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Electroforming-free resistive switching memory effect in transparent *p*-type tin monoxide

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We report reproducible low bias bipolar resistive switching behavior in *p*-type SnO thin film devices without extra electroforming steps. The experimental results show a stable resistance ratio of more than 100 times, switching cycling performance up to 180 cycles, and data retention of more than 10³ s. The conduction mechanism varied depending on the applied voltage range and resistance state of the device. The memristive switching is shown to originate from a redox phenomenon at the Al/SnO interface, and subsequent formation/rupture of conducting filaments in the bulk of the SnO layer, likely involving oxygen vacancies and Sn interstitials. © 2014 AIP Publishing LLC.

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Resistive switching (RS) memory devices have been intensively studied recently for next generation nonvolatile memory applications. This type of memory is attractive due to its low operating power, high density, and high switching speed.^{1,2} Since its discovery in 1960s, several materials have been studied as RS media, such as perovskites,³ solid electrolytes,⁴ binary transition metal oxides,⁵ organics,⁶ bio-materials,⁷ etc. Different RS characteristics have also been observed including bipolar and unipolar switching. However, the oxide resistive memory research has mostly focused on *n*-type semiconducting oxides, and therefore RS devices with reasonable performance have been limited to *n*-type materials. Although the RS performance of *p*-type oxides have received less attention than *n*-type oxides, several studies in fact have already been published using oxides, such as Cu₂O, NiO, CuAlO_x, and Co₂O₃, for RS applications.^{8–11}

Recently, *p*-type oxides have attracted great attention due to their potential advantage in some applications such as gas sensing and low-power transparent complementary logic circuits.^{12,13} It is therefore important to investigate if the RS phenomenon exists in these oxides and to explain their behavior. Among few *p*-type oxide materials, tin monoxide (SnO) is attractive owing to its relatively high mobility compared to other *p*-type oxides, an effect that is due to its hybridized orbitals and increased dispersion at the top of the valence-band.^{14,15} There have been no reports on RS behavior in SnO. Therefore, we have investigated the RS effect in SnO and have been able to demonstrate that RS does in fact occur in *p*-type SnO films. Furthermore, we propose a mechanism to explain the underlying physico-chemical phenomena involved in the RS behavior of SnO.

The fabrication process starts with the cleaning of indium-tin-oxide (ITO) coated glass substrates sequentially with acetone, 2-propanol, and DI water in an ultrasonic bath for about 5 min each. A thin SnO film (~30 nm) was then deposited by DC reactive sputtering using a Sn target at

room temperature with 20 W DC power in 13% oxygen at a base pressure of 1.8 mTorr (0.24 Pa). Finally, the top electrode was defined by depositing ~80 nm thick Al film using thermal evaporator system through a shadow mask having an area of $\sim 1.96 \times 10^{-3} \text{ cm}^2$ to complete the full device structure, as shown in inset of Fig. 1. The optical transmittance, X-ray diffraction (XRD), and Raman spectrum of the SnO films were measured using Evolution 600 UV-VIS spectrophotometer (Thermo Scientific), Bruker D8 Discover thin film X-ray diffractometer, and Horiba aramis UV spectrometer, respectively. The electrical properties were measured using Keithley 4200 semiconductor parameter analyzer in voltage sweeping mode at room temperature. All of the operating voltages were applied on the top electrode (Al), while the ITO bottom electrode was grounded.

Figure 1 shows the optical transmission spectrum (from 300 to 800 nm) of the as-deposited SnO films on ITO coated glass substrate. The baseline transmission was corrected using a similar ITO coated glass substrates. A high transmittance of more than 90% was obtained across most of the visible region, which established the film to be transparent. The XRD patterns of the as deposited and thermally annealed (200 °C for 30 min in air) SnO thin films are shown in Fig. 2(a). A number of diffraction peaks are observed, indicating that the films are polycrystalline. The most intense peak observed comes from the (101) planes at $2\theta = 29.77^\circ$ which is consistent with the formation of the tetragonal phase ($a = b \neq c$) of SnO with lattice constants of $a = 3.8 \text{ nm}$ and $c = 4.848 \text{ nm}$ (JCPDS 00-055-0837). The sharp, strong diffraction peaks indicate good crystallinity of the annealed SnO film. The lack of SnO diffraction peaks in the as-deposited film suggests it's amorphous in nature. The relatively minor and broad peaks at 43.2° and 63.8° , observed in both the as-deposited and annealed films are attributed to small amount of metallic tin, (JCPDS 03-065-0296), consistent with our previous study.¹³ The Raman active phonon modes were investigated in the as-deposited and annealed SnO film, as shown in Fig. 2(b). Two sharp peaks can be observed, one at 113.2 cm^{-1} and the other at

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FIG. 1. Experimentally measured transmission spectrum of SnO thin film (~ 30 nm) deposited on glass/ITO substrate. Inset shows schematic device structure of the SnO based RS devices used in this study.

211.1 cm^{-1} corresponding to the A_{1g} and B_{1g} vibrational modes, respectively, for the tetragonal SnO structure, which is consistent with the previously reported results.^{16,17}

Typical hysteretic current-voltage characteristics obtained from the as-deposited SnO RS device are shown in Fig. 3(a). During the measurements, the current compliance was limited to 10 mA to protect the device from permanent (hard) breakdown and the applied voltage was swept in the sequence of $0 \rightarrow -4 \text{ V} \rightarrow 0 \rightarrow +4 \text{ V} \rightarrow 0$. Initially, the virgin device was in OFF-state, i.e., in high resistance state (HRS, arrow 1). When the applied voltage was swept from 0 to -4 V , the injection current abruptly increases by a factor

FIG. 2. (a) X-ray diffraction patterns and (b) Raman spectrum obtained from as-deposited and annealed SnO films.

FIG. 3. (a) Bipolar reversible and nonvolatile RS characteristics of as-deposited SnO memory device and variation of the V_{SET} and V_{RESET} during the DC switching cycling measurement (inset). (b) Current conduction mechanism in double log scale and P-F plot of the HRS state at higher voltage region (inset).

of around 10^2 at $\sim -0.8 \text{ V}$ (V_{SET}) and the low resistance state (LRS) or ON condition is achieved (arrow 2). The ON state of the device retains its low resistance value during the reverse negative voltage sweep and also under positive voltage sweep (arrows 3, 4, and 5) up to $\sim 2.2 \text{ V}$ (V_{RESET}). After that, a sudden increase in the resistance occurs beyond V_{RESET} , resulting in low value of the leakage current (arrow 6) and this situation holds until the V_{SET} again is applied to the device (arrows 7 and 1). Since, the SET and RESET process occurred in opposite polarity sides, the RS performance is clearly clock-wise bipolar in nature. Importantly, no significant RS behavior observed from the annealed SnO devices (see supplementary material, Fig. S1).¹⁸

Normally, an electroforming process is necessary to switch “ON” the RS devices; however, here the switching properties were observed without extra electroforming steps. Hence, it may be assumed that a self-electroforming process occurs during the DC voltage sweep in these SnO devices. The underlying mechanism of the electroforming-free RS behavior and its relationship to the microstructure of SnO are not very clear at this point. However, we believe that the presence of small amount of metallic Sn and Sn interstitials (Sn_i^{2+}) play a critical role in the electroforming-free RS behavior in SnO memory devices. The low DC voltage value needed to switch these devices, together with the fact that no extra forming process is needed, makes these devices attractive for low power consumption applications.¹⁹ Furthermore, it can be observed that after 180 DC switching cycles the current values of HRS in either polarity are higher than the first DC sweep cycle, while the current values in LRS is almost the same, as shown in Fig. 3(a). On the other hand, the values of V_{SET} and V_{RESET} differ from their previous

values during the DC switching cycles, as shown inset of Fig. 3(a). The V_{SET} and V_{RESET} values were distributed in the range of -0.46 V to -1.88 V and 1.45 V to 2.99 V, respectively, which shows randomness in the HRS to LRS or LRS to HRS transition. These broad distributions of the SET and RESET voltages signify the formation and rupture of the conductive filaments. However, the average V_{SET} and V_{RESET} were found ~ -0.7 V and ~ 2.3 V, respectively. Both of these effects can be explained by the existence of residual filaments in the SnO film during the cyclic measurement, as will be discussed later. However, the key point that should be highlighted here is that this previously unreported bi-stable RS effect in SnO is reversible and stable.

To gain an insight into the conduction and switching mechanisms for both LRS and HRS, the hysteretic I - V characteristics are re-plotted on a log-log scale, as shown in Fig. 3(b). It can be observed that slope of the $\ln |I|$ versus $\ln |V|$ curve (denoted as A) is close to unity in the LRS. In contrast, the slope (denoted as B) of the HRS is close to unity only in the low voltage region, which suggests an Ohmic type conduction process. However, it can be observed that the conduction mechanism of HRS in the higher voltage region is different. The slope of the line in this region (denoted as "C"), is around 1.5, which indicates that conduction in this high voltage region is not Ohmic. To determine the nature of the conduction mechanism in the high voltage region, the current-voltage characteristics are plotted in $\ln(I/V)$ vs. $\text{Sqrt. } V^{1/2}$, as shown in inset of Fig. 3(b). Now, it can be clearly seen that a linear relationship is obtained, which indicates that the Poole-Frenkel (P - F) conduction may be dominating in this region.²⁰ Hence, it may be concluded that multiple conduction mechanism exists in ITO/SnO/Al memory structure, depending on the memory state.

Next, the DC switching cycling and retention performance of the SnO RS devices were evaluated. Figure 4(a) shows 180 times sweeping cycles operation in a consecutive mode for the SET and the RESET operations, with a READ voltage of $+1$ V. The average value of HRS/LRS ratio is found to be $\sim 10^2$ during the whole test without noticeable degradation. The values of LRS are found to be almost constant during the cycling test, while the HRS values are found to fluctuate. On the other hand, during the retention tests as shown in Fig. 4(b), both LRS and HRS exhibit robust stability and show undetectable signs of degradation even after 10^3 s at room temperature, confirming the nonvolatile nature of these devices. Hence, this device not only holds well under the switching cycling test but also shows good retention characteristics. These results imply that SnO based RS devices have good nonvolatile memory characteristics.

In order to understand the RS memory behavior in SnO, we studied memory performance as a function of electrode materials and found that the electrode/SnO interface plays a critical role. Specifically, good and stable resistive switching behaviors were observed in the case of Al as top electrode (Fig. 3(a)), but no significant RS properties were observed in the case of Pt and Ag top electrodes (see supplementary material, Fig. S2). To explain the electrical behavior and electrode dependence in our RS memory devices, we note the following: it has been reported that ITO, which is used as

FIG. 4. (a) DC Switching cycling test and (b) retention characteristics of the ITO/SnO/Al memory structure.

bottom electrode in all our devices, acts as a source or reservoir of oxygen ions (O^{2-}) and oxygen vacancies.²¹ Hence, under the application of a positive bias on the top electrode, migration of the O^{2-} towards the Al/SnO interface is expected and as a result Al should become partially oxidized at the Al/SnO interface via an oxidation process ($Al + O^{2-} \rightarrow AlO_x$), leading to the formation of very thin AlO_x interfacial barrier layer, as illustrated in Fig. 5(a) and as has been previously observed in other oxide systems.²² This type of reaction is expected since the standard Gibbs free energy (ΔG) for formation of Al_2O_3 ($\Delta G \sim -1582.3$ kJ/mol)²³ is far lower than that of SnO ($\Delta G \sim -251.9$ kJ/mol),²³ which leads to this interfacial oxidation process. Hence, formation of higher band gap barrier layer (AlO_x) as compare to SnO at the interface results in the lower value of current in HRS state. In contrast, the poor RS behavior in case of Pt and Ag top electrodes is believed to be due to the absence of such

FIG. 5. Illustration of the proposed physical model to explain the switching mechanism in SnO based RS device for (a) HRS and (b) LRS state.

interfacial barrier layer, since both of these electrodes have higher ΔG of oxide formation than SnO ($\Delta G \sim 167.8$ kJ/mol for PtO₂ and $\Delta G \sim -11.20$ kJ/mol for Ag₂O).²³

Under the application of a negative bias on the top Al electrode, we observe that the conductivity of the device increases significantly (arrow 2 in Fig. 3(a)). One possible explanation for this behavior is that during the application of negative bias on Al top electrode, a reduction process may lead to O^{2-} release from the interface and ultimately dissolution of the AlO_x barrier layer occurs ($AlO_x \rightarrow Al + O^{2-}$), which leads to increase the current in LRS state (Fig. 5(b)). An additional factor that may contribute to the abrupt increase of current in LRS is the formation of conducting filaments (CFs), which is a commonly reported phenomenon in oxide-based resistive switching devices.²⁴ This filament formation concept is illustrated in Fig. 5(b) and can be explained from our previous study as well as from literature reports. It has been reported that Sn interstitials (Sn_i^{2+}) and O vacancies (V_o^{2+}) are the two most common defects present in SnO.^{14,15} Hence, we surmise that migration of Sn_i^{2+} and V_o^{2+} towards the top electrode takes place during the application of negative bias on the top electrode. Furthermore, it is possible that sufficiently large numbers of these positively charged defects are accumulated to the point where a CF that traverses the entire film thickness may be formed at a critical value of negative bias (V_{SET}).²⁵ It has been reported that each CF behaves like a metallic wire due to the existence of high charge carrier concentration in each filament and hence Ohmic-like conduction can be observed during the LRS.^{26,27} Hence, we surmise that the abrupt change in the conductivity of the device due to the formation/rupture of conducting filaments. Since, the current in LRS state is controlled by these stable CFs, the resistance values in LRS are found to be stable compared to the HRS state during the switching cycling measurements. However, during the application of positive bias on top electrode (arrow 6 in Fig. 3(a)) a transition to the HRS starts (beyond V_{RESET}), and re-arrangement of Sn_i^{2+} and V_o^{2+} occurs by means of moving away from the top electrode, leading to the dissolution/rupture of the CFs.

The precise nature of how these filaments rupture cannot be discerned directly in these samples, but it has been suggested that filament rupture in oxide RS memories is localized in the middle portion of the filaments (with respect to its length) due to a Joule heating mechanism.²⁸ In this process, all filaments may not dissolve completely, resulting in the existence of residual small filaments during the HRS state (Fig. 5(a)). These residual CFs are directly involved in the conduction process and result in the Ohmic-like conduction observed in our samples in the low-field region of the HRS state.²⁹ However, it appears that such concentration of residual CFs in consecutive RS cycles may not be identical, which may explain the observation of dispersion in the resistance values in HRS.³⁰

In summary, RS behavior has been observed in *p*-type SnO thin film devices. A reasonable memory performance was observed for this *p*-type semiconductor with HRS/LRS ratio of $\sim 10^2$, more than 10^3 s retention times, DC switching cycling stability, and low voltage operation. It is observed that the conduction mechanism in the LRS is Ohmic over the

entire voltage range. In contrast, the HRS shows a transition from Ohmic to Poole–Frenkel conduction at high voltage. This previously unreported RS effect in SnO could be explained by a filament model involving the exchange and migration of oxygen and Sn interstitials along with the interfacial effect.

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