Bipolar resistance switching in high-performance Cu/ZnO : Mn/Pt nonvolatile memories: active region and influence of Joule heating

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Abstract. Manganese-doped ZnO dielectric films sandwiched between Cu and Pt electrodes were prepared and investigated for nonvolatile resistive memory applications. These structures exhibit promising bipolar resistive switching (RS) behavior with a large ON/OFF ratio (∼10³), suitable threshold voltages (1.4 and −0.7 V for SET and RESET, respectively), long retention (>10⁴ s at 85 °C) and low write current (10 µA). A study on the ZnO : Mn thickness dependence of threshold voltages reveals that RS should be an interfacial effect rather than bulk behavior. By elevating current compliance during the SET process, an anomalous transition from bistable memory switching to monostable threshold switching was observed, which is attributed to the instability of conductive filaments induced by Joule heating effects. Apart from this, fast voltage sweep cycles without efficient heat dissipation were also found to accelerate the hard dielectric breakdown of the device, reflecting the impact of accumulative Joule heating. These results reveal the possible influences of Joule heating effects on bipolar resistance switching and thus the necessity of avoiding them in future high-density memory applications. Conceivable solutions are considered to be reducing the operating currents and improving the heat dissipation of memory devices based on our experiments.

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1. Introduction

There is a surge of scientific interest in next-generation nonvolatile memory technologies at present, because traditional flash memory is rapidly approaching its fundamental scaling limit due to the increasing difficulty of retaining electrons in shrinking dimensions [1]–[3]. On this background, resistance-change random access memory (RRAM), a nonvolatile memory concept based on resistance change between two or more resistance states, has attracted extensive attention due to its high response speed, high scalability, multi-bit storage potential and simple structure [3]–[7]. Resistive switching (RS) effects have been reported in various materials, including solid electrolytes [8]–[10], perovskites [4]–[7], [11]–[15], binary transition metal oxides (BTMOs) [16]–[19], amorphous silicon [20] and even organics [21]. Among them, BTMOs have advantages of simpler compositions, lower deposition temperatures and better compatibility with complementary metal–oxide–semiconductor (CMOS) processes, which makes them promising candidates for practical applications. As one of the most important BTMOs at present, ZnO has found wide applications in electronics, optics, optoelectronics, spintronics and energy generators because of its versatile favorable properties and facile preparations [22]–[25]. Therefore, the development of ZnO-based RRAM would be of both scientific and commercial interest.

Although controversies still exist in the microscopic mechanism of RS effects, there is now consensus that RS is mediated by the so-called conductive ‘filaments’ formation and rupture process in many systems [1, 3, 4, 8]–[10, 16]. In our previous work, we have directly observed the presence of metallic Ag filaments in low-resistance state (LRS) Ag/ZnO : Mn/Pt RRAM devices under a transmission electron microscope, thus fundamentally underpinning the filamentary model [26]. As a result, the filamentary mechanism, especially the physics involved in the SET process, is quite clear. However, there still exist some issues in RRAM that are not clearly understood, for instance, the active region where RS occurs and the role of Joule heating effects in bipolar RS. As is widely known, Joule heating is considered as the driving force of RESET switching in unipolar RS [3, 4, 16], whereas the influence of Joule heating on bipolar RS still remains elusive. This question would become more urgent when the memory density gets higher and higher. In this study, Cu/ZnO : Mn/Pt electrochemical metallization memories with bipolar RS were prepared and investigated for RRAM applications. Device performance was characterized and the above-mentioned issues were elucidated.
2. Experimental details

A total of 2 at.% Mn-doped ZnO dielectric films with a series of thicknesses (15, 30, 60 and 120 nm) were deposited on Pt/Ti/SiO$_2$/Si(100) substrates by means of direct current reactive magnetron cosputtering. The base vacuum of the chamber was better than $5 \times 10^{-4}$ Pa, and the working gas was a mixture of argon (0.4 Pa) and oxygen (0.4 Pa). The substrates were heated to 200 °C during deposition. Subsequently, Cu top electrodes were fabricated by positioning a shadow mask on the top of the ZnO : Mn films and sputtering an 80 nm thick Cu layer. The Cu electrodes are circular in shape and 300 µm in diameter, defining the lateral geometry of the devices. The obtained two terminal Cu/ZnO : Mn/Pt memory devices were sequentially delivered to a Keithley 4200 semiconductor characterization system for electrical transport characterizations. The crystal structure of the as-prepared ZnO : Mn films was analyzed by x-ray diffraction (XRD) (Rigaku D/max-2500) utilizing Cu $K\alpha$ radiation. A scanning electron microscope (SEM) equipped with an energy dispersive x-ray spectroscopy (EDX) attachment was used to examine the changes on the Cu anode after the device underwent permanent failure.

3. Results and discussion

3.1. Structural characterization and measurement configuration

Figure 1 shows a representative $\theta$–$2\theta$ XRD scan pattern obtained in 2 at.% Mn-doped ZnO films with a thickness of 30 nm. The films were found to be highly c-axis oriented. Apart from the wurtzite (002) peak, no additional diffraction lines of ZnO could be detected in the scanned region of 30–80°, which indicates a fine wurtzite structure with a strong c-axis texture. The inset of figure 1 depicts a schematic view of the memory cell structure and the measurement setup in this study.
setup in this work. As can be seen, all the bias voltages were applied on the Cu anode with the Pt cathode grounded.

3.2. Resistive switching characteristics in Cu/ZnO : Mn/Pt capacitors

Figure 2(a) shows the current–voltage (I–V) characteristics measured from the first voltage sweep cycle on the pristine Cu/ZnO : Mn/Pt memory device with a ZnO : Mn thickness of 30 nm. The initial state of the device exhibits high resistance at $\sim 10^8\text{--}10^9\,$Ω, and the voltage is swept in four parts following a sequence of 0 → positive → negative → 0, as denoted in figure 2(a). One can see that a forming process occurs at about 1.9 V, which triggers an abrupt change from a high-resistance state (HRS or OFF) to a low-resistance state (LRS or ON). A current compliance (CC) of 5 mA is adopted herein to avoid permanent dielectric breakdown of the device. The resistance in LRS is found to be randomly distributed around $10^2\,$Ω, which does not show significant dependence on the film thickness. This kind of distribution was also reported recently by Soni et al [8]. Subsequently, when we sweep the voltage reversely to $\sim -0.6\,$V, a RESET switching is observed. Positive biases were also tried to RESET the devices but had no success, indicating a completely bipolar nature and thus confirming electrochemical redox reactions as the driving force in RS instead of thermal fuse/antifuse [3]. It should be noted that the first RESET process cannot fully restore the high resistance in the initial state. Instead, an OFF state with a relatively lower resistance ($\sim 10^5\,$Ω) was reached, which is in agreement with the observation of Wang et al [27]. It might be attributed to the incomplete dissolution of the conductive filaments created in the forming process. These remnant parts of filaments percolate in the insulating matrix in some manner, decreasing the overall difficulty of charge transport through the cell.

After the first cycle, stable bipolar RS could be reproducibly observed. Figure 2(b) shows a typical I–V curve measured in subsequent cycles, where a CC of 5 mA is also adopted in the SET process. The voltage required in SET is generally lower than that in forming. Moreover, one can see in figure 2(b) that the electrical transport behavior in LRS exhibits a completely linear character, coinciding with ohmic conduction through metallic Cu filaments. It is worthwhile pointing out that Mn doping is not indispensable for the presence of RS effects. The Cu/undoped ZnO/Pt cells are also able to display bipolar RS, as exhibited in the inset of figure 2(b). However, since undoped ZnO is intrinsically an n-type semiconductor, the resistance of the as-prepared device composed of pure ZnO is only $\sim 10^7\,$Ω. Mn doping is thus employed to increase the resistivity of ZnO films, because Mn is a deep donor in ZnO and can significantly depress the concentration of intrinsic donors such as interstitial zins or oxygen vacancies [28, 29].

Figure 2(c) replots the I–V curve in figure 2(b) in a semilogarithmic scale, from which one can clearly see that different resistance states, namely, HRS and LRS, exist under zero bias, confirming the potential of utilizing the present structure for nonvolatile memory applications. Furthermore, figure 2(d) shows the log–log plot and linear fitting results of the previous I–V curve for the positive branch, in which the conduction mechanisms in the ON and OFF states could be determined as ohmic conduction and trap-controlled space charge limited conduction (SCLC) [30], respectively. The SCLC in the OFF state reflects the intrinsic charge transport behavior of ZnO : Mn films. Thus the entirely different conduction behavior in the ON state confirms that ohmic conduction is a local transport behavior through Cu filaments [26].

Figure 2(e) shows the distributions of the SET and RESET threshold voltages of Cu/ZnO : Mn (30 nm)/Pt memory devices. When the cells are repeatedly switched between
Figure 2. Resistive switching characteristics of the Cu/ZnO : Mn (30 nm)/Pt memory device. (a) Forming cycle of the device. (b) $I$–$V$ characteristics of the cell obtained in subsequent cycles. The inset shows RS effects in the Cu/undoped ZnO/Pt memory device. (c) Semilogarithmic plot of the $I$–$V$ curve in (b). (d) Log–log plot and linear fitting of the $I$–$V$ curve in (b) for the positive branch. (e) Distributions of SET and RESET threshold voltages. (f) Data retention properties of the device at $85 \, ^\circ C$. 

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ON and OFF states, $V_{\text{RESET}}$ distributes in a range of $-1.3$ to $-0.2$ V, whereas $V_{\text{SET}}$ shows more scattering with a wider distribution of $0.4$–$2.0$ V. The average values of $V_{\text{RESET}}$ and $V_{\text{SET}}$ are $-0.7$ and $1.4$ V, respectively, which are quite suitable for practical applications in view of their compatibility with CMOS processes, power consumption and immunity to possible electrical disturbances in the circuits. The data retention properties of the device were also examined at $85^\circ$C to simulate a real device operating temperature. One can see in figure 2(f) that both the memory states exhibit little degradation within $10^4$ s, and the ON/OFF ratio is stably kept as $>10^3$, demonstrating good reliability of data storage.

3.3. The active region of RS

A controversial issue concerning the mechanism of RRAM lies in the active region of RS, namely, whether RS is a bulk effect or an interfacial one. To elucidate this issue better in the present system, Cu/ZnO : Mn/Pt memory cells with different ZnO : Mn thicknesses of 15, 30, 60 and 120 nm were prepared and investigated. Figure 3 displays the ZnO : Mn thickness dependence of average threshold voltages in forming, SET and RESET processes. One can see that $V_{\text{forming}}$ shows an almost linear dependence on film thickness. The thicker the film, the higher the $V_{\text{forming}}$. It could be regarded as the increased difficulty of creating longer conductive filaments in a thicker ZnO : Mn matrix for the first time. As for $V_{\text{SET}}$ and $V_{\text{RESET}}$, however, little or weak dependence on film thickness is observed, which means that the bias voltage may mainly drop on a local effective region, and the thickness of this region does not significantly vary with bulk thickness. It seems that RS is a local effect rather than a global one, which is inclined to the interfacial model. Similar experimental results have also been obtained in Cu/SiO$_2$/Pt and Pt/Fe$_2$O$_3$/Pt cells [9, 18]. Furthermore, Janousch et al [11] and Yang et al [19] have shown experimental evidence indicating the electrode/dielectric interface as the above-mentioned local effective region, which corroborates the interfacial model more firmly. Therefore, a possible scenario of RS might be as follows: the RESET process corresponds to
Figure 4. (a) Bipolar RS characteristics of the Cu/ZnO : Mn (30 nm)/Pt memory device when different CCs (10 µA, 100 µA, 1 mA, 5 mA, 10 mA) are adopted in the SET process. The $I–V$ curve for the 10 µA CC case is also shown in the inset in semilogarithmic scale. (b) Threshold switching characteristics of the Cu/ZnO : Mn (30 nm)/Pt memory device when the CC is increased to 50 mA.

an incomplete dissolution of conductive filaments at the electrode/dielectric interface, and the subsequent SET process only needs to connect this local area instead of rebuilding the whole conductive path.

3.4. Role of Joule heating effects in bipolar RS

A systematic study on the effect of Joule heating was conducted by varying the CC in the SET process and recording corresponding $I–V$ characteristics. As shown in figure 4(a), bistable RS can be successfully achieved by tuning the CC in a wide range from 10 µA to 10 mA for the Cu/ZnO : Mn (30 nm)/Pt memory cell. The inset of figure 4(a) displays the $I–V$ curve for the 10 µA case in semilogarithmic scale, from which bistable RS could be more clearly observed,
Figure 5. Fast cycling characteristics of the Cu/ZnO : Mn (30 nm)/Pt memory device in cycles 1–64 after the forming process. The inset shows that RS fails in cycle 65.

demonstrating that the write current could be reduced to such a low level without interrupting the RS effects. In contrast, when we increase the CC up to 50 mA, it is interesting to find that bistable memory switching has transformed to monostable threshold switching, as shown in figure 4(b). Although the cell also exhibits resistance switching from HRS to LRS, the LRS could not be retained; thus it is not suitable for application as a nonvolatile memory device. Chang et al [16] have also observed the memory switching → threshold switching transition in Pt/NiO/Pt cells when heat dissipation is not efficient enough, which is considered to make the conductive filaments unstable at high temperatures. In the present case, we could invoke this interpretation to explain our phenomenon well. Since more severe Joule heating would be generated when larger currents (determined by the value of CC) pass through the as-formed filaments in the SET process, the Cu filaments would be at elevated temperatures. The mass transport electromigration of Cu atoms contained in the filaments would thus be accelerated, leading to possible ruptures of the filaments and instability of the ON states. Our results reflect that the influence of Joule heating effects is not negligible when write currents above ~10 mA are involved for Cu/ZnO : Mn/Pt cells, which coincides very well with the viewpoint of Guo et al [31].

An anomalous feature in figure 4(a) is that the resistance in LRS has not shown apparent dependence on the value of CC, which deviates from the experiential relationship $I_{\text{reset}} \approx I_{\text{comp}}$ ($I_{\text{reset}}$ denotes the current where RESET switching occurs, whereas $I_{\text{comp}}$ is the value of CC) [32], especially for low $I_{\text{comp}}$ cases (e.g. 10 and 100 $\mu$A). This deviation could be attributed to a transient current flowing through the parasitic capacitance ($C_p$) of the measurement configuration (the inset of figure 1) when forming or SET transitions occur [33]. This is the reason why the deviation is more severe in the cases of low $I_{\text{comp}}$. By introducing a 1T1R configuration or using an ideal current limiter without $C_p$, the deviation might be alleviated, as indicated by the work of Kinoshita et al [33], which would be considered in our following work.

To further disclose the role of Joule heating in bipolar RS, another experiment, namely, fast sweep cycling, was performed on the Cu/ZnO : Mn/Pt cells. As shown in figure 5, bipolar $I$–$V$
characteristics were repeatedly measured on a single cell without time intervals after forming, and the CC in the SET processes was fixed to 1 mA. Although the Joule heating effects in a single cycle are weakened compared to the case in figure 4(b), this fast cycling has led to a quick failure of the cell since the heat generated during the write/erase operations does not have enough time to get dissipated. One can see that bipolar RS repeats successfully for 64 cycles, whereas a RESET failure takes place in cycle 65, leaving the device in the ON state permanently (see the inset). At this time, highly bright patterns can be observed on the Cu anode by in-situ optical microscopy, which indicates a very high temperature. These types of patterns can be later found and recorded under SEM, as shown in figure 6(a), part of which is further magnified and displayed as figure 6(b). One can clearly see that the patterns are composed of cracks whose shapes are similar to those of lightning. Compositions of the areas inside and outside the patterns, as denoted in figure 3(c), are also analyzed by EDX. The results show that there are no apparent compositional differences between the two kinds of areas, and figure 6(d) displays a typical EDX spectrum for the two cases. All these features indicate that the switching failure of the device is actually induced by a hard dielectric breakdown, and emergence of the patterns on the anode could serve as a signal. In contrast, if we leave intervals such as 2 min between neighboring cycles to aid in heat dissipation, the emergence of these kinds of patterns could be effectively depressed while memory switching does not
fail within 100 cycles. Therefore, it is proven that accumulative Joule heating effects have accelerated the hard dielectric breakdown of the cell, which is also harmful in practical memory applications.

Apparently, the avoidance of deleterious thermal effects would be necessary toward a practical application of RRAM, and this requirement is more urgent in future high-density data storage. In fact, the experiments in figures 4 and 5 have indicated possible routes, which may mainly fall into two categories. The first choice is certainly reducing operating currents, which is the goal of all electronic devices. However, this solution might not always be omnipotent, since accumulative Joule heating is proven to be harmful as well. Therefore, the second method, improving heat dissipation, becomes indispensable. Further studies on these issues are certainly beneficial for the field.

4. Conclusions

In summary, we fabricated Cu/ZnO : Mn/Pt electrochemical metallization memories, which exhibit promising bipolar RS behavior with a large ON/OFF ratio, suitable threshold voltages, long retention and low write current. The study on ZnO : Mn thickness dependence of threshold voltages reveals that RS should be interfacial behavior. Furthermore, our experimental results have disclosed the role of Joule heating in decreasing the stability of Cu filaments and accelerating the hard dielectric breakdown of electrochemical metallization memories. The avoidance of deleterious thermal effects would be necessary in future high-density packing, which might be achieved by reducing the operating currents and improving the heat dissipation.

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