

Phase transitions in $\text{Ge}_{1-x}\text{Te}_x$ alloys

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ABSTRACT

The crystallization kinetic of 50nm thick $\text{Ge}_x\text{Te}_{1-x}$ ($x=0.37, 0.49, 0.64$) films deposited by sputtering on a thermally grown SiO_2 layer has been investigated. Time Resolved Reflectivity measurements during the annealing of non-stoichiometric alloys showed the presence of an intermediate step in the reflectivity versus temperature curve during the transition from the amorphous to the crystal. Detailed TEM observation of partially transformed samples indicated that the phase separation occurs by the formation of crystalline Te precipitates in Te-rich alloy unlike Ge-rich alloy in which amorphous Ge precipitates are initially formed. For what concern cyclability we observed that the crystallization rate of amorphous layers produced by laser irradiation of crystalline non-stoichiometric GeTe alloys follows the same trend of as-deposited amorphous layers. Samples re-amorphized by ion irradiation exhibit lower crystallization temperatures since this process is unable to mix the atomic species over long distance.

Key words: GeTe, phase transitions, non-stoichiometric

1. INTRODUCTION

Stoichiometric GeTe has been proposed as active medium in electronic phase change memories [1]. The most interesting characteristic of this alloy is the high crystallization temperature (175°C), compared with other chalcogenide (GST 130°C), that could permit to use this material as active medium in devices with high operating temperature. It has been shown that non-stoichiometric $\text{Ge}_x\text{Te}_{1-x}$ exhibits higher crystallization temperature with respect to the stoichiometric alloy [2]. This enhancement is likely due to the precipitation of the excess element required before crystallization of the stable GeTe phase. However, the whole process of phase separation and GeTe crystallization as well as the influence of the phase separation on cyclability are not known in detail [3].

2. EXPERIMENTS

Amorphous $\text{Ge}_{1-x}\text{Te}_x$ ($x=0.37$ and 0.64) films, 50 nm thick, were deposited at room temperature on thermally grown SiO_2 layer using a rf magnetron co-sputtering from elemental targets. The crystallization kinetics was investigated by *in situ* time resolved reflectivity (TRR) using a 5 mW He-Ne laser probe during the annealing (6°C/min). The crystallization temperature is experimentally defined as the maximum in the first derivative of the reflectivity versus temperature curve. Structural characterization of crystallized film by transmission electron microscopy was performed using a JEOL JEM 2010F TEM. Melt quenched amorphous was obtained by irradiation with a pulsed (12 ns) Nd:YAG laser ($\lambda=532$ nm) with energy density of 175 mJ/cm². Ion irradiated amorphous was prepared by implanting 130 keV Ge^+ ions at a fluence of 1×10^{14} ions/cm² at RT.

3. RESULTS & DISCUSSION

Time Resolved Reflectivity measurements during isothermal annealing of non-stoichiometric alloys showed the presence of an intermediate step in the reflectivity versus temperature curve during the transition from the amorphous to the crystal. Transmission electron microscopy analyses on partially transformed samples allowed associating this step to the precipitation of the excess species that, at any composition, was found to precede the crystallization of stoichiometric GeTe. The Ge-rich alloy exhibited higher crystallization temperature (355°C) with respect to both Te-rich alloy (245°C) and stoichiometric GeTe (175°C). It is reasonable to assume that this feature is related to the mobility of the excess atomic species since GeTe crystallization is triggered by the phase separation between the stable phase and the excess species in the non stoichiometric alloys.

Detailed TEM and EFTEM images of partially transformed samples are shown in figure 1. The first series (a, b, c) refers to the Te-rich alloy and it shows that the phase separation occurs by the formation of crystalline Te precipitates (a) followed by GeTe crystallization (b, c). In the Ge-rich alloy amorphous Ge precipitates are initially formed (bright regions in figure 1d) and then we observe the simultaneous crystallization of Ge and GeTe (e, f).

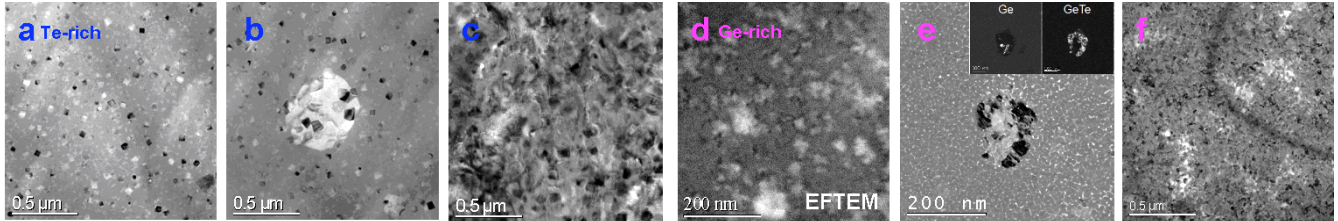


Figure 1 TEM images at different times during the crystallization process of non-stoichiometric GeTe alloys: the first series (a, b, c) refers to the Te-rich composition while the second one to the Ge-rich alloy. Precipitation of the excess species is required before the GeTe crystallization. In the Te-rich alloy the phase separation occurs by the formation of crystalline Te precipitates (a) followed by GeTe crystallization (b, c). In the Ge-rich alloy amorphous Ge precipitates are initially formed (d) and then we observe the simultaneous crystallization of Ge and GeTe. (inset e, f).

We have compared also the crystallization rate of amorphous layers produced by ion or laser irradiation of both crystalline non-stoichiometric alloys. The crystallization rate and temperature of the melt quenched amorphous resulted very similar to that of the as-deposited amorphous indicating that even in melt quenched non stoichiometric alloys the crystallization is triggered by the precipitation of the excess species. The crystallization temperature of the ion implanted alloys decreases down to a value close to stoichiometric GeTe. The difference relies on the method to re-amorphize the phase separated crystalline samples since ion implantation can't induce a long range atomic mixing and only amorphization occurs unlike pulsed laser irradiation in which fast atomic mixing and dissolution of precipitates occurs in liquid phase.

4. CONCLUSION

The precipitation process involved during the crystallization of non-stoichiometric alloys is the reason of the higher crystallization temperature measured in these materials with respect to stoichiometric GeTe. On the other hand the atomic mobility of the excess species is responsible of the higher crystallization temperature measured changing the stoichiometry from Te-rich to Ge-rich. It is clear that if we want to preserve this feature we must be sure that during the amorphization process the melting and the mixing of the atomic species occur.

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Biographies

Egidio Carria was born in Catania, Italy in 1984 and received his first level degree (2006) and second level degree (2008) in Physics from the University of Catania, Italy. In 2008 he began his PhD in Physics working on the phase transitions in GST and GeTe. He is studying also laser and ion irradiation as processes to induce variation in the local order of amorphous chalcogenide as well as instruments to amorphize phase change materials.