. Examples include pressure and temperature sensing based on the capacitive, piezo- or pyroelectric response of electrets. For pressure sensing, soft ferroelectrets with a strong longitudinal piezoelectric response, negligible pyro- and transverse piezoelectricity seem ideal.

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