Opto-electronic characterization of electron traps upon forming polymer oxide memory diodes

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Metal-insulator-polymer diodes where the insulator is a thin oxide (Al_2O_3) layer are electroformed by applying a high bias. The initial stage is reversible and involves trapping of electrons near the oxide/polymer interface. The rate of charge trapping is limited by electron transport through the polymer. Detrapping of charge stored can be accomplished by illuminating with light under short-circuit conditions. The amount of stored charge is determined from the optically induced discharging current transient as a function of applied voltage and oxide thickness. When the charge density exceeds $8 \times 10^{17}/m^2$, an irreversible soft breakdown transition occurs to a non-volatile memory diode. © *2011 American Institute of Physics*. [doi:10.1063/1.3628301]

Non-volatile memories are being developed for data storage applications. A promising candidate is a resistive random access memory. The memory consists of a simple metal-insulator-metal stack based upon organic or inorganic semiconductors and oxide layers or nanoparticles. Diodes comprising as insulator an oxide have to be formed by applying a high electric field corresponding to soft breakdown. After forming the memory can be programmed reversibly between a high resistance off-state and a low resistance on-state.[1–4] The memories show excellent data retention and programming cycle endurance. The electroforming mechanism however remains elusive.[5]

Here, we investigate the photophysics of electroforming in Al/Al_2O_3/polyspirofluorene/Ba/Al memories. By applying a bias voltage on pristine diodes, electron traps are populated and the release of trapped charge is investigated by photoexcitation. The traps are located at the oxide-polymer interface.[6–8] The density of traps is determined from the temporal behavior of the photocurrent as a function of the thickness of the oxide layer. The trapped electrons provide the driving electric field for electroforming of the memory.

The diode structure (inset of Fig. 1) consists of an Al bottom electrode, a sputtered layer of Al_2O_3 (20 nm), a spirofluorene polymer (80 nm), and a Ba/Al (5 nm/100 nm) top electrode that forms an Ohmic contact with the polymer. The devices with an active area of 1 and 9 mm^2 were encapsulated to exclude O_2 and H_2O. In all cases, positive bias voltage refers to the bottom Al electrode being positive with respect to the top Ba electrode. Current–voltage (*J-V*) curves were obtained using a Keithley 487 picoammeter. A blue LED ($350 \leq \lambda \leq 650$ nm and $\lambda_{max} = 440$ nm) was used as optical excitation source. The light intensity inside the diode could not be calibrated but was kept constant throughout the series of measurements.

Figure 1 illustrates the electroforming of the diode. The bias voltage was swept at a ramp rate of 0.1 V/s up to 10 V and the current density recorded with time. The *J-V* characteristic shows three distinct regions. At applied voltages below 6 V (region I), the current density has the characteristics of a displacement current, approaching an almost constant value depending on the ramp rate. The diode behaves as a capacitor.

The charging of the capacitor can be followed by applying a step voltage. The charging current (*I*) decays with time (*t*), following a power law $I(t) = 1/t^{\alpha}$. Where α is a constant parameter. The inset of Fig. 2 shows the linearity of log (*I*) *vs* log (*t*) over four decades with a slope $\alpha \sim 1.06$. An explanation of this remarkable behavior is given below.

Upon reversing the direction of the voltage sweep, the current is negligible (not shown). This implies that the charges are trapped. With impedance spectroscopy or
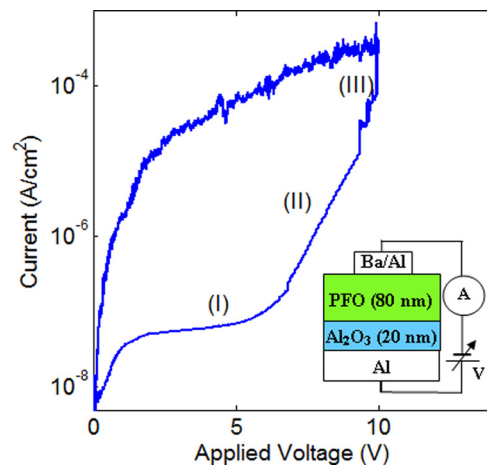

FIG. 1. (Color online) Typical current-voltage characteristics during electroforming of a Al/Al_2O_3/polyspirofluorene/Ba/Al diode. Inset shows the layout of the diode.

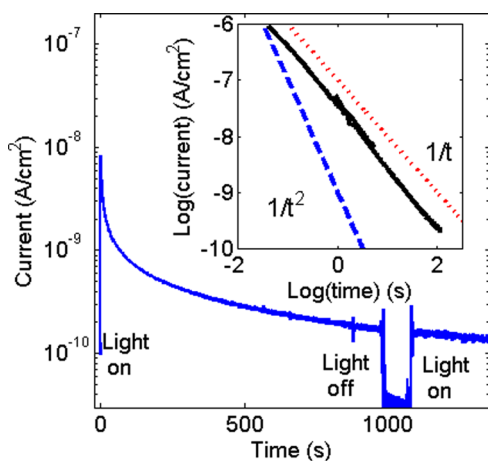a)Electronic mail: hgomes@ualg.pt.

FIG. 2. (Color online) Light-induced discharge current in a Al/Al2O3/poly-spirofluorene/Ba/Al diode as a function of time, after the application of a trap filling voltage step of 2 V. Near 1000 s, the illumination is briefly interrupted to probe the current background. The inset shows the trapping current transient after the application of a voltage step of 2 V. The current decay follows $1/t^{\alpha}$ over more than four orders of magnitude with $\alpha = 1.06$. The experimental data is shown together with the $1/t^2$ and $1/t$ behavior.

FIG. 3. (Color online) Schematic band diagram of the diode under short circuit and illumination. The neutralization of the electrons trapped at the polymer-oxide interface by photogenerated holes is schematically depicted. J_R is the recombination current.

capacitance transients, the trapping of the charges cannot be observed, hence the trap levels must be deep. This is confirmed by the fact that under short-circuit conditions, it takes days to discharge. Once emptied, identical J-V traces are measured; charging in region I is reversible.

In region (II), at bias voltages between 6 V and 10 V, the current rises exponentially with bias and is due to tunneling of electrons through the oxide. In this regime, the J-V characteristics are reversible; no hysteresis is observed.

In region III, near 10 V, the current rises steeply and becomes noisy which are both typical characteristics of soft breakdown of the oxide. This process is irreversible; the electrical characteristics have changed permanently. The formed device behaves as a non-volatile memory, as reported previously.[9,10] The resistance of the diode can now be switched between a low resistive on-state and a high resistance off-state.

The trapped charge in region I can be neutralized by photogenerated charge carriers. Under illumination, transient discharge currents are observed on the time scale of hundreds of seconds. Optical detrapping is only observed for light with photon energies higher than the polymer band gap (3.1 eV) showing that the charge carriers inducing the neutralization are generated in the polymer. Furthermore, detrapping transients are faster for higher optical power, in agreement with first order kinetics. Once the traps have been emptied optically, the filling of the traps can be repeated. Charging and optical discharging are found to be fully reversible processes.

Figure 2 shows a typical current transient upon exposure of a charged diode to light. Before the experiment, the traps in the diode were filled by applying a voltage ramp of 0.1 V/s up to 2 V. When the light is switched on, a relatively large current transient is observed that slowly decays with time. Turning off the light source momentarily near 1000 s, the current goes back to zero and recovers when turning the illumination back on. The current follows the original decay until all the traps are emptied. This confirms that the current
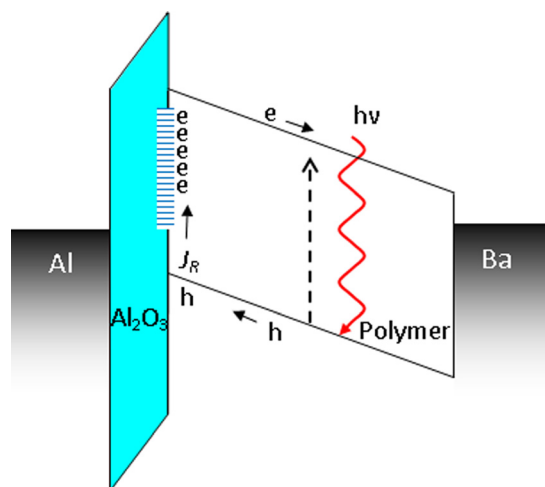
under illumination is not a simple photocurrent but originates from detrapping of electrons from impurity/defect sites with ionization energies that lie in the semiconductor band gap. This is illustrated schematically in Fig. 3.

In order to obtain information on the amount of trapped charge, a series of trap filling and emptying cycles was performed with increasing voltage from 1.5 V up to 6 V in steps of 1 V. Charging J-V sweeps are shown in Fig. 4(a), and the corresponding optical discharging transients recorded after the sweeps and under the same optical power are shown in Fig. 4(b). From the discharge transient, the density of trapped charge was calculated from the area under the optically induced current transient.

The inset in Fig. 4(b) shows the total amount of charge released upon illumination as a function of the maximum applied charging voltage in the preceding charging J-V sweep. The amount of charge released depends linearly on the applied maximum charging voltage. Extrapolation to the voltage necessary to fully electroform the device (10 V, see Fig. 1) predicts that a total amount of $8 \times 10^{17}/m^2$ charges must be stored in the device before soft-breakdown occurs and memory characteristics are induced. This density of trapped charge (ρ_t) corresponds to a critical electric field strength for electroforming ($\rho_t/\varepsilon_0\varepsilon_{ox}$) of 1.5×10^9 V/m, which is close to the field strength required for electrical breakdown of Al_2O_3 (10^9 V/m.[11,12]). Furthermore ρ_t is in agreement with previous findings using quasi-static capacitance-voltage techniques.[8] The oxide thickness was varied. The amount of stored charge when applying the same bias voltage for charging varies with oxide thickness. Yet, the amount of charge needed to reach the critical electrical field strength for electroforming remained the same.

We propose a tentative model to explain both the trapping and the light induced detrapping process. Under a positive applied voltage, electrons injected from the Ba electrode drift through the polymer and accumulate at trapping sites located at the polymer/oxide interface (see Fig. 3). The current through the diode can be expressed as
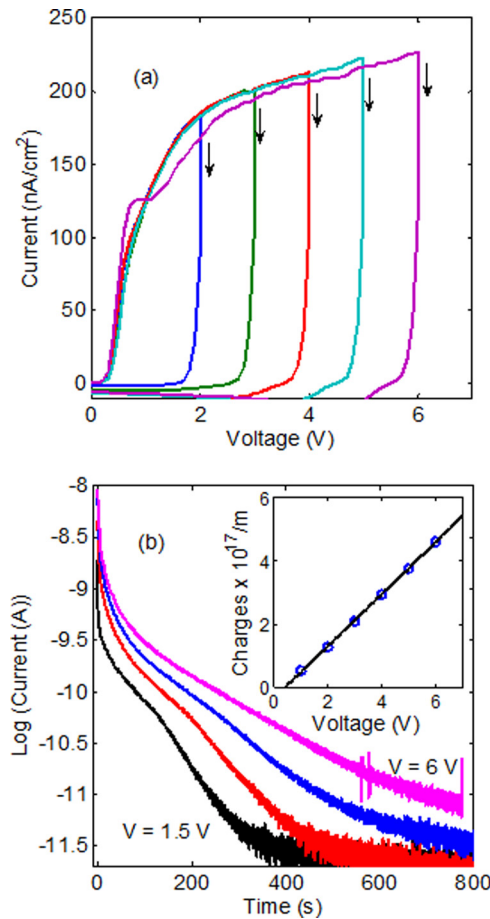
FIG. 4. (Color online) (a) Trapping *J-V* loops with increasing maximum filling voltages. After each trapping loop, optically induced discharge transients were recorded as shown in (b). The number of detrapped electrons is calculated from the area under each current transient. The inset of (b) shows the number of detrapped charges as a function of the filling voltage (1.5 V to 6 V).

$$I(t) = C\frac{dV(t)}{dt} = \frac{V(t)}{R_{pol}(V(t))}, \qquad (1)$$

where C is the capacitance associated with the oxide layer and R_{pol} is the resistance of the semiconducting polymer. Transport of electrons through π-conjugated polymers is trap limited.[13] One can phenomenologically approximate R_{pol} by

$$R_{pol}(V(t)) = \frac{r}{V(t)^n}, \qquad (2)$$

where r and n are parameters that depend on the energy distribution of the traps. For films of π-conjugated polymer, n usually falls in the range 3–7. The differential equation for $V(t)$ contained in Eq. (1), can be solved by integrating by parts, yielding the following expression for the current

$$I(t) = \frac{1}{r}\left(\frac{1}{\frac{n}{rC}t + \left(\frac{1}{V_0}\right)^n}\right)^{1+1/n} \propto t^{-(1+1/n)} \; for \; t \gg (rC/nV_0^n), \qquad (3)$$

where, V_0 is the initial voltage drop over the polymer. From the experiment, we obtain a power-law dependence of the current I on time with an exponent of 1.06. We fabricated electron-only diodes of the present poly(spirofluorene) and obtained superlinear *J-V* characteristics following Eq. (2) with exponent n around 5. This is in good agreement with the exponent $\alpha = 1.06$ from time domain measurements as described by Eq. (3).

If the electric field across the oxide is increased, hole injection from the aluminum anode into the oxide will be favored. Hole trapping in the oxide encourages further accumulation of electrons at the interface, creating a layer of increasing polarization which eventually causes soft-breakdown across the oxide. We suggest that this process is responsible for the oxide electroforming.

In summary, we have determined density and spatial location of electron traps in polymer-oxide memories employing an electro-optic method. The trapped charges establish an electric field across the oxide. When this field reaches a critical value, soft breakdown occurs, yielding an active memory diode.

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