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Impact of Al and Cu electrodes on GeO_x/W for high-performance crossbar resistive switching memories

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1. Introduction

Resistive switching random access memory (RRAM) devices have shown promise to develop future low power nanoscale nonvolatile memory (NVM) technology [1, 2]. RRAM devices using several materials with different structures have been proposed by several groups [3-6]. Although many materials using different structures have been reported, but the GeO_x material using Cu and Al top electrodes (TE) on GeO_x/W layers in the crossbar architecture have not been reported yet. In this study, enhanced resistive switching memory performances using novel Al/Cu/GeO_x/W crossbar structure are reported. The RESET current scalability is observed for Cu top electrode (TE) than that of the Al TE, which is very important in future nanoscale memory application. Long read endurance of $>10^5$ and excellent data retention at 85^{o}C for more than 500 hrs with high resistance ratio of $>10^4$ have been obtained for Cu TE. In addition, stable switching cycles and data retention at a current compliance (CC) of 1 nA and RESET current of <1 nA are obtained for Cu TE devices, which is useful for very low power operation for nanoscale nonvolatile memory applications.

2. Experiment

First, a tungsten (W) bottom electrode (BE) with a thickness of 200 nm was deposited by RF sputtering on SiO_2/Si wafers. Then the BE was defined and patterned by standard photo-lithography and wet etching process. To design the crossbar architecture, photo-lithography and etching were used to pattern W BE. Then, GeO_x film (~8 nm-thick) was deposited by RF sputtering. A thin WO_x layer (~2nm) was formed on W BE. Following this, copper (Cu) TE (~40 nm-thick) was deposited using thermal evaporator. To protect the Cu from surface oxidation for high temperature measurement, the aluminum (Al) layer (~160nm-thick) was deposited. Al TE without Cu layer was also deposited on GeO_x film. Finally, lift-off process was performed to obtain the crossbar memory devices.

3. Results and discussion

Fig. 1 shows the optical image, schematic view and HRTEM image of Al/Cu/GeO_x/W and Al/GeO_x/W memory devices. The thickness of the GeO_x film is ~ 8 nm. Different layers such as W, GeO_x, WO_x, AlO_x and Cu are confirmed by both EDX and XPS analyses (not shown here). It is observed the formation of AlO_x layer at the Al/GeO_x interface. Considering the Gibbs free energies of Al_2O_3 (-1582 kJ/mole), GeO_2 (-518.8 kJ/mole), CuO (-129.7 kJ/mole), and Cu_2O (-149 kJ/mole) at 300K, the formation of AlO_x at the Al/GeO_x interface will be easily as compare to others, and the AlO_x film will be more defective. Due to the AlO_x/GeO_x bilayers, a high formation voltage of ~6 V is needed for Al TE, as shown in first cycle of Fig. 2. The RESET current is independent for all CCs, which is due to the defective AlO_x layer at the Al/GeO_x interface. For Cu TE devices, typical I-V hysteresis characteristics with CC of 1 nA-50 µA are shown in Fig. 3. Initially, all memory devices was in the high resistance states (HRS). Slightly high voltage ~ 1 V is necessary to switch the memory device from HRS to low resistance states (LRS), as shown in first cycle. After formation process, the device shows normal bipolar resistive switching behavior. The memory device can be operated at low CC of 1 nA, and cylindrical type filament can be expected because the HRS is the same after RESET operation. A change of HRS state is observed at CC of 50 µA. At a higher CC of 50 µA, the filament diameter is increased and the shape of the filament will be a conical-type. After RESET operation, the Cu filament remains at the GeO_x/W interface. Corresponding SET/RESET currents versus CCs for both TEs are shown in Fig. 4. The RESET current is independent and higher (~1 mA) with different CCs for the Al TE. This suggests that the RESET current scalability as well as device scaling is difficult for the Al TE devices, which is larger filament diameter formation even a small CC of 1 nA. On the other hand, an excellent scaling of RESET current is observed for the Cu TE devices with CCs from 1 nA- 50 µA. Further, the RESET current is lower than the SET current which proves no current overshoot effect even 1R configuration. This suggests that the Cu nano-filament diameter can be controlled by CCs. Tight distributions of SET/RESET voltages [Fig. 5 (a)] and LRS [Fig. 5(b)] are obtained for the Cu TE devices. Applicable SET/RESET voltages and high HRS/LRS ratio of $>10^4$ at a small CC of 50 A are observed as compared to that of the Al TE devices at high CC of 500 µA. Larger SET/RESET voltages are obtained for the Al TE devices, which is difficult for low power operation. Fig. 6 shows the schematic illustration of resistive switching mechanisms for Cu and Al TEs. The copper ions (Cu^{z+}, z= 1 or 2) as a positive charge was migrated through the defects into the GeO_x film and started to grow first from W BE under SET operation through a reduction process (Cu^{z+} +ze^-→Cu^o) at the GeO_x/W interface [Fig. 6(a)]. The Cu nano-filament was started to dissolve at the Cu/GeOx interface under RESET operation through a dissolution process (Cu^o→Cu^{z+} + ze^-) [Fig. 6(b)]. Considering the energy gap and electron affinity of GeO_2, and work functions of Cu and W electrodes, the Cu ion as a positive charge (hole) can be injected through the GeO_x film rather than the electron injection because of lower barrier height of holes (not shown here). Due to the defective AlO_x layer formation at the Al/GeO_x interface, uncontrolled oxygen vacancy filament formation [Fig. 6(c)] and oxidation by O^{2-} ions [Fig. 6(d)] process can be observed under SET and RESET operations, which will hinder the scaling of the device. This suggests that Cu TE device has superior performance. The LRS decreases linearly with increasing CCs from 1 nA-50 µA for different structure devices (Fig. 7), which is very useful for multi-level data storage. Excellent read endurance of $>10^5$ times (Fig. 8) and data retention characteristics of >500 hrs (Fig. 9) with a large resistance ratio of $>10^4$ at 85^{o}C are achieved. Stable switching cycles and retention characteristics at small CC of 1 nA are also obtained (Fig. 10), which is useful for nanoscale memory.

4. Conclusions

Superior resistive switching memory performances in terms of high resistance ratio ($>10^4$), long endurance of $>10^5$ cycles, excellent data retention (>500 hrs) at 85^{o}C for CC of 50 µA, and excellent scalability potential are observed for the Al/Cu/GeO_x/W devices as compared to the Al/GeO_x/W devices. The switching mechanism occurs because of the lower barrier height for hole (Cu^{z+}) injection rather than electron injection. Controllable Cu nano-filament with a small CC of 1nA is also obtained. This study is very useful for future high-density low power 3D architecture.

Acknowledgment

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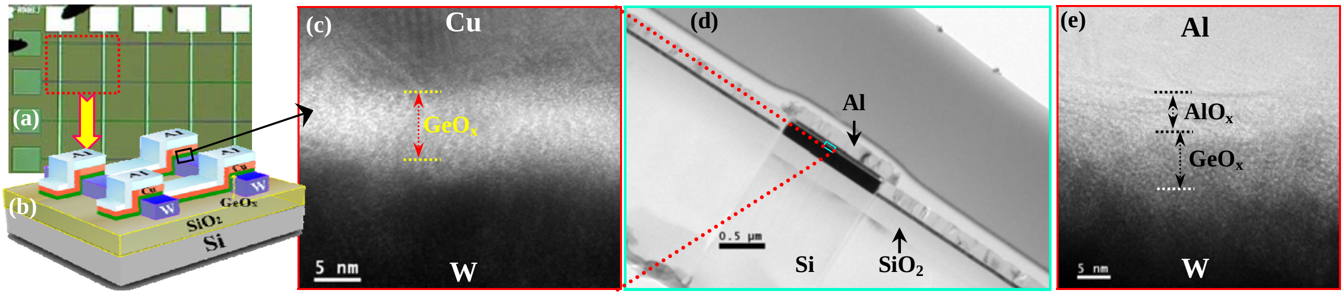

Fig. 1 (a) Optical image, (b) schematic view, and HRTEM image of (c), (d) Al/Cu/GeO_x/W and (e) Al/ GeO_x/W crossbar resistive switching memory device. Formation of thin AlO_x layer at the Al/GeO_x interface is observed. The thickness of GeO_x layer is approximately 8 nm. The thickness of AlO_x layer is approximately 5 nm.

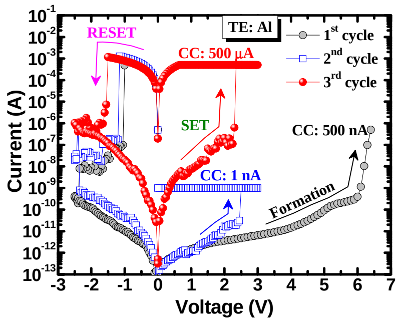

Fig. 2 Typical I-V hysteresis of Al/GeO_x/W RRAM device. The formation voltage is >6 V. The RESET currents are almost independent (~1 mA) with CCs from 1 nA-500 μA.

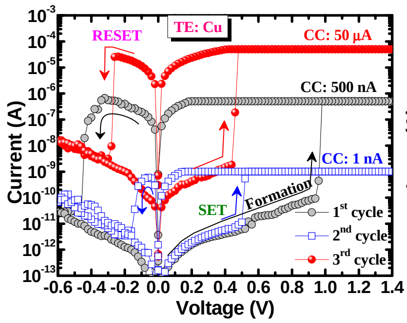

Fig. 3 Typical I-V characteristics of Al/Cu/GeO_x/W CBRAM device. Initially, slightly high voltage (~1V) is needed to switch the device into LRS. The SET voltage is ~0.5V.

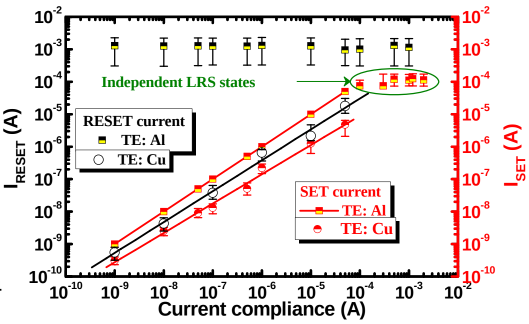

Fig. 4 SET/RESET currents versus CCs curve. SET current are increasing as increases CCs for both the devices. The RESET current increases as increases the CCs for Cu TE, however, the RESET current is not scalable for Al TE because of AlO_x formation.

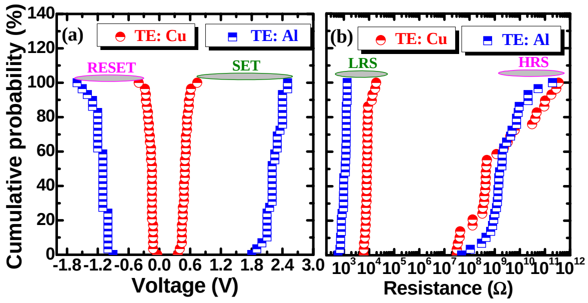

Fig. 5 Cumulative distributions of (a) SET/RESET and (b) LRS/HRS states for Cu (CC: 50 μA) and Al TE (CC: 500 μA) devices. The Al TE devices can be operated at higher power. SET/RESET voltages are lower for Cu TE devices. Tight distributions and lower SET/RESET voltages are obtained for Cu TE. High HRS/LRS ratio is found to be >10[4] for the Al/Cu/GeO_x/W device.

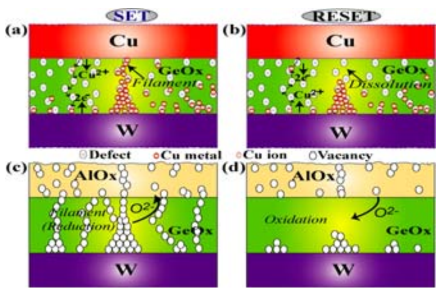

Fig. 6 Resistive switching mechanism is due to Cu nano-filament (a) formation and (b) dissolution of the CU TE. However, oxygen vacancy filament (c) formation and (d) oxidation are the switching mechanism for Al TE. The filament diameter is independent with CC for Al TE because of uncontrollable.

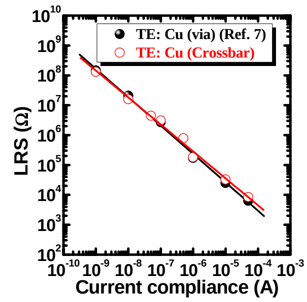

Fig. 7 LRS versus CCs for crossbar and via structure (Ref. 7) devices. LRS states are similar for both structures with different CCs. The device can be operated as low current as 1 nA.

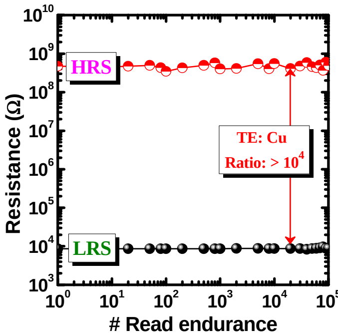

Fig. 8 Excellent read endurance of >10[5] times with a large resistance ratio of >10[4] for Al/Cu/GeO_x/W crossbar memory is obtained.

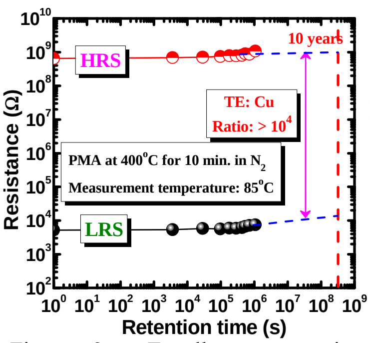

Fig. 9 Excellent retention characteristic of >500 hrs is observed at 85°C measurement temperature after PMA treatment.

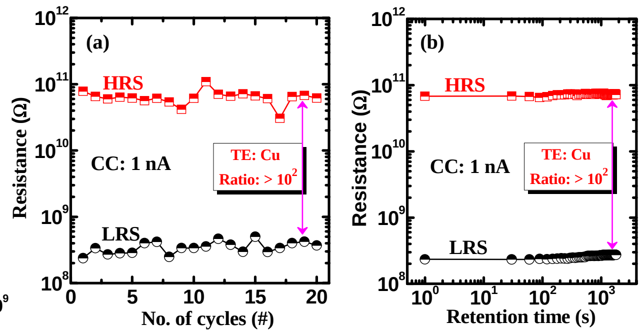

Fig. 10 Good (a) switching cycles and (b) retention characteristics are observed at 1 nA CC for Al/Cu/GeO_x/W crossbar memory, which can be applicable for future low power high-density non-volatile memory applications.