Resistance Switching Behavior Dependent of Substrate Temperature for $ZnMn_2O_4$ Films Deposited by Magnetron Sputtering

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Abstract. The effect of substrate temperature on the resistance switching properties and the endurance characteristics of $ZnMn_2O_4$ films, deposited on p-Si substrate by magnetron sputtering, was investigated. The $ZnMn_2O_4$ films deposited at various substrate temperatures are polycrystalline with spinel structure. The $ZnMn_2O_4$ films deposited at a substrate temperature of 500℃ have the highest R_{HRS}, the biggest R_{HRS}/R_{LRS} and the highest V_{ON}. Good endurance characteristics have been observed in $Ag/ZnMn_2O_4$/p-Si devices deposited at 100℃ and 300℃, the R_{HRS}/R_{LRS} ratio maintained at about 10^3 after successive 1000 switching cycles, and the stable resistive switching repeat cycles is over 1400, but the repeatable resistive switching cycles for the specimens deposited at 500℃ is just 50. These results indicated that the substrate temperature has significant influence on the endurance characteristic of $Ag/ZnMn_2O_4$/p-Si device.

Introduction

Resistive switching is a phenomenon by which a material can undergo reversible changes in electrical resistance. As one of the candidates for the next generation non-volatile memories (NVMs), there is a world-wide effort to elucidate the underlying physics and to develop a resistive random access memory (RRAM) due to their simple structure, high speed and non-volatile [1]. The resistive switching effect was observed in many materials systems, including binary oxide thin films, such as NiO [2], TiO_2 [3], and ZrO_2 [4], and perovskite materials, such as $SrZrO_3$ [5], $SrTiO_3$ [6], $Pr_{0.7}Ca_{0.3}MnO_3$ [7], $Bi_4Ti_3O_{12}$ [8]. ZnO and doped ZnO demonstrate resistive switching characteristics [9,10]. The Mn-Zn-O ternary system is interesting in terms of its interesting electrical and magnetic properties. However, the switching behaviors in Mn-Zn-O ternary oxides have been less investigated compared with the binary counterparts.

$ZnMn_2O_4$ films grown by sol-gel method and chemical solution method have recently shown resistive switching behavior [11,12]. However, there have been few reports on the resistive switching behavior of $ZnMn_2O_4$ films or $ZnMn_2O_4$-based RRAM device prepared by magnetron sputtering. In this paper, $ZnMn_2O_4$ films with a structure of $Ag/ZnMn_2O_4$/p-Si were prepared by magnetron sputtering, and the effect of substrate temperature on microstructure, resistive switching properties and endurance characteristics was investigated.

Experiments

The $ZnMn_2O_4$ films were deposited on heavily doped p-Si substrates by magnetron sputtering. With a size of 12mm×10mm, the p-Si substrates were ultrasonically cleaned in acetone, rinsed in alcohol and then dried. $ZnMn_2O_4$ ceramic with a diameter of 60mm was used as sputtering target, and high purity argon gas and oxygen gas were used as the sputtering and reaction gas. During the sputtering, the working pressures were held at 1 Pa, and sputtering power was 100W. For different film specimens, the substrate temperatures were maintained at 100℃, 300℃, 500℃, respectely. The sputtering time was held on 90min according to the film thickness of 2.10μm. After deposition, the films were annealed at 600°C for 1 hour in the air. For the test of electric properties, some devices with a structure of $Ag/ZnMn_2O_4$/p-Si have been fabricated, and Ag, as top electrode, was fabricated by vacuum evaporation with a thin aluminum sheet which has some circular hole.

X-ray diffraction (XRD) (D8-Advance, Bruker Inc., Germany) was used to characterize the phase and crystalline structure of $ZnMn_2O_4$ films. The microstructure morphology of $ZnMn_2O_4$ films was analyzed by a scanning electron microscope (SEM, JSM5610LV, JEOL). *I-V* characteristics and resistance switching performances were examined by a source meter (Keithley 2400, USA).

Results and Discussion

Fig.1 is the XRD patterns of $ZnMn_2O_4$ films deposited at different substrate temperatures. From Fig.1, the XRD patterns show that the substrate temperature has not significant influence on the spinel structure of $ZnMn_2O_4$ films, and the films were polycrystalline, in which the (103), (312), (303), and (224) planes are agreement with JCPDS card No.24-1133. No peaks from other phases are detected. However, the substrate temperature is a key factor for the crystallizability of $ZnMn_2O_4$ films, which can be confirmed by the surface SEM images $ZnMn_2O_4$ films in Fig.2. When the substrate temperature increases from 100℃ to 500℃, the grain becomes more and more large and the average grain sizes increase from 12.1nm to70.7nm. When the substrate temperature is not over 300℃, the grain boundaries of $ZnMn_2O_4$ films are clear, and dense, smooth. Crack-free surface morphologies can be observed in the $ZnMn_2O_4$ film samples deposited at a substrate temperature below 300℃, which suggests that these samples are homogeneous and compact. When the substrate temperature is 500℃, some abnormal larger grains are observed in the samples, which indicate that the grains are easy gather closely together to come into being clusters when the substrate temperature too high.

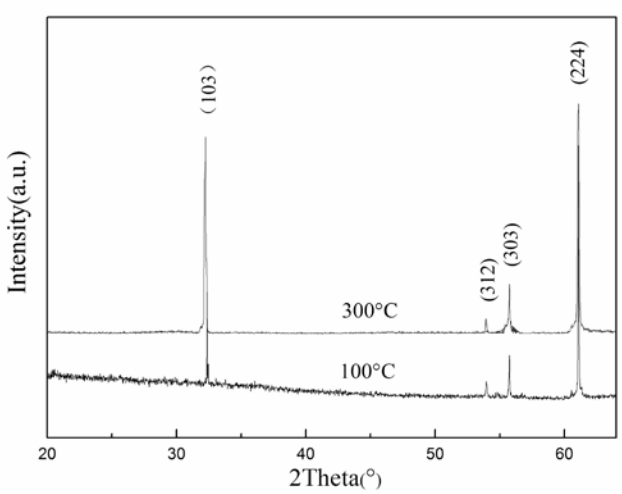

Fig.1 XRD patterns of $ZnMn_2O_4$ films deposited at different substrate temperatures

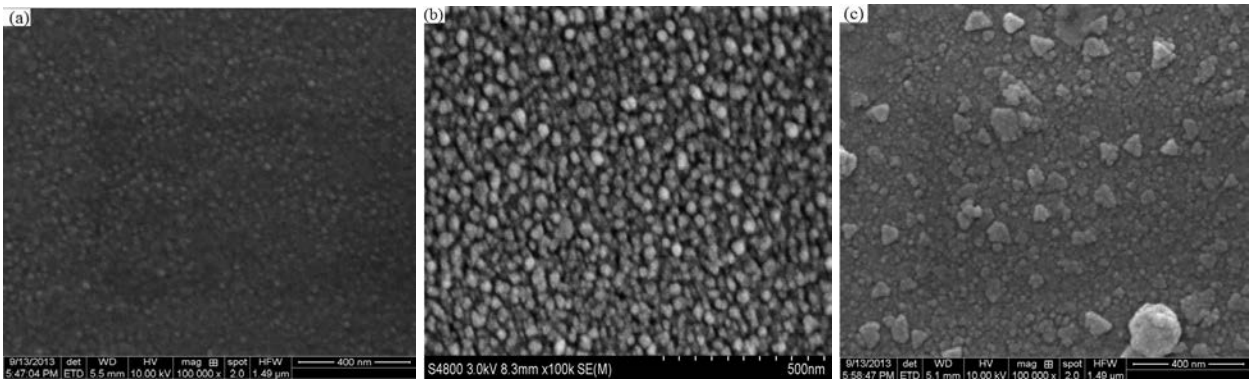

Fig. 2 Surface SEM images of $ZnMn_2O_4$ films deposited at different substrate temperatures: (a) 100℃; (b) 300℃; (c) 500℃

To reveal the resistance switching behavior $ZnMn_2O_4$ films deposited at different substrate temperatures, the current-voltage (*I-V*) curves device of Ag/$ZnMn_2O_4$/p-Si based different film specimens were measured at room temperature, and the results are shown in Fig.3. The measurement

was performed by sweeping the bias voltage of the top electrode in the sequence of $0 \rightarrow V_{max} \rightarrow 0 \rightarrow -V_{max} \rightarrow 0$ V. From Fig.3, it can be seen that two distinct resistance states with a hysteresis loop in *I-V* curves are observed in the three specimens at different substrate temperatures, which indicated that all Ag/$ZnMn_2O_4$/p-Si devices exhibit bipolar resistance switching behavior and the substrate temperature has not an influence on the bipolar resistance characteristics of those devices. The "Set" process occurs when the resistance of $ZnMn_2O_4$ films changes from high to low at $V_{ON,}$ meaning the resistance state of device change from high resistance state (HRS) to low resistance state (LRS). The other way round, the "Reset" process occurs when the resistance changes from low to high at $V_{OFF,}$ which indicate that the device has changed from LRS to HRS. Before the saltation occurs, the device will maintain the high resistance (R_{HRS}) or the low resistance (R_{LRS}). For those devices deposited at a substrate temperature of 100℃ or 300℃, the voltage values of V_{ON} both are 7.5V, but it is 15V for the device deposited at a substrate temperature of 500℃. Corresponding to the above three samples, the R_{HRS} are $3.5\times10^4\Omega$、$4\times10^4\Omega$、$6\times10^4\Omega$, respectively, meanwhile resistance at LRS (R_{LRS}) all are about $10^2\Omega$, which indicated that the $ZnMn_2O_4$ films deposited at a substrate temperature of 500℃ have the highest R_{HRS} and the biggest R_{HRS}/R_{LRS} ratio, but also have the highest V_{ON}.

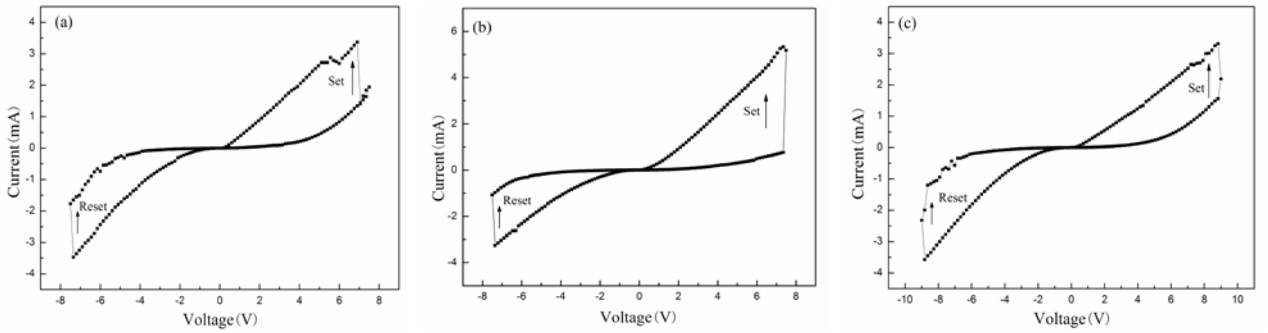

Fig.3 *I-V* curves of Ag/$ZnMn_2O_4$/p-Si deposited at different substrate temperatures: (a) 100℃; (b) 300℃; (c) 500℃

The read/write endurance properties characterize the controllability, reversibility, and reproducibility of the switching between HRS and LRS, which is important for the actual application of RRAM devices. Fig.4 is the resistance at HRS and LRS of Ag/$ZnMn_2O_4$/p-Si devices deposited at different substrate temperatures dependent of the switching cycles. From Fig.4, it can be seen that the resistance values of the HRS and the LRS distribute in a certain range after hundreds switching cycles and the variation trends of resistance at HRS and LRS in Ag/$ZnMn_2O_4$/p-Si device deposited at substrate temperatures are similar. And more, for the specimens deposited at 100℃ and 300℃, the R_{HRS}/R_{LRS} ratio maintained at about 10^3 after successive 1000 switching cycles, and the stable resistive switching repeat cycles is over 1400, but the repeatable resistive switching cycles for the specimens deposited at 500℃ is just 50. These results indicated that the substrate temperature has significant influence on the endurance characteristic of Ag/$ZnMn_2O_4$/p-Si device.

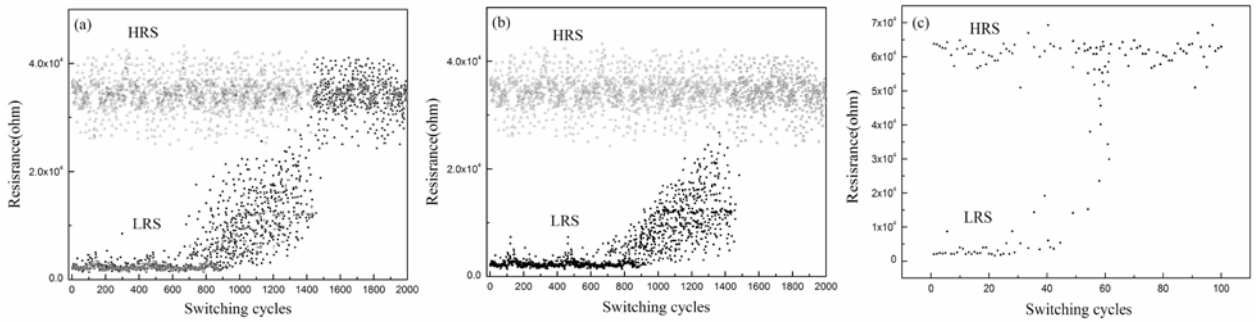

Fig.4 Endurance characteristics of $ZnMn_2O_4$ films deposited at different substrate temperatures: (a) 100℃; (b) 300℃; (c) 500℃

Summary

The substrate temperature has not significant influence on the phase structure of $ZnMn_2O_4$ films, but it effect obviously on the grain size and the resistive switching properties. The $ZnMn_2O_4$ films deposited at various substrate temperatures are polycrystalline with spinel structure. $ZnMn_2O_4$ film samples deposited at a substrate temperature below 300℃ are homogeneous and compact, but the grains are easy gather closely together to come into being clusters when the substrate temperature too high. The substrate temperature has not an influence on the bipolar resistance characteristics of $Ag/ZnMn_2O_4$/p-Si devices. The $ZnMn_2O_4$ films deposited at a substrate temperature of 500℃ have the highest R_{HRS} and the biggest R_{HRS}/R_{LRS} ratio, but also have the highest V_{ON}. Good endurance characteristics have been observed in $Ag/ZnMn_2O_4$/p-Si devices deposited at 100℃ and 300℃, the R_{HRS}/R_{LRS} ratio maintained at about 10^3 after successive 1000 switching cycles, and the stable resistive switching repeat cycles is over 1400, but the repeatable resistive switching cycles for the specimens deposited at 500℃ is just 50. These results indicated that the substrate temperature has significant influence on the endurance characteristic of $Ag/ZnMn_2O_4$/p-Si device.

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