Resistive switching in polymethyl methacrylate thin films

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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.

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 morestraight forward 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/cm^2 [1—6].

Several materials have been studied to optimize the active medium for ReRAM technology, which includes oxides such as TiO_2 [7,8], ZnO [9,10], WO_x [11], ZrO_2 [12,13] etc., and sulphides such as Ag_2S [14] and $CuZn_xAl_{1-x}S$ [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

(Al$^+$) from the electrode causes the change in the resistance of the devices [17]. Another possibility is the electroforming process [29]; the formation of islands of metal atoms from the electrodes when an applied electric field. Besides these, the formation of multiple filament pathways has been proposed to explain resistance switching in organic materials [30]. 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 mm^2 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 $10^4\Omega$. 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 $J = 9\mu k/8d^3V^2$ where, μ 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 7.6×10^{-5} cm^2/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 cm^2/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
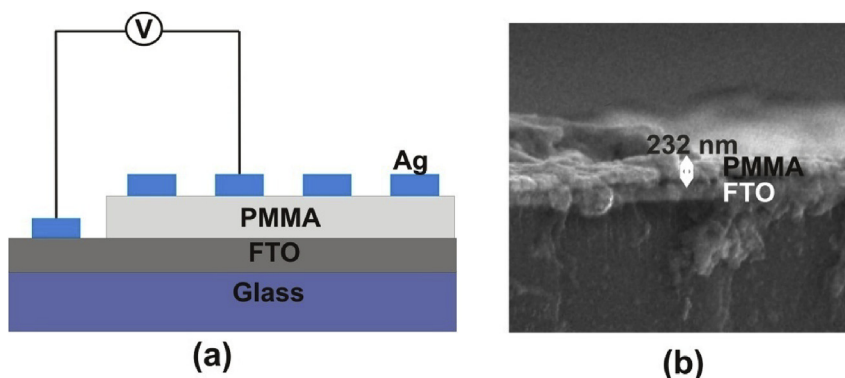

Fig. 1. (a) Structure of the PMMA ReRAM devices, spin-coated on FTO glass substrate. Thermally evaporated Ag was used as the top electrode on PMMA and on FTO. (b) The cross-sectional secondary electron image of the device, showing approximately 230 nm thick PMMA coated on FTO film.