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Flexible resistance memory devices based on Cu/ZnO:Mg/ITO structure

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Resistance memory devices based on a Cu/Mg-doped ZnO/indium-tin-oxide structure on a PET (polyethylene terephthalate) flexible substrate were fabricated. The devices showed stable bipolar resistance switching property and good flexibility. The high to low resistance ratio was larger than 30 times, the endurance was more than 10^2 cycles, and the resistance retention was longer than 10^4 s. The resistance values of both high and low resistance states were not significantly changed by bending in a radius (≥20 mm) for more than 10^3 times. This resistance switching phenomenon of our devices can be explained by creation/rupture of metal conductive channels induced by electrochemical migration of Cu ions.

1 Introduction Flexible electronic devices formed on a flexible substrate are expected to enable future applications that traditional planar integrated circuits cannot provide, such as flexible thin film transistor, flexible liquid crystal panel, and flexible organic light-emitting diode display [1]. As an important part of electronic devices, flexible nonvolatile memory is also needed to be developed. Recently, resistive random access memory (RRAM) has attracted intense attention due to its simple structures, nonvolatile, high scalability, and compatibility to the complementary metal–oxide–semiconductor (CMOS) technology [2]. RRAM utilizes the electric-field-induced resistance switching of a metal–insulator–metal structure between high resistance state (HRS) and low resistance state (LRS) to record information. The resistance switching phenomenon has been found in various materials, such as NiO, TiO_2, CuO_x, ZrO_2, ZnO, etc. [3–7]. These oxides have simple composition and good compatibility with CMOS technology. Furthermore, they can work with polycrystalline structure and therefore can be prepared on various substrates with different lattice constants and orientation, such as glass and plastic substrates. This will allow the design of flexible RRAM devices. Recently, some flexible RRAM devices have been prepared using Al_2O_3, ZnO, and TiO_2 on stainless steel and polyethersulfone (PES) substrates [8–11]. In our previous work, we have studied resistance switching of an indium-tin-oxide (ITO)/Mg-doped ZnO (ZnO:Mg)/F-doped SnO_2 (FTO) structure, where the ZnO:Mg films were deposited by pulsed laser deposition (PLD) at 400 °C [12]. The high deposition temperature will be detrimental to many flexible substrates, especially to the plastic substrates due to their weak heat tolerance. In this letter, a ZnO:Mg/ITO structure was prepared at 80 °C on polyethylene terephthalate (PET) substrate for flexible RRAM application. The resistance switching characteristics and mechanical endurance of the devices were examined and the resistance switching mechanism was discussed.

2 Experiment An ITO bottom electrode of ~300 nm was deposited on PET substrate by a PLD system (KrF eximer laser, $\lambda = 248$ nm) using a commercial ITO ceramic target (In_2O_3:SnO_2 = 9:1) with substrate temperature of 80 °C and oxygen pressure of 0.5 Pa. Then, ZnO:Mg films of ~300 nm thickness were deposited on the ITO/PET substrates by the PLD system using a home-made ceramic target (ZnO:MgO = 8:2) with substrate temperature of 80 °C and oxygen pressure of 10 Pa. Cu and TiN top electrodes were prepared on the ZnO:Mg film surface by the PLD system at 80 °C under vacuum condition (<10^4 Pa) subse-

quently. Au top electrodes were prepared on the ZnO:Mg film surface by an ion sputtering system at room temperature. All electrode sizes were 100 μm in diameter, defined by a shadow mask. X-ray diffraction (XRD), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS) were used to characterize the crystal structure, surface morphology, and oxidation state of the samples, respectively. Current–voltage (I–V) characteristics were measured by the standard two-probe methods, using a computer-controlled Keithley SourceMeter 2611. The voltage that drives the current flowing from top to bottom electrodes is defined as positive.

3 Results and discussion Figure 1a shows a photograph of the Cu/ZnO:Mg/ITO/PET device bended by fingers. Figure 1b shows the XRD pattern of the ZnO:Mg/ITO films on PET substrate. The weak (002)-wurtzite peak and (111) (200)-cubic peaks indicate the coexistence of two phases with weak crystallinity. No diffraction peak of ITO was observed, indicating that the ITO film deposited at 80 °C is amorphous. An SEM image shows that the ZnO:Mg films have uniform grains with the size of ~50–100 nm (see inset in Fig. 1b). The XPS results in Fig. 1c, d show the peaks of Zn $2p_{3/2}$ and Mg 2p at the binding energy of 1022.2 and 49.9 eV, respectively, indicating that Zn and Mg were fully oxidized in the film. The binding energy of Zn $2p_{3/2}$ and Mg 2p lower than 1022.5 eV (Zn–O) and 50.25 eV (Mg–O), respectively, should be due to the existence of Zn–Mg band. The atomic ratio of Zn to Mg, estimated from integrated intensity, is about 3:2, lower than that of the target. That might be caused by the volatilization loss of Zn during the film deposition.

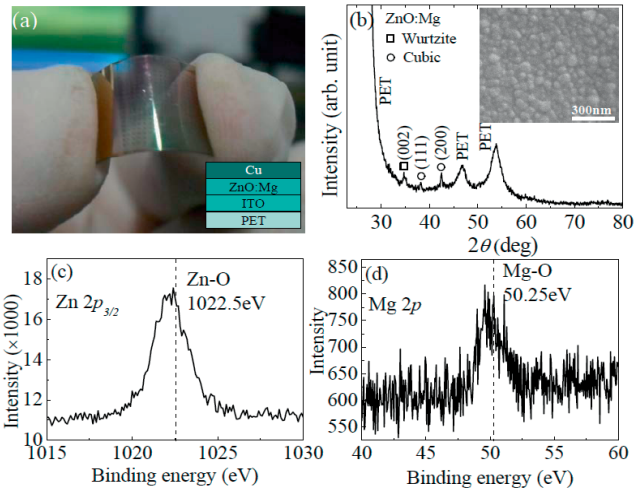

Figure 1 (online color at: www.pss-rapid.com) (a) Photograph of the Cu/ZnO:Mg/ITO/PET device. Inset in (a) shows the schematic diagram of the device structure. (b) XRD pattern of ZnO:Mg films on ITO/PET substrates. Inset in (b) shows SEM image of ZnO:Mg film surface. (c)–(d) Respective XPS spectra of Zn $2p_{3/2}$ and Mg 2p lines.

The I–V characteristics of the Cu/ZnO:Mg/ITO/PET devices were measured by sweeping voltage in the sequence of 0 V → 3 V → 0 V → 1.5 V → 0 V at a speed of 10 mV/s. As shown in Fig. 2(a), the current increased abruptly at $V_{forming}$ = 2.6 V in the first voltage sweep, indicating that the sample resistance was changed to a low resistance state (LRS). The LRS was maintained during sweeping back to 0 V. With sweeping the voltage from 0 V to 1.5 V, the current suddenly decreased at a certain voltage (V_{reset}). Then the device changed to the HRS. In the subsequent sweep, repeatable I–V curves were obtained with a HRS-to-LRS switching voltage (V_{set}) lower than $V_{forming}$. We call the first sweeping from 0 V to 3 V as electroforming process, which activates the resistance switching of the devices. We also performed the negative voltage sweeping initially. However, we could not observe the electroforming process but a permanent breakdown. That means, only the positive voltage can trigger the forming process. Figure 2b shows the retention characteristics of the obtained LRS and HRS at room temperature. At least a HRS/LRS ratio of 30 was maintained for 4 hours. During the continuous resistance switching, both the obtained resistance values (HRS and LRS) and the switching voltage (V_{set} and V_{reset}) have a relatively narrow distribution, as shown in Fig. 2c and 2d. These results indicate a good reliability of our devices for nonvolatile memory application.

The stability of the resistance states against mechanical bending is crucial for application in flexible nonvolatile memories. To demonstrate the flexibility, the devices were tested after being physically bended with a bending apparatus, in which the edges of the devices were gripped and

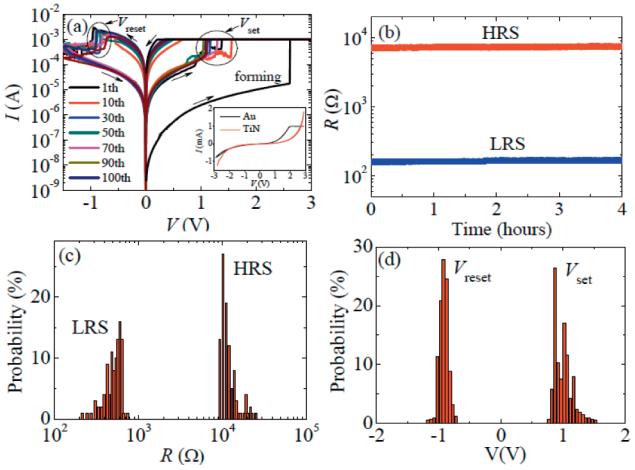

Figure 2 (online color at: www.pss-rapid.com) (a) Semi-logarithmic I–V curves with 100 cycles of voltage sweeping for the Cu/ZnO:Mg/ITO/PET devices. Inset in (a) shows the I–V curves with Au and TiN top electrodes. (b) Retention property of device resistance at room temperature. (c) and (d) show the resistance and the switching voltage (V_{set} and V_{reset}) distribution during 100 cycles of voltage sweeping, respectively. All resistance values were read at 0.1 V.

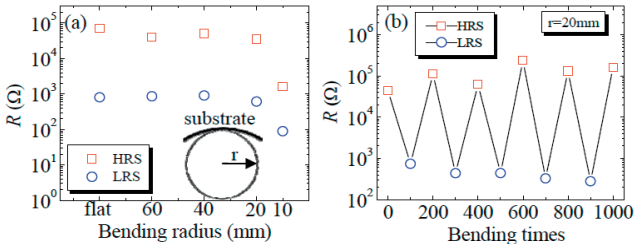

Figure 3 (online color at: www.pss-rapid.com) (a) Resistance retention as a function of bending radius. (b) Resistance switching with bending, in which each resistance was read after 100 times of bending. All resistance values were read at 0.1 V.

then the devices were bended from flat to a half-circle with a radius of r. As shown in Fig. 3a, the obtained HRS and LRS were almost unchanged when decreasing the bending radius to 20 mm. When the bending radius reached 10 mm, both the HRS and LRS resistance decreased. That might be caused by the cracking of the ZnO:Mg films and ITO bottom electrode. The mechanical endurance was evaluated by repeated bending test. During the bending process, the sample was initially triggered to the LRS by applying 1.5 V with time of 0.1 s, bended 100 times, and then the resistance value was read by applying 0.1 V. After that, the sample was triggered to the HRS by applying −2 V with time of 0.1 s and compliance current 1 mA, bended 100 times, and then the resistance value read by applying 0.1 V. Subsequently, the trigger/bend/read cycle described above was repeated. As shown in Fig. 3b, both the HRS and LRS exhibit good endurance against continuous bending for 10^3 times, demonstrating that the devices are still operating after significant bending.

The resistance switching mechanism is still an open question, although many models have been proposed [13, 14]. To study the effects of electrode materials, we prepared Au and TiN electrodes for comparison. As shown in the inset of Fig. 2a, the I–V curves exhibit no hysteresis. That supports the crucial role of Cu top electrode in the resistance switching of our devices. It has been demonstrated that Cu can act as a fast mobile ion in oxides, such as WO_3, SiO_2, and Ta_2O_5, and Cu metal filaments can be formed due to an electrochemical reaction [15–17]. The XRD and SEM results of the ZnO:Mg films show that our films are weakly crystalline with small grain size, indicating that large grain boundaries exist. From these reports and our results, it would be feasible for Cu to diffuse rapidly along the grain boundaries of ZnO:Mg films to form filamentary channels. During the electroforming process, we speculate that the Cu top electrode was oxidized under positive bias and acted as Cu ion source. Driven by the positive electric field, Cu ions moved to the bottom electrode and then were reduced to Cu atoms in the cathode gradually. With Cu atom accumulation, a conductive filamentary channel was created to bridge the top/bottom electrodes. Then the device was switched to LRS. Since Cu can be oxidized easily as the anode and the Cu ion bear positive charge, the electroforming process only occurred under positive bias. When applying negative bias after electroforming, the conductive channel was re-oxidized and the Cu ions moved back to the top electrode, resulting in rupture of the conductive channel. Thus the device was restored to the HRS. Compared with Cu, it is difficult for Au to be oxidized and then diffuse in the films. Therefore, the conductive channel cannot be electroformed in the Au/ZnO:Mg/ITO devices. TiN can be easily oxidized and often plays a role of oxygen reservoir in oxygen defect based resistance switching systems [18]. However, no resistance switching occurred in our devices with TiN top electrode, implying that oxygen-related defects, such as oxygen vacancies, might not play the dominant role for resistance switching in our devices.

4 Conclusion Flexible resistance memory devices have been fabricated by sandwiching ZnO:Mg films between Cu and ITO electrodes on a PET substrate. In addition to good repeatable and stable resistance switching, the devices exhibit good flexibility and mechanical endurance. A possible switching mechanism was presented based on the creation/rupture of a Cu conductive channel induced by electrochemical migration of Cu ions. This flexible device gives RRAM a promising application in flexible electronic systems.

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