E*PCOS2010

Phase change behavior of $Ge_1Cu_2Te_3$ thin films

Yuji Sutou*, Toshiya Kamada, Yuta Saito, Masashi Sumiya and Junichi Koike
Department of Materials Science, Tohoku University, 6-6-11 Aoba-yama, Sendai 980-8579
*ysutou@material.tohoku.ac.jp

ABSTRACT

The electrical resistance on the crystallization process of sputtered-deposited $Ge_1Cu_2Te_3$ film was investigated by a two-point probe method. It was found that the amorphous $Ge_1Cu_2Te_3$ film crystallized into a single $Ge_1Cu_2Te_3$ phase with a chalcopyrite structure, which lead to a large resistance drop. The crystallization temperature of the $Ge_1Cu_2Te_3$ amorphous film was about 240 °C, which was about 70 °C higher than the conventional $Ge_2Sb_2Te_5$ amorphous film. The activation energy for the crystallization of the $Ge_1Cu_2Te_3$ amorphous film was higher than that of the $Ge_2Sb_2Te_5$ amorphous film. The $Ge_1Cu_2Te_3$ compound with a low melting point can be expected to be suitable as a phase change material for PCRAM.

Key words: $Ge_1Cu_2Te_3$, low melting point, high crystallization temperature.

1. INTRODUCTION

Phase change random access memory (PCRAM) has been regarded as one of the promising candidates for the next-generation nonvolatile memories because of low production cost and excellent scalability. Generally, a phase change material for PCRAM needs to possess a low melting point for low power consumption, a high crystallization temperature for long data retention, and to show crystallization without phase decomposition for excellent repeatability. Currently, $Ge_2Sb_2Te_5$ compound (GST) is attracting considerable attention as a phase change material for PCRAM. The amorphous GST crystallizes first into a NaCl structure, and then transforms into a more stable hexagonal structure by further heating [1, 2]. However, the GST has a high melting point (~ 632 °C), and its crystallization temperature is relatively low (~ 150 °C). Therefore, it is required to develop a new phase change material with a low melting point and a high crystallization temperature. A Ge-Cu-Te system is known to be glassy alloys [3-6] and thermoelectric material [7]. In this system, there is a ternary calcogenide compound of $Ge_1Cu_2Te_3$, which has a low melting point of about 520 °C [8]. Therefore, the $Ge_1Cu_2Te_3$ compound is expected to be suitable as PCM from the viewpoint of equilibrium phase stability. However, the amorphization and crystallization of the compound have not been studied. In this study, phase change behavior and the corresponding electrical resistance change of the $Ge_1Cu_2Te_3$ film deposited by RF sputtering were investigated.

2. EXPERIMENTS

$Ge_1Cu_2Te_3$ (GCT) films with 200 nm thickness were deposited on SiO_2(20nm)/Si substrates by sputtering of Ge-Cu-Te alloy target. The composition of the alloy target was set to $Ge_{24}Cu_{33}Te_{43}$ to obtain the $Ge_1Cu_2Te_3$ film. The film composition was determined by transmission electron microscopy (TEM) with energy dispersive spectroscopy (TEM-EDS). The deviation from the stoichiometric composition of $Ge_1Cu_2Te_3$ was found to be less than 8% for all the elements. In-situ electrical resistance measurement during annealing process of the film was performed by a two point probe method. X-ray diffraction (XRD) analysis was employed for the structural identification of the film using an X-ray diffractometer with Cu-Kα radiation. TEM analysis was carried out to investigate the microstructure and to identify crystalline structure.

3. RESULTS & DISCUSSION

An as-deposited GCT film was confirmed to be amorphous by XRD and TEM. Figure 1 shows the temperature dependence of the electrical resistance for the GCT film at a heating rate of 10.6 °C/min. It was found that the as-deposited GCT film showed abrupt electrical resistance change by more than 10^2 ohm because of crystallization at about 240 °C. The crystallization temperature of the GCT was higher than that of GST (170 °C). The amorphous GCT film crystallized into a stable orthorhombic $Ge_1Cu_2Te_3$ structure. The activation energy for the crystallization E_a of the GCT film was higher than that of the GST film. The E_a of the GCT was estimated to be 2.81 eV from the Kissinger method, while the E_a of GST was estimated to be 2.33 eV. Moreover, it was estimated from isothemal annealing that the GCT film shows 10-year lifetime at the maximum temperature of 144 °C [9], which is higher than that of GST film. These results suggest that the amorphous GCT exhibits a higher thermal stability than the amorphous GST. The GCT film with a low melting point and a high crystallization temperature holds great promise as a new phase change material for PCRAM.

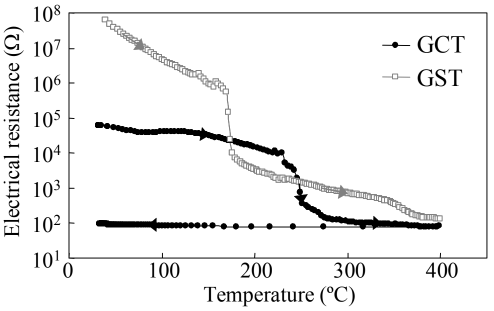

Figure 1. Temperature dependence of the electrical resistance of GCT and GST films.

4. CONCLUSION

We investigated the electrical resistance change with the crystallization and the thermal stability of the $Ge_1Cu_2Te_3$ (GCT) amorphous film. The results obtained were as follows:

1. The GCT amorphous phase crystallized into a single $Ge_1Cu_2Te_3$ crystalline phase with a chalcopyrite structure, which lead to a large electrical resistance drop. The crystallization temperature of the GCT film was about 70 °C higher than that of the $Ge_2Sb_2Te_5$ (GST) film.
2. The electrical resistances of the amorphous phase and the crystalline phase of the GCT film were lower than those of the GST film. Also, the difference of the electrical resistance between the amorphous and the crystalline phases of the GCT film was smaller than that of the GST film.
3. The maximum temperature for 10-years lifetime of the GCT film was evaluated to be 144 °C. Therefore, the GCT compound with a low melting point can be expected to be a promising phase change material for PCRAM.

REFERENCES

1. N. Yamada, E. Ohno, K. Nishiuchi, N. Akahira and M. Takao: “Rapid-phase transitions of GeTe-Sb_2Te_3 pseudobinary amorphous thin films for an optical disk memory”, J. Appl. Phys. **69** (1991) 2849
2. I. Friedrich, V. Weidenhof, W. Njoroge, P. Franz, M. Wuttig: “Structural transformations of $Ge_2Sb_2Te_5$ films studied by electrical resistance measurements”, J. Appl. Phys., **87** (2000) 4130
3. Z.U. Borisova: Glassy Semiconductor, Plenum, New York, 1985, p. 463.
4. R.A. Ligero, M. Gasa-Ruiza, M.P. Trujillo, A. Grozco, R. Jimenez-Garay: “Thermal-Stability and Crystallization Kinetics of Cu-Ge-Te and As-Ge-Te Glassy Systems with a High Tellurium Content“, Phys. Chem. Glasses **35** (1994) 115
5. K. Ramesh, S. Asocan, K.S. Sangunni, E.R.S. Gopal: “Crystallization studies on $Cu_xGe_{15}Te_{85-x}$ glasses”, J. Phys. Condens. Matter. **8** (1996) 2755
6. J. Vazquez, P.L. Lopez-Alemany, P. Villares, R. Jimenez-Garay: “A study on the thermal stability of some alloys in the Cu–Ge–Te glassy system by differential scanning calorimetry”, Thermochimica Acta **327** (1999) 191
7. A.P. Goncalves, E.B. Lopes, O. Rouleau, C. Godart: “Conducting glasses as new potential thermoelectric materials: the Cu–Ge–Te case”, J. Mater. Chem. **20** (2010) 1516
8. M. Dogguy, C. Carcaly, J. Rivet et Jean Flahaut: “Description du système ternaire Cu---Ge---Te”, J. Less-Common Metals **51** (1977) 181
9. Y. Sutou, T. Kamada, Y. Saito, M. Sumiya, J. Koike: “Crystallization behavior of $Ge_1Cu_2Te_3$ amorphous film”, Mater. Res. Soc. Symp. Proc. **1251** (2010) H05-08

Biographies

Yuji Sutou was born in Gumma, Japan, in 1974. He studied materials science at Tohoku University, Japan and received his PhD at the same University in 2001. He is an associate Professor of Department of Materials Science, Tohoku University. His current research field is alloy design and microstructural control of shape memory alloys, thin film, coating etc.