

# A study on phase change characteristics of Ge-Cu-Te ternary alloy thin films

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## Abstract

The  $(\text{GeTe})_{1-x}(\text{CuTe})_x$  films were deposited on  $\text{SiO}_2/\text{Si}$  substrate by co-sputtering of GeTe and CuTe targets. It was found that the reflectance of the amorphous Ge-Cu-Te film was independent on composition, while the reflectance of the crystalline Ge-Cu-Te film decreased monotonically with increasing CuTe content. The GCT ( $x = 2/3$ ) crystalline film showed a lower reflectance than the amorphous GCT film. The crystallization speed became slow when the composition of the film was deviated from stoichiometric composition. The crystallization starting time of the GCT amorphous film was only a slightly longer than that of the GST amorphous film.

**Keywords:**  $(\text{GeTe})_{1-x}(\text{CuTe})_x$ , optical contrast, crystallization speed

## 1. Introduction

Phase change random access memory (PCRAM) has attracted much attention as a new class of non-volatile memories because of its low production cost and high scalability.  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  (GST) film has been widely studied as a phase change material for PCRAM because GST shows a fast crystallization speed and a good reversibility between the amorphous and crystalline states [1,2]. However, GST has a low crystallization temperature  $T_x$  of about  $150^\circ\text{C}$  and a high melting point  $T_m$  of over  $600^\circ\text{C}$  [1,3], which limits data retention capability and causes high power consumption for reset operation, respectively.

Very recently, the present authors have found that a  $\text{GeCu}_2\text{Te}_3$  (GCT) amorphous film had a high crystallization temperature of over  $200^\circ\text{C}$  [4]. The GCT memory devices showed memory switching behaviors and exhibited a 10% lower power consumption for the reset operation than the conventional GST memory devices because of its low melting point of about  $500^\circ\text{C}$  [5]. In addition, the GCT amorphous film was found to show a thickness increase of 2.0% with the crystallization. In the present study, we investigated the phase change characteristics including resistance and reflectance changes upon crystallization and phase change speeds of the Ge-Cu-Te ternary alloy films using static laser tester.

## 2. Experiments

The  $(\text{GeTe})_{1-x}(\text{CuTe})_x$  films with 200nm in thickness were obtained by controlling the RF power of GeTe and CuTe targets.  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  (GST) films were also prepared by sputtering of a stoichiometric  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  alloy target for comparison. The crystallization temperature of the films was measured by a two-point probe method during heating at a heating rate of  $10^\circ\text{C}/\text{min}$  in Ar atmosphere. The reflectance of the amorphous and crystalline films was measured relative to an Al reference mirror

with spectrophotometer in the range of wavelength between 250-1000 nm. The crystallization speed of the as-deposited GCT and GST amorphous films with a thickness of 200 nm was measured using a static laser tester based on the reflectance results. The wavelength of both the pump and probe laser was 830 nm.

### 3. Results and discussions

#### 3-1. Electrical resistance

Fig. 1 shows the temperature dependence of the electrical resistance for the films with GeTe ( $x=0$ ), GCT ( $x=2/3$ ) and CuTe ( $x=1$ ). It was confirmed by XRD measurement that the as-deposited films show an amorphous state except the CuTe binary film. In the amorphous state, the GeTe binary film shows the highest electrical resistance and the electrical resistance of the amorphous state decreases with increasing Cu content. The as-deposited CuTe binary film had a crystalline state. The as-deposited films showed a drastic decrease in electrical resistance during heating, which is caused by crystallization. The small abrupt decrease in electrical resistance observed in the CuTe binary film was confirmed by XRD measurement to be caused by a structural change. Fig. 2 shows the compositional dependence on crystallization temperature ( $T_x$ ) for the  $(\text{GeTe})_{1-x}(\text{CuTe})_x$  films, where the x-axis is plotted by RF power ratio ( $Pr$ ) defined as  $(\text{Power of GeTe target})/(\text{Power of GeTe target} + \text{Power of CuTe target})$ . The  $Pr$  of about 0.6 corresponds to the composition of the GCT. The  $T_x$  increases with increasing the  $Pr$  and reached to a maximum  $T_x$  of about 250°C at  $Pr \sim 0.3$  and then decreases with further increasing CuTe content. The GCT film showed the highest  $T_x$  in the compounds which exist along with GeTe-CuTe composition line.

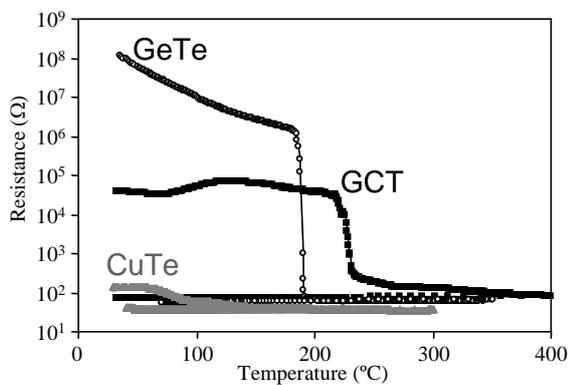


Fig 1. Temperature dependence of the electrical resistance of GeTe, GCT and CuTe films.

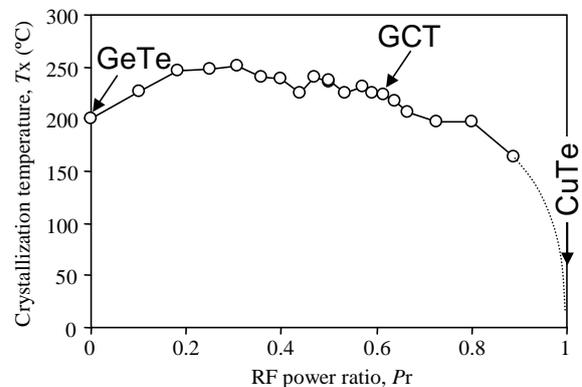


Fig 2. Composition dependence on the crystallization temperature  $T_x$  for  $(\text{GeTe})_{1-x}(\text{CuTe})_x$  films.

#### 3-2. Reflectance

In this section, we show the results of the reflectance of the amorphous and crystalline  $(\text{GeTe})_{1-x}(\text{CuTe})_x$  films. Fig. 3 shows the reflectance of the as-deposited and annealed GCT films, where the annealed sample was heated up to 400°C for complete crystallization. It is noteworthy that the reflectance of the GCT crystalline film is lower than that of the GCT amorphous film in the

wavelength range of 250-1000 nm [6]. Such the opposite reflectance change upon crystallization has also been recently observed in Sb-Ge [7] and Fe-Te [8] binary films. The reflectance of the amorphous film was found to be almost independent on CuTe content, while the reflectance of the crystalline film decreased monotonically with increasing CuTe content. The difference of the reflectance  $\Delta R$  ( $=R_{\text{crystalline}} - R_{\text{amorphous}}$ ) of GeTe binary film was more than 30%, while the GCT film showed a negative reflectance change of about  $\Delta R = -10\%$  upon crystallization at a wavelength of 830 nm. When the  $Pr$  reached at about 0.5, the  $\Delta R$  became almost zero [9].

### 3-3. Crystallization speed

In this study, the crystallization starting time ( $t_s$ ) of the GCT amorphous film was measured using a static laser tester based on the results of reflectance change upon crystallization. Fig. 4 shows the reflectance change induced by laser irradiation at power of 11.0 mW and wavelength of 830 nm as a function of pulse duration (0-50 ns) for the GCT amorphous film. The result of the GST amorphous film was also shown for comparison. Since the reflectance was measured using a Si photo-diode, the raw data were obtained in the form of voltage. The photo-diode voltage ratio  $V/V_0$  is plotted on the vertical axis, where  $V_0$  and  $V$  are the detected voltage before and after the pump pulse laser irradiation. The GST film showed the reflectance increase upon crystallization because the GST crystalline film has a higher reflectance than the GST amorphous film. In the GST film, the  $V/V_0$  starts to relatively sharply increase at about 23 ns defined as  $t_s$ , which should mean nucleation time [6]. Meanwhile, in the GCT film, the  $V/V_0$  starts to relatively sharply decrease at  $t_s \approx 26$  ns, which should be due to crystallization. This result indicates that the GCT amorphous film shows a fast crystallization speed. The crystallization speed became slow when the composition of the film was deviated from stoichiometric composition such as GeTe and GCT. In addition, it was confirmed that the amorphization speed of the GCT film was much faster than that of the GST film because the GCT had a lower melting point than the GST.

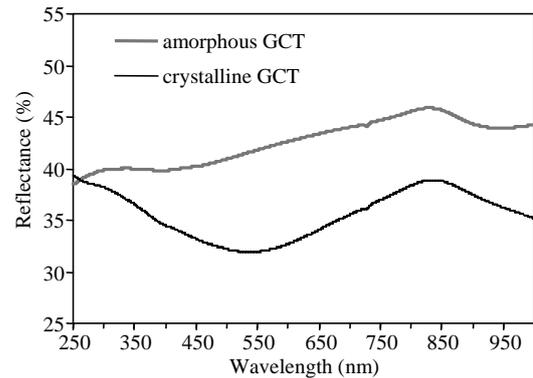


Fig. 3. Reflectance of as-deposited amorphous GCT and annealed crystalline GCT films.

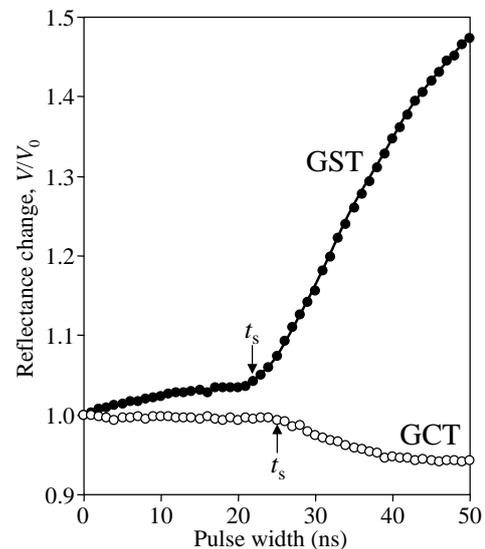


Fig. 4. Reflectance change of the GCT and GST amorphous films induced by laser irradiation with a fixed power of 11.0 mW as a function of laser pulse width.

#### 4. Conclusion

We investigated the phase change characteristics including resistance and reflectance changes upon crystallization, and phase change speeds of the Ge-Cu-Te ternary alloy films by laser irradiation.

It was found that the GCT showed the highest crystallization temperature in the compounds which exist along with GeTe-CuTe composition line. The electrical resistance of the amorphous state decreased with increasing CuTe content. Meanwhile, the reflectance of the amorphous film was found to be independent on CuTe content, while the reflectance of the crystalline film decreased monotonically with increasing CuTe content. Interestingly, the GCT crystalline film showed a lower reflectance than the amorphous GCT film. The crystallization starting time of the GCT amorphous film was only a slightly longer than that of the GST amorphous film. Meanwhile, the GCT film showed much faster amorphization speed than the GST film.

The present results indicate that the GCT film with a low melting point, high thermal stability of the amorphous phase and a high phase change speed is a promising PCM for PCRAM application.

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