Synthesis and resistive switching behaviour of ZnMnO_3 thin films with an $\text{Ag/ZnMnO}_3/\text{ITO}$ unsymmetrical structure

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Abstract. Single-phase MnZnO_3 films were prepared on glass substrates coated with the use of indium tin oxide (ITO) as transparent bottom electrode *via* the sol–gel method. The effects of annealing temperature on structure, resistance switching behaviour and endurance characteristics of the ZnMnO_3 films were investigated. The stable resistive switching behaviour with high resistance ratio in $\text{Ag/ZnMnO}_3/\text{ITO}$ unsymmetrical structure was observed. No second phase is detected, and the crystallinity of the MnZnO_3 films is improved with the increase in annealing temperature from 350 to 400°C. The MnZnO_3 films annealed at 350–450°C with an $\text{Ag/MnZnO}_3/\text{ITO}$ structure exhibit bipolar resistive switching behaviour. Ohmic and space-charge-limited conduction are the dominant mechanisms at low and high resistance states, respectively. V_{ON} , V_{OFF} and $R_{\text{HRS}}/R_{\text{LRS}}$ of the MnZnO_3 films increase with the increase in annealing temperature. Improved endurance characteristics are observed in the samples annealed at 350 and 400°C. The endurance of the MnZnO_3 films degrades when annealed at >450°C.

Keywords. MnZnO_3 ; resistive switching; annealing temperature; sol–gel.

1. Introduction

In recent years, metal–insulator–metal structures with resistive switching memories have been considered as one of the most promising candidates for next-generation nonvolatile memory devices; in these structures, an external electrical stimulus reversibly switches resistance between high-resistance state (HRS) and low-resistance state (LRS) to store data.^{1–6} Resistive switching phenomena exhibiting different performance characteristics have been observed in numerous material systems, including perovskites^{7–9} and binary transition metal oxides.^{10–14} Mn-doped ZnO has attracted significant attention as a potential room-temperature diluted magnetic semiconductor material.¹⁵ Mn-doped ZnO and Mn–Zn–O ternary systems with metal/insulator/metal structure demonstrate efficient resistive switching performances.^{16,17} For optical–electrical application, electrodes with substrates coated with transparent oxide are needed. Indium tin oxide (ITO)-coated glass substrates have been widely used in manufacturing transparent conductors. However, resistive switching memories in devices with unsymmetrical metal/Mn–Zn–O/ITO structure have not been reported. In this study, ITO was used as bottom electrode, and then MnZnO_3 thin films were synthesized at low temperature *via* the sol–gel method to fabricate an $\text{Ag/MnZnO}_3/\text{ITO}$ structured device, which can be applied in transparent electronics. The effects of annealing temperature on resistive

switching behaviour and characteristics of the prepared structure were determined.

2. Experimental

MnZnO_3 films were prepared on ITO-coated glass substrates *via* the sol–gel method. $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (Mn:Zn=1:1 molar proportion) were used as source materials; and 2-methoxyethanol and diethanolamine were selected as solvent and stabilizer, respectively. Stable and homogeneous solutions (0.3 mol l^{-1}) were prepared after continuous stirring at room temperature. The films were prepared by spin coating the homogeneous solutions at 3000 r.p.m. for 30 s. Each layer was heated at 250°C to remove organic residuals before the next layer was spun. To prevent cracking and disruption caused by crystallization, each spun layer should be thin enough to ensure simultaneous evaporation of the solvent. The spin coating and preheating procedures were repeated until the desired thickness was achieved. The obtained MnZnO_3 thin film samples were then annealed at 350, 400 and 450°C for 30 min in ambient air.

For electrical measurement, top Ag electrodes (200 μm diameter) were deposited by radiofrequency magnetron sputtering using a metal shadow mask to form an $\text{Ag/MnZnO}_3/\text{ITO}$ structured device cell. In the resistive switching experiments, a forward bias was applied to the device; this forward bias is the current flowing from the top Ag

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electrode, through the MnZnO_3 films, and then to the bottom ITO electrode. Current–voltage (I – V) characteristics of resistive switching behaviour were obtained using a semiconductor parameter analyzer (Keithley 2636A-System Source Meter, USA). The crystalline phase was determined by X-ray diffraction (XRD) with $\text{Cu K}\alpha$ radiation at 30 kV and 20 mA. Surface microstructures of the annealed samples were observed using an atomic force microscope (AFM). The thickness of the prepared MnZnO_3 films, which was approximately 350 nm, was measured using an XP-100 surface profilometer (XP-100, USA).

3. Results and discussion

Figure 1 shows typical XRD spectra of MnZnO_3 films annealed at different temperatures. The peak at $2\theta = 50.46^\circ$ (labelled by an asterisk) is attributed to conductive ITO, whereas the other diffraction peaks, such as (220) and (311), belong to the ZnMnO_3 phase for all of the samples annealed at temperatures between 350 and 450°C . No diffraction signal related to ZnO or ZnMn_2O_4 is detected. The ZnMnO_3 phase is formed at 350°C , which is lower than that of MnZnO_3 synthesized *via* oxalate precursors through the co-precipitation technique.¹⁸ Based on figure 1, the diffraction peaks of MnZnO_3 phase increase and sharpen along with the increase in sintering temperature from 350 to 400°C , thereby promoting crystallization of MnZnO_3 films. Nevertheless, a significant improvement in crystallization is observed in the samples annealed at 450°C . Although phase evolution in a Mn–Zn–O system with the addition of Mn is very sensitive to synthesis conditions, single-phase MnZnO_3 films are obtained at certain favourable synthesis conditions. Zn/Mn ratio in the source precursor is desirable; both ions in the single-source precursor were already mixed in the source precursor. Moreover, the full-width at half-maximum of the diffraction peak decreases slightly,

indicating that grain size increases along with the increase in annealing temperature, which was also been confirmed in figure 2. Thus, the crystallinity of MnZnO_3 is improved by annealing.

Figure 2a–d shows typical AFM images of MnZnO_3 films annealed at 350 and 400°C , respectively, which reveal that the films are uniform and dense. Surface morphology of both MnZnO_3 samples is evidently similar, except in terms of grain size and uniformity. Figure 2c and d shows that the MnZnO_3 films annealed at 400°C are composed of equiaxial grains instead of cluster grains, and the grains are more uniform.

Figure 3 shows the I – V curves in a semilog scale of the memory cell based on an $\text{Ag}/\text{MnZnO}_3/\text{ITO}$ structure annealed at different temperatures. The I – V curves were obtained at room temperature. The inset shows the schematic diagram of the device and test structures. Sweeping voltage ($0 \rightarrow 3 \rightarrow 0 \rightarrow -3 \rightarrow 0$ V) was employed in obtaining the I – V curves.

Two distinct resistance states can be observed in all of the samples (figure 3), with the device with an $\text{Ag}/\text{MnZnO}_3/\text{ITO}$ structure exhibiting bipolar resistive switching (BRS) behaviour; no electroforming process and current compliance are required to activate memory effect. The ‘RESET’ process implies resistive switching from LRS to HRS, whereas the ‘SET’ process is resistance switching from HRS to LRS. Turn-off voltage (V_{OFF}) is defined as the sweeping voltage when the ‘RESET’ process occurs, whereas turn-on voltage (V_{ON}) is the sweeping voltage when the ‘SET’ process takes place. When a direct current–voltage applied on the Ag electrode is swept from 0 to 3 V, the ‘SET’ process occurs at approximately 0.75, 0.90 and 0.95 V for samples annealed at 350, 400 and 450°C , respectively. LRS is maintained while voltage decreases from 3 to 0 V. When a direct current–voltage applied on the Ag electrode is swept from 0 to -3 V, the ‘RESET’ process occurs; the current significantly decreases at -1.6 , -2.3 and -2.7 V for samples annealed at 350, 400 and 450°C , respectively. Resistance ratio ($R_{\text{HRS}}/R_{\text{LRS}}$) of MnZnO_3 films annealed at various temperatures is > 10 , which increases with the increase in annealing temperature. The behaviour that negates the need for the forming process can be attributed to abundant oxygen vacancy clusters pre-existing in the films,⁵ which result in forming a voltage approximately equal to the set voltage.

To understand the conduction mechanism of BRS behaviour in $\text{Ag}/\text{MnZnO}_3/\text{ITO}$ structure devices, I – V curves of the samples annealed at different temperatures in positive voltage regions are redrawn in a logarithmic plot; linear fitting results are shown in figure 4a–c. For all of the samples, the $\log I$ – $\log V$ plots in LRS are completely linear with a slope of approximately 1, thereby indicating Ohmic conduction mechanism.¹⁹ However, fitting lines in HRS exhibit three regions with slope values at different application fields. Electrical transport behavior in HRS at a low-voltage section also follows Ohmic conduction mechanism (the slope is approximately 1 in $\log I$ – $\log V$ plots). A narrow trap-free region with a slope ranging from

Figure 1. XRD patterns of MnZnO_3 films annealed at different temperatures.

Figure 2. AFM images of surface microstructures of MnZnO_3 films annealed at: (a) 3D image at 350°C , (b) 2D image at 350°C , (c) 3D image at 400°C and (d) 2D image at 400°C .

Figure 3. I – V curves of $\text{Ag/MnZnO}_3/\text{ITO}$ devices annealed at different temperatures. The inset is the schematic diagram of the device structure and the test structure. Arrows indicate the sweeping directions.

4.76 to 5.31 is observed. At the high-voltage section, nonlinear effects in $\log I$ – $\log V$ plots with a slope of approximately 2 are observed. This behaviour is typical in trap-controlled space-charge-limited conduction (SCLC^{17,20}), in which current increases as a result of injecting excess space charges, and current density is squarely proportional to voltage.¹⁹

Based on the leakage analysis, the samples annealed at different temperatures exhibit similar conduction mechanisms.

However, as annealing temperature increases, the range of the succeeding Ohmic conduction mechanisms extends to higher voltages in HRS, whereas SCLC conduction behaviour weakens. BRS behaviour in $\text{Ag/MnZnO}_3/\text{ITO}$ devices is related with oxygen vacancies, grain boundaries and interstitial atoms in MnZnO_3 films. When a voltage is applied, grain boundaries and dislocations facilitate diffusion of oxygen vacancies at high electric fields, resulting in percolating conduction filaments. The carriers transport or hop through the filament path, thereby exhibiting Ohmic conduction behaviour and maintaining LRS until the tiny filaments are ruptured; the device then switches to HRS. The rupture of conduction filaments in $\text{Ag/MnZnO}_3/\text{ITO}$ devices can be due to disappearance of oxygen vacancies near the $\text{MnZnO}_3/\text{ITO}$ interface caused by oxygen diffusion from ITO, which serves as an oxygen reservoir.²¹ In addition to oxygen diffusion, Ag oxidation easily occurs in high electric fields; the drift of mobile Ag^+ cations transforms the oxide into a metallically conducting phase.⁵ The metallic filaments may not be destroyed completely during HRS→LRS process, and the remaining fragments cause inhomogeneous conduction in MnZnO_3 films. Hence, BRS behaviour is induced upon formation/disruption of conducting filaments. At higher annealing temperature, fewer defects and less grain boundaries are found within conducting paths, thereby increasing V_{ON} , V_{OFF} and R_{LRS} .^{22,23}

Endurance characteristics of the $\text{Ag/MnZnO}_3/\text{ITO}$ devices were determined to evaluate the fatigue performance of resistive switching memory in HRS and LRS. Figure 5 illustrates the resistance evolution in HRS (R_{HRS}) and LRS (R_{LRS})

(a)

(b)

(c)

Figure 4. $\log I - \log V$ plots in the positive voltage regions of samples annealed at: (a) 350°C, (b) 400°C and (c) 450°C. The lines show the fitting results in both HRS and LRS.

of Ag/MnZnO₃/ITO devices measured under 0.5 V reading voltage within 300 switching cycles. The initial R_{LRS} and R_{HRS}/R_{LRS} of Ag/MnZnO₃/ITO devices evidently increase as annealing temperature increases from 350 to 450°C.

(a)

(b)

(c)

Figure 5. Endurance characteristics of MnZnO₃/ITO devices annealed at: (a) 350°C, (b) 400°C and (c) 450°C.

Good endurance characteristics are observed in the samples annealed at 350 and 400°C, during which R_{LRS} and R_{HRS}/R_{LRS} remain retentive after 300 switching cycles. By contrast, the R_{LRS} and R_{HRS}/R_{LRS} in the MnZnO₃ films

annealed at 450°C decline sharply at >200 switching cycles. Thus, the MnZnO_3 films annealed at 450°C exhibit low endurance. Furthermore, fluctuations in HRS resistance values are observed during the initial testing cycles, and such values become relatively stable after further switching cycles. After the 'RESET' process, a low amount of tiny filaments are found in HRS. These filaments can be the primary cause of resistance fluctuation in MnZnO_3 films during the initial testing cycles. Nevertheless, the amount of tiny filament increases along with the increase in switching cycles. A mass of tiny filaments stabilizes the fluctuations in resistance values and R_{HRS} decreases after further switching cycles. This phenomenon is also observed in ZnO -based resistive switching materials.^{15,24}

4. Conclusions

MnZnO_3 films with ITO as transparent bottom electrode can be prepared *via* the sol-gel method at low synthesis temperatures. Annealing temperature remarkably affects the structure, resistance switching behaviour and endurance characteristics of ZnMnO_3 films. A single-phase ZnMnO_3 is formed at 350°C , and crystallinity of MnZnO_3 films is improved along with the increase in annealing temperature. V_{ON} , V_{OFF} and $R_{\text{HRS}}/R_{\text{LRS}}$ increase with the increase in annealing temperature, which can be attributed to the defect-healing effect of MnZnO_3 films. For $\text{Ag/MnZnO}_3/\text{ITO}$ devices, the conduction mechanism involved in LRS follows Ohmic behaviour; the electrical transport behaviour in the low-voltage section of HRS also follows Ohmic conduction mechanism. By contrast, the conduction behaviour in the high-voltage section of HRS is characterized by SCLC conduction mechanism. MnZnO_3 films annealed below 450°C exhibit better endurance characteristics. The low amount of tiny filaments in HRS after the 'RESET' process can be the primary cause of resistance fluctuations of MnZnO_3 films during the initial testing cycles. Certain mass of tiny filaments stabilizes the fluctuations in resistance values and decreases R_{HRS} after further switching cycles.

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