Effects of Sputtering Power on Resistance Switching Properties of $ZnMn_2O_4$ Films Deposited by Magnetron Sputtering

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Abstract. $ZnMn_2O_4$ films with a structure of $Ag/ZnMn_2O_4$/p-Si were fabricated on p-Si substrate by magnetron sputtering. The effects of sputtering power on microstructure, resistance switching properties and endurance characteristics of $ZnMn_2O_4$ films were investigated. $ZnMn_2O_4$ films are spinel structure and the sputtering power has not changed their phase structure. $ZnMn_2O_4$ film samples deposited at a sputtering power below 100W are homogeneous and compact, but too high sputtering power would degrade the quality of $ZnMn_2O_4$ films. Bipolar resistive switching behavior and good endurance characteristics have been observed in $Ag/ZnMn_2O_4$/p-Si devices deposited at different sputtering power. The $ZnMn_2O_4$ films deposited at a sputtering power of 80W have the highest R_{HRS}, biggest R_{HRS}/R_{LRS} ratio, but the $ZnMn_2O_4$ films deposited at a sputtering power of 100W have the lowest V_{ON} and V_{OFF}. The resistive switching for all specimens can be repeated stably for over 1000 cycles, which indicated that the sputtering power has not significant influence on the read/write endurance characteristic.

Introduction

As one of the most promising candidates for the next generation non-volatile memories (NVMs), resistance random access memories (RRAM) are attracting a great deal of attention due to their simple structure, high speed and non-volatile [1]. In the past decade, many materials systems have been investigated for RRAM application, including perovskite materials, such as $Pr_{0.7}Ca_{0.3}MnO_3$ [2], $La_{0.7}Ca_{0.3}MnO_3$ [3], $SrZrO_3$ [4], $SrTiO_3$ [5], $Bi_4Ti_3O_{12}$ [6], and binary metal oxides, such as TiO_2 [7], NiO [8], Cu_xO [9], and ZrO_2 [10]. ZnO and Mn doped ZnO demonstrate resistive switching characteristics [11]. 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.

Recently, it is reported that the $ZnMn_2O_4$ films grown by sol-gel method and chemical solution method demonstrate resistive switching behavior [14,15]. Nevertheless, there have been few reports on $ZnMn_2O_4$ films or $ZnMn_2O_4$-based RRAM device prepared by magnetron sputtering and its resistive switching behavior. In this paper, $ZnMn_2O_4$ films deposited on p-Si substrate and a device with $Ag/ZnMn_2O_4$/p-Si structure were prepared by magnetron sputtering, and the effects of sputtering power on microstructure, resistive switching properties and endurance characteristics were 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, 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 the substrate temperature was maintained at 300°C. 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 different film specimens, sputtering power was 80W, 100W, 150W, respectively. As top electrode, Ag 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 various sputtering powers. The intensity of the XRD characteristic diffraction peaks of $ZnMn_2O_4$ films deposited at various sputtering powers are obvious different, but the XRD patterns show that the sputtering power has not changed the phase structure of $ZnMn_2O_4$ films. From Fig.1, it can be seen that the films were polycrystalline, and the diffraction peaks at 2θ of 32.23°, 53.92°, 55.73°, and 61.07° are ascribed to the reflection of (103), (312), (303), and (224) planes of spinel structure $ZnMn_2O_4$, which is in agreement with JCPDS card No.24-1133. No peaks from other phases are detected. When the sputtering power is 80W, the intensity of the characteristic diffraction peaks is unconspicuous, but as the sputtering power increased, the peaks in XRD patterns became sharper and the relative intensity of the peaks became stronger, indicating a better crystallization and larger grain size.

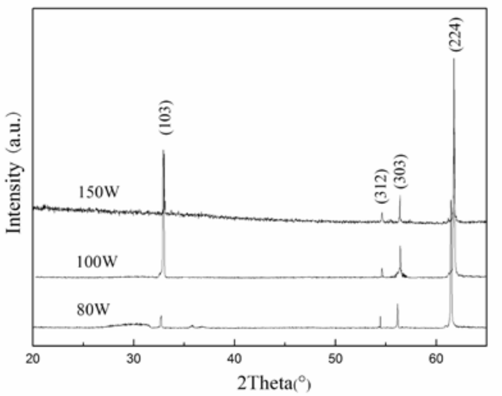

Fig.1 XRD patterns of $ZnMn_2O_4$ films deposited at various sputtering powers

In order to illustrate the surface morphology of the films, Fig.2 shows the surface SEM images of $ZnMn_2O_4$ films deposited at a sputtering power of 80W, 150W. Corresponding to the above two samples, the average grain sizes are 45nm and 28nm. Dense, smooth and crack-free surface morphologies can be observed in the $ZnMn_2O_4$ film samples deposited at a sputtering power below 100W, which suggests that these samples are homogeneous and compact. When the sputtering power is 150W, a little abnormal larger grains and crack are observed in the samples, indicating the films become of low quality.

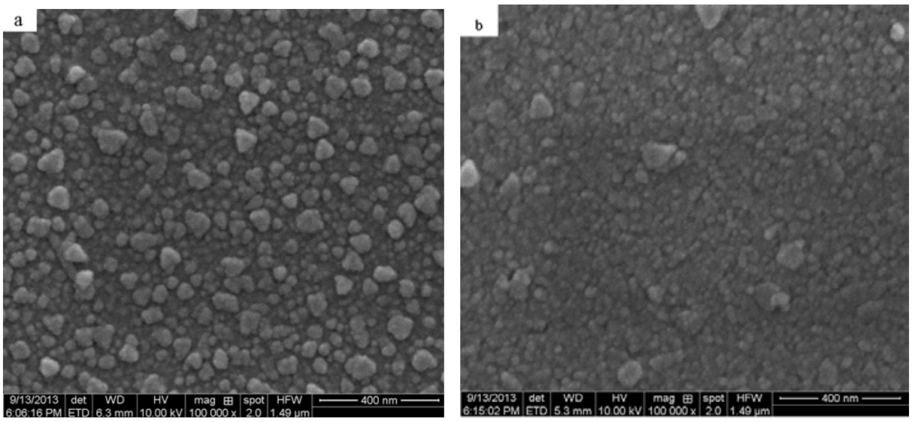

Fig. 2 Surface SEM images of $ZnMn_2O_4$ films deposited at a sputtering power: (a) 80W; (b) 150W

To reveal the resistance switching behavior of Ag/$ZnMn_2O_4$/p-Si device deposited at different sputtering powers, the typical current-voltage (*I-V*) curves of Ag/$ZnMn_2O_4$/p-Si devices were measured, shown in Fig.3, in which the $ZnMn_2O_4$ films deposited at a sputtering power of 80W, 100W, 150W, respectively. 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 the three Ag/$ZnMn_2O_4$/p-Si devices all exhibit bipolar resistance switching behavior with a hysteresis loop in *I-V* curves and the sputtering power have not an influence on their bipolar resistance characteristics. Two distinct resistance states are observed in all specimens deposited at various sputtering powers. When the dc voltage applied to the Ag electrode is swept from 0 to a certain voltage value (V_{ON}), the resistance decreases dramatically, which indicate that the resistance state changes from high resistance state (HRS) to low resistance state (LRS), meaning the “Set” occurs. The device will maintains the LRS while the dc voltage is swept to a certain negative voltage value (V_{OFF}), then the resistance increases sharply, which indicate the device changes back from LRS to HRS, meaning the “Reset” occurs. Corresponding to the above three samples, the voltage values of V_{ON} are 15V, 7.5V, 9V, and the resistances at HRS (R_{HRS}) are $5\times10^4\Omega$、$4\times10^4\Omega$、$2.5\times10^4\Omega$, respectively, meanwhile resistance at LRS (R_{LRS}) all are about $10^2\Omega$, which indicated that the $ZnMn_2O_4$ films deposited at a sputtering power of 80W have the highest R_{HRS}, biggest R_{HRS}/R_{LRS} ratio, but the $ZnMn_2O_4$ films deposited at a sputtering power of 100W have the lowest V_{ON} and V_{OFF}.

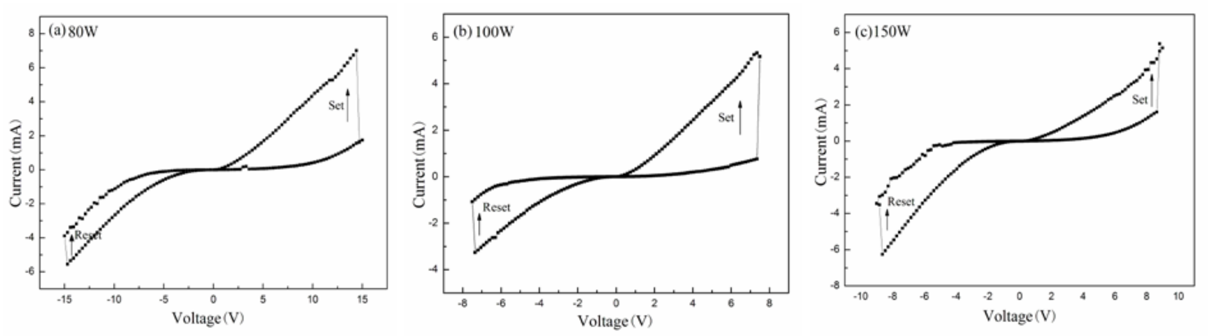

Fig.3 *I-V* curves of Ag/$ZnMn_2O_4$/p-Si deposited at: (a) 80W; (b) 100W; (c) 150W

The read/write endurance characteristic is very important for the actual application of RRAM devices. Good endurance properties could ensure that the switching between ON and OFF states is highly controllable, reversible, and reproducible. To evaluate the endurance characteristics of Ag/$ZnMn_2O_4$/p-Si devices deposited at different sputtering powers, a repeating switching test is carried out and the results are given in Fig.4. From Fig.4, it can be seen that the Ag/$ZnMn_2O_4$/p-Si device deposited at different sputtering powers have the similar change trend, and the resistive switching can be repeated stably for over 1000 cycles under bipolar resistive switching mode, which indicated that the sputtering power has not significant influence on the read/write endurance characteristic. After successive 1200 switching cycles, the resistance values of the HRS and the LRS distribute in a certain range, but the HRS, and the R_{HRS}/R_{LRS} ratio maintained over 10^2, which indicated that the Ag/$ZnMn_2O_4$/p-Si device has better endurance characteristics.

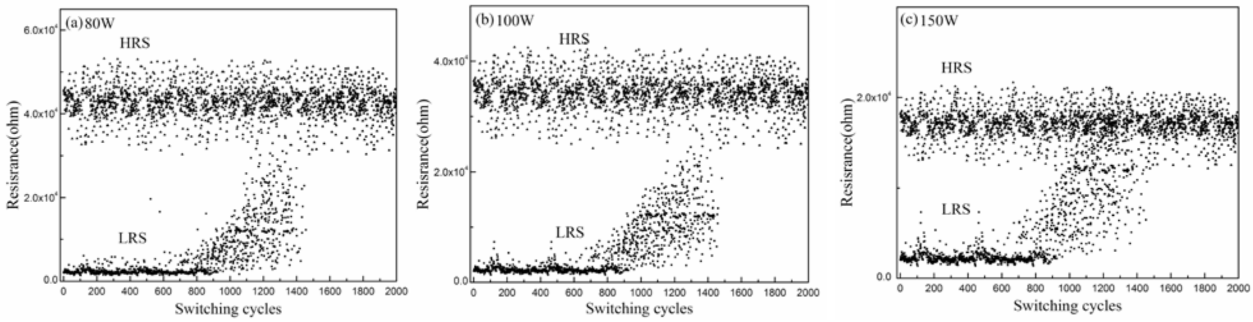

Fig.4 Endurance characteristics of $ZnMn_2O_4$ films deposited at: (a) 80W; (b) 100W; (c) 150W

Summary

The intensity of XRD diffraction peaks of $ZnMn_2O_4$ films deposited at different sputtering powers are distinguishing, but the $ZnMn_2O_4$ films all are spinel structure and the sputtering power has not changed their phase structure. $ZnMn_2O_4$ film samples deposited at a sputtering power below 100W are homogeneous and compact, but too high sputtering power would degrade the quality of $ZnMn_2O_4$ films. Bipolar resistive switching behavior and good endurance characteristics have been observed in Ag/$ZnMn_2O_4$/p-Si devices deposited at a sputtering power of 80W, 100W, 150W. The $ZnMn_2O_4$ films deposited at a sputtering power of 80W have the highest R_{HRS}, biggest R_{HRS}/R_{LRS} ratio, but the $ZnMn_2O_4$ films deposited at a sputtering power of 100W have the lowest V_{ON} and V_{OFF}. The resistive switching for all specimens can be repeated stably for over 1000 cycles under bipolar resistive switching mode, which indicated that the sputtering power has not significant influence on the read/write endurance characteristic.

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