Phase change behavior of $Ge_1Cu_2Te_3$ thin films

Toshiya Kamada*, Yuta Saito, Masashi Sumiya, Yuji Sutou and Junichi Koike
Department of Materials Science, Tohoku University, 6-6-11 Aoba-yama, Sendai 980-8579
*a9tm5309@s.tohoku.ac.jp

ABSTRACT

The electrical resistances on the crystallization process of co-sputtered Ge-Cu-Te films were 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, which lead to a large resistance drop. The crystallization temperature of the $Ge_1Cu_2Te_3$ amorphous film was 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 (PCM) for PCRAM needs to possess a low melting point (T_m) for low power consumption, a high crystallization temperature (T_x) 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 PCM. 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 ^oC), and its crystallization temperature is relatively low (~ 160 ^oC). According to International Technology Roadmap for Semiconductors 2007, the expected operating temperature for PCRAM that guarantees a minimum operating data retention capability of 10-year is set to 125 °C on and after 2011 for high temperature operation, e.g., automotive application. Therefore, a new PCM with a low T_m and a high T_x is expected to be developed. 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 T_m 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-Cu-Te films deposited by RF sputtering were investigated.

2. EXPERIMENTS

Ge-Cu-Te films with 200 nm thickness were deposited on SiO_2(20 nm)/Si substrates by co-sputtering of GeTe, Te and Cu targets. The compositions of co-sputtered samples lie on Cu_2Te– $Ge_{33.3}Te_{66.7}$ pseudobinary line. The compositions of these films were $Ge_{23.8}Cu_{17.1}Te_{59.1}$, $Ge_{20.4}Cu_{29.1}Te_{50.5}$ and $Ge_{16.7}Cu_{33.3}Te_{50}$ (hereafter, we called each sample GCT17, GCT29 and GCT33), where the composition of the films was determined by transmission electron microscopy (TEM) with energy dispersive spectroscopy (TEM-EDS). The composition of the GCT33 film almost corresponds to that of $Ge_1Cu_2Te_3$ compound film. 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

Figure 1 shows XRD patterns of the as-deposited Ge-Cu-Te films. From XRD patterns, these films were confirmed to be amorphous. Figure 2 shows the temperature dependence of the electrical resistance for the Ge-Cu-Te films at a

heating rate of 10 °C/min. It is found that the electrical resistance of amorphous state decreases with increasing Cu content and the as-deposited Ge-Cu-Te films show abrupt electrical resistance change by more than 10^2 ohm because of crystallization at about 200 °C. The temperature dependence of the electrical resistance for GST film is also shown in Fig. 2. The crystallization temperatures of the Ge-Cu-Te films are higher than that of GST film. The electrical resistances of the amorphous and the crystalline phases of the Ge-Cu-Te films are lower than those of the GST film. And also, the difference of the electrical resistance between the amorphous and the crystalline phases of the Ge-Cu-Te films is smaller than that of the GST film. Figure 3 shows the crystallization temperatures of the Ge-Cu-Te films on $Cu_2Te - Ge_{33.3}Te_{66.7}$ pseudobinary phase diagram, where T_x was determined from the minimum value of the temperature derivative of the electrical resistance. It is found that the crystallization temperature slightly decreases with increasing Cu content. Figure 4 shows XRD patterns of Ge-Cu-Te films heated up to 300 ℃. It is seen from these patterns that phase decomposition occurred in GCT17 and GCT29. The GCT17 and GCT29 amorphous films crystallize into three phases ($Ge_1Cu_2Te_3$, GeTe and Te), and two phases ($Ge_1Cu_2Te_3$ and Te), respectively, while GCT33 crystallizes into a $Ge_1Cu_2Te_3$ single crystalline phase. In this study, the activation energy E_a for crystallization of GCT33 was estimated by Kissinger method. Figure 5 shows Arrenius plots of the dependence of heating rate on crystallization temperature. From these plots, the E_a of the GCT33 is estimated to be 2.52 eV, which is higher than that of GST (E_a=2.33 eV). Moreover, it was estimated that the $Ge_1Cu_2Te_3$ amorphous film shows 10-year lifetime at the maximum temperature of 171 ºC. These results suggest that the amorphous GCT exhibits a higher thermal stability than the amorphous GST. Therefore, the $Ge_1Cu_2Te_3$ film with a low melting point and a high crystallization temperature holds great promise as a new PCM for high temperature operation.

4. CONCLUSION

We investigated the electrical resistance change with the crystallization and the thermal stability of the Ge-Cu-Te amorphous films. The results obtained were as follows:

1. The off-stoichiometric amorphous Ge-Cu-Te films crystallized into two or three-phase crystalline state, while the $Ge_1Cu_2Te_3$ amorphous film crystallized into a single $Ge_1Cu_2Te_3$ crystalline phase. The crystallization temperature of the co-sputtered $Ge_1Cu_2Te_3$ film was about 40 °C higher than that of the $Ge_2Sb_2Te_5$ (GST) film.
2. The electrical resistances of the amorphous and the crystalline phases of the Ge-Cu-Te films were lower than those of the GST film. Moreover, the difference of the electrical resistance between the amorphous and the crystalline phases of the Ge-Cu-Te films was smaller than that of the GST film.
3. The activation energy for the crystallization of the $Ge_1Cu_2Te_3$ amorphous film was higher than that of the GST amorphous film.

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

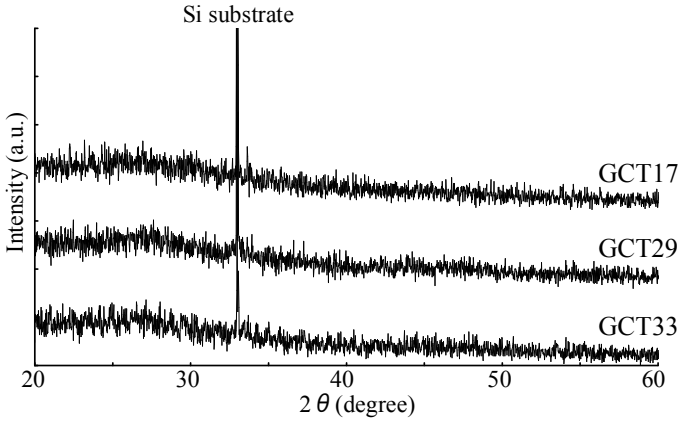

Figure 1. XRD patterns of as-deposited GCT17 , GCT29 and GCT33.

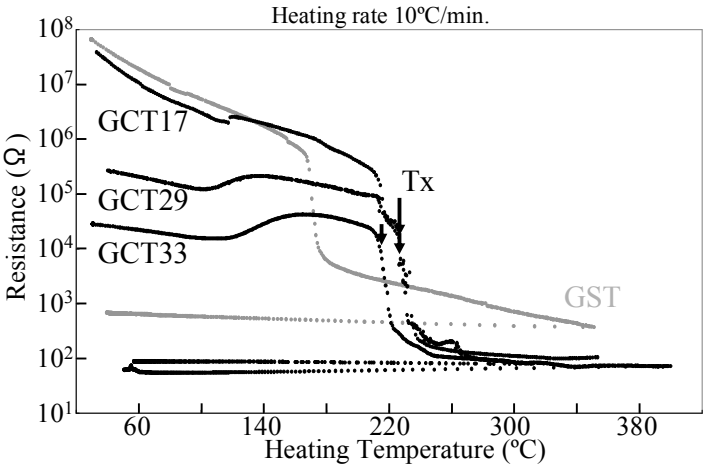

Figure 2. Temperature dependence of the electrical resistance of GCT17, GCT29 and GCT33.

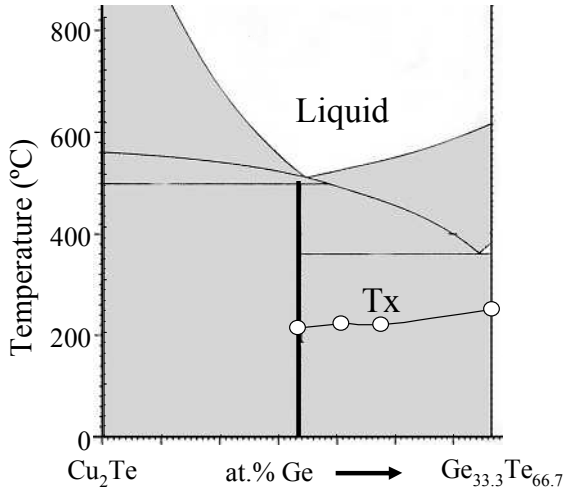

Figure 3. Crystallization temperatures of GCT17, GCT29 and GCT33 on Cu_2Te-$Ge_{33.3}Te_{66.7}$ pseudobinary phase diagram.

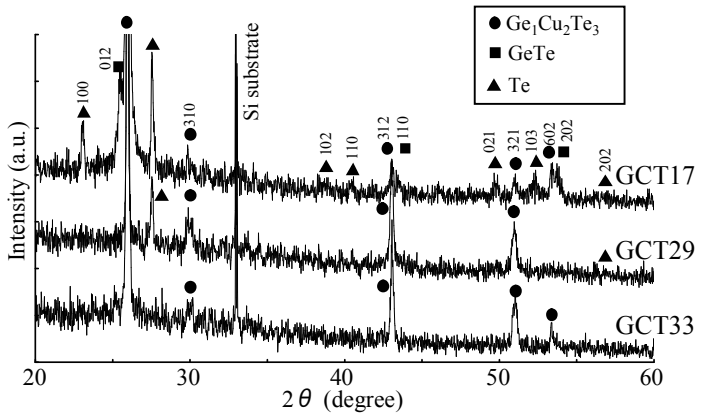

Figure 4. XRD patterns of GCT17, GCT29 and GCT33 heated up to 300 ºC.

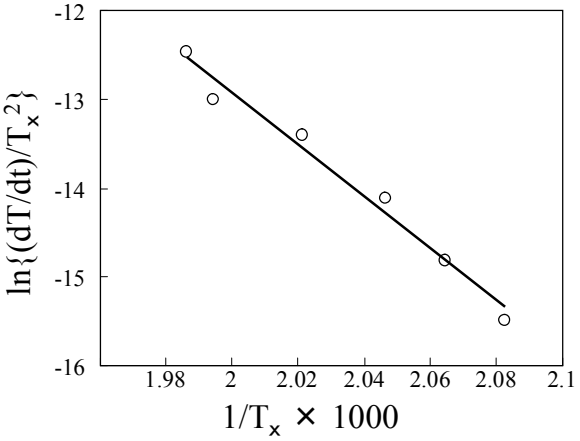

Figure 5. Kissinger plot for crystallization of GCT. The activation energy E_a is estimated to be 2.52 eV.