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Formation free resistive switching memory device using $Ge_{0.4}Se_{0.6}$ solid electrolyte

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1. Introduction

Different types of nonvolatile memory devices such as flash memory [1], phase changeable memory (PCM), magnetic random access memory (MRAM), ferroelectric RAM (FeRAM), resistive memory (RRAM) [2-4], etc. have been reported to fulfill the requirements of the International Technology Roadmap for semiconductors (ITRS). Among those memory devices the resistive switching memory device is one of the very promising candidates to overcome those problems such as scalability potential, switching power, nonvolatility and reliability aspects. Different resistive memory devices by using binary oxides such as ZrO_2, NiO, Ta_2O_5, etc. have also been reported by several groups [2-6]. Kozicki *et al*.[7] and Kund *et al.* [8] reported the Ag conductive bridging formation in the GeSe or GeS chalcogenide materials under certain bias condition on the memory device. However, the Ag as a mobile ion cannot be used fairly in the CMOS technology. To avoid this problem, Cu is one of the best choices for using metal chain in the $Ge_{0.4}Se_{0.6}$ solid electrolyte. Furthermore, Cu can be commonly used in the interconnection of CMOS technology. In this study, we have investigated resistive switching memory device using Cu metallic chain formation/removal in the Al/Cu/$Ge_{0.4}Se_{0.6}$/W structure without formation process which is useful for application.

2. Experiment

At first the bottom electrode of tungsten (W) metal was deposited by sputtering on 8 inch Si/SiO_2 substrate. Then, the SiO_2 with a thickness of 150 nm was deposited. The device sizes of 0.2-8 μm were defined by lithography and etching process. Then, the 40 nm thickness of $Ge_{0.4}Se_{0.6}$ film was deposited by electron gun (E-Gun). The Cu as a top electrode was deposited by thermal evaporator. The thickness of Cu was 40 nm. To protect the Cu, 160 nm of Al was deposited by thermal evaporator. Lift-off process was used to fabricate the memory device. The schematic structure of our memory device is depicted in the Fig. 1. Memory characteristics such as current-voltage (I-V), cycling and retention were performed using HP4156C semiconductor measurement analyzer.

3. Results and discussion

The memory characteristics of our resistive switching devices in an Al/Cu/$Ge_{0.4}Se_{0.6}$/W structure have been described. Current-voltage (I-V) hysteresis characteristics are shown in Fig. 2. Initially, the device was in the OFF-state, R_{High} (arrow 1). By applying a positive voltage on the top electrode, there is an instantaneous switching from the high resistance (low current: R_{High}) state to the low resistance (high current: R_{Low}) state (arrow 2) at a large threshold voltage (V_{th}) of +0.6 V. To form the conductive path of Cu chain into the solid electrolyte, the applied bias should be larger than the V_{th}. The memory device can continue the low resistance state (ON-state: R_{Low}) until the negative voltage of -0.24 V (arrows 3-6). The resistive memory device is going to be the high resistance state (R_{High}) if the applying voltage is more negative (V_e<-0.24V) as shown in arrow 7. A large erase current (I_e) of -78μA is needed for removal of Cu chain. The values of V_e and I_e increase with increasing the programming current compliances (not shown here). It means that the metallic Cu chain could be stronger by controlling the external power. The high resistance state will continue as shown in arrows 8 & 9. The corresponding resistance-voltage (R-V) hysteresis characteristic are shown in Fig. 3, which is calculated from Fig. 2. The ratio of resistance (R_{High}/R_{Low}) is large enough (~ $1.9x10^2$) for multi-level data storage (MLC) application. The switching mechanism of our resistive switching memory device is due to the reduction and oxidation process which can be explained as follows (Fig. 4). Initially the device was in the OFF state. Under the programming condition by applying the positive bias on the top electrode, the Cu ions will diffuse into the GeSe solid electrolyte film. Therefore, Cu metallic chain can be formed between two electrodes. Due to the metallic chain, the low resistance state could be observed [Fig. 4(a)]. Under the erasing condition by applying negative bias on the top electrode, the Cu metallic chain can be broken and the Cu ions will flow back to the top electrode. In this case, the high resistance state could be observed [Fig. 4(b)]. This formation and removal of the metallic pathway are due to the electro-migration and oxidation, respectively. The mechanism of our resistive switching memory device is not related with the oxygen vacancy mechanism, which is confirmed by X-ray photoelectron spectroscopy (XPS) analysis. The XPS spectra of Ge*3d* (Fig. 5) and Se*3d* (Fig. 6) core levels composed to the GeSe and $GeSe_2$ states. The GeO_x or SeO_x peaks are not observed in the GeSe solid electrolyte. Furthermore, the O*1s* peak is not also observed in the solid electrolyte. Indirectly, we can say that the resistive switching mechanism of our memory device is not related to the oxygen vacancy. Fig. 7 shows the Weibull plot of R_{Low} and R_{High} resistance states. The ratio of R_{High}/R_{Low} is > 10^2 in the maximum distributed region which is high enough for MLC application. Weibull plot of the V_{th} and V_e is shown in Fig. 8. The maximum V_e and V_{th} are showing in the range between -0.1 V to -0.3 V and 0.4 V to 0.6 V, respectively. Large V_{th} are obtained due to the composition (40:60) of the $Ge_{0.4}Se_{0.6}$ solid electrolyte. The memory devices are showing the erase current with the range of 50-100 μA (Fig. 9), which confirm the strong Cu chain formation under programming current of 200 μA.. Good endurance characteristics of >$2.5x10^5$ cycles are observed (Fig. 10). The OFF-state is unstable which can be improved by using series transistor on the memory element. The excellent data retention characteristics up to 50 hours are observed for a low programming current of 200 μA at 85°C (Fig. 11), due to the strong Cu chain formation into the $Ge_{0.4}Se_{0.6}$ solid electrolyte.

4. Conclusions

The nonvolatile resistive switching memory device with a low programming current of ~200 μA, large V_{th} of ~0.6V, high R_{High}/R_{Low} of 1.9×10^2, good endurance (>$2.5x10^5$ cycles) and excellent retention (>50 hours) at 85°C is reported. Furthermore, a strong Cu chain formation can be monitored by investigating the erase voltage and current. It is believed that this memory device can be useful in future 22 nm nonvolatile memory technology.

Acknowledgments

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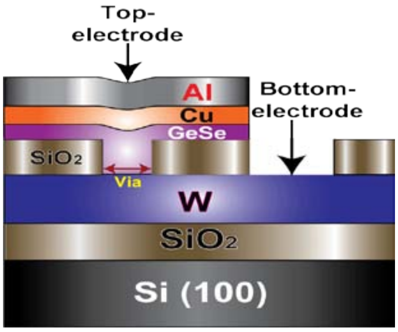

Fig. 1 Schematic of the resistive memory device using Al/Cu/$Ge_{0.4}Se_{0.6}$/W structure. The thickness of $Ge_{0.4}Se_{0.6}$ film is 40 nm.

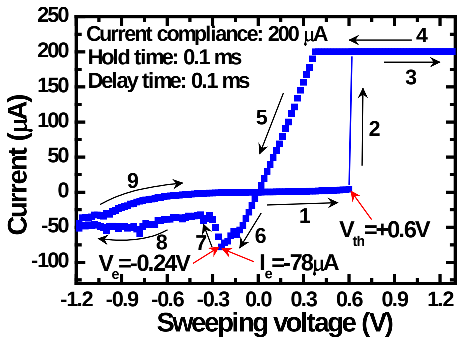

Fig. 2 Current versus voltage (I-V) hysteresis characteristics of the Al/Cu/$Ge_{0.4}Se_{0.6}$/W resistive memory devices. The size of the memory device is 0.2 μm.

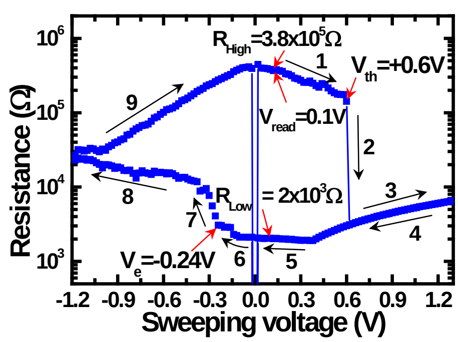

Fig. 3 R-V hysteresis characteristics have been calculated from Fig. 2. A high resistance ratio (R_{High}/R_{Low}) of $1.9x10^2$ is observed. Extra formation process is not needed to get such a switching of the memory device.

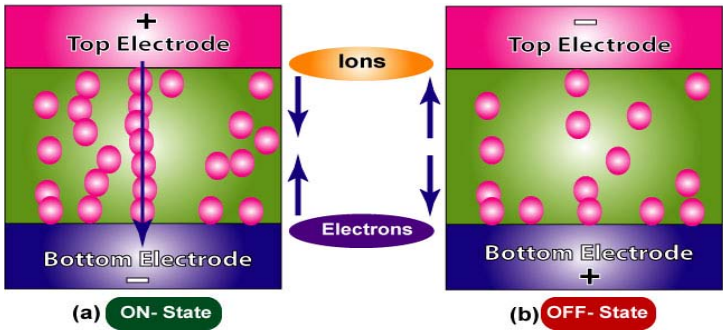

Fig. 4 Resistive switching mechanism of our memory device in Al/Cu/$Ge_{0.4}Se_{0.6}$/W structure. (a) Formation of Cu metallic chain due to reduction process by applying positive bias on the top electrode. (b) Removal of Cu metallic chain due to oxidation process by applying negative bias on the top electrode.

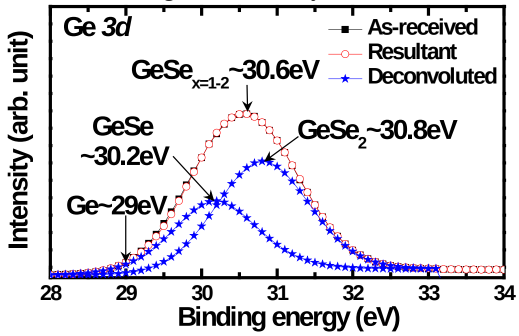

Fig. 5 X-ray photoelectron spectra of Ge*3d* core levels. The oxidation state of Ge is not observed in our $Ge_{0.4}Se_{0.6}$ solid electrolyte. It means that the switching mechanism of our memory device is not related to the oxygen vacancy.

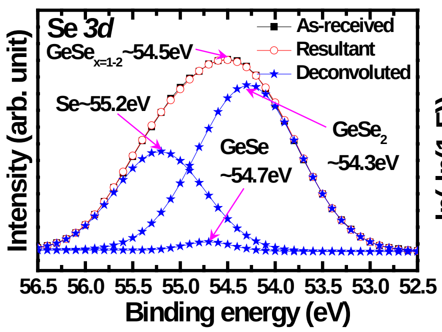

Fig. 6 X-ray photoelectron spectra of Ge*3d* core levels. The oxidation state of Se is not also observed. The solid electrolyte is composed with the GeSe and $GeSe_2$ states.

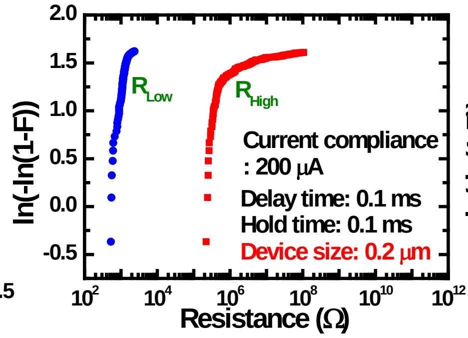

Fig. 7 The cumulative distribution (~150 devices) of R_{Low} and R_{High} is fitted with Weibull function. The ratio of R_{High}/R_{Low} is about 10^2 for all devices, which is high enough for MLC application.

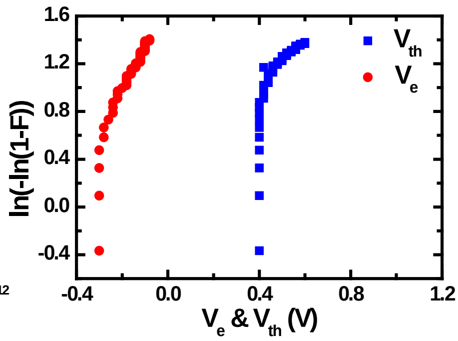

Fig. 8 Weibull plot of negative voltage (V_e) and threshold voltage (V_{th}) at 200 μA programming current. The device size was 0.2 μm.

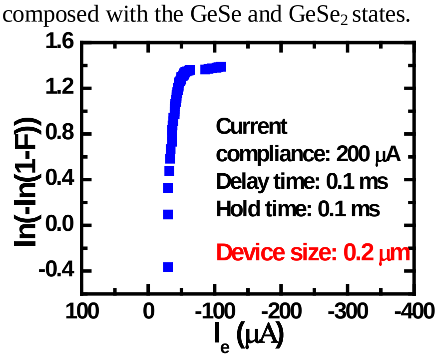

Fig. 9 Weibull plot of erase current (I_e) at 200 μA programming current. The maximum number of I_e is showing in the range from 50-100 μA. The erase current proves that the Cu chain was strong enough under such a programming current of 200 μA.

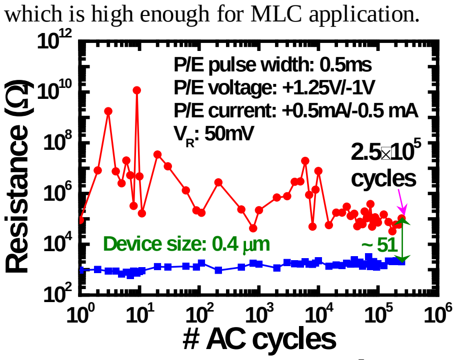

Fig. 10 Good endurance ($>2.5x10^5$ cycles) characteristics of the Al/Cu/$Ge_{0.4}Se_{0.6}$/W memory devices are obtained. The high resistance state could be stable if the series transistor is used in the memory elements. The resistance ratio (R_{High}/R_{Low}) is more than 51 after the $2.5x10^5$ cycles.

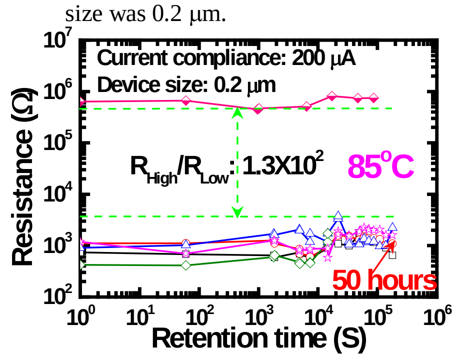

Fig. 11 Excellent retention characteristics of an Al/Cu/$Ge_{0.4}Se_{0.6}$/W resistive memory device are observed at the measurement temperatures of 85°C. A high resistance ratio of $1.3x10^2$ is achieved after 50 hours of retention time. To confirm the data, five memory devices are measured at 85°C.