Phase transition characteristics of $GeCu_2Te_3$ thin film

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ABSTRACT

Recently, the present authors have found that a $GeCu_2Te_3$ (GCT) amorphous film has a high crystallization temperature of over 200˚C. In this study, we investigated the optical properties and the density change upon crystallization of the GCT film. And also, the thermal conductivities of the amorphous and crystalline GCT films were investigated. It was found that the amorphous GCT shows a higher refractive index than the crystalline GCT in the wavelength range of over 500 nm. Consequently, it was confirmed that the reflectance of amorphous state is higher than that of crystalline state in the wavelength range of 300-1000 nm. XRR measurements showed that the densities of the amorphous and crystalline GCT are 6.06 g/cm^3 and 5.80 g/cm^3, respectively, which means that the amorphous GCT is denser than the crystalline GCT. It was found by thermoreflectance technique that the amorphous GCT has almost the same thermal conductivity as amorphous GST, while the crystalline GCT shows about two times higher thermal conductivity than crystalline GST.

Key words: Ge-Cu-Te, volume change, optical properties, thermal conductivity

1. INTRODUCTION

$Ge_2Sb_2Te_5$ (GST) is the most widely studied for PCRAM application because it shows a fast crystallization [1,2]. However, the GST needs a high reset current which causes high power consumption because of its high melting point (~ 630˚C). Moreover, the thermal stability of GST amorphous film is relatively low because of its low crystallization temperature of about 150˚C. Therefore, it is necessary to develop new PCMs with a low melting point, maintaining a high crystallization temperature.

Recently, the present authors have found that a $GeCu_2Te_3$ (GCT) amorphous film has a high crystallization temperature of over 200˚C [3]. The GCT memory device shows memory switching behavior and exhibits lower power consumption for the reset operation than conventional GST memory device because of its low melting point of about 500˚C [4]. It is noteworthy that the reflectance change in the wavelength range of 400-1000 nm and thickness change upon crystallization of the GCT film are opposite to those of conventional phase change materials, such as GST and GeTe [5]. Moreover, it was found that the GCT film shows a fast phase change [6]. In this study, to understand the transition behaviors of GCT film, we investigated the density change upon crystallization and the optical properties of the GCT film. And also, the thermal conductivities of the amorphous and crystalline GCT films were investigated.

2. EXPERIMENTS

GCT films with 200 nm in thickness were deposited on SiO_2/Si substrate by co-sputtering of GeTe and CuTe targets. The film composition was determined by inductively-coupled plasma mass spectrometry and the deviation from the stoichiometric composition $GeCu_2Te_3$ was found to be less than 1% for all elements. The densities of amorphous and crystalline states of the GCT films were measured by X-ray reflectivity (XRR). The optical properties were investigated by ellipsometry. The thermal conductivity of the amorphous and crystalline GCT film was evaluated by thermoreflectance technique.

3. RESULTS AND DISCUSSION

3-1. Density change

It was found from XRR measurements that the densities of the amorphous and crystalline GCT are 6.06 g/cm^3 and 5.80 g/cm^3, respectively. This indicates that the amorphous GCT shows a volume expansion of about 4.3% upon crystallization. The value of the volume change is nearly equal to the increase in thickness of about 3.4% upon crystallization measured with atomic force microscopy (AFM). Figure 1 shows the density change (thickness change) upon crystallization in GCT, GST and GeTe films, where the crystalline film was heated to 350ºC. It is seen that the GCT shows a smaller volume change than the conventional PCMs. And, it is noteworthy that the volume change of the GCT shows an opposite sign to that of conventional PCMs. Very recently, it was suggested by *ab initio* molecular-dynamics (AIMD) simulations that the high density of amorphous GCT might be related to shorter Cu bonds compared to crystalline GCT [7].

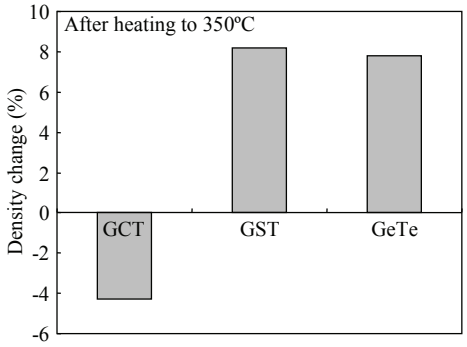

Fig. 1 Density change upon crystallization of GCT, GST and GeTe films. The density change was defined by $(d_{cry}-d_{amo})/d_{amo}$. The result of the GST was taken from reference [8]. The result of the GeTe was estimated from the film thickness change by AFM.

3-2. Optical properties

Fig. 2(a) shows the refractive index n and extinction coefficient k for the amorphous (as-deposited) and crystalline (heated to 350ºC) GCT films. It is seen that the amorphous GCT shows a higher refractive index than the crystalline GCT in the wavelength range of over 500 nm. Meanwhile, amorphous GST has been reported to show a lower n than crystalline GST [1]. Based on the results in Fig. 2(a), the vertical reflectance of amorphous and crystalline GCT films was calculated as shown in Fig. 2(b). It is seen that the reflectance of amorphous state is higher than that of crystalline state in the wavelength range of 300-1000 nm. The reflectance of amorphous and crystalline state obtained by AIMD simulations are also shown in Figure 2(b) [7]. It is seen that the simulated reflectance spectra are almost the same

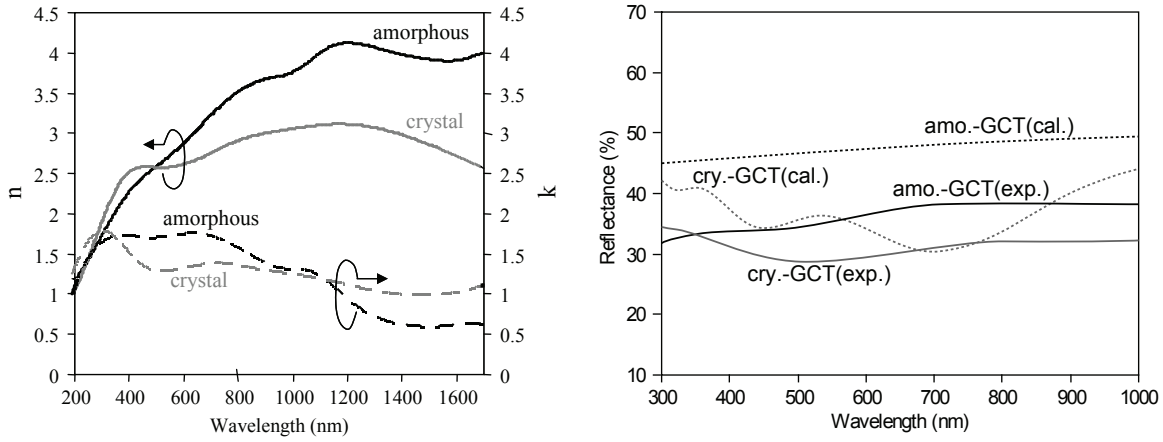

Fig. 2 (a) Refractive index n and extinction coefficient k for the amorphous (as-deposited) and crystalline (heated to 350ºC) GCT films. (b) Reflectance of amorphous and crystalline GCT films calculated based on the results of (a). The dotted lines indicate the reflectance simulated by AIMD [7].

tendency with the experimentally observed spectra, that is, the amorphous phase shows a higher reflectivity than the crystalline phase across a 300–1000 nm wavelength range.

Figure 3 shows the relationship between reflectance change (optical contrast = $\Delta R/R = (R_{cry}-R_{amo})/R_{cry}$) and density change in various phase change materials [6]. It is seen that there is a clear correlation between optical contrast and density change. Generally, it has been suggested that a PCM showing a large optical contrast has a crystal structure with a high coordination number Z, such as NaCl and cubic structures (Z=6) [9]. Meanwhile, a PCM like $AgInTe_2$ with a small coordination number, such as chalcopyrite and wurtzite structures (Z=4) shows almost no optical contrast. The GCT crystal is known to have a chalcopyrite structure (Z=4), but the GCT shows a relatively large optical contrast. Therefore, the present results indicate that rather than the coordination number, the density change shows a better correlation with the optical contrast. It has been also suggested from AIMD simulation that the higher reflectance of amorphous CGT may be due to a higher degree of electron delocalisation, in particular of the Cu d electrons [7].

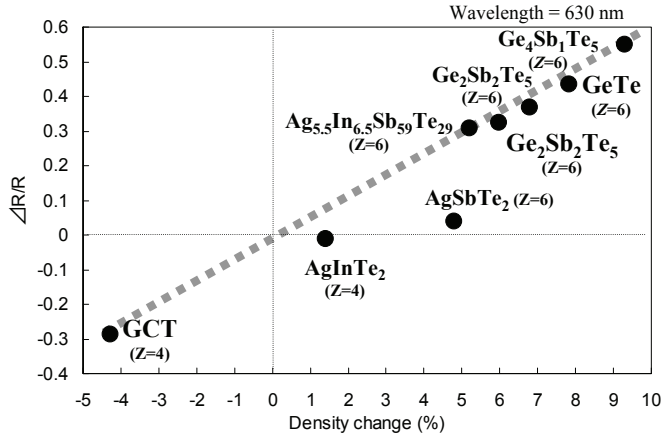

Fig. 3. Relationship between reflectance change (optical contrast) and density change in various phase change materials, where the optical contrast was defined as $\Delta R/R = (R_{cry}-R_{amo})/R_{cry}$.

3-3. Thermal conductivity

Table 1 indicates the thermal conductivity of GCT and GST film obtained in this study. It is seen that the amorphous phase shows a lower thermal conductivity than the crystalline phase in both films. The amorphous GCT has almost the same thermal conductivity as the amorphous GST, while the crystalline GCT shows about two times higher thermal conductivity than the crystalline GST.

Table 1. Thermal conductivity of GCT and GST.

	phase	Annealing temperature (ºC)	Thermal conductivity ($W\times m^{-1}\times K^{-1}$)
GCT	amorphous	-	0.14
	crystal	350	1.9
GST	amorphous	-	0.12
	crystal(hcp)	400	1.1

4. CONCLUSION

The amorphous GCT showed a larger density than the crystalline GCT and consequently, the GCT showed the volume increase upon crystallization, which was the opposite behavior of the conventional PCMs, such as GST and GeTe. The GCT also showed an opposite sign in reflectance change upon crystallization to the conventional PCMs. It was found that there is a clear correlation between optical contrast and density change in various PCMs. Moreover, it was found that the crystalline GCT showed a higher thermal conductivity than the crystalline GST.

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