Short Communication

Theoretical and experimental investigation into environment dependence and electric properties for volatile memory based on methyl-red dye thin film

Marcos A.L. Reis a,*, Tamires C.S. Ribeiro b, Carlos E. Cava c, Lucimara S. Roman c, Jordan Del Nero b

a Pós-graduação em Eng. Elétrica, Universidade Federal do Pará – UFPA, 66075-900 Belém-PA, Brazil
b Departamento de Física, Universidade Federal do Pará – UFPA, 66075-110 Belém-PA, Brazil
c Departamento de Física, Universidade Federal do Paraná – UFRP, 81531-990 Curitiba-PR, Brazil

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Abstract

The environment dependence and electric properties of Ni/methyl-red/Ni organic device were both theoretically and experimentally investigated at room temperature. This volatile memory consists of methyl-red layer (~200 nm) with a planar geometry. The results demonstrated that (a) applying low-voltage pulses increases conductivity from $10^{-8}$ cm$^{-1}$ (OFF) to $10^{-5}$ cm$^{-1}$ (ON); (b) measurements of current–voltage show a peak-to-valley ratio of 8:1 [10:1] under positive [negative] bias; (c) the electric feature of this dye memory is due the Schottky barrier in the metal/methyl-red interface with negative differential resistance effect. These semiconductor characteristics indicate that this azo aromatic compound is promising for applications in volatile memory arrays.

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1. Introduction

Organic materials in microelectronics applications have great advantages such as low cost, flexibility and easy production [1–6]. An important effect of organic devices is the possibility to create many conduction states. This fact can be useful to design a Random Access Memory (RAM) through an easier and cheaper manufacturing way. Nowadays, single-molecule memory cells can be considered a promising solution to the limit-scaling problem (Moore’s law), but there are some challenges in these devices manufacture [2–4]. Nevertheless, there are some solutions to address this problem, namely the production of planar devices based on the protonated organic thin films for storing more information in the same cell [5–7]. This can be achieved by the reaction between some gases and molecules of the thin film, i.e., for a particular bias voltage, the conductivity levels lead to data storage. With higher applied bias, the same behavior is achieved but at different current level. The information can be erased with opposite applied bias [8,9].

In this paper, we present the development of a memory device based on methyl-red (MR), 2-[4(dimethylamino)phenylazo] benzoic acid with the molecular formula $(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{N}=(\text{CH}_3)\text{C}_6\text{H}_4\text{COOH}$. The physisorption between atmospheric gases and molecules of the organic thin-film dye as well as their effects on electric dipole moment was theoretically studied, and both the electric properties and conductivity levels programmable were characterized. The device showed a good negative differential resistance (NDR) in both bias voltages. In this case, the single-layer device is a typical azo aromatic compound usually used as acidic/basic indicator, and its color changes from pink to yellow depending on the pH environment. Recently, this property of the MR has been used as Schottky diode and solar cells [10,11], but its use as active element in electronic memory is not well known.

2. Methodology

2.1. Experimental details

MR was purchased from Sigma–Aldrich, and a 10% (w/v) solution was prepared in 50 μL of ethanol and deposited between electrodes on glass substrate by spin-coating with an angular rotation of 1000 revolutions per minute (rpm) with an approximate thickness of 200 nm. The nickel electrodes were fabricated by vapor deposition under high vacuum with 45 μm of the gap length and 60 nm of thickness. The current–voltage ($I–V$) characteristics and write-ON-erase-OFF cycles were performed by a Keithley 6487 sourcemeter. During the electrical measurements, the device was kept in a chamber at environment atmosphere. The electronic absorption spectra measurements were obtained using a Shimadzu
UV–2401PC Spectrophotometer, between wavelengths of 200 and 800 nm, where it is possible to find the exact signature for MR structure present in the thin film.

2.2. Theoretical methodology

Density Functional Theory (DFT) by B3LYP/6-31G** calculations implemented by Gaussian program was used to obtain the minimal energy geometry of the molecular structure [12]. The interactions were simulated by sequential Monte Carlo (MC) computational calculations [13] and references therein. These simulations were performed at room temperature and atmospheric pressure to obtain the electric dipole moment of each molecular interaction. The dipole moment presented indicates an increase in charge-transfer between the molecules involved [14]. Therefore, changing the dipole moment of the organic semiconductor by physisorption of environment molecules can change the current flowing through the metal/methyl-red interface.

3. Results and discussion

The superposition of the main interaction sites of environment molecules such as water vapor (H2O), oxygen and nitrogen gases (O2 and N2) with acid methyl-red molecule species is shown, respectively, inset Fig. 1a. After 75 uncorrelated configurations generated by 1.5 × 10^3 MC step simulations, we verified the electric dipole moment increase in MR among nitrogen and oxygen gas to MR among water vapor. The results of the interactions can be seen in Fig. 1a, in the order of 2.64 D (Debye) ± 0.26 and 2.95 D ± 0.28 to 3.44 D ± 0.24, i.e., nitrogen and oxygen to water vapor, respectively. Furthermore, the small dipole moment resulting from MR–nitrogen interaction is evidence of poor or null electric charge transport, just like it is experimentally observed for this device.

Thin films of acid MR are obtained after drying (ethanol used as solvent is evaporated), and its absorbance spectrum shows a clear signature at 490 nm, Fig. 1b (inset). This molecule has the azo β-nitrogen as its active site and shows absorption spectrum centered in 494 nm [15]. The theoretical absorbance maximum of 477.15 nm ± 3.89 obtained by the presented methodology is in agreement with the experimental absorbance maximum obtained, which can be seen in Fig. 1b. This feature is achieved by adsorption on the protonated film of oxygen atoms, mainly due to electrons of oxygen molecule and water vapor. The atmosphere dependence in the memory effect is observed in other devices with different adsorption process [4,5].

Fig. 2 shows current switching with NDR effect in both bias voltages (negative/positive) with peak current densities at 10^3 A/cm². These effects start at ±2.7 V in both sweep voltages due to the charge tunneling through the Schottky barrier of metal/methyl-red interface when the energy levels are aligned [16], i.e., the nickel ions are injected from the electrodes tunneling through of the inhomogeneous barrier (doped by oxygen from environment) at a specific bias voltage. This found in organic tunneling diodes, organic thin-film memory and molecular rectifiers [17,18]. Fig. 2 (inset up) shows the device structure and molecule geometry of the acid MR dye with a diimide central group, N(b) = N(a), where protonation-deprotonation and charge recombination occur [19]. This azo group combined with aromatic rings is responsible for delocalized molecular orbital and promoting charge recombination with molecular active layers. Moreover, Fig. 2 (inset down) shows the results for the device under air and nitrogen atmospheres. It is possible to see an increase in current levels for air atmosphere due to mainly the physisorption caused by oxygen and water vapor. This result is in accordance with the preliminary theoretical result regarding the increase in the electric dipole moment with current levels.

**Fig. 1.** (a) Convergence of electric dipole moment of acid methyl-red in different environments (nitrogen, water vapor and oxygen). (b) Theoretical and experimental absorption spectra for acid MR molecule in atmosphere with N2, O2 and H2O compared with MR thin film.

**Fig. 2.** Current–voltage characteristics. The arrows indicate the direction of the scanning (±50 mV/s) and NDR effect. The device structure and electric behavior under air (ambient atmosphere) or nitrogen atmosphere are showed inset up and down, respectively.
The working cycles showing no degradation process is shown in Fig. 3. It was maintained more than 30 write/erase cycles (it is showed 90 s of regular operation). This figure presents the following aspects: (a) Initially, the memory is set in write position (−5.0 V) and ON (read) pulse is applied in 0.96 s; (b) The high (ON) and low (OFF) conductivity states were obtained at +3.0 V; (c) An erase pulse is applied at +5.0 V; (d) OFF (read) pulse is measured at 3.15 s.

Fig. 4a shows that the difference between ON/OFF states is 145 nA, corresponding to semiconductor state at $10^{-5}$ S cm$^{-1}$ (ON) and insulating state at $10^{-6}$ S cm$^{-1}$ (OFF). The MR thin film is a semiconductor when bias scanning from 0 to +5.0 V with current densities of 0.2 mA/cm$^2$ at +3.0 V. In reverse bias scanning from +5.0 V to 0, the device presents insulating behavior with current densities down to $10^{-3}$ mA/cm$^2$ at +3.0 V. Furthermore, the bit retention time was measured at room temperature, as shown in Fig. 4b. This time corresponds to the period of time that a cell memory can hold electric charge without being refreshed. In this work, the electric current was calculated as an exponential decay with a time constant ($\tau$) of 4.50 s, and results were fitted using the following Eq. (1), being the variables $t$ and $A_0$ time and current measured, respectively.

$$A(t) = A_0 e^{-t/\tau}.$$  \hspace{1cm}  (1)

This prospect is $10^3$ times more efficiency than inorganic memories based on silicon like Dynamic Random Access Memory (DRAM), e.g., bit retention time for commercial DRAM is around at $10^{-3}$ s [20,21], but the MR–DRAM owns a small current density and not speed access time. Moreover, if compared with similar volatile organic memories, this device does not show a good retention time because was performed by organic self-assembled monolayers fabricated with donor and acceptor electrons molecular groups. Despite that, the peak current for this devices is less than 2.5 nA, very small compared with our memory device [22].

4. Conclusions and perspectives

In conclusion, we have investigated and manufactured electrical switching semiconductor device based on acid MR thin film. The theoretical results indicate an increase in physisorption of oxygen and water vapor by dipole moment analyses with good agreement of electrical signature of the device in environmental atmosphere. We also obtained theoretical/experimental absorbance spectra with good accordance. This result corresponds to an error less than 3.5% comparing with experimental ones and indicates the exact chemical structure present in the organic thin film. Concerning the electric characterizations, the planar device shows ON/OFF current ratio equal to 8:1 and 10:1 for forward and reverse bias, respectively. This memory effect has been attributed to NDR in the current–voltage characteristics and current densities at $10^{-3}$ A/cm$^2$ (peak, ON state) and $10^{-5}$ A/cm$^2$ (valley, OFF state). In future works, we hope to obtain better retention time and increases in the current density with increasing the doping levels by physisorption onto thin film. However, the low cost and facility of manufacture with multiple programming cycles obtained for this MR–DRAM device bring us confidence that this system is very promising for future applications as memory elements or intelligent sensors.

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References