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Article in Organic Electronics · February 2016
DOI: 10.1016/j.orgel.2015.11.017

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Resistive switching in polymethyl methacrylate thin films

Jimmy Mangalam a, Shivani Agarwal b, A.N. Resmi b, M. Sundararajan c, K.B. Jinesh b, * 

a Amity Institute of Nanotechnology, Amity University, Noida, 201301, Uttar Pradesh, India
b Indian Institute of Space-Science and Technology (IIST), Veliyamala, Thiruvananthapuram, 695547, Kerala, India
c National Institute of Interdisciplinary Science and Technology (NIIST), Pappanamcode, Thiruvananthapuram, 695547, Kerala, India

ARTICLE INFO

Article history:
Received 29 June 2015
Received in revised form 19 November 2015
Accepted 19 November 2015
Available online xxx

Keywords:
ReRAM
Electrical bistability
PMMA
Resistive switching

ABSTRACT

The origin of the resistive switching in Polymethyl methacrylate (PMMA) films is studied in this work, analysing the switching mechanism of Ag/PMMA/FTO devices. Significant improvement in the performance occurs upon annealing the sample, indicating that the evaporation of the solvent plays a significant role in the memory behaviour of the devices. The shift in the space-charge-limited conduction regime after the set process shows that the electron mobility has been enhanced by two orders of magnitude upon switching. Voltage stress analyses show that the switching from high-resistive phase to low resistive phase occurs only when the silver electrode is positively biased, which confirms that the origin of switching is Ag* filament formation through PMMA. The performance of the devices at different temperatures shows that the set and reset voltages increase with temperature. This observation is explained based on the vitrification of the PMMA layer as a result of the increased evaporation of the solvent at higher temperatures.

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1. Introduction

Resistance switching observed in materials under applied voltage has potential applications in upcoming Random Access Memory (RAM) technology. There are few reasons behind the technological relevance of this phenomenon; firstly, measuring the resistance is more straightforward than measuring the threshold voltage of a transistor in the flash-type memory elements to determine its programmed state. Secondly, being simple metal-insulator-metal capacitor structures, the device fabrication and the process technology is far simpler than the conventional transistor fabrication processes. Thirdly, Resistive RAM (ReRAM) technology has excellent compatibility with the standard CMOS process technology [1,2]. Besides, the physical phenomena that lead to the switching between resistive states are properly understood. Since most of the resistive switching happens due to a conductive filament formation [3,4], the underlying mechanisms are similar to the physics of the dielectric breakdown events. As the filament formation occurs at sub-nano scale, the scaling down of the device to nanometer dimensions is viable, which promises a bit density as high as 10 Gb/cm² [1–6].

Several materials have been studied to optimize the active medium for ReRAM technology, which includes oxides such as TiO₂ [7,8], ZnO [9,10], WO₄ [11], ZrO₂ [12,13] etc., and sulphides such as Ag₂S [14] and CuZn₄Al₁₋₅S [15]. Pan et al. has published a detailed review on the ReRAM materials and their performances [2]. Further, for the development of flexible memory devices, organic materials such as polymethyl methacrylate (PMMA) [16–18], pentacene [19], anthracene [20] and polystyrene have been widely investigated together with their hybrid structures [21–25]. Among organic materials for ReRAM applications, PMMA has attained a special attention because it shows reasonably good switching, also since it is a standard resist material for submicron ReRAM lithography [26]. Several studies have been dedicated to the resistive switching characteristics of PMMA-based hybrid systems [27,28]. However, the investigations to understand the intrinsic resistive memory switching in PMMA films are scarce, and the actual switching mechanism in this material remains ambiguous. PMMA being a low-cost and easy-to-process dielectric material has lots of interests in flexible memory devices. Therefore, understanding the nature of its electrical bistability is imperative to characterize the switching behaviour of the PMMA-based hybrid materials.

Different charge transport mechanisms have been explored to explain the mechanism involved in the switching behaviour of organic materials. Avila-Nino et al. have studied the switching in PMMA and concluded that the introduction of the aluminium ions...
coating. To avoid the impact of toluene, the film thickness of the PMMA layer was increased to 230 nm. In this manuscript, the electrical bistability of Ag/PMMA/FTO devices is studied at different temperatures to identify possible mechanisms behind the switching phenomenon.

2. Experimental

The PMMA films were prepared by spin-coating 1% solution of PMMA (99.99%, from Sigma–Aldrich) in toluene on fluorine doped tin oxide (FTO) substrates. The film was spun at 1000 rpm for 60 s, yielding a film thickness of approximately 230 nm on single coating. To avoid the impact of toluene, the films were baked at 60 °C for 20 min after spin-coating, after which, 100 nm thick silver electrodes were deposited onto the PMMA layer using a thermal evaporator (Fillunger Thermal Coating system). A shadow mask with an electrode area of 1 mm² and pitch length of 3 mm was used for the deposition of the top electrodes. The diagram and the secondary electron image of the cross-section of the device are shown in Fig. 1, which shows 230 nm thick PMMA films on the FTO-coated glass substrates. A two-probe station connected to Agilent 4200 A parameter analyzer was used to do the electrical measurements of the devices.

3. Result discussion

Fig. 2(a) shows the typical current–voltage (I–V) behaviour of the Ag/PMMA/FTO device. No forming process was applied to trigger the device prior to the electrical switching experiment. Fig. 2(b) shows the comparison between the switching behaviour of Ag/PMMA/FTO devices with the as-deposited PMMA and annealed at 100 °C for 30 min. The devices with as-spun PMMA exhibits hysteresis, but no evident abrupt transitions. When the PMMA layer is annealed prior to the electrode deposition, the device shows sharp switching characteristics. This strongly indicates the vitrification of the PMMA layer as a result of the solvent evaporation upon annealing.

The device is initially at its natural high resistance (Off) state, with a resistance of 10⁶Ω. When it switches to a low resistance (On) state, the resistance drops to 60Ω. Generally, the switching mechanism is attributed to four different phenomena, namely, space-charge limited conduction (SCLC) resulting from the accumulation of charges at the PMMA-electrode interface, charge transfer between donor-acceptor levels of PMMA, switching due to the change in the electrochemical state of the interface and metallic filament formation through the active layer [31,32]. Among these possibilities, the filament theory has been widely accepted as the general origin of resistive switching. However, the switching can be more complicated in PMMA, as it is a polar molecule with glass transition temperature of 110 °C [33] and therefore, its molecular ordering has a strong electric field dependence [34]. PMMA molecules have been reported to have considerable variation in its dielectric function when grown under an external electric field, because of the aforementioned alignment of the molecules [35]. The electric field at the switching voltage of the ReRAM device shown in Fig. 2 comes in the range of 0.13 MV/cm, which is high enough to induce molecular reordering in the film.

A log–log plot of the I–V curve shown in Fig. 2 is given in Fig. 3(a), which depicts that the initial conduction mechanism in PMMA is due to the trapped charges that follow the applied electric field linearly (and is a very low current, as represented by the large noise). The trapped charges follow Ohm’s law, as depicted by the slope (~1) of the initial part of the curve. At a higher voltage, the charge transport is restricted by the space-charge limited conduction (SCLC), governed by Child’s law given by $J = \frac{9\mu k}{8dV^2}$, where, $\mu$ is the charge mobility, $k$ is the dielectric constant of the active medium and $d$ is the film thickness [36]. The presence of SCLC indicates the presence of defects either at the Ag/PMMA interface [30] or in the PMMA layer. Extrapolating the linear fit to the Child’s law at the SCLC regime, the electron mobility in PMMA can be roughly calculated to be $7.6 \times 10^{-5} \text{ cm}^2/\text{V.s}$, which is a typical mobility of electrons in insulators. The transition voltage ($V_{Tr}$) at which the Ohmic conduction changes to SCLC is around 0.4 V in this case. After the switching, the conduction mechanism is dominated by Ohmic charge injection and $V_{Tr}$ shifts to 1.4 V. Ohmic conduction is related to the trapped charges in the dielectric medium and it predominates over the space-charge limited conduction when the volume charge density is larger than the injected charge density [36]. The extension of the Ohmic regime by an additional 1 V shows the generation of large number of volume charges in the PMMA film. Therefore, we can conclude that this shift of the SCLC regime after switching is not primarily due to the polarization change in the medium, but rather it indicates the formation of a conductive path in PMMA. This conductive path comprises a large density of ions contributing to the overall conduction of the medium. Extrapolation of the SCLC regime after switching gives a carrier mobility of 0.01 cm²/V.s; more than two orders of magnitude higher than the mobility before switching. This drastic increase in electron mobility is indicative of a sudden conductivity enhancement, and it could not be merely due to the polarization change in PMMA. The formation of islands of metal atoms from the electrodes when the vitri
Thus, the blue-shift in SCLC regime and the substantial enhancement in the carrier mobility support the filament formation theory, rather than the polarizability variation of PMMA molecules. Further, it is noticeable that the trap-filled limited conduction (TFLC), which is due to the sphere of influence of the filled traps, is not observed after switching. This means that the lifetime of the transient electrons in the conductive filaments is too small to limit further charge injection to the PMMA layer\footnote{\ref{35}}. The lifetime of the transient electrons is a crucial parameter in determining the eventual speed of the ReRAM devices when connected in an array.

To validate the filament formation further, the resistance of the device at the On-state has been measured as a function of temperature. As Fig. 3(b) shows, the resistance declines with increasing temperature, indicating behaviour similar to semiconducting materials. This negative temperature coefficient of resistance strongly points out the hopping mechanism of electrons from traps over the adjacent potential barriers. The traps here are the silver ions and the barrier is the PMMA molecules separating the Ag\textsuperscript{+} ions. This mechanism is further validated by plotting the Arrhenius behaviour of the On-state current as a function of $1/T$, yielding the activation energy of electron hopping through adjacent Ag\textsuperscript{+} ions in the filament Fig. 3(c). The potential barrier height varies linearly with applied bias as a result of the Schottky barrier lowering. Fig. 3(d) shows the activation energy of electron hopping plotted against the bias voltage, and the linear extrapolation gives the barrier height (at zero bias voltage) of $0.021 \pm 0.001$ eV. This activation energy is close to the thermal energy of electrons (0.024 eV) at room temperature, and therefore, electrons hopping through the Ag\textsuperscript{+} ions would follow simple Ohmic conduction as Fig. 3(a).

Further, the Ag/PMMA/FTO devices were subjected to constant voltage stress (CVS) measurements as shown in Fig. 4 to check the
polarity of onset of the filament growth. Both positive and negative voltages were applied to allow charge injection from Ag electrodes and FTO substrate. When a positive bias is applied to Ag electrode, the current sampling shows drastic jumps in conductivity, the frequency of which increases as the bias voltage increased (not shown here). In this case, the electron injection occurs from the FTO. When the top Ag substrate is negatively biased, no abrupt jumps in the current is observed (even for devices that were already switched earlier), showing that switching is initiated by the Ag electrode, rather than by the PMMA dielectric medium. If the switching was due to the molecular rearrangements in PMMA, it would have happened regardless of the polarity of the voltages. Thus, it confirms that the filament formation of Ag$^+$ ions in the PMMA matrix is the origin of resistive switching in these devices. It has been pointed out by S. Gao et al. that for switching media with low cationic mobility, the filament formation is a cumulative process, where filament growth. Both positive and negative voltages were applied to allow charge injection from Ag electrodes and FTO substrate. When a positive bias is applied to Ag electrode, the current sampling shows drastic jumps in conductivity, the frequency of which increases as the bias voltage increased (not shown here). In this case, the electron injection occurs from the FTO. When the top Ag substrate is negatively biased, no abrupt jumps in the current is observed (even for devices that were already switched earlier), showing that switching is initiated by the Ag electrode, rather than by the PMMA dielectric medium. If the switching was due to the molecular rearrangements in PMMA, it would have happened regardless of the polarity of the voltages. Thus, it confirms that the filament formation of Ag$^+$ ions in the PMMA matrix is the origin of resistive switching in these devices. It has been pointed out by S. Gao et al. that for switching media with low cationic mobility, the filament formation process occurs from the anode, opposite to the electrochemistry of high-mobility cationic solid electrolyte [37]. This again confirms the Ag$^+$ filament formation in the PMMA medium.

The Ag$^+$ filament formation in PMMA is a cumulative process that increases with the applied bias, and the process resembles the dielectric breakdown phenomenon, where the final breakdown event is due to the accumulated charged defect sites such as vacancies. Therefore, in order to understand the reliability of switching in PMMA, the set and reset voltages can be plotted as Weibull distributions. The cumulative distribution function is given by $F(x) = 1 - \exp(-x^\beta)$, where $\beta$ is shape parameter of the distribution [38]. In the present scenario, the parameter $x$ represents the write/erase switching voltages, yielding $\ln(-\ln(1 - F(V))) = \beta \ln(V)$. A plot of $\ln(-\ln(1 - F(V))) = \beta \ln(V)$ against $\ln(V)$ gives the Weibull distribution of the cumulative switching process. Fig. 5 shows the Weibull distributions of set and reset voltages at 40°C and 70°C (for representation purpose, $\ln(-\ln(1 - F(V)))$ versus Voltage is depicted here). At higher temperatures, the Weibull distributions exhibit two distinct slopes indicating to different mechanisms of switching. The higher slopes ($\beta \geq 2$) are similar for both temperatures indicating the same switching mechanism, while the lower slope indicates a different origin of the switching behaviour. This different origin of switching could be the contribution from the temperature-dependent polarization, or the vitrification process in the film as will be discussed later. Fig. 5 also indicates that the Weibull zero’s of the set and reset have been shifted to higher values at higher temperatures. A similar trend has been observed with increasing the layer thickness as well, (please see the Supporting Information, Fig. S.I-1). The filament formation is an electric field-assisted phenomenon, and therefore, the set and reset voltage have a strong dependence on the thickness of the PMMA layer (please see Supporting Information, SI-1). This is an additional evidence for the filament formation in the PMMA layer.

Fig. 6 shows the temperature dependence of the set and reset voltages, indicating that the set-reset window is gradually increasing with temperature. From the point of view of the filament formation, this result is counterintuitive, since the activation of the silver atoms to ionize and the mobility of the Ag$^+$ ions to form the filament should be enhanced at elevated temperatures. Thus, a gradual reduction in set-reset voltages would be expected with increasing the temperature.

Since the Ag$^+$ ion dynamics at elevated temperatures can only lead to faster electrical switching, the increasing set-rest voltages should be associated with the changes in the PMMA film itself. More precisely, this increase should be related to the structural relaxation of the PMMA layer. It has been reported that during the isothermal vitrification of polymer films (with similar thickness reported here), the solvent evaporation plays a crucial role in the thickness and density of the films [36]. Due to this, the volume relaxation of the film becomes time-dependent. The Ag$^+$ ions will have a constant value when the fractional thickness of the film becomes nearly same as the volume fraction of the solvent at the vitrification point. Solvent evaporation is a strongly temperature dependent process. Therefore, the structural relaxation occurs on a smaller timescale at elevated temperatures. Thus, the increasing set-reset voltages with temperature could be explained as due to the densification of the film resulting from the solvent evaporation and consequent structural relaxation of the PMMA layer.

The write–erase cycle performance of the PMMA device was tested by applying a square-pulse with peak at ±2 V and measuring the corresponding current. In this case, the device sets On at 1.5 V and sets Off at –1.5 V. The pulse peaked at 2 V sets the device On and a pulse of -2 V erases the data. Fig. 7(a) shows the cycling performance of the device (shown only for 200s for clarity), where the symbols represents the current measured and the solid line is the programming voltage pulse. The erase (Off-state) current has less scattering compared to the On state, which reflects the scattering of the on-set threshold of the Ag$^+$ filament formation. The endurance of the On and Off states have been measured by sampling the current at these states, as shown in Fig. 7(b), where the mean On/Off ratio is $10^3$.

4. Conclusions

The solvent evaporation and the subsequent vitrification of the film have a significant influence on the switching mechanism of PMMA. The current–voltage analyses of the annealed Ag/PMMA/FTO devices show that the initial breakdown of the device is followed by the space-charge limited current (SCLC), leading to a final switching behaviour. After switching, the current follows a purely Ohmic behaviour, and the SCLC regime is shifted to a larger voltage range, indicating the formation of a conducting path through the layer. However, this experiment proves only that a rapid enhancement in the trap density of the films occurs, but does not explain the switching mechanism. For getting a conclusive picture, temperature dependence of the On-state current and resistance were measured as a function of temperature. The conduction indicates an electron hopping mechanism through the Ag$^+$ ions, separated by a barrier height of nearly 0.021 eV. Constant voltage stress (CVS) analysis was performed on these devices, from which we observe that switching happens only when the Ag electrode is positively biased, not when the FTO substrate is positively biased.
This depicts that the origin of the resistive switching is mainly due to the Ag electrode, which in turn supports the Ag$^+$ filament formation hypothesis. At elevated temperatures, the Weibull distributions of the set and reset voltages exhibit an additional lower-slope branch, indicating certain phenomena responsible for the early breakdown of the devices. The devices exhibit a linear increase in set and reset voltage with increasing temperature, counterintuitive to a reduced operational voltage due to the enhanced diffusion of the Ag ions at larger temperatures. This enhancement in the set/reset voltages with temperature could be mainly due to the structural relaxation in the PMMA films resulting from the gradual evaporation of toluene from the film and the subsequent vitrification of the film. Our observations shows that understanding the intrinsic switching behaviour of the PMMA layer is films is imperative to analyze more complex PMMA-based hybrid active layers.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.orgel.2015.11.017.

References


Fig. 5. Weibull distributions of the Ag/PMMA/FTO samples at (a) 40 °C and (b) 70 °C.

Fig. 6. Temperature dependence of the SET and RESET voltages of the Ag/PMMA/FTO devices.

Fig. 7. (a) Write-erase cycles of the Ag/PMMA/ITO device with switching shown in Fig. 2(b). The voltage pulses were with peaks ±2 V. The solid line is the programming voltage pulse and the blue symbols show the corresponding current measured. (b) The endurance of the device at On and Off states. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)


