Compositional dependence on phase change characteristics in Ge-Cu-Te ternary phase change materials

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ABSTRACT

Compositional dependences on the crystallization temperature, thickness change with crystallization and optical reflectance were investigated in the Ge-Cu-Te ternary alloy film along the pseudobinary composition line of GeTe-CuTe. The crystallization temperature increased and then decreased with increasing CuTe content. It was found that the Ge-Cu-Te films with higher CuTe content, including $Ge_1Cu_2Te_3$ compound, showed the increase in film thickness and the decrease in reflectance with crystallization. The thickness and reflectance changes of the Ge-Cu-Te films with higher CuTe content are the opposite to those observed in other conventional phase change materials.

Key words: Ge-Cu-Te, Crystallization behavior, Volume change, Reflectance change

1. INTRODUCTION

Phase change random access memory (PCRAM) has been attracting considerable attention as a next-generation nonvolatile memory because of their low production cost and high scalability. $Ge_2Sb_2Te_5$ (GST) has been the most widely studied as a phase change material (PCM) for PCRAM. The GST shows a fast crystallization speed and a good reversibility between amorphous and crystalline phases. However, since GST shows a low crystallization temperature of about 150ºC, GST is unsuitable for high temperature operation. Thus, new PCM with a high crystallization temperature is expected to be developed for improving the thermal stability of PCRAM. Recently, Sutou et al. has reported that amorphous $Ge_1Cu_2Te_3$ (GCT) shows a higher thermal stability than GST amorphous film and an estimated failure time is well beyond the data retention requirements of the ITRS 2011 [1]. Meanwhile, the compositional dependences on the phase change characteristics of Ge-Cu-Te ternary alloy film have not been investigated yet. GCT exists on the pseudobinary composition line of GeTe-CuTe. In this work, we present the compositional dependences on the crystallization temperature, thickness change during crystallization and optical reflectance for Ge-Cu-Te ternary alloy films along the GeTe-CuTe pseudobinary composition line.

2. EXPERIMENTS

$(GeTe)_{1-x}(CuTe)_x$ films ($0 \leq x \leq 0.67$) with about 200 nm in thickness were deposited on SiO_2/Si substrates by co-sputtering of GeTe and CuTe targets. The different compositional samples were obtained by controlling the RF power of each target. *In situ* electrical resistance measurements were performed during heating and cooling process by a two-point probe method at 10 ºC/min under Ar atmosphere. An energy dispersive X-ray spectrometer attached to scanning electron microscopy (SEM) was used to determine the sample composition. Volume changes were evaluated by measuring the thickness change of the films by atomic force microscopy (AFM) before and after annealing. The reflectance of the amorphous and crystal films were measured relative to an Al reference mirror with spectrophotometer in the range of wavelength between 250 - 1000 nm.

3. RESULTS & DISCUSSION

Fig. 1 shows the compositional dependence on the crystallization temperature T_x and the thickness change of the film upon crystallization, where the x-axis is plotted by RF power ratio of GeTe and CuTe targets. The RF power ratio (P_r) of about 0.6 corresponded to the composition of $Ge_1Cu_2Te_3$ (GCT). Thickness change was defined as the ratio of the thickness (t_{an}/t_{as}) of the as-deposited amorphous film (t_{as}) and film after annealing to 350ºC for complete

crystallization (t_{an}). The T_x increased with increasing the RF power ratio and reached to the maximum T_x of about 250ºC at P_r ~ 0.3 and then decreased with further increasing CuTe content. The T_x of the GCT film was about 25ºC higher than that of the GeTe film. Thickness change upon crystallization monotonically increased with increasing the RF power of CuTe target. The amorphous GeTe film showed about 8% thickness decrease upon crystallization, which is a similar tendency with GST showing a 6.5% decrease [2], while the GCT showed the thickness increase of about 3% upon crystallization which is in good agreement with the previous report [3]. The dashed line in Fig. 1 shows the thickness change of 1.00 which means the thickness does not change upon crystallization. It is seen that the films deposited at P_r = 0.4~0.5 shows negligible thickness change with crystallization. Fig. 2 shows the compositional dependence on the reflectance of amorphous ($R_{amo.}$) and crystalline phases ($R_{cry.}$) measured at 830 nm of wavelength. It is noteworthy that the $R_{amo.}$ has almost same value regardless of CuTe content, while the $R_{cry.}$ decreases monotonically with increasing CuTe content. The difference of the $R_{cry.}$ and $R_{amo.}$ ($\Delta R=R_{cry.}-R_{amo.}$) of GeTe was more than 30%, while the GCT film showed negative reflectance change of about ΔR=-10% upon crystallization. When the P_r reaches at about 0.5, the $R_{cry.}$ becomes almost the same as the $R_{amo.}$ i.e. ΔR=0. According to GeTe-CuTe pseudobinary phase diagram, the films with the composition on GeTe - GCT line are considered to have the mixture of GeTe and $Ge_1Cu_2Te_3$ phases after crystallization. Since the volume fraction of the $Ge_1Cu_2Te_3$ phase increases with increasing CuTe content and consequently, such monotonic compositional dependence on thickness change and reflectance may be shown along the GeTe- GCT line.

4. CONCLUSION

In this study, we investigated the compositional dependences on the phase change characteristics in the GeTe-CuTe pseudobinary alloy films. The crystallization temperature increased and then decreased with increasing CuTe content. It was found that thickness change monotonically increased with increasing CuTe content and the films with higher CuTe content showed the increase in film thickness with crystallization. The reflectance of the amorphous film is independent on CuTe content, while the reflectance of the crystalline film decreased monotonically with increasing CuTe content. The film with higher CuTe content showed the decrease in the reflectance with crysatllization.

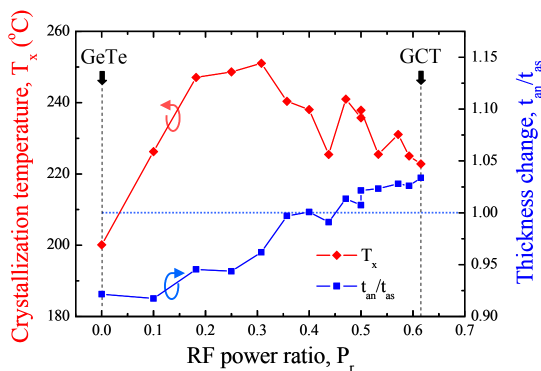

Fig. 1. Compositional dependence on the crystallization temperature (T_x) and thickness change (t_{an}/t_{as}).

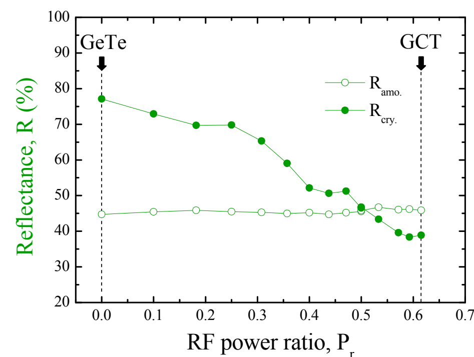

Fig. 2. Compositional dependence on the reflectance of the amorphous ($R_{amo.}$) and crystalline phases ($R_{cry.}$).

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Biographies

Yuta Saito was born in 1985 in Japan. He received his B.S. and M.S. degrees from Tohoku University, Japan in 2008 and 2010, respectively. He has been a doctoral student in Tohoku University since 2010. He is a Research Fellow of the Japan Society for the Promotion of Science (JSPS) during 2010-2013. His research topic includes the development of phase change materials and the investigation of phase change behaviors for next generation non-volatile memory.