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Studies on nonvolatile resistance memory switching in ZnO thin films

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Abstract. Six decades of research on ZnO has recently sprouted a new branch in the domain of resistive random access memories. Highly resistive and *c*-axis oriented ZnO thin films were grown by us using d.c. discharge assisted pulsed laser deposition on Pt/Ti/SiO_2/Si substrates at room temperature. The resistive switching characteristics of these films were studied in the top-bottom configuration using current–voltage measurements at room temperature. Reliable and repeated switching of the resistance of ZnO thin films was obtained between two well defined states of high and low resistance with a narrow dispersion and small switching voltages. Resistance ratios of the high resistance state to low resistance state were found to be in the range of 2–5 orders of magnitude up to 20 test cycles. The conduction mechanism was found to be dominated by the Ohmic behaviour in low resistance states, while Poole–Frenkel emission was found to dominate in high resistance state. The achieved characteristics of the resistive switching in ZnO thin films seem to be promising for nonvolatile memory applications.

Keywords. ZnO thin film; pulsed laser deposition; resistive switching; nonvolatile memories.

1. Introduction

Current research to find alternative materials for nonvolatile memories focuses on accomplishing greater packing density, faster switching rate, lower power consumption and low voltage operation compared to the commonly used MOS transistor based flash memory devices. Some of the recently emerged ideas in this domain are silicon–oxide–nitride–oxide–silicon based memory (SONOS) (White *et al* 2000), magneto-resistive random access memory (MRAM) (Akerman 2000), ferroelectric random access memory (FeRAM) (Scott and Paz de Araujo 1989), conducting-bridge random access memory (CBRAM) (Kund *et al* 2005), phase change random access memory (PRAM) (Lai 2003) and resistive random access memory (RRAM) (Choi *et al* 2005). The SONOS memory devices are similar in structure to MOS transistor based flash memory with the exception that they have a silicon oxide and silicon nitride sandwich layer structure as the gate oxide. Charge is stored in deep level traps in the oxide–nitride sandwich layer structure. The SONOS memories have a lower programming voltage and a higher operational endurance than conventional polysilicon based flash memories. The MRAM utilizes the switching of resistance of the structure containing a thin insulating layer sandwiched between two magnetic layers, on application of an external magnetic field. The FeRAMs are designed by replacing the dielectric layer of a MOS capacitor with a ferroelectric layer to achieve non-volatility. The CBRAMs, also known as programmable metallization cell (PMC), are based on the change in the resistance of the solid thin film electrolyte sandwiched between two electrodes due to relocation of ions on application of an appropriate electric field and the PRAMs are based on the principle of switching of the phase of chalcogenide glasses between two structural states viz. crystalline (usually low-resistance state) and amorphous (usually high-resistance state), with the application of heat produced by the flow of electric current. Far from all these memory systems the RRAM or resistive random access memories rely on the simple phenomenon of resistance switching observed in the specific form of the thin films of some of the metal oxides such as ZrO_2 (Wu *et al* 2007), TiO_2 (Choi *et al* 2005), NiO (Seo *et al* 2004), MnO_2 (Zhang *et al* 2009) and recently, ZnO (Chang *et al* 2008). Some of the perovskite oxides such as $SrTiO_3$ (Beck *et al* 2000) also show this phenomenon. The current–voltage (I–V) characteristics of these metal oxides show extreme changes in resistance between high and low resistance states on application of suitable bias voltage. The phenomenon of the resistance change in RRAM differs from that observed in PRAM in the sense that there is no phase change involved in the thin film of the material during switching between the low and high resistance states (Choi *et al* 2005). The advantages of RRAM systems over the other competing modes are the lower operating voltages and power consumption, faster switching rate, smaller and simpler bit cell structure and higher packing density (Chang *et al* 2008).

Amongst the known metal oxides currently being explored for the development of RRAM, ZnO has been demonstrated to be a potential candidate primarily due to

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its abundant availability in nature, rugged structural and chemical behaviour, highly evolved growth technologies, environmental friendliness and compatibility with complementary metal oxide semiconductor technology. ZnO has direct and wide bandgap of ~3·3 eV at room temperature and is thus highly transparent in visible spectral region. It is nominally *n*-type degenerate semiconductor but its conductivity can be tailored in a broad range from metal like to insulator like by suitable impurity doping or controlling the nature and concentration of point defects due to control on the growth methodology. Therefore, it is possible to develop a fully transparent RRAM entirely based on ZnO and its variants. In recent past there have been some reports on the resistance switching behaviour in ZnO thin films (Chang *et al* 2008); however, a clear understanding of the switching mechanism and underlying physical and chemical processes responsible for this exciting observation are still the areas of thorough studies. In this report we have investigated the resistance switching characteristics of highly resistive ZnO thin films grown by d.c. discharge assisted pulsed laser deposition as a first step towards the development of transparent nonvolatile resistive random access memory devices based completely on ZnO. The results of these studies are presented and discussed in detail in this paper.

2. Experimental

ZnO thin films of thickness, ~90 nm, were grown on commercially obtained Pt/Ti/SiO_2/Si substrates using an in-house developed variant of the pulsed laser deposition (PLD), which was based on the controlled d.c. discharge in oxygen ambient. The deposition chamber was initially evacuated to a base pressure of $\sim 1 \times 10^{-6}$ Torr using a turbo molecular pump and then filled with oxygen ambient at a partial pressure of $\sim 2{\cdot}0 \times 10^{-2}$ mbar during the deposition. It was known that the normal PLD grown ZnO films show high *n*-type conductivity without any intentional doping presumably due to non-stoichiometry i.e. presence of oxygen vacancies (Kukreja *et al* 2008) as one of the possibilities. To achieve highly resistive ZnO, it is, therefore, imperative to replenish these oxygen vacancies in grown ZnO thin films either through post annealing treatment or somehow during the growth itself. We used a novel in-house developed d.c. discharge assisted PLD scheme to grow insulating ZnO films (Misra *et al*, to be published). The electric discharge in oxygen ambient at a partial pressure of $\sim 2{\cdot}0 \times 10^{-2}$ Torr in the PLD chamber was struck by applying a positive d.c. voltage of ~800 V on an interposing copper electrode with respect to the growth chamber which was kept at ground potential. The discharge in the oxygen ambient appeared uniformly spread inside the entire PLD chamber. The 3rd harmonic of a *Q*-switched Nd : YAG laser (355 nm, 10 Hz and 6 ns) was used at a fluence of ~1 J/cm^2 for the deposition of the ZnO thin films. All the depositions were carried out at room temperature. ZnO target used in the depositions was made by pelletizing high purity (99·999%) powder of ZnO which was subsequently sintered at 1200°C for 2 h to get a high density pellet. The structural characteristics of the grown ZnO layer were studied using high resolution X-ray diffraction (Phillips HRXRD) and atomic force microscopy. The current–voltage characteristics of the grown ZnO film were investigated using Keithley 206 measurement unit in the top-bottom configuration. For that the top contact was made by placing a platinum pressure contact of a tip of ~250 micron diameter on the ZnO films whereas the bottom platinum layer of substrate acted as the bottom contact. The direction of current flow was kept from top to bottom electrode and the measurements were carried out in voltage sweeping mode.

3. Results and discussion

The $\omega - 2\theta$ scan of high resolution X-ray diffraction (HRXRD) from the ZnO thin films grown on Pt/Ti/SiO_2/Si substrates at room temperature using the aforesaid d.c. discharge assisted PLD is shown in figure 1. The diffraction peaks corresponding to the ZnO (0002) plane of the grown film and that of Pt and Si originating from the substrate can be seen in the diffraction pattern indicating purely *c*-axis oriented growth of the ZnO films. The (0002) peak of ZnO was found to be rather broad indicating presence of structural defects and other inhomogeneities, which are expected because of the much lower temperature during the growth compared to the optimum value of ~750°C (Misra and Kukreja 2004). The atomic force micrograph of a typical ZnO film grown through this methodology is shown in figure 2. The surface topogra-

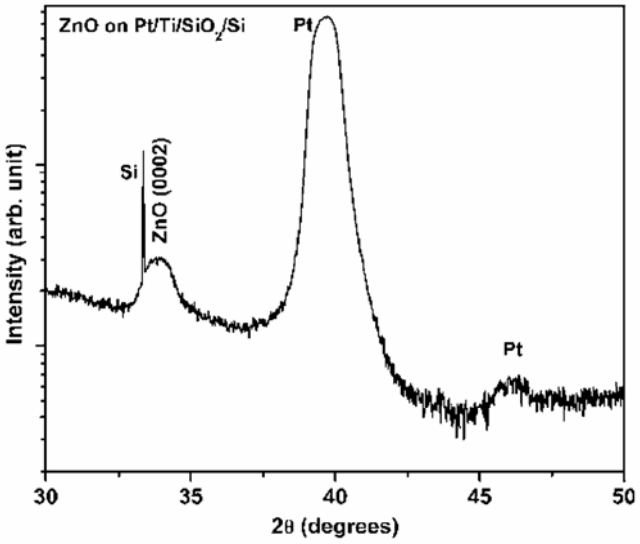

Figure 1. $\omega - 2\theta$ scan of HRXRD of ZnO thin film grown on Pt/Ti/SiO_2/Si substrate.

phy indicates particulate free surface with irregularly shaped columnar grains of average size of ~ 50 nm.

The resistance of the ZnO thin films was measured in top bottom configuration through room temperature *I–V* measurements. The as grown ZnO thin film was found to be in a high resistance state (~ 30 kΩ measured at ~ 0·16 V) and did not show any resistance switching behaviour until the applied bias voltage was increased to ~ 3·5 V. At that voltage the resistance of the ZnO film was found to drop suddenly to a low value of ~ 30 Ω (measured at ~ 0·16 V). This is the low resistance state (LRS) of ZnO film and the process is known as the initial forming process wherein the virgin ZnO thin film is transformed from its initial high resistance state (HRS) to LRS on application of an external bias voltage known as the initial forming voltage (Seo *et al* 2008). During this initial forming process current compliance was kept fixed at 5 mA to avoid the breakdown or burning of the ZnO film due to high current flow in low resistance state. The low resistance state of ZnO once formed persisted even when the applied voltage was reduced to zero. The initial forming voltage of ~ 3·5 V in our case corresponds to an applied electric field of ~ 0·39 MV/cm across the ZnO film, which compares favourably with the recently reported forming voltages in ZnO films of nearly similar thickness by Chang *et al* (2008) and much smaller than those reported for other metal oxides (Lee *et al* 2007; Wu *et al* 2007).

After this initial forming process which renders the ZnO film in low resistance state, the voltage was again swept from 0 to 1·1 V in small steps while measuring the current. A sudden drop in current was observed at a voltage of ~ 0·55 V indicating abrupt increase in the resistance of ZnO film and switching from low resistance state into high resistance state. This is known as the 'reset' process (Chang *et al* 2008) and the resulting HRS of ZnO film remained preserved even when the applied bias voltage was removed. In the high resistance state again as the voltage was swept from 0 to 2·0 V, a sudden drastic increase in current was observed at ~ 1·8 V i.e. the resistance decreased drastically and the ZnO film again switched into LRS state. This is called the 'set' process (Chang *et al* 2008). During the set process current compliance was set at 10 mA to protect the ZnO film from permanent damage. The current compliance is very important and merely changing this parameter during the set process can change the resistance of the LRS. In the LRS state by sweeping the voltage from 0 to 1·0 V again, the reset process could be repeated and the ZnO film switched to HRS. Similarly by sweeping the voltage from 0 to 2·5 V after the reset process the device could again be set back to LRS. The *I–V* characteristics of ZnO film for the two consecutive set and reset processes after the initial forming process is shown in figure 3. Thus the resistance of the ZnO film can be switched between two states of low and high resistance repeatedly by sweeping the applied voltage.

By repeating the set and reset processes over 20 cycles it was observed that the reset voltage is spread (not shown in figure 3) over a small window of voltage between ~ 0·55 and 0·71 V. This reset voltage observed in our device is less than the reported values for Pt/ZnO/Pt capacitor (Chang *et al* 2008). By contrast, the set voltage was seen to have a comparatively larger spread over the 20 cycles of testing between ~ 1·5 and 2·5 V. However, these values of reset and set voltages clearly show a non-overlapping window of operational voltages between the two resistance states i.e. LRS and HRS, which is essential for the nonvolatile RAM applications. The observed resistive switching phenomenon is fully reversible and repeatable provided that the current compliance is correctly set.

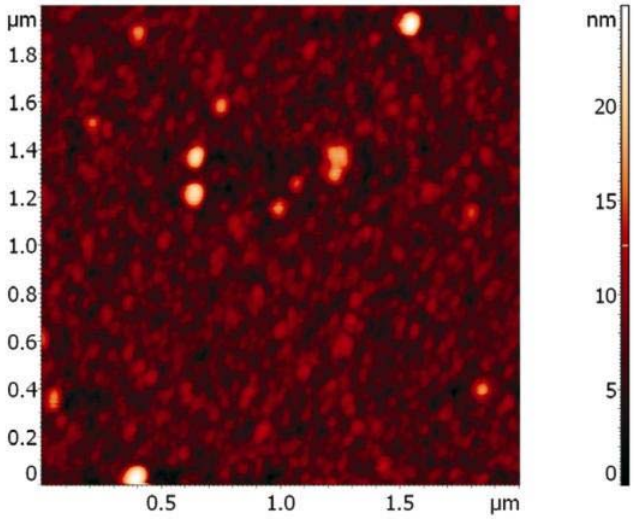

Figure 2. Atomic force micrograph of the ZnO film grown on Pt/Ti/SiO_2/Si substrate.

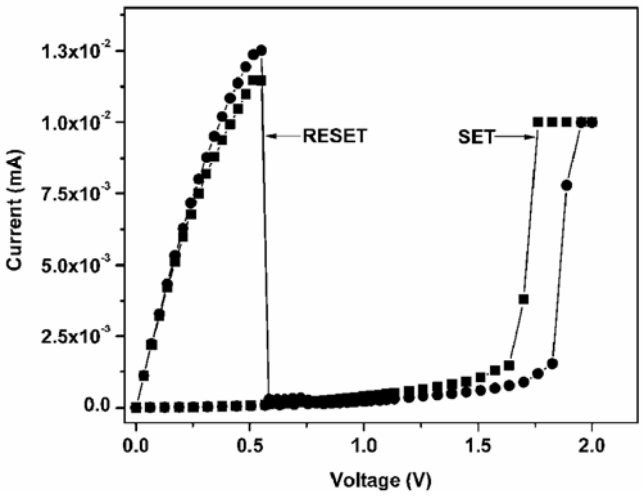

Figure 3. Current–voltage (*I–V*) plot of ZnO thin film showing resistive switching.

The mechanism of the resistance switching in ZnO thin film is not yet fully understood in the literature. One of the models that have been adopted by a number of researchers to explain the resistive switching behaviour of various metal oxide films such as TiO_2, NiO, CuO, ZnO and MgO etc is the filamentary model (Choi *et al* 2005). In this model the switching between the low and high resistance states of material has been ascribed to the creation and subsequent rupture of conducting filaments which are distributed throughout the film material (Choi *et al* 2005). Conducting filaments are a kind of extended defects in insulating ionic crystals which can be created by the alignment of the pre-existing as well as the field induced structural defects such as oxygen vacancies, Zn interstitials and dislocations etc along the grain boundaries due to the presence of a strong electric field during the initial part of the formation process. On application of electric field, charge trapped in these aligned defects can overcome the defect potential and the filaments conduct current (Seo *et al* 2008). Since these filaments are metal-like in nature, current flow suddenly increases manifolds and initially an insulating material in HRS switches to LRS. In LRS the current through the material increases rapidly with increasing bias voltage till the reset voltage (V_{reset}) is reached. At this voltage, it is believed that the current flow through the filaments is large enough so that the corresponding Joule heating can rupture most of the conducting filaments bringing the material in HRS. This explains the switching from LRS to HRS (Choi *et al* 2005). However, some tiny filaments can still exist in the material even in the HRS as reflected by the finite resistance of material. As the bias voltage is again increased to the set voltage, these tiny filaments could grow leading to the switching from HRS to LRS.

To understand the current conduction mechanisms in LRS and HRS of ZnO in view of the aforesaid filamentary model, the corresponding I–V graphs were plotted in log–log scale. Figure 4 shows the I–V plot of ZnO thin film in the LRS in a double logarithmic scale. It can be seen from figure 4 that in the low voltage region (< 0·2 V) the I–V characteristic is linear with the slope of ~ 0·95 indicating metal like ohmic conduction. However, at higher bias voltages (> 0·2 V), the I–V curve showed slight deviation from the initial linearity. Such a deviation from linear I–V characteristics at high voltages has been observed by others also (Kim and Hwang 2009) and can be attributed to the heating induced increase in the resistance of metal like conducting filaments before the onset of rupture process due to excess heating, which leads the film to HRS (Kim and Hwang 2009). The I–V characteristic of ZnO film in the HRS plotted in double logarithmic scale is shown in figure 5. As can be seen in figure 5, the I–V characteristic in HRS of ZnO is also linear in the low voltage regime like that in LRS. The linear I–V characteristic of ZnO in HRS can be attributed to the presence of small concentration of leftover conducting filaments even after the rupture process (Seo *et al* 2004). However, at higher bias voltages the I–V characteristic showed nonlinear behaviour. This nonlinear I–V characteristic and the corresponding conduction mechanism of ZnO film in HRS at higher electric field can be explained by the Poole–Frenkel (P–F) emission mechanism (Frenkel 1938). According to P–F emission mechanisms the functional form of the current density (J) is given by

$$\ln(J/E) \propto \exp(\sqrt{e^3/\pi\varepsilon_0\varepsilon_r}/rkT) \times E^{1/2}, \quad (1)$$

where E is the applied electric field, e the electronic charge, ε_r the dynamic dielectric constant of the material, ε_0 and k are, respectively permittivity of free space and Boltzmann's constant, T the temperature and r the coefficient ranging between 1 and 2 (Yeargan and Taylor 1968). For $r = 1$, the conduction mechanism is called normal PF effect while $r = 2$ corresponds to the trap modified P–F effect and generally occurs in insulators containing some amount of traps. The plot of $\ln(J/E)$ vs $E^{1/2}$ for the ZnO films in high voltage regime has been shown in the inset of figure 5. The linear fit of the straight portion of this graph gives a slope of $\sim 7{\cdot}1 \times 10^{-4}$ SI unit. From the slope of the linear $\ln(J/E)$ vs $E^{1/2}$ relation, the dynamic dielectric constant, ε_r and hence refractive index (n) of the material can be estimated using the well known relation, $n = \sqrt{\varepsilon_r}$. The refractive index obtained from the fitting of the modified P–F emission in our case was ~ 2·04, which is in close agreement with the experimentally observed values of refractive index of ZnO (Yeh 1988). Therefore, the conduction mechanism in HRS in the high voltage or field regime resembles well with the trap modified P–F emission. This is possible since the ZnO films grown at room temperature generally contain a considerable amount of point and structural defects which may act as carrier traps during the conduction process.

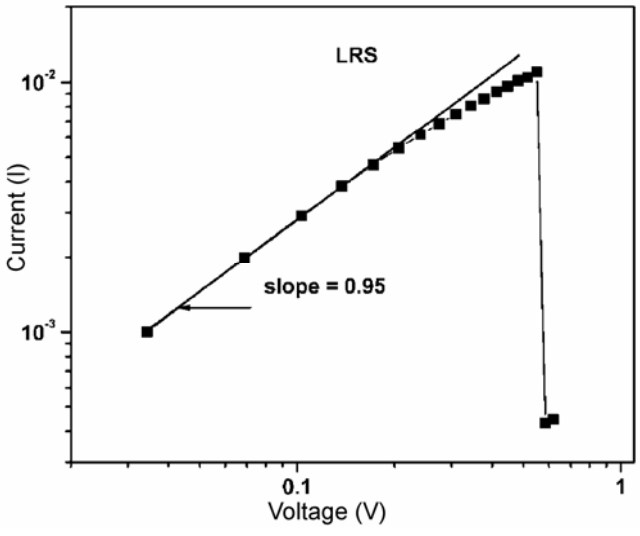

Figure 4. Log–log plot of current–voltage (I–V) of ZnO film in LRS.

The resistances of the ZnO thin film in the two well resolved states of LRS and HRS were measured at a bias voltage of 0·16 V for different switching cycles to study the device endurance, which are shown in figure 6. It can be seen that the resistances of ZnO film in LRS at different switching cycles up to 20 were pretty steady at around ~ 30 Ω, while in HRS the resistance of ZnO film varied in the range of ~ 1·5 kΩ–1·5 MΩ. The large fluctuations in the resistance of ZnO film in the HRS with switching cycles has also been observed by others (Chang *et al* 2008) and can be explained in terms of the aforementioned filamentary model of the resistive switching phenomenon. According to this model, it is likely that the reset process may not completely rupture all the conducting filaments formed during the set process. Some tiny filaments may still persist in HRS even after the reset process and their number may vary at different switching cycles, thereby providing significant variation of the resistance with switching cycle. In spite of this large fluctuation in the resistance of ZnO film in HRS, there exists a non overlapping window of resistances between LRS and HRS of ZnO film which is suitable for nonvolatile memory applications.

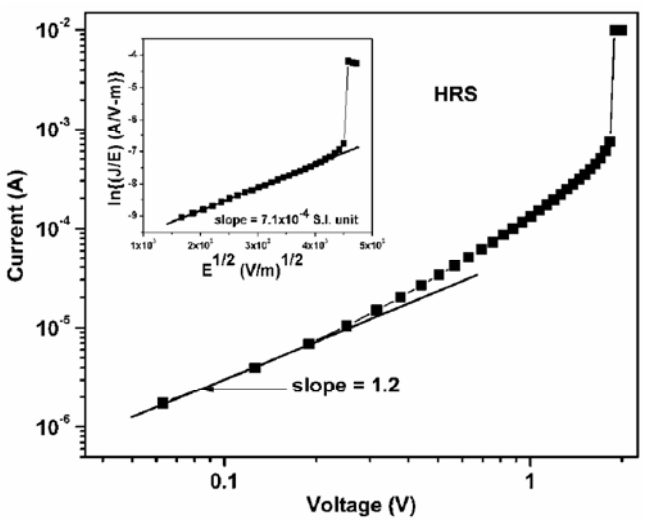

Figure 5. Log–log plot of current–voltage (I–V) of ZnO film in HRS. Inset shows the plot of ln(J/E) as a function of $(E)^{1/2}$ in high voltage regime.

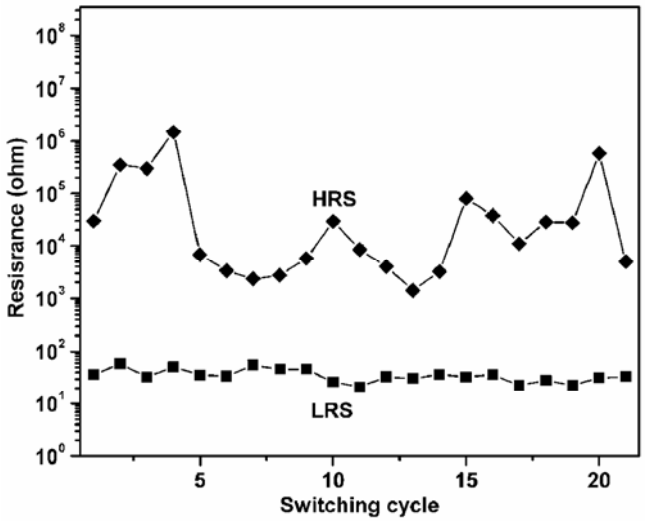

Figure 6. Functional dependences of resistances in HRS and LRS on switching cycle.

4. Conclusions

We have grown highly resistive ZnO thin films on Pt/Ti/SiO_2/Si substrates at room temperature using d.c. discharge assisted pulsed laser deposition methodology and studied their resistive switching behaviour at room temperature. The as grown films were found to be *c*-axis oriented in nature with particulate free surface. The resistance of ZnO films in top bottom configuration was found to switch between a high resistance and low resistance states with well defined window by the application of suitable bias voltages. The conduction behaviour was found to be dominated by ohmic behaviour in the LRS and Poole–Frenkel emission in the HRS. Reliable switching characteristics such as low switching voltages, good retention with switching cycles observed from these films grown at room temperature opens up the possibility of realizing transparent nonvolatile memory devices even on flexible substrates.

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