The effects of substrate temperature on ZnO-based resistive random access memory devices*

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Ag/ZnO/Zn/Pt structure resistive switching devices are prepared by radio frequency magnetron sputtering. The ZnO thin films are grown at room temperature and 400 °C substrate temperature, respectively. By comparing the data, we find that the latter device displayed better stability in the repetitive switching cycle test, and the resistance ratio between a high resistance state and a low resistance state is correspondingly increased. After 10^4-s storage time measurement, this device exhibits a good retention property. Moreover, the operation voltages are very low: –0.3 V/–0.7 V (OFF state) and 0.3 V (ON state). A high-voltage forming process in the initial state is not required, and a multistep reset process is demonstrated.

Keywords: ZnO, resistive switching devices, magnetron sputtering

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1. Introduction

Recently, resistive random access memory (ReRAM), which is based on resistance switching characteristics, has received much attention as a new type of storage.[1,2] The resistive switching phenomenon is observed in many materials, such as polymers[3] and solid electrolytes.[4] However, these materials have their own certain limitations. For example, polymers suffer from low endurance, a need for the solid electrolyte to have a high write operation voltage, etc. Relative to these materials, transition metal oxides (TMOs), such as ZnO, ZrO_2, NiO, and TiO_2,[5−11] are widely researched due to their simple structures, excellent scalabilities, high densities, and good compatibilities with complementary metal–oxide semiconductor (CMOS) technology. Despite these advantages, the stability of TMO ReRAM needs to be improved. Therefore, we choose ZnO for device fabrication and research in this paper. There are a large number of oxygen vacancies in a ZnO thin film which could be used to grow conductive filaments. In addition, ZnO semiconductor material has been widely studied, so the relevant instruments and preparation technology are relatively mature.[12−14] We use radio frequency (RF) magnetron sputtering to grow ZnO thin film. In order to obtain a device with good stability, good-quality ZnO is strongly required. For this reason, we remold our instrument by using a light tube to heat the substrate to a high temperature (about 500 °C; only 200 °C could be reached before). We compare two different devices. One of them is fabricated at room temperature (RT) and the other at 400 °C. We find that not only the quality of the ZnO thin film but also the performance of the device is improved when it is fabricated at 400 °C.

2. Experiment

A 20-nm Zn buffer layer was deposited on the Pt/Ti/SiO_2/Si substrate for fabricating Ag/ZnO/Zn/Pt structure ReRAM devices. Then about 100-nm ZnO thin films were grown by RF magnetron sputtering at room temperature and 400 °C using a metallic Zn target, respectively. Subsequently,

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the ZnO thin film was annealed in an O_2 gas ambient for 20 min. The structure of the device is shown in Fig. 1. A thin Ti layer was inserted between the layers of Pt and SiO_2/Si to enhance the adhesion of the Pt electrode to the Si substrate. A 100-nm Ag layer was used as a top electrode. The electrode with a diameter of 200 μm was deposited by RF magnetron sputtering with a metal shadow mask. The current (I)–voltage (V) characteristic was measured by using a Keithley 2612. The crystal structure was characterized by using an X-ray diffractometer (Bruker D8 advance).

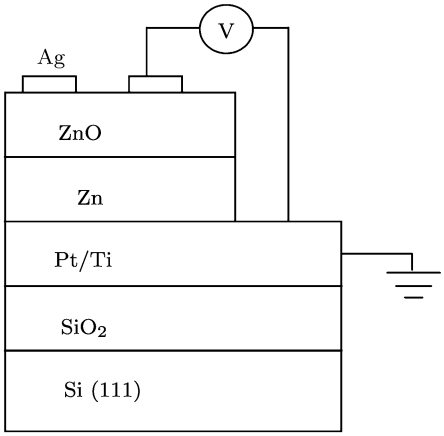


Fig. 1. Schematic structure of the designed memory stack.

3. Results and discussion

Figure 2 shows the XRD patterns of the ZnO thin films at different substrate temperatures. Figure 1(a) shows the ZnO thin film grown at RT, whose peak is not obvious, exhibiting poor crystallinity. Figure 1(b) displays the ZnO thin film deposited at 400-°C substrate temperature, which is preferentially grown along the c axis. Apart from the (002) peak, no additional diffraction lines of ZnO can be detected in the scanned region of 30°–60°, which indicates a good wurtzite structure with a strong c-axis texture. Another diffraction peak corresponds to Pt (111). The XRD patterns indicate that after 400-°C heating of the substrate, the quality of the ZnO thin film is improved.

To analyse the resistive switching performances of the Ag/ZnO/Zn/Pt structure devices, the current–voltage (I–V) characteristics are investigated by DC voltage sweeps and plotted in a semi-logarithmic scale, as shown in Fig. 3. During the electrical measurements, the Ag top electrode (TE) is positively biased, while the Pt bottom electrode (BE) is grounded.

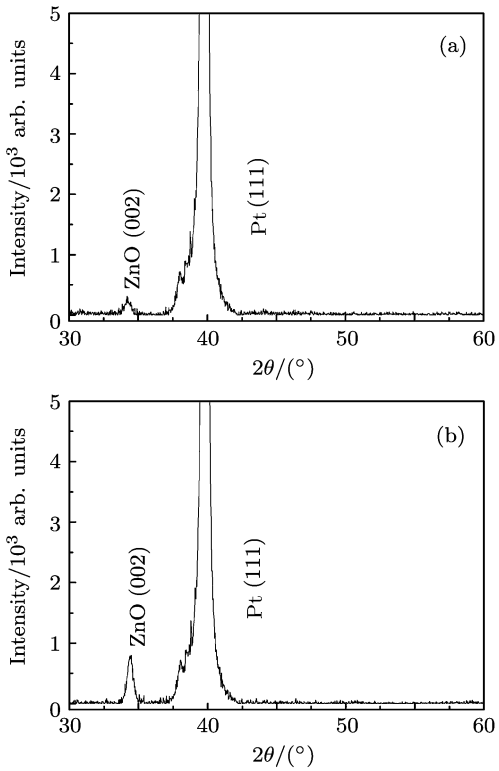


Fig. 2. XRD patterns of the ZnO thin flims at substrate temperatures of: (a) room temperature and (b) 400 °C.

A current compliance (CC) of 10 mA is adopted herein to avoid permanent dielectric breakdown of the device in the SET process. Typical I–V characteristics of ZnO deposited at room temperature are exhibited in Fig. 3(a). The ReRAM device switches to a low resistance state (LRS) (ON state) at about 0.5 V when the voltage sweeps from zero to a positive value. At the negative part, the cell reaches a high resistance state (HRS) (OFF state) at about –0.35 V. Figure 3(b) shows the switching characteristics of ZnO deposited at 400 °C. We can see in the SET process that the threshold voltage is about 0.3 V. In the RESET process, the first switching occurs at about –0.3 V, and the second switching takes place at about –0.7 V. This phenomenon is due to the fact that the device contains both a Ag filament and an oxygen vacancy filament.[15] The multistep switching process indicates that a multilevel ReRAM device with a cache system can be obtained by using a step voltage, which can effectively solve the contradiction between large-capacity and high-speed in memory devices. Moreover, the operating currents of the two devices are very low (∼20 mA), which indicates a low power consumption. The electroforming process is not needed in the initial state. This property is beneficial to high-density

ReRAM device applications, laying the foundations for the preparation of large capacity memory.[16]

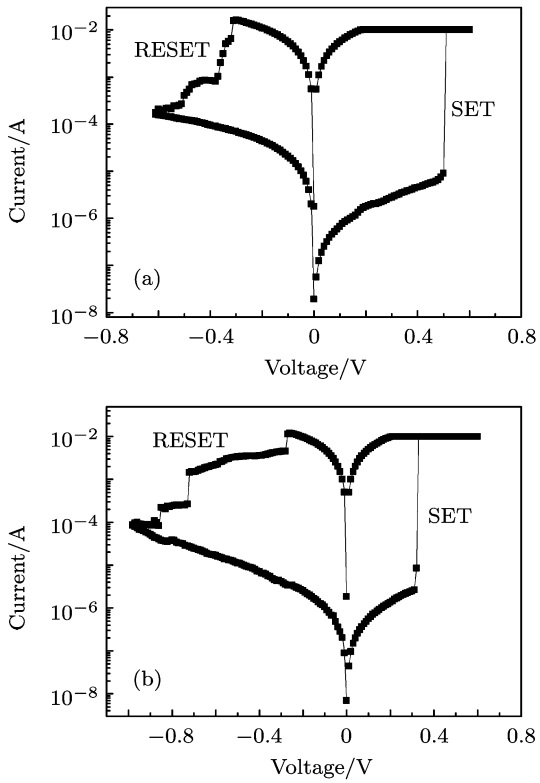


Fig. 3. Typical I–V characteristics of the Ag/ZnO/Zn/Pt memory device at substrate temperatures of: (a) room temperature and (b) 400 °C.

To further analyse the memory performance, measurements of the repetitive switching cycles are carried out and shown in Fig. 4. Both devices are SET by a positive sweep voltage and RESET by a negative sweep voltage. Resistance values are obtained at 0.1 V. As shown in Fig. 4(a), the resistance ratio between HRS and LRS is about 5×10^2, but the HRS resistance of the RT device is unstable. Figure 4(b) shows the switching cycling characteristics of Ag/ZnO/Zn/Pt devices at a 400-°C substrate temperature. As can be seen, the low resistance values are distributed in a narrow range around 20 Ω, while the high resistance values are about 2×10^4 Ω. The resistance ratio between HRS and LRS is about 10^3, and the HRS resistance is more stable than that of LRS. This illustrates that after the 400-°C heating of the substrate, the device stability and the resistance ratio between HRS and LRS are both increased correspondingly.

Storage time performance is also an important parameter of memory devices, so we measure the capability of a Ag/ZnO/Zn/Pt device fabricated at a 400-°C substrate temperature to retain both resistance states and it is shown in Fig. 5. During the measurement, first, the device is turned ON or OFF by DC voltage sweep and then a sustained readout voltage (0.1 V) is applied to the Ag TE. As shown in this figure, after 10^4 seconds of test, the HR and LR remain almost unchanged, and the resistance ratio between HRS and LRS is kept stable when the ratio $> 10^3$, which suggests that the data retention characteristic of this memory device is very good.

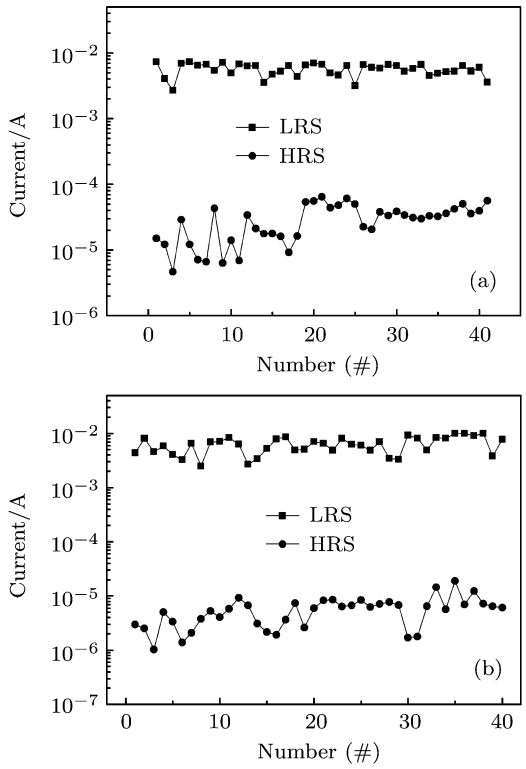


Fig. 4. Switching cycling characteristics in the HR state and the LR state of the Ag/ZnO/Zn/Pt memory device at different substrate temperatures: room temperature and 400 °C, with the resistance measured at 0.1 V.

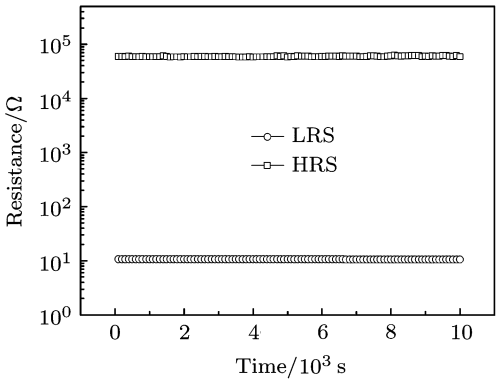


Fig. 5. Retention property of the Ag/ZnO/Zn/Pt memory device at 400-°C substrate temperature.

The mechanisms for resistive switching of the transition metal oxides are interesting but still controversial. From many proposed models, the conductive filament formation and rupture mechanism are adopted to explain the resistive switching effect in this work. Under application of an electric field, defects such as oxygen vacancies and Ag cations align to form tiny conducting filaments in the HRS and these tiny conducting filaments gather together to form stronger and more conducting filaments leading to the transition to the LRS.[17] These are in agreement with the models of the electrochemical metallization memory effect (ECM) and the valence change memory effect (VCM).[18] Take the VCM model for example, in the SET process, the oxygen ions which are generated by soft excitation can be stored by the Ag TE. When the DC sweep voltage varies from zero to negative, the oxygen ions which have been stored in Ag TE can infiltrate through the ZnO film into oxidized oxygen vacancies, leading to the rupture of conducting filament[19] and the device transforming to HRS. The ECM model is very similar to the VCM model in process, but their difference is that Ag atoms, instead of oxygen vacancies, play a main role. The oxidation and reduction reactions of Ag atoms have the most effect on conductive filament formation and rupture process.[15]

In this work, we select ZnO to study the ReRAM device, because the ZnO thin film contains a large number of oxygen vacancies which could be used to grow conductive filaments. Therefore, the electroforming process is not needed in the initial state. Compared with the TMO materials of NiO or ZrO_2,[20,21] it has an improved characteristic for practical application. Although the oxygen vacancies play an important role in forming filaments, their excess can still affect the performance of ReRAM devices, thereby reducing the resistance of the HR state and thus the resistance ratio between HRS and LRS. So we use the method of heating the substrate to improve the quality of ZnO thin films, thus reducing the excess number of oxygen vacancies. Hence, the resistance ratio between HRS and LRS increases, and the device has a better stability than the RT device. These demonstrate that the better quality polycrystalline ZnO thin film meets the requirements of ReRAM devices.

4. Conclusion

By using the method of heating the substrate, we improve the quality of ZnO thin film, and achieve more stable resistive switching characteristics of the Ag/ZnO/Zn/Pt ReRAM. A low operation voltage ($<$ 1 V), low operation current ($\sim$20 mA), high resistance ratio ($\sim 10^3$), good retention characteristic ($> 10^4$ s), non-electroforming process, and multistep reset process are obtained. Taking these excellent switching performances into consideration, the Ag/ZnO/Zn/Pt memory device shows strong promise for future nonvolatile resistive switching memory applications.

References

[1] Meijer G I 2008 *Science* **319** 1625
[2] Waser R and Aono M 2007 *Nat. Mater.* **6** 833
[3] Kwan W L, Lei B, Shao Y and Yang Y 2010 *Curr. Appl. Phys.* **10** e50
[4] Terabe K, Hasegawa T, Nakayama T and Aono M 2005 *Nature* **433** 47
[5] Seo J W, Park J W, Lim K S, Kang S J, Hong Y H, Yang J H, Fang L, Sung G Y and Kim H K 2009 *Appl. Phys. Lett.* **95** 133508
[6] Xu N, Liu L F, Sun X, Chen C, Wang Y, Han D D, Liu X Y, Han R Q, Kang J F and Yu B 2008 *Semicond. Sci. Technol.* **23** 075019
[7] Son J Y and Shin Y H 2008 *Appl. Phys. Lett.* **92** 222106
[8] Sun B, Liu Y X, Liu L F, Xu N, Wang Y, Liu X Y, Han R Q and Kang J F 2009 *J. Appl. Phys.* **105** 061630
[9] Park C, Jeon S H, Chae S C, Han S, Park B H, Seo S and Kim D W 2008 *Appl. Phys. Lett.* **93** 042102
[10] Yang L, Kuegeler C, Szot K, Ruediger A and Waser R 2009 *Appl. Phys. Lett.* **95** 013109
[11] Tsunoda K, Fukuzumi Y, Jameson J R, Wang Z, Griffln P B and Nishi Y 2007 *Appl. Phys. Lett.* **90** 113501
[12] Özgür Ü, Alivov Y I, Liu C, Teke A, Reshchikov M A, Doğn S, Avrutin V, Cho S J and Morkoçd H 2005 *J. Appl. Phys.* **98** 041301
[13] Bao S Y, Dong W J, Xu X, Luan T B, Li J and Zhang Q Y 2011 *Acta Phys. Sin.* **60** 036804 (in Chinese)
[14] Qin J M, Zhang Y, Cao J M, Tian L F, Dong Z W and Li Y 2011 *Acta Phys. Sin.* **60** 036105 (in Chinese)
[15] Yang Y C, Pan F, Liu Q, Liu M and Zeng F 2009 *Nano Lett.* **9** 1636
[16] Yang Y C, Pan F, Zeng F and Liu M 2009 *J. Appl. Phys.* **106** 123705
[17] Chang W Y, Lai Y C, Wu T B, Wang S F and Chen F 2008 *Appl. Phys. Lett.* **92** 022110
[18] Waser R, Dittmann R, Staikov G and Szot K 2009 *Adv. Mater.* **21** 2632
[19] Lin C Y, Wu C Y and Tseng T Y 2007 *J. Appl. Phys.* **102** 094101
[20] Chang S H, Lee J S, Chae S C, Lee S B, Liu C, Kahng B, Kim D W and Noh T W 2009 *Phys. Rev. Lett.* **102** 026801
[21] Liu Q, Long S and Wang W 2009 *IEEE Electron Dev. Lett.* **30** 1335