Opto-electronic characterization of electron traps upon forming polymer

Citation for published version (APA):

DOI:
10.1063/1.3628301

Document status and date:
Published: 01/01/2011

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.

Download date: 30. Jun. 2020
Opto-electronic characterization of electron traps upon forming polymer oxide memory diodes

Qian Chen,1 Benjamin F. Bory,3 Asal Kiazadeh,1 Paulo R. F. Rocha,1 Henrique L. Gomes,1,a) Frank Verbakel,2 Dago M. De Leeuw,2 and Stefan C. J. Meskers3
1Center of Electronics Optoelectronics and Telecommunications (CEOT), Universidade do Algarve, Campus de Gambelas, Faro 8005-139, Portugal
2Philips Research Laboratories, Professor Holstlaan 4, Eindhoven 5656 AA, The Netherlands
3Molecular Materials and Nanosystems, Eindhoven University of Technology, P.O. Box 513, Eindhoven 5600 MB, The Netherlands

(Received 30 June 2011; accepted 28 July 2011; published online 23 August 2011)

Metal-insulator-polymer diodes where the insulator is a thin oxide (Al2O3) 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 \(8 \times 10^{17}/\text{m}^2\), an irreversible soft breakdown transition occurs to a non-volatile memory diode.

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/Al2O3/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 Al2O3 (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 mm2 were encapsulated to exclude O2 and H2O. 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 ≤ λ ≤ 650 nm and \(\lambda_{\text{max}} = 440\) 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 \(\alpha\) 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

![Figure 1: Typical current-voltage characteristics during electroforming of a Al/Al2O3/polyspirofluorene/Ba/Al diode. Inset shows the layout of the diode.](image-url)
mental data is shown together with the $J$-$V$ 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 ($C_e$) corresponds to a critical electric field strength for electroforming ($\rho_s e_{f_{ox}}$) of $1.5 \times 10^9$ V/m, which is close to the field strength required for electrical breakdown of Al$_2$O$_3$ ($10^9$ V/m). Furthermore, $\rho_s$ 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 electric 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

\[ J_R = \frac{1}{t} e \text{ } \text{cgs units, for any time constant } t. \]
\[ I(t) = \frac{1}{r} \left( \frac{1}{n} t + \left( \frac{1}{V_0} \right)^n \right)^{1+1/n} \approx r^{-1} \times (rC/nV_0^n)^{(1+1/n)} \]

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 \( a \approx 1.06 \) 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.

We gratefully acknowledge Ton van den Biggelaar from Philips and Martijn Kuik from the University of Groningen for preparing the devices. This work was financially supported by the Dutch Polymer Institute (DPI), Project No. 704, Fundação para Ciência e Tecnologia (FCT) through the research Unit, and Center of Electronics Optoelectronics and Telecommunications (CEOT).