Research Article

Triggering WORM/SRAM Memory Conversion by Composite Oxadiazole in Polymer Resistive Switching Device

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Electrical characterization indicates that the nonvolatile write once read many (WORM) times/volatile static random access memory (SRAM) conversion was triggered by the composite of the oxadiazole small molecule. FTO/PMMA/Ag device possesses nonvolatile WORM memory behavior, while the FTO/PMMA+oxadiazole/Ag device shows vastly different volatile SRAM feature. The FTO/PMMA/Ag and FTO/PMMA+oxadiazole/Ag memory devices both exhibit high ON/OFF ratio nearly $10^4$. The additive oxadiazole small molecule in the polymethyl methacrylate was suggested to form an internal electrode and serve as a channel during the charge transfer process, which is easy to both the charge transfer and back charge transfer, as a consequence, the WORM/SRAM conversion upon oxadiazole small molecule complexation was triggered. The results observed in this work manifest the significance of oxadiazole small molecule to the memory effects and will arouse the research interest about small molecule composite applied in memory devices.

1. Introduction

Resistive random access memory (RRAM) devices has aroused the research scholar’s widespread interest on the account of their fast operation speed, simple construction, low power dissipation, and compatibility with conventional CMOS technique [1–4]. RRAM devices are probably a promising solution to traditional memory technologies facing the physical limit. On account of their widespread applications in nonvolatile data memory [5], logic operation [6–8], neuromorphic circuits [9], and programmable analogue circuits [10]. For resistive switching effect, the device could be repeatedly converted between the OFF state and the ON state, once an appropriate voltage is applied. Up till now, resistive switching has been reported in a variety of materials, for instance, perovskites [11], binary oxides [12], organics [13–16], TiO$_x$ [17], MoSe$_2$-doped ultralong Se microwires [18], Fe$_2$O$_3$ solid electrolyte [8], and chalcogenide [19]. In particular, resistive switching memory integrated with nanogenerators for self-powered device has been developed recently [20]. During the last several years, organic resistive switching memory device has attracted special attention, such as polyvinyl carbazole [21], epoxy methacrylate resin [22], and poly(vinyl alcohol) [23]. Taking these into account, organic memory shows excellent mechanical flexibility, high ductility, excellent bendability, low cost, and the possibility for molecular design through chemical synthesis [24]. The charge transfer mechanisms in RRAM memory devices could be ascribed to various physical and/or chemical behavior theory and still needs more work [25].

In a variety of organic materials that were applied in the resistive switching memory devices, polymer has drawn a lot of attention on account of easy processing, favourable environmental stability, easiness in the fabrication of thin films, and low cost [26]. The application of the polymer made the flexible RRAM film devices possible. Flexible devices promise a broad application prospect [27, 28]. Integrating polymer with small molecule material has been recently investigated with the purpose of realizing preferable synergetic effects with the two materials [29].

Polymethyl methacrylate (PMMA) has been verified a polymeric matrix in resistive switching application [30, 31], which being a low cost and easily processed organic material, has more and more interest in flexible resistive switching
devices owing to its favourable switching and for its function as a normative resistance material in submicron RRAM lithography [32]. Simultaneously, oxadiazole derivatives were intensively reported as ideal electron acceptor materials in electronic devices [33–39]; 2-(4-tert-butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole was one of the most efficient electron-transporting materials on account of its high electron affinity. In the present work, PMMA is used as the host body for forming a thin film. And it was used to form the nanocomposite with 2-(4-tert-butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole to demonstrate resistive switching characteristics. And 2-(4-tert-butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole functions as the donor.

2. Experimental

The 2-(4-tert-butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole ($M_w = 354$, MDL: MFCD00003101) and PMMA (average $M_w = 150,000$, MDL: MFCD00134349) were both purchased from Sigma-Aldrich. The chemical structures of oxadiazole and PMMA are shown in Figure 1. To prepare PMMA+oxadiazole nanocomposites, 1 g of 2-(4-tert-butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole powder was mixed to 20 g of PMMA, then 5 g of the prepared composite was added to 50 ml of chlorobenzene solvent and PMMA in chlorobenzene solvent of 10 mg/ml with subsequent magnetic stirring for 48 h. After that, the PMMA+oxadiazole composite solution (filtered by polytetrafluoroethylene membrane, pore size of 0.22 mm) and PMMA of chlorobenzene solvent were spin-coated on a cleaned SnO$_2$ doped with fluorine (FTO) glass (purchased from Guluo Co. Ltd. Luoyang, China) at 800 rpm for 15 s, and then 4000 rpm for 60 s. Afterwards, the spin-coated FTO glasses were baked in 40°C for overnight on a hot plate to remove the residual solvent. The top Ag electrode with a thickness of 200 nm was deposited by using thermal evaporation under the pressure of $1 \times 10^{-4}$ Pa. The fabricated structure of the memory device is schematically exhibited in Figure 2. The morphology of the cross-section properties of the active layer was tested by scanning electron microscopy (SEM; Nova Nano 450). All electrical measurements were performed by using a semiconductor characterization system (Keithley 4200) at room temperature. The bottom FTO electrode was grounded in the process of the resistive switching performance test, and an external voltage was applied to the top Ag electrode.

3. Results and Discussion

The cross-section SEM images of the PMMA and PMMA+oxadiazole composite films before the deposition of the top Ag electrode are shown in Figure 3.

The electrical memory behavior of the two devices was characterized by the current-voltage ($I-V$) curves of the FTO/PMMA/Ag and FTO/PMMA+oxadiazole/Ag sandwich devices. Figure 4(a) shows the $I-V$ curves of the FTO/PMMA/Ag memory device, which indicates a typical nonvolatile WORM performance. As seen in Figure 4(a), the FTO/PMMA/Ag device is initially in the high resistance state (the OFF state). In the process of the first positive voltage sweep, a sudden increase in current happened at the voltage of about 1.25 V, indicating the transition of the FTO/PMMA/Ag device from the high-resistance state to the low-resistance state (ON state) with an ON/OFF ratio up to $10^4$ as shown in Figure 4(b). On this transformation, the FTO/PMMA/Ag device retains this ON state in the process of the succeeding positive scan (2nd sweep) and negative scan (3rd sweep) and cannot retrieve to its initial high-resistance state even though power supply shut down (4th sweep), manifesting its nonreversible nonvolatile nature and write once read many (WORM) times memory properties. Broadly speaking, the quantitative evaluation of resistive switching was assessed with the $I_{OFF}/I_{ON}$ ratio at each applied voltage. This would help in providing information about the optimum operation parameters of the threshold resistive switching voltage ($V_{th}$) and the range of applied voltage for observing the obvious ON and OFF, and the amount of distinctiveness ($I_{OFF}/I_{ON}$) can result in defining the critical process parameters for the preparation of memory device structures with an efficient bipolar resistive switching behavior. Figure 4(b) describes the evaluated values for $I_{OFF}/I_{ON}$ depending on the applied bias of the representative FTO/PMMA/Ag device structures. In order to assess the stability and reliability of the
FTO/PMMA/Ag memory behavior, Figures 4(c) and 4(d) show the performance of retention time and stimulus read pulse under the ON and OFF states of the FTO/PMMA/Ag device. Both ON and OFF states were tested under constant voltage stress and continuous pulse. No significant attenuation in current was observed, and both the ON and OFF current responses were fairly stable which reached up to $2 \times 10^4$ s and $10^4$ continuous read pulses, manifesting favourable stability and reliability of the FTO/PMMA/Ag device.

Figure 5(a) shows the $I-V$ curves of the FTO/PMMA+oxadiazole/Ag device. Totally different from the FTO/PMMA/Ag memory device, the added 2-(4-tert-butylphenyl)-
5-(4-biphenylyl)-1,3,4-oxadiazole small molecule indicates a reversible volatile SRAM memory property, manifesting the important role of oxadiazole small molecule in the PMMA composite. As shown in Figure 5(a), in the process of the first positive sweep from 0 to 6 V, the FTO/PMMA+oxadiazole/Ag device maintains its OFF state until a threshold switching voltage of 1.30 V was reached. The current of the FTO/PMMA/Ag device then increased suddenly from $10^{-6}$ A to $10^{-2}$ A, converting the FTO/PMMA+oxadiazole/Ag device to the ON state. The FTO/PMMA+oxadiazole/Ag device stably maintained in the ON state in the process of the continued positive and negative scan (2nd and 3rd sweeps). Nevertheless, the subsequent tests exhibit that the ON state can only be maintained transiently and will relax to the original OFF state spontaneously once cutting off power supply for over 3 min, manifesting its actually ”volatile” feature. Then, in the fourth scan, the FTO/PMMA+oxadiazole/Ag device can be converted to the ON state again, manifesting its volatile static random access memory (SRAM) properties.

The $I-V$ curves in Figure 5(a) indicate that the FTO/PMMA+oxadiazole/Ag takes on the volatile but reprogrammable electrical bistability, which could be applied in SRAM devices in digital information technology. The cumulative distributions of resistive switching voltage ($V_{th}$) and resistance of ON and OFF states ($R_{ON}$ and $R_{OFF}$) for FTO/PMMA+oxadiazole/Ag and FTO/PMMA/Ag device are shown in Figures 6(a)–6(d). For the sake of comparison and evaluation, the variation coefficients of all switching parameters have been calculated by $\sigma/\mu$ (where $\sigma$ is the standard deviation and $\mu$ is the average value). Figure 6(e) shows the variation coefficients of $V_{th}$, $R_{ON}$, and $R_{OFF}$, respectively.

Figure 7 shows the UV-vis absorption spectra of the PMMA and the composite film of PMMA and oxadiazole small molecule. The PMMA and PMMA+oxadiazole show a distinct absorption peaks near 345.5 nm, respectively, both of which are corresponding to the $\pi-\pi^*$ transition of PMMA. Obviously, the $\pi-\pi^*$ absorption of the oxadiazole small molecule is blue-shifted, manifesting that the addition of oxadiazole in the PMMA matrix was beneficial to the $\pi-\pi^*$ electron transitions of the PMMA, for which one considered reason is the ameliorated molecular coplanarity of the methacrylate methacrylic ring after oxadiazole small molecule composite. Whereas a weak absorption peak appeared at 301.5 nm, the absorption transitions were wholly blue-shifted to a lower wavelength region, manifesting the possible formation of oxadiazole chains aggregation, which will facilitate charge transfer in the PMMA bulk when the external bias was applied.

To better catch on the resistive switching mechanism, the $I-V$ characteristics were redrawn in the double-log coordinate system as exhibited in Figure 8. The ON state of the FTO/PMMA/Ag and FTO/PMMA+oxadiazole/Ag devices shows linearity in the $I-V$ relationship and the slope of the plot is nearly 1 (1.04 and 1.02), manifesting that the ohmic conduction through the conducting filament is dominant. In the OFF state of the FTO/PMMA/Ag and FTO/PMMA+oxadiazole/Ag device, the ohmic conduction was observed in a low voltage region, and the slope increased to over 2 (2.94, 1.19, and 3.78), manifesting that the space-charge-limited conduction (SCLC) among the disconnected portion of the conducting filament governs in a high voltage region. These conduction properties in

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**Figure 5:** (a) $I-V$ curves of FTO/PMMA+oxadiazole/Ag device. (b) Switching ratio ($I_{ON}/I_{OFF}$) depends on the applied bias, as estimated from the $I-V$ sweeps recorded for FTO/PMMA+oxadiazole/Ag device.
ON and OFF states are also in keeping with those in the previous report [40–42]. The experimental results indicate that the resistive switching property have a high association of the oxadiazole small molecule additives in polymer host. At initial stage, the charge carriers have no sufficient energy to overcome the charge injection barrier between PMMA molecules; the built-in electric field between the interface was formed [43–45], at the same time, the formation of built-in electric field will further hinder the injection of carriers. Thus, the FTO/PMMA/Ag device is on the high resistance state. Once the voltage scanning is up to the \( V_{th} \), the occurrence of intermolecular charge transfer leads to transition in the FTO/PMMA/Ag device from OFF to ON state. The formed

![Graphical representation of cumulative distributions and variation coefficients](image-url)
charge transfer was in favour of the holding of the generated charge carriers, which may be related to the nonvolatility of the resulting data-storage devices. As indicated above, oxadiazole small molecule complexation has facilitated electron accepting in active layer and endows the active layer with a quasireversible \(n\)-doping feature, suggesting that the oxadiazole moieties in PMMA could act as mediators to facilitate the intramolecular charge transfer. Here, the quasireversible features of the oxadiazole group are supposed to be partially responsible for the reversible volatile SRAM memory behaviors for the FTO/PMMA+oxadiazole/Ag device. Because of the quasireversible and unstable charge transfer, the charge transfer state immediately dissociates via the back charge transfer or a recombination process of the separated charges after taking out the external power supply, which leads to volatile memory characteristic in FTO/PMMA+oxadiazole/Ag device.

4. Conclusions

In summary, small molecule oxadiazole was composited with polymer PMMA, which easily formed a thin film in this work for memory applications, that effectively avoids the defect of crystallization of small molecules during the formation of thin film. The FTO/PMMA/Ag device show irreversible nonvolatile WORM feature. However, after oxadiazole was added, the FTO/PMMA+oxadiazole/Ag device exhibits reversible volatile SRAM memory properties. More importantly, the added oxadiazole forms an internal electrode and serves as a medium in the process of charge transfer, which facilitates the forth and back charge transfers, furthermore triggering the conversion from WORM to SRAM memory. This work indicates the feasibility of oxadiazole in electronic resistive switching memory and demonstrates the consequence of oxadiazole complexation in the resistive switching memory effects, which would probably attract the interest of academic researchers to prepare desirable memory device by using small molecule oxadiazole species and the memory effect of WORM to SRAM conversion application.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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