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Band tailoring by annealing and current conduction of Co-doped ZnO transparent resistive switching memory

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Abstract. The switching characteristics of ITO/$Zn_{1-x}Co_xO$/ITO transparent resistive random access memories were studied. 5 mol% cobalt doped ZnO resistive layer improves bipolar switching properties. In addition, the redshift in band energy caused by doping of cobalt (Co) was studied. The doped memory device also showed a change in band energy by 0.1 eV when subjected to annealing of 400 °C. Annealing below 400 °C temperature did not show any characteristic changes. The film morphology analysis suggested the increase in roughness with annealing temperature, which can be seen from FESEM and AFM images. In this study annealing and Co doping effect on ZnO based non-volatile memory device is presented. Moreover, transparent memory devices with 90% transmittance at 550 nm wavelength have been reported. At low field and high field region Schottky emission and ionic conduction are dominated respectively.

Keywords: resistive switching memory, transparent device, doped ZnO, annealing effect, current conduction

1. Introduction

Transparent resistive switching memory (RRAM)has earned a tremendous attraction in transparent electronics as well as use in future non-volatile memory devices [1–6]. The selection of insulating active material in transparent Metal-Insulator-Metal **(**MIM**)**RRAM is very crucial as it is the main factor defining the device characteristics [7–14].Due to the wide direct band gap of 3**.**3 eV, ZnO can be a potential active material for the transparent electronic devices as transparent RRAM [15,16].The presence of excess native defects such as oxygen vacancies and zinc interstitials degrades the overall memory performance of pure ZnO [17–24].The study suggests that the switching performance of RRAM can be improved by controlling the number of defects present, which governs the creation and annihilation of conductive filaments (CFs) in the RRAM [25–30].

Doping is often used to control the defect concentration. Co-doped ZnO(Co:ZnO) has gained a great interest in past years owing to its capability in the field of magnetic semiconductor applications [30–32]. To magnify the potential of Co-doped ZnO resistive switching for application in non-volatile memories (NVM), more studies should be performed on the electrical and other characteristics properties of these devices. Here, we report the annealing effect on the structural, optical, and switching properties of Co:ZnORRAM devices.

2. Methods

All films were deposited byRF sputtering for its low temperature and low cost fabrications as compared to other methods [2,33,34]. A CoO doped (5 mol. %) ZnO thin film of thickness 38-nm weresputtered at room temperature on a commercial indium tin oxide (ITO) coated glass substrate (Merck & Co., Inc.). During deposition the working pressure of10 mTorr, rf power of 60W and Ar/O_2 gas flow ratio of20/10 sccm, respectively were sternly maintained. A top electrode (TE) of ITO was sputtered at room temperature from ITO (purity 99.99 %) target at Ar ambient of 10 mTorr using a stainless-steel shadow mask havinga diameterof150 µm. Annealing of the sample was done at 200 °C, 300 °C, and 400 °C for 10 minutes to vary the native defects. The electrical switching properties and optical transparency of the devices were investigated by using a B1500A semiconductor device analyzer (Agilent Technologies, Inc.) and an UV-Vis spectrophotometer (UV-1800, Shimadzu), respectively. Atomic force microscopy (AFM) (VEECO Nanoscope IV) was investigated to observe the topography of the Co-doped ZnO film.

3. Result and discussion

Current-Voltage (I-V) switching curve of the said RRAM were measured by applying an external bias at the top electrode with grounded bottom electrode, shown in **Figure 1a**. By the application of positive voltage sweep, the device is turned into the low resistance state (LRS) from initial pristine high resistance state (HRS), which is named as forming process. In this given device, a forming voltage of 3.5 V is necessary to start the resistive switching. Bipolar resistive switching is observed in the device with the 1.2 V SET voltage of and the -1.7 V RESET voltage. A compliance current of 5 mA is maintained during measurement in order to evade the device breakdown. The switching curves are fitted with different conduction mechanisms in different regions (not shown here).

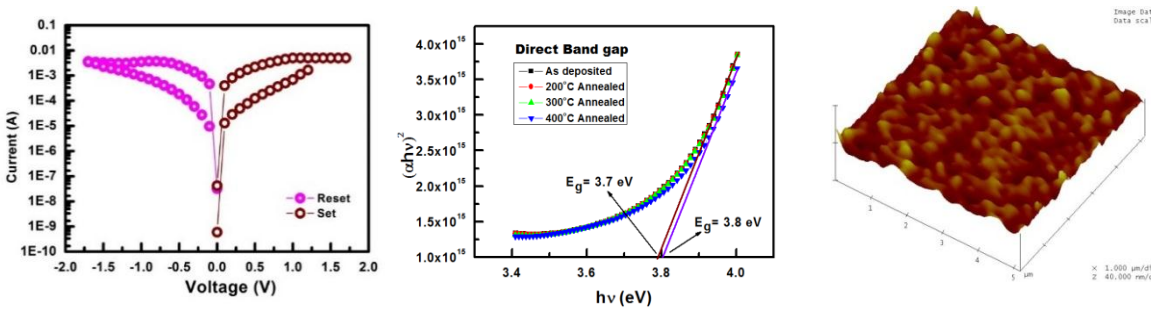

Figure 1. a) I-V switching curve; b) Tauc's plot of of ITO/Co:ZnO/ITO RRAM at different annealing; c) 3D AFM topography of 200° C annealed Co:ZnO surface.

The Tauc plot of the Co:ZnO sample at different annealing conditions obtained from the transmittance spectra as shown in **Figure 1b**.We can infer from the number that the device of ~ 390 nm thickness is very transparent in the visible region and suitable for the use in transparent

electronic devices. It is observed from the figure that the energy gap value of the device is 3.7 eV and 3.8 eV depending on the annealing temperature, which differs from the energy gap value of pristine ZnO (3.3 eV). This redshift of the energy band gap in the Co doped ZnO from the pristine one can be attributed to the effect of Co doping [35]. The strong sp-d exchange interaction between the band electrons and localized 'd'electrons are mainly responsible for the increase in the energy gap or band gap [36]. This results supported by the literature of oxide thin films grown by different techniques, where there is an increase of band gap in Co:ZnO is observed [35,36].

Singh *et al.* also explained the change in band gap in their Co-doped ZnO sample on the basis of the smaller ionic radius of Co ions compared to that of Zn [37]. A blue shift in absorption peak indicates an increase in band gap, which may be due to the enhances of carrier concentration by Burnstein–Moss effect [38]. The deviation in optical properties can be seen after the sample annealed at 400 °C. The annealing temperature of 200 °C and 300 °C had no or very minimal effect on the optical property and retained the same as the as-deposited sample.

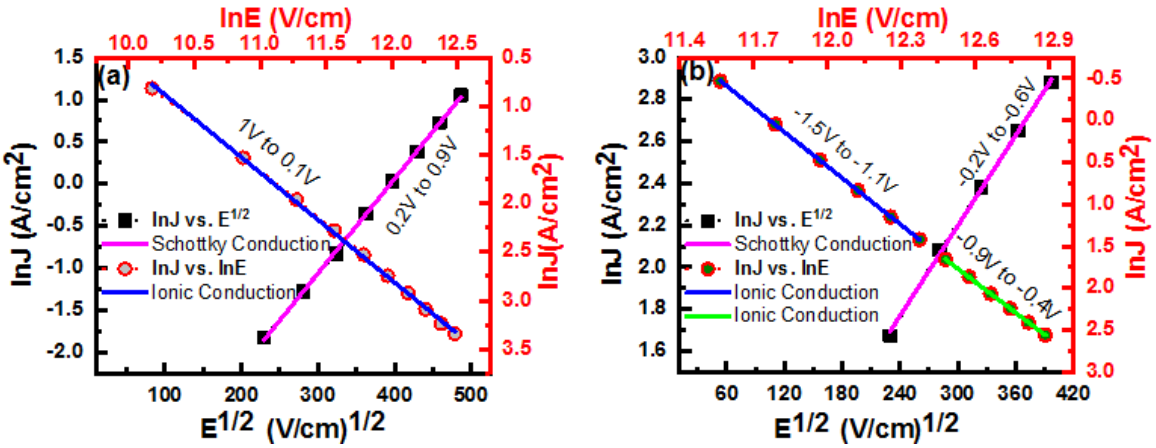

Figure 2. current conduction fittings of the a) LRS and b) HRS, indicating Schottky and ionic conduction mechanisms in low and high electric field region respectively.

From the figure we can infer that for the annealing temperature at 400 °C, a change in electrical energy band gap was found. The energy band gap of the device has increased to 3.8 eV from 3.7 eV when the samples are annealed at 400 °C. This increase in energy band gap may be accredited to the increase of the size of the particle with the increase of annealing temperature [39] and also can be due to the degradation of density of localized states during the annealing process [40]. The calculated band gap is also verified using the photo-luminescence study (not shown here). In order to know the size of the particle and surface morphology of the active layers, the AFM has been studied. **Figure 1c** shows the typical tapping mode AFM topography of Co:ZnO surface annealed at 200° C. The surface of the film is quite smooth (~2.3 nm); however, the roughness increases after annealing. The AFM topography corroborates with the FESEM surface morphology.

For exploring the current conduction mechanism of the ITO/Co:ZnO/ITO memory device, the set/ reset curves are fitted with all conduction mechanisms in different regions using the equations 1 and 2 [41], as shown in **Figure 2**.

$$\ln(J) = \left(\frac{q\sqrt{\frac{qE}{4\pi\varepsilon_0\varepsilon_r}}}{kT} \right) + \left(\ln A^* T^2 - \frac{q\varphi_B}{kT} \right) \quad (1)$$

$$J = J_0 \exp[-(\frac{-q\emptyset_B}{KT} - \frac{Eqd}{2KT})] \quad (2)$$

Where, J, q, ε_0 ,ε_r, A^*, k, T, $\emptyset_B$ and d are the corresponding current density, the charge of an electron, permittivity in vacuum, relative dielectric constant, effective Richardson constant, Boltzmann's constant, temperature, the potential barrier height and jumping distance between two nearby defects respectively. All other symbols have their usual meaning.

It is undoubtedly found that the low electric field region is controlled by Schottky emission, which is mainly due to the jumping of electrons into the conduction band of the oxide after gaining sufficient energy [42]. However, at high electric field region, the conduction mechanism is governed by ionic conduction, which may be because of the shifting of oxygen vacancies by the application of the electric field inside the oxide material[43].

4. Conclusion

In conclusion, the optical properties of highly transparent ITO**/**Co:ZnO**/**ITO resistive memory devices were studied.Increase in the bandgap energy from 3.3 eV for pristine ZnO to3.7 eV for Co:ZnO due doping is reported**.** The response to 200 °C, 300 °C and 400 °C of the RRAM device resulted in a change in band energy.The energy increased to 3.8 eV from 3.7 eV when annealed in 400 °C and did not show any difference when annealed at lower temperatures of 200 °C and 300 °C with respect to pristine Co:ZnO device.The roughness of the surface increases with annealing temperature, which was analyzed by FESEM and AFM. Schottky emission is dominated in the low field region, whereas at high filed ionic emission is dominated. This report not only showing anencouragingmethod of the upcoming transparent non-volatile memory using doping to improve the device property but also provides a brief understanding, which can be useful for the fabrication of next-generation non-volatile memories.

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