Extended Abstracts of the 1992 International Conference on Solid State Devices and Materials, Tsukuba, 1992, pp. 319-321 **PC3-6**

Nonvolatile Memory Based on Phase Transition in Chalcogenide Thin Film

Toshiya Kitagawa, Kazuya Nakayama, Shuichi Okano*, Masashi Ohmura and Masakuni Suzuki

Faculty of Technology, Kanazawa University,Kodatsuno 2-40-20,Kanazawa, 920,Japan
**Ishikawa College of Technology, Tsubata 923-03,Japan*

Electrically erasable nonvolatile memories based on the reversible amorphous- crystalline phase transition in As-Sb-Te films were studied. The pulse current for the phase transition could be reduced by increasing the width of the pulse. When the current pulse for the transiton from the crystalline to the amorphous state was small, the deterioration of high resistive amorphous state proceeded with the repetition of the phase transitions. The deterioration occurred due to the accumulation of segregated crystallites. In the appropriate set- and reset-conditions, more than 10^5 repetition cycles of write/erase were attained.

1. Introduction

The phase transition between the amorphous and crystalline state in chalcogenide semiconductor films can be controlled by electric pulses or pulsed laser beam,[1-4] so chalcogenide semiconductor films would be applied to electrically erasable nonvolatile memories, where the high resistive amorphous states and low resistive crystalline states are assigned to binary states.

Tellurium based alloys are favorable materials for such nonvolatile memories using reversible phase transitions, since their melting and crystallization temperatures can be set up by controlling the composition so as to crystallize and amorphize in appropriate temperature cycles.[5-7] In this study, we examined the possiblity of the nonvolatile memory device based on reversible phase transitions in As-Sb-Te ternary systems.

2. Sample Preparation and Experiments

$As_xSb_yTe_z$ bulks were prepared from the melt of the mixtures of high purity (99.999 %) As, Sb and Te where the ranges of x, y and z are 40>x>0, 40>y>0 and 80>z>60 respectively, but z=100 - x - y. Thin $As_xSb_yTe_z$ films, which were prepared by the flash-evaporation of $As_xSb_yTe_z$ powders, were sandwiched between the upper and lower electrodes as shown in Fig.1. There might be a slight differnce in the composition of the prepared thin film from the starting bulk material. The active region of the memory devices was limited to the opening of $10\mu m$ in the polyimid film defined by photolithography. Ni films as the lower electrode were deposited on glass substrates. The upper electrode consisted of Sb and Al double layers.

$As_xSb_yTe_z$ powders, as the evaporation source were prepared in N_2 ambient to avoid oxidation. The thickness of evaporated $As_xSb_yTe_z$ films was fixed to about 2000Å , and the thickness of polyimid films, which separate the upper electrode from the lower electrode, was about $1\mu m$.

The phase transition between the high resistive amorphous state and the low resistive crystalline state was caused by the set-pulse and the reset-pulse, which were fed through the micro-computer controlled circuits. In the set operation, a current

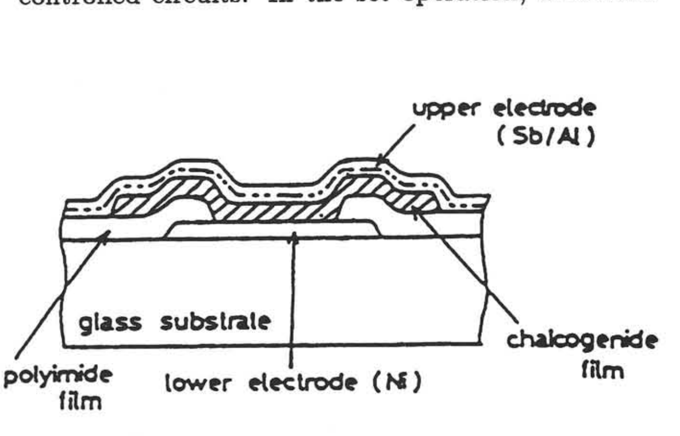

Fig.1 Cross sectional view of a memory cell.

limiting resistance ($> 1k\Omega$) was connected to the memory cell to limit the current after the switching, while in the reset operation a current limiting resistance was removed. The resistance of memory device was monitored using the reading pulse after every set and reset operation. The height and width of the set- and reset-pulse were varied to study the conditions causing the phase transition and the phenomena induced by electric pulses.

3. Results and Discussion

Typical waveforms for the reversible phase transtion are shown in Fig.2. When the voltage across $As_xSb_yTe_z$ films exceeded V_T, the memory cells switched into low resistance states due to the formation of a high conductive filament. The threshold field for the switching was typically of the order of 10^5 V/cm.

The high conductive filament crystallized when the temperature in the conductive filament exceeded the crystallization temperature of amorphous $As_xSb_yTe_z$ film, so the holding time to crystallize a high conductive filament varied with the intensity of the current of the set-pulse as shown in Fig.3 (a). The set operation could be made with the set-pulse lower than 5 V.

The diameter of the crystallized filament was estimated to be about 1 μm from its conductance. The crystallized filament could be brought back to the amorphous state by the reset-pulse which heated up the filament above the melting point. In this case, the high cooling rate was, however, necessary to quench the melt, so the wide reset-pulse could not cause the transition back to amorphous states as shown in Fig.3 (b).

Figure 4 shows the variation of resistance of both amorphous and crystalline states caused by the set- and the reset-pulses. The stability of resistance of the amorphous state strongly depended on the reset current. The number of the repetition cycle of the phase transition increased with increasing the

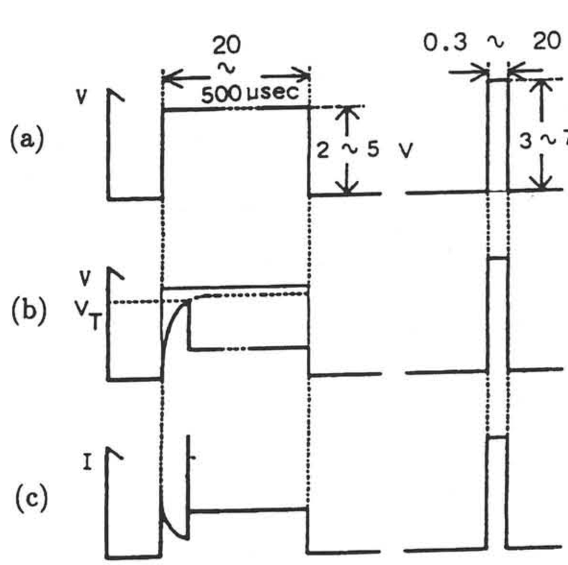

Fig.2 Voltage and current waveforms of the set- and the reset-pulses. (a)Voltage waveform of the applied pulses. (b)Voltage across the cell. (c)Current flowing through the cell.

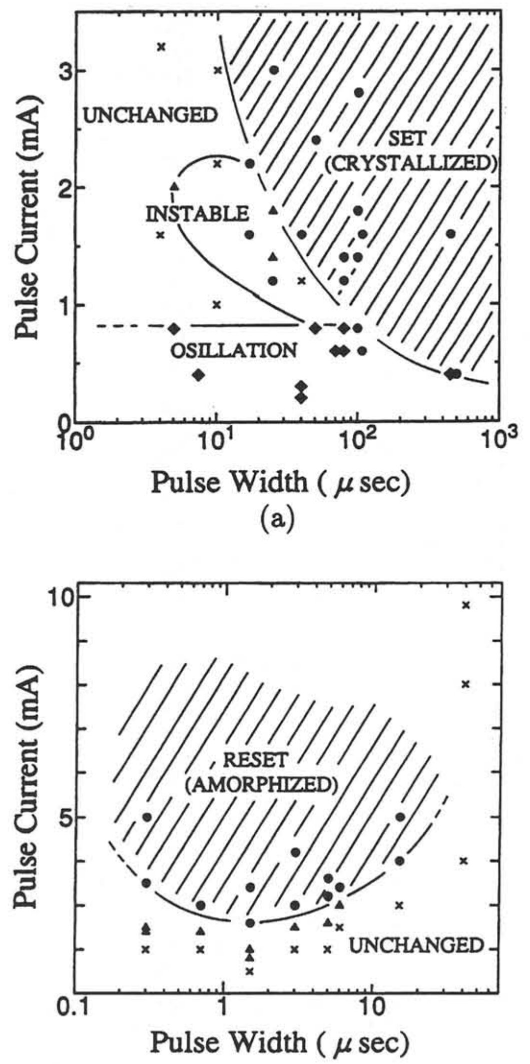

Fig.3 The relation of the current and width of the pulses causing the set and the reset operations in the memory cell of $As_{20}Sb_{10}Te_{70}$.(a) set operaiton. (b) reset operation.

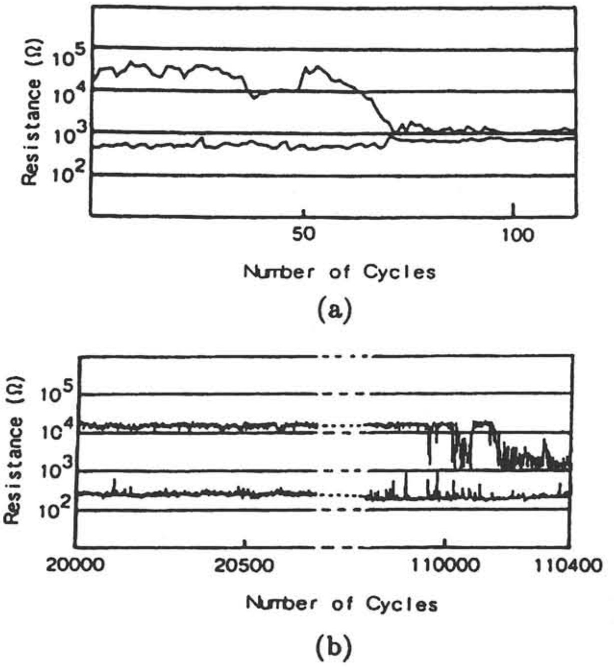

Fig.4 Variation of the resistance of crystalline and amorphous states with the repetition cycle of the phase transition in the memory cell of $As_{20}Sb_{10}Te_{70}$. The width of the reset pulse was 0.3 μsec. (a) I_{reset}= 4.8 mA. (b) I_{reset}= 44 mA.

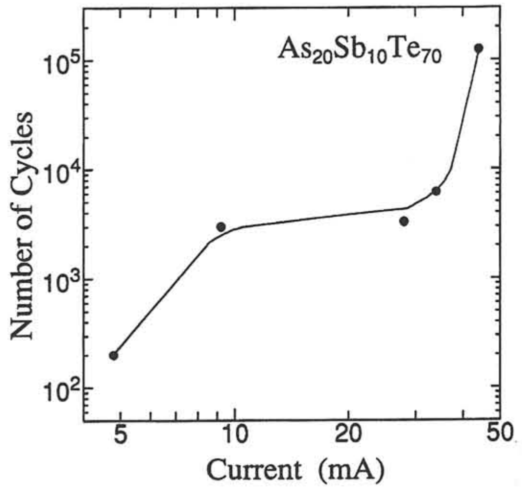

Fig.5 Maximun repetition cycles of the phase transition as a function of the reset current. The width of the reset pulse was fixed to 0.3 μsec.

reset current up to 40 mA as shown in Fig.5. More than 10^5 repetition cycles of the phase transition were attained with the reset pulse with more than 40 mA.

When the reset current was small, the deterioration, which is the drop of the resistance of amorphous states, occurred in a small number of the repetition cycle of the transition, and the phase transtion at last came to a halt. Those deteriorated cells, however, could be resurrected many times by applying larger current reset-pulse. In fact, the original amorphous state with high resistivity was restored, and the set- and reset-operation again became possible.

From these result, the deterioration of memory device is considered to be caused by the gradual segregation of crystallites in and outside the filament. To avoid this, memory materials should have those compositions which generate the crystalline phases of low melting point. From this point of view, the $As_xSb_yTe_z$ film with 15>x>10, 10>y>5 and 80>z>70 are fairly satisfying materials.

The reduction of the cell size down to the scale of the filament formed by the switching event would be also effective to avoid the accumulation of crystallites. This must be effective for lowering the reset current. The suppression of heat flow through the metal electrodes would be useful to some extent for the reduction of the reset current.

4. Conclusion

In the $As_xSb_yTe_z$ films, the repetition cycle of the phase transition was attained to a value more than 10^5. The deterioration of memory cells is due to the accumulation of segregated crystallites during transition processes. The stability of the set and the reset operation may be achieved by the reduction of the cell size and the improvement of the cell structures.

Acknowledgement

We would like to thank Dr.A.Kitagawa and Mr.Y.Kakimoto for their useful discussions, and Dr. D.P.Gosain and Mr.K.Ohtsuka for their Collaborations. This work was partly supported by Betsukawa Foundation.

References

1) S.R.Ovshinsky, Phys.Rev.Lett. 21(1968)1450.
2) S.H.Holmberg et al, J.Electron.Mater. 8(1979)333.
3) J.Kotz et al, J.Appl.Phys. 55(2),15(1984)427.
4) Y.Maeda et al, Tr.I.E.I.C.E. Vol.J74-C-II. No4 (1991)243.
5) J.Bicerano et al, J.Non-Cryst.Solids. 74(1985)75.
6) D.P.Gosain et al, J.Mater.Sci. 26(1991)3271.
7) D.P.Gosain et al, Jpn.J.Appl.Phys. 28(1989)1013.