Organic Nonvolatile Memories Based on PMMA and PHEMA Dielectric Layers

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1. Introduction

Recently, organic and polymer materials for future molecular-scale memory applications have been extensively investigated. Their attractive features include good processability, miniaturized dimensions and the possibility for molecular design through chemical synthesis [1]. Advantages of organic and polymer memories also include simplicity in device structure, good scalability, low-cost potential, low-power operation, multiple state property, 3D stacking capability and large capacity for data storage [2,3]. Organic/polymer memory devices with different architecture, including capacitor-type, transistor-type, and resistor-type memories, have been proposed for various demands. For resistor-type memories, data storage is based on the electrical bistability (ON and OFF states) of materials arising from changes in certain intrinsic properties, such as charge transfer and phase change, in response to the applied electric field [4]. They are especially with low power dissipation, high switching speed, and simple fabrication process. In previous reports, inorganic ferroelectric materials or nanoparticles were often incorporated in device structures to exhibit the memory effect [5-7]. In this article, we have fabricated the bistable nonvolatile memories with poly(2-hydroxyethyl methacrylate) PHEMA and poly(methyl methacrylate) PMMA, respectively, acting as the dielectric layer. Most specifically, our devices are without ferroelectric materials or nanoparticles incorporated, which can significantly simplify the device process and increase the reliability. The results exhibited that memories with PMMA layer are with the ON/OFF current ratio about 10⁴, long retention time over 10000 sec, and better writing/reading/erasing stability.

2. Experimental Details

To fabricate the memory devices, glass substrates with an ITO layer (~140 nm, 15 $\Omega/$) were firstly cleaned by detergent, acetone, and isopropyl alcohol. Subsequently, the dielectric layer, which was PHEMA or PMMA, was spin-coated onto the ITO/glass substrates from their PHEMA-methanol or PMMA-toluene solutions. Their concentration was controlled to obtain the dielectric layers with identical thickness of 180 nm. Finally, after baked at 70 °C for 1 hour, the substrates were transferred to a thermal coater to evaporate a 150-nm-thick Al thin film through a metal mask with 1 mm×1 mm square patterns as the top anode. The completed devices were preserved in a glove-box with H₂O and O₂ content less than 1 ppm. For



Fig. 1 *I-V* curves of PHEMA-devices and PMMA-devices. The arrows indicate the bias sweeping direction

convenience, the device with PHEMA and PMMA dielectric layer were respectively called PHEMA-devices and PMMA-devices in the following descriptions.

3. Results and Discussion

Fig. 1 shows the current-voltage (I-V) characteristics of PHEMA- and PMMA-devices in semi-log scale. As indicated by the arrows, the devices were initially swept from 4 to -2 V, and immediately swept from -2 to 4 V. With the reverse bias increasing, the as-fabricated device shows a high-resistance state (HRS) until the threshold voltage (writing bias) where the device is switched to a low-resistance state (LRS). Once the transition is achieved, the devices remain at the LRS even after the applied voltage is removed, indicative of the non-volatile switching property. However, the LRS will be erased when the applied forward bias is larger than certain value which was called the erasing bias. For PHEMA- and PMMA-devices, the writing bias is identically happened at ~ 0.5 V while the erasing action is carried out at 2.6 and 1.9 V, respectively. The conductance of LRS is different from that of HRS by a factor of 10⁴ at room temperature. The mechanism of the rapid increase of current after biasing a voltage larger than 0.5 V can be explained as follows. By applying voltage above threshold, the localized trap sites in the polymer are filled by electrons and then the trap-filling process creates electromigrating and filamentary paths. The charge carriers will continuously hop or tunnel among electron-filled traps



Fig. 2 Retention measurements of the devices. Filled triangle/circle and opened triangle/circle represent the LRS/HRS of PHEMA-/PMMA-devices, respectively.

and that increases the conductivity of polymers.

Two important properties of memory devices are retention time and rewritable/re-erasable ability. The retention measurement of the devices was carried out by applying a bias at 1 V (read voltage), as shown in Fig. 3. No obvious change in the current of LRS was observed in PMMA-devices for whole test duration. The current fluctuations of the HRS are attributed to the incomplete erasing of trapped charges after an erasing process. For PMMA-devices, the fluctuation is getting smaller and more stable with time, and the ON/OFF current ratio becomes larger. Long retention time over 10000 sec is thus guaranteed.

The rewritable/re-erasable ability was tested by periodically writing, reading, and erasing the states. As shown in Fig. 3(a), firstly, a writing voltage of -1.5 V was applied to set the device in ON state. Subsequently, a reading voltage of 1 V was applied several times to evaluate the stability,



Fig. 3 (a) Variation of applied voltage as a function of time. The reading current of HRS and LRS of (b) PMMA- and (c) PHE-MA-devices, as a response of applied voltage.

followed by an erasing voltage of 3 V and several reading tests. The procedure was repeated every 11 sec. Figs. 3(b) and 3(c) shows the responses of PMMA- and PHE-MA-devices, respectively. The LRS current shows relatively high stability than the HRS current does. Nonetheless, in cycles 2 and 5, the LRS current rapidly decreases within few reading in PHEMA-devices. It indicates that the trapped charges are readily detrapped even though the reading voltage is well-below the erasing voltage. As a consequence, the ON state may be mis-reading as the OFF state. In contrast, although the fluctuation of HRS current is over one order $(4x10^{-7} \sim 6x10^{-6} \text{ A})$ in PMMA-devices, the ON/OFF current ratio is large enough and the mis-reading can be avoided. Therefore, all the device characteristics including I-V cureves, retention time test, and reliability test, have suggested that PMMA is much suitable for organic/polymer memories.

4. Conclusions

In conclusion, we have fabricated the resistor-type memories with poly(2-hydroxyethyl methacrylate) PHEMA and poly(methyl methacrylate) PMMA active layer, respectively. From the *I-V* characteristics, the devices with PMMA active layer have a lower erasing voltage (1.9 V) than that (2.6 V) of PHE-MA-devices. Both devices can be easily turned as the ON state by applied a writing voltage of -0.5 V. Higher stability and reliability in retention and writing/reading/erasing measurement also suggested that PMMA is a better candidate for organic/polymer memories.

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