Crystallization of primed amorphous $Ge_2Sb_2Te_5$ studied by Transmission Electron Microscopy

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ABSTRACT

The crystallization kinetics of 50nm thick $Ge_2Sb_2Te_5$ films, deposited by sputtering on a thermally grown SiO_2 layer, has been investigated by transmission electron microscopy (TEM) and time resolved reflectivity (TRR) measurements during isothermal annealing in the range between 120°C and 130°C. Three different amorphous states have been analyzed: as deposited, primed and melt quenched. At the same temperature, the primed amorphous sample exhibits a higher nucleation rate whereas the melt quenched film shows an enhancement of both nucleation and growth rates with respect to the as deposited film. This behavior can be explained taking into account the effects of laser irradiation on the local order and on the population of subcritical nuclei in the amorphous phase.

Key words: $Ge_2Sb_2Te_5$, polymorphism, primed amorphous, TEM, crystallization

1. INTRODUCTION

Phase change materials are used for optical and electrical non-volatile memories. The storage mechanism is based on the large difference in reflectivity and resistivity that these compounds exhibit during the transition from the amorphous to the crystalline phase or vice versa [1]. In particular, $Ge_2Sb_2Te_5$ is the most investigated alloy since it seems to have the best combination of electrical, optical, and phase changing properties [2]. It is known that the degree of short range order in amorphous solids depends on the sample processing. Differences in the crystallization velocity between as deposited, primed and melt quenched amorphous samples have been already reported [3]. In particular, laser irradiated amorphous GST shows a faster crystallization with respect to the as deposited film. We have estimated this effect measuring at different temperatures, by *ex situ* TEM, both the nucleation and the growth rate.

2. EXPERIMENTS

Amorphous $Ge_2Sb_2Te_5$ films, 50 nm thick, were deposited from stoichiometric target at room temperature on thermally grown SiO_2 layer using rf-magnetron sputtering. Primed amorphous samples have been prepared by irradiation with a pulsed (12 ns) Nd:YAG laser (λ=532 nm) using an energy density of 60 mJ/cm^2. According to numerical simulations, the corresponding annealing temperature is ~700K. The thermal treatment is short enough to avoid crystallization. The melt quenched amorphous has been obtained tuning the irradiation fluence (180 mJ/cm^2) to overcome the melting temperature (916K). The cooling rate (~10^{10} K/s) is high enough to avoid crystallization during the quenching of the liquid phase. The diameter of the laser beam (~3mm) is large enough to allow measurements on a large area. The different samples have been partially crystallized and analysed ex situ by TEM using a JEOL JEM 2010F TEM. . The nucleation and growth rates have been then estimated.

3. RESULTS & DISCUSSION

In fig.1 TEM micrographs (dark field), collected at different times, are reported for the case of as deposited, first row, and primed amorphous samples, second row. Primed samples have a nucleation rate (2.7×10^6 cm^{-2}s^{-1}) about 6-7 times higher and an incubation time of about a factor three smaller, while growth velocities (53 pm/s) are quite similar to the values measured in the as deposited film. The third row of fig.2 shows a comparison between the different amorphous samples annealed at 125°C for 15min. Melt quenched sample has a nucleation rate one order of magnitude higher than primed sample and a growth velocity at least four time faster.

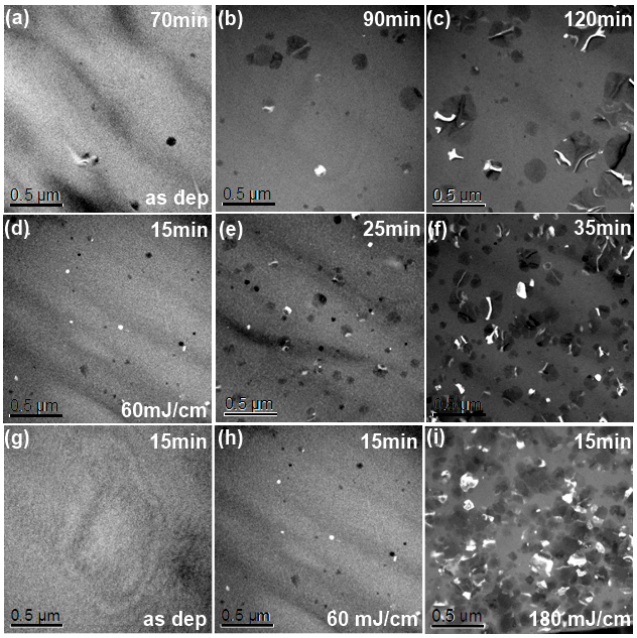

Figure 1 TEM images, collected at different times, during the crystallization process at 125°C of different amorphous GST alloys: as deposited, primed and melt quenched. The **(a)(b)(c)** images refer to the as deposited film whereas the second row refers to a primed amorphous sample. The last row shows the different amorphous films after 15min of thermal treatment. The as deposited film **(g)** is completely amorphous, the primed sample **(h)** shows a low crystalline fraction whereas the melt quenched **(i)** is almost completely crystallized.

In the case of primed amorphous GST, the higher nucleation rate of the crystalline phase can be explained taking into account the change in the population of subcritical nuclei. During the laser irradiation process, the formation of ordered structures, before crystallization, has been already reported [4]. On the other hand, the higher growth velocity measured in melt quenched amorphous can be justified by a change in the local order of the as deposited material upon irradiation [5]. In particular a reduction of homopolar bonds (Ge-Ge and Te-Te) after the processing promotes the system to a state closer to the crystalline phase since it is known that these bonds are not allowed in the crystalline phase and then they inhibit the phase change process.

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Biographies

Egidio Carria was born in Catania, Italy, in 1984. He has received his first level degree (2006) and second level degree (2008) in Physics from the University of Catania. In 2008 he began his PhD in Physics working on the phase transitions in GST and GeTe alloys. He has defended with success his Ph.D. dissertation in 2012. During the last years, he has investigated laser and ion irradiation processes to induce variation in the local order of amorphous chalcogenide as well as instruments to amorphize and dope phase change materials.