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Research paper

Nonvolatile organic resistive switching memory based on poly(*o*-methoxyaniline) film

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ABSTRACT

Resistive switching memories have attracted considerable attention for their potential applications in next-generation nonvolatile memory devices due to high switching speed, high volume storage, low power consumption, and non-destructive readout. In this paper, a controllable and nonvolatile rewritable bipolar organic memory based on the active poly(*o*-methoxyaniline) (POMA) film is demonstrated. The capacitive device structure of Al/POMA/ITO exhibits good bistable resistive switching characteristics with a high ON/OFF current ratio of ~10^3, low switching voltage, good cycling endurance, and long retention time of over 10^4 s. The observed bipolar switching phenomena could be elucidated by the formation and annihilation of conductive filaments, which corresponded to oxidation and reduction of metal Al top electrode and/or POMA polymer molecule chains.

1. Introduction

Resistive random access memories (RRAM) with two terminal cross-bar device structures are one of the most potential alternatives for up-coming nonvolatile memory applications due to their high storage density, low power consumption, good size scalability, simple structure, non-destructive readout, etc. [1–4]. In addition, their exceptional electrical memory performance with high response speed, low operation voltage, and multi-bit storage potential satisfies the requirements well for new emerging memory technologies [5]. One aspect of the electrical bistable resistive memory that has received considerable attention in recent years is organic-based RRAMs due to their material varieties and advantageous properties such as feasible solution-processed fabrication, low cost, large area processing, and flexibility. There are various organic materials that have been found to exhibit resistive switching effect including small organic molecules [6–8], polymers [9–12], π donor–acceptor complexes [13–15], systems containing mobile ions and redox species [16–17], hybrid organic–inorganic systems [18–20], and so on [21–26]. There are also a variety of mechanisms to explain the conductance switching phenomena on the basis of filament formation [1,5], electric field induced charge transfer effect [8,15], charge trapping/detrapping, the potential barrier changing related tunneling effects [12], etc. To date, the continuous research for a stable and reliable resistive switching behavior has resulted in many findings on various material combinations, device configurations, and operating mechanisms.

Conjugated polymer usually possesses the specific physical properties as a semiconducting/conducting material. The π-π interactions between the conjugated groups along polymer molecular chain give the feasible structural control and functionality for the applications on organic electronics. Conjugated polymer poly(*o*-methoxyaniline) (POMA), a derivative of polyaniline (PANI), contains a methoxy (–OCH_3) group in the aromatic ring in the *ortho*-position to the amino group. The presence of the electron donor –OCH_3 substituent increases the processability and solubility of POMA in organic solvents, while maintaining similar optical and electronic properties comparing to PANI [27–29]. With other advantages of low production cost, being environmentally benign, good thermal stability, and robust biocompatibility, POMA has been extensively studied in the applications of electronic, photovoltaic and optic properties [30–34]. However, the studies for POMA (including its composites) focus mainly on the device applications in organic thin film transistors, solar cells, and sensors [35–40]. However, the bistable resistance switching behavior in RRAM memory device with POMA as an active layer has not been explored yet. As known, bistable electrical-switching and the nonvolatile rewritable memory effect have been found in a two-terminal device with PANI or PANI composites as an active layer [17,41]. Having similar structure and electrical property as PANI, PMOA device is expected to exhibit good resistive switching performance. The research for the resistive switching characteristics of POMA-based RRAM devices has a certain significance to broaden the applications of PANI derivatives in organic electronics.

In this study, we report the electrically bistable resistive memory device characteristics based on the conjugated polymeric material of

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POMA. The memory behavior was measured based on a simple metal–polymer–metal configuration of the spin-coated POMA film sandwiched between an aluminum top electrode and indium-tin oxide (ITO) coated glass. The effect of top electrode area on the electrical switching properties was explored, and the resistive switching mechanism was inferred. These results could provide the new insight for high-performance organic electrical memory applications.

2. Materials and methods

POMA used in this study was obtained commercially from Alfa Aesar. A fresh solution of 1 wt.% of POMA dissolved in *N*,*N*-dimethyl formamide (DMF) was spin-coated onto ITO glass substrate at 500 rpm for 5 s and 5000 rpm for 60 s with N_2 blowing. The N_2 blow to the ITO electrode surface can improve the uniformity of POMA layer and accelerate the DMF solvent evaporation during the deposition. Prior to the POMA film deposition, the ITO coated glass was cleaned in acetone, methanol, and finally de-ionized water with ultrasonic cleaning for a duration of 15 min each, and the solution was filtered through a 0.22 μm filter. The spin-coating procedures were repeated four times to yield the desired film thickness of ~50 nm. Prior to the next spin-coating deposition, the POMA film was annealed at 100 °C for 10 min in a vacuum of ~10^{-3} Pa. After the final film deposition, POMA was vacuum annealed for 2 h at the above temperature to enhance the film densification and uniformity. For top electrical contact, Al electrodes with a thickness of 200 nm were deposited on the POMA layer by electron-beam evaporation through a shadow mask. Different electrode diameters ranging from 200 μm, 300 μm, 400 μm, and 500 μm were chosen to investigate the dependence of the conductance switching behavior on the cell area. For bottom electrical contact, the edge of the spin-coated POMA film was removed with acetone to expose the underlying ITO substrate. Fig. 1 shows the schematic of the Al/POMA/ITO device and POMA molecular structure. The electrical characterization of the memory device was performed on an Agilent B1500A semiconductor parameter analyzer under ambient conditions. During electrical measurement, the ITO bottom electrode was grounded, and all electrical biasing was applied onto the Al top electrode. The resultant film morphology and thickness were determined using a NanoScope Multimode and NanoScope Dimension 3100 Atomic Force Microscopy (AFM).

3. Results and discussion

The Al/POMA/ITO structure devices with 50-nm-thick active layer exhibit very interesting bistable electrical behavior. Fig. 2 shows the typical current density-voltage (*J*-*V*) characteristics of a POMA RRAM device with 0.05 V sweeping step. As other RRAM devices, a pre-electroforming process was necessary in POMA memory for stable and reproducible switching characteristics. In the forming process, a strong positive bias on the top Al electrode from 0 to 5 V was applied, turning the device into a low resistance state (LRS) and then a sequence electric stimuli 5 V → 0 V → −5 V → 0 V applied to switch the device back to a high resistance state (HRS) again. However, not all POMA RRAMs have an initial HRS, some memories showed an electrically conductive state (LRS). In any cases, the electroforming process was necessary for the subsequent stable switching operation. In switching property measurement, a negative voltage was first swept from 0 to −3 V (sweep 1) and then returned to 0 V (sweep 2), followed by a positive-voltage sweep from 0 to 5 V (sweep 3) and returned to 0 V (sweep 4) again. In sweep 1, an abrupt increase in current density occurred at a threshold voltage of −1.15 V (V_{SET}), indicating a device transition ("SET" process) from the HRS (OFF) to LRS (ON). The device remained in the LRS in sweep 2 even removing the power supply. Then, a positively biased sweep 3 is applied and program the LRS back to the initial HRS ("RESET" process) with sufficient magnitude of 2.9 V (V_{RESET}). The HRS of the device can be maintained in sweep 4 and re-programmed to the LRS again in the subsequent negative sweeps. The ratio of current ($I_{ON/OFF}$) in HRS to that in LRS of the device is about 10^3 at a read voltage of 0.5 V, which is high enough to promise the low misreading rate through precisely controlling the LRS and HRS states. The operation cycles can be repeated with fairly good accuracy (see inset in Fig. 1) despite minor variation in the SET and RESET voltages, indicating that the POMA device exhibited stable bipolar resistive switching characteristics with low switching voltage.

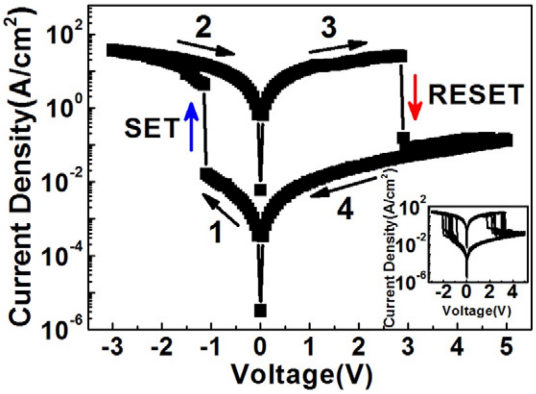

Fig. 2. Typical *J*-*V* curves of Al/POMA/ITO device. The inset shows the *J*-*V* characteristics in 10 switching cycles.

In order to investigate the endurance performance of the Al/POMA/ITO memory, cyclic switching operations were conducted. Fig. 3a and b illustrate the evolution of resistance of the two well-resolved states and the cumulative probability at 0.5 V in 100 cycles, respectively. As shown in Fig. 3a, although the resistance values exhibited some fluctuations in both LRS and HRS, the resistances of HRS and LRS maintained good stability with a ratio of 10^3 and did not show markedly degradation within 100 switching cycles. Fig. 3c and d report the evolution and statistical distribution of V_{SET} and V_{RESET} in 100 switching cycles. When the cell was repeatedly switched between LRS and HRS, the V_{RESET} changed in a range from 1.85 V to 3.8 V, while the V_{SET} changed between −2.1 V and −0.7 V. Fig. 3e displays the retention performance of the memory cell under ambient conditions. Little degradation of the memory device in both the LRS- and HRS-resistances and relatively narrow distribution in both the SET- and RESET-voltages indicate that the switching between the ON and OFF states of the device is reliable. Both the LRS and

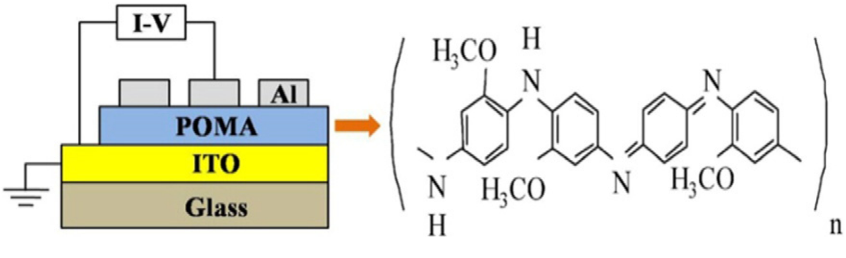

Fig. 1. Schematic of Al/POMA/ITO device and the molecular structure of POMA.