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Improved resistive switching memory characteristics using higher Ge content in $Ge_{x(0.2-0.5)}Se_{1-x}$ solid-electrolytes

S. Maikap[1,*], S. Z. Rahaman[1], Y. H. Wu[1], C. S. Lai[1], H. Y. Lee[2], W. S. Chen[2], F. T. Chen[2], M. J. Kao[2], and M. J. Tsai[2]

[1]Thin Film Nano Tech. Lab., Department of Electronic Engineering, Chang Gung University, Tao-Yuan, Taiwan
[2]Electronic and Opto-Electronic Research Lab., Industrial Technology Research Institute, Hsinchu, Taiwan
[*]Corresponding author: Tel: 886-3-2118800 ext. 5785 Fax: 886-3-2118507 E-mail: sidhu@mail.cgu.edu.tw

1. Introduction

Recently, conductive bridging resistive switching random access memory (CBRAM) devices with different solid-electrolytes [1-5] have been investigated for future low power with high speed, high scalability potential, simple process, and low cost. The kinetics of Ag or Cu filament formation/dissolution in the oxide based CBRAM are quite different as compared to the chalcogenide based devices [6]. In the last decade, higher (80%) Se content in the Ge_xSe_{1-x} solid electrolyte based CBRAM devices was also reported extensively due to more understandable switching mechanism and promising memory performance for future applications. Due to structural flexibility in the higher Se content devices, very small SET voltage (~0.2V) and uncontrolled filament formation/dissolution at elevated temperature (>85°C) can hinder for future memory applications. However, higher (50%) Ge content (or lower (50%) Se) in the Ge_xSe_{1-x} based devices has not been reported yet. In this study, improved resistive switching memory performance, such as higher SET voltage (~0.6V), stable endurance (>10^5 cycles), and stable retention with a high resistance ratio of >10^4 at 85°C for the Al/Cu/$Ge_{0.5}Se_{0.5}$/W structure have been reported for the first time. The Cu filament was also observed by HRTEM. Furthermore, stable low current operation (1 nA) with more than atomic scale of 0.25Å filament diameter, as calculated by new approach is also reported. A large memory size of 1300 Pbit/in^2 is obtained.

2. Experiment

Tungsten metal (W) with a thickness of ~100 nm was deposited by RF sputtering on SiO_2/Si substrate. To form a small via size of 150x150 nm^2, the SiO_2 layer (150 nm-thick) was deposited. Then, Ge_xSe_{1-x} (x=0.2, 0.3, 0.4, 0.5) films with a thickness of ~40 nm was deposited by E-beam evaporator. Then, Cu as a top electrode was deposited. To measure the device at elevated temperature, the Al layer was deposited on Cu layer by thermal evaporator. Finally, the lift-off process was performed to fabricate the memory device.

3. Results and discussion

Fig. 1(a) shows a typical high-resolution transmission electron microscope (HRTEM) image of the fabricated resistive memory device with a size of 150x150 nm^2. After 6000 program/erase (P/E) cycles with current compliance (CC) of 500 µA and pulse width of 500 µs, this TEM image was obtained. The thickness of Ge_xSe_{1-x} solid-electrolyte film is approximately 40 nm. A crystalline Cu filament with a diameter of 30 nm is observed [Fig. 1(b)]. All layers of W, Ge_xSe_{1-x}, Cu filament, and Cu are confirmed by EDX spectra [Fig. 1(c)]. As-received Ge_xSe_{1-x} film shows amorphous [Figs. 2(a) & (b)]. Figs. 3 & 4 shows x-ray photo-electron spectroscopy (XPS) of Ge*3d* and Se*3d* core-level electrons with different Ge_xSe_{1-x} films. The binding energies of Ge*3d* (Fig. 3) and Se*3d* (Fig. 4) are found to be 29 and 55.2, respectively. The binding energies of the different Ge_xSe_{1-x} films have shown different owing to the Ge*3d* and Se*3d* core-level electrons. Typical current-voltage (I-V) hysteresis characteristic of an Al/Cu/$Ge_{0.5}Se_{0.5}$/W device with a CC of 8 µA is shown in Fig. 5. Average SET voltage increases from 0.2 to 0.6 with increasing Ge content from 0.2 to 0.5 in Ge_xSe_{1-x} films owing to the less defective film for Cu^{z+} (z=1 or 2) ions. Good DC endurance with a high resistance ratio of >10^4 at CC of 8 µA is observed for high Ge content devices owing to good control of Cu filament formation/dissolution (Fig. 7). LRS decreases with increasing CCs from 1nA-1mA owing to filament diameter increased. At CC of <10 µA, the LRS of $Ge_{0.2}Se_{0.8}$ device is lower than that of $Ge_{0.5}Se_{0.5}$ device (Fig. 8). This suggests that Cu ions can be easily migrated through higher Se content, which results in a large variation of HRS. Figs. 9(a) & (b) show the schematic illustration of resistive switching mechanisms for Cu filament formation/dissolution. The copper ions as a positive charge was migrated through the defects into the Ge_xSe_{1-x} film and started to grow first from W BE under SET operation through a reduction process ($Cu^{z+} + ze^- \rightarrow Cu^o$) at the Ge_xSe_{1-x}/W interface [Fig. 9(a)]. The Cu filament was started to dissolve at the Cu/Ge_xSe_{1-x} interface under RESET operation through a dissolution process ($Cu^o \rightarrow Cu^{z+} + ze^-$) [Fig. 9(b)]. The Cu ions are migrated through the defects in $Ge_{0.2}Se_{0.8}$ film. Capacitance-voltage hysteresis shows defective film 9not shown here). It is suggested that the Cu ion as a positive charge (hole) can be injected through the Ge_xSe_{1-x} film rather than the electron injection. It is noted that the memory devices using $Ge_{0.2}Se_{0.8}$ and $Ge_{0.3}Se_{0.7}$ films show inferior P/E cycles (collapsed after 10^5 cycles), while higher Ge content memory devices show robust and long P/E cycles of >10^5 because of well controlled Cu filament formation/dissolution under external bias (Fig. 10). Highly stable LRS/HRS and excellent data retention of >48 hrs at 85°C are observed for higher Ge content resistive switching memory device (Fig. 11). This suggests that it may be lower thermal stability of higher Se content devices. This memory device is highly scalable because the device can be operated as low current as 1 nA (Fig. 8). The filament diameter (D) is calculated below.

$$D = \sqrt{\frac{4.L.\rho_{filament}}{\pi.LRS}} \qquad (1)$$

where L is the length (thickness of $Ge_{0.5}Se_{0.5}$, ~40 nm) and $\rho_{filament}$ is the resistivity (~200 µΩ.cm [7]). Using LRS and CC as obtained from Fig. 8 and eq. (1), the filament diameter was found to decrease linearly with CC (Figure 12). The nanoscale filament diameter was 15.8 nm–0.25Å as the CC decreased from 1mA to 1 nA. These calculated filament diameters were generally consistent with those in some reports [3,7-10]. The small diameter of 0.25Å shows a stable retention of >30 mins for CC of 1nA, indicating scalability beyond atomic scale. A memory size of 3.2 Tbit/in^2 can be obtained at CC of 1mA. If a low current operation of 1nA is achieved, then an even larger memory size of 1300 Pbit/in^2 can be obtained.

4. Conclusion

Improved resistive switching memory characteristics, such as higher SET voltage of 0.6V, stable long endurance of >10^5 cycles, long retention with a high resistance ratio of >10^4 at 85°C, low current operation of 1 nA for the Al/Cu/$Ge_{0.5}Se_{0.5}$/W structure have been reported. The Cu nanofilament is also observed by HRTEM. A large memory size of 1300 Pbit/in^2 is obtained to design for future high-density low power nanoscale nonvolatile memories.

Acknowledgment

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References

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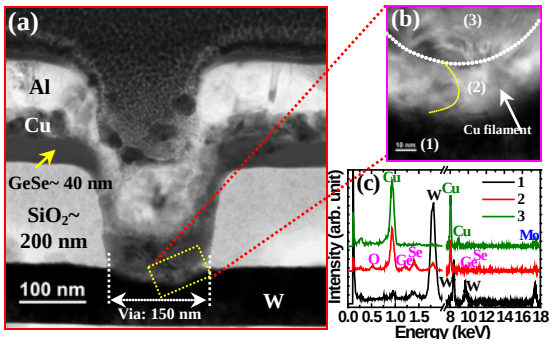

Fig. 1 (a) & (b) TEM image of an Al/Cu/$Ge_{0.2}Se_{0.8}$/W memory structure after 6000 P/E cycles. The size of the memory device is approximately 150×150 nm^2. The Cu filament diameter is ~30 nm. (c) EDX analysis.

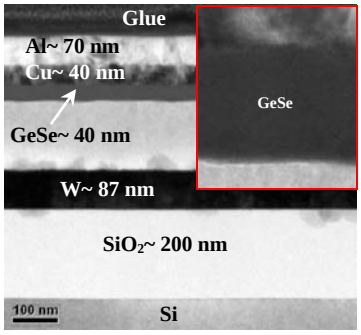

Fig. 2 Typical TEM image of as-received Al/Cu/$Ge_{0.2}Se_{0.8}$/W memory device. The $Ge_{0.2}Se_{0.8}$ film shows amorphous (inset).

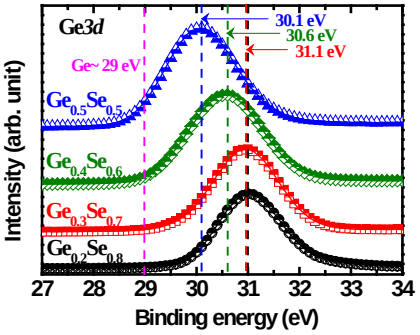

Fig. 3 XPS characteristics of Ge*3d* for all solid electrolytes. The binding energy of Ge*3d* electrons are increased (30.1 to 31 eV) with increasing the Se contents.

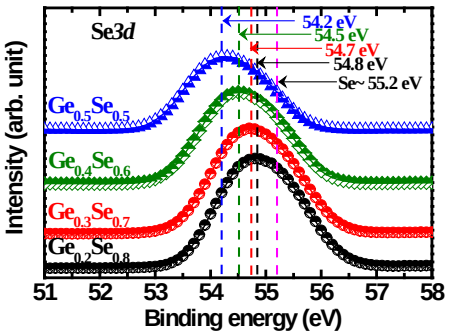

Fig. 4 XPS characteristics of Se*3d*. The binding energy of Se*3d* electrons are increased (54.2 to 54.8) eV with increasing the Se contents. All compositions are confirmed from the XPS.

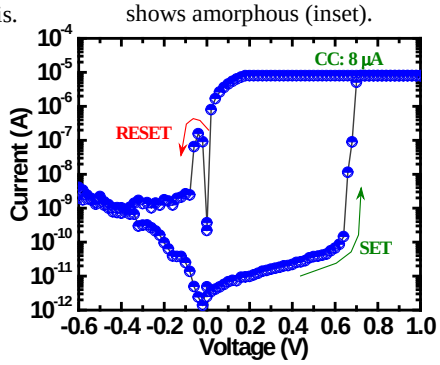

Fig. 5 Typical I-V hysteresis characteristics of an Al/Cu/$Ge_{0.5}Se_{0.5}$/W memory device at aCC of 8 μA. The SET voltage of ~0.6V is high enough for circuit design.

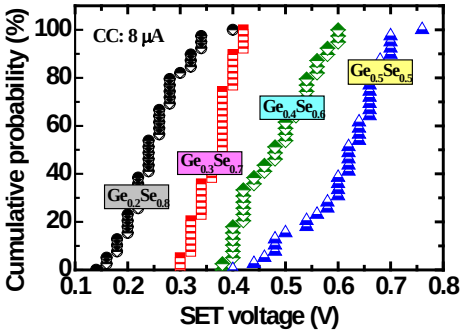

Fig. 6 SET voltages are decreasing with increase of Se contents in Ge_xSe_{1-x} film. Increase Ge contents, which will allow less structural flexibility as well as higher SET voltage.

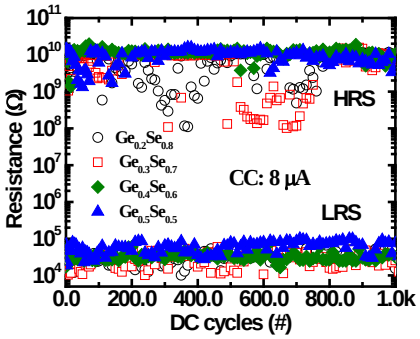

Fig. 7 Large variations of resistance states can be found for higher Se contents owing to the structural flexibility and uncontrolled Cu nano-filament diameter under SET/RESET operation. Therefore, higher Ge content is better.

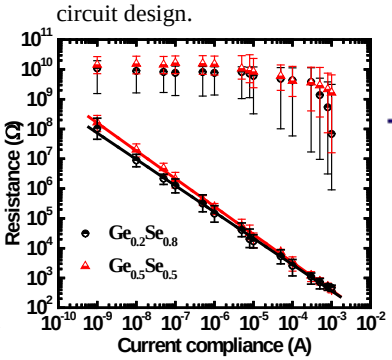

Fig. 8 LRS decreases with increasing CCs owing to the copper nano-filament diameter increased. Lower LRS for higher Se contents proves the higher migration and larger filament diameter at small CC of <10 μA.

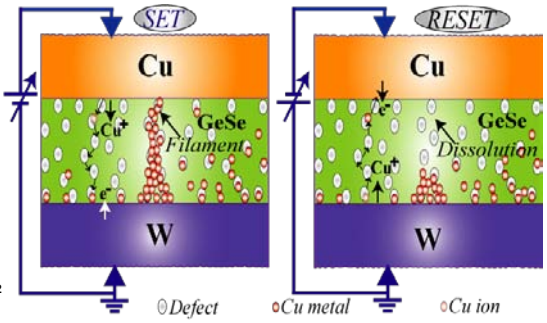

Fig. 9 Schematic views of the filament (a) formation and b) dissolution under SET and RESET operations are shown. Cu ions will migrate through defects inside the Ge_xSe_{1-x} solid electrolytes. The filament was started to grow at the Ge_xSe_{1-x}/W interface and to dissolve at the Cu/ Ge_xSe_{1-x} interface.

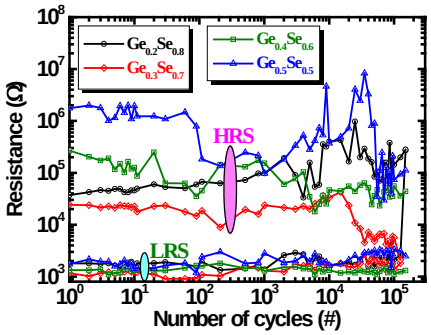

Fig. 10 Good ac endurances of ~10^5 cycles are observed for all devices. However, more stable endurance is observed for higher Ge content device because controllable filament formation/dissolution under external bias.

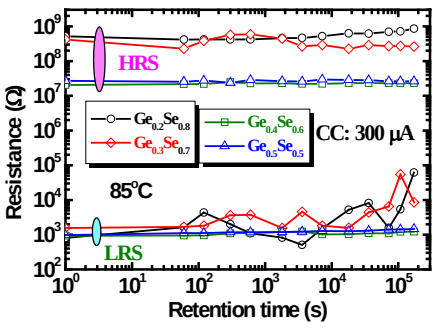

Fig. 11 Stable retention characteristics of >48 hrs at 85°C are obtained for $Ge_{0.4}Se_{0.6}$ and $Ge_{0.5}Se_{0.5}$ devices as compared to the higher Se content devices. This suggests that higher Se has thermal stability issue.

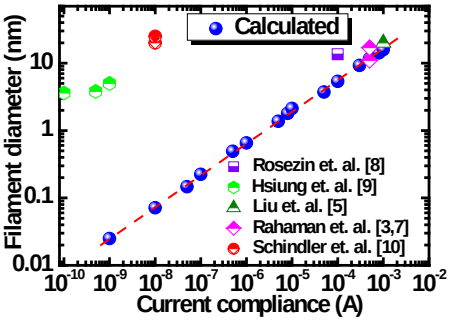

Fig. 12 The nanofilament diameter versus CCs for $Ge_{0.5}Se_{0.5}$ devices, as calculated using the new approach and verified by experimental data. A small diameter of (0.25 Å) and large memory size (~1300 Pbit/sq in.) can be obtained.