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Isothermal and CW laser crystallization of amorphous $Ge_2Sb_2Te_5$ thin films

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ABSTRACT

Transmission electron microscopy results are presented for as-deposited amorphous $Ge_2Sb_2Te_5$ thin films after theirs isothermal annealing and CW laser illumination. Obtained microphotographs suggested that the crystallization process was driven solely by heterogeneous nucleation on the film boundary. The simplified model of steady-state crystallization process was developed for the case of heterogeneous nucleation mechanism. The values of nucleation rate and growth rate for isothermal and CW laser crystallization are calculated. The calculated values are in reasonable agreement with both our experimental data and with results previously published by the other authors.

1. Introduction

In this study, the crystallization behaviour of $Ge_2Sb_2Te_5$ (GST225) amorphous thin films was examined with the goal of determining the features of crystallization mechanism under isothermal heating and continuous-wave (CW) laser irradiation. GST225 composition is one of the extensively examined phase change memory (PCM) materials, which is currently used for rewritable data storage applications based on structural phase transitions. Bits of information can be stored as amorphous marks in a crystalline matrix utilizing the different optical or electrical properties of the two phases [1,2]. As-deposited GST225 films are amorphous and must be crystallized before being used in a PCM device. Amorphous marks are produced with melting microscopic areas of the film by means of a pulsed laser beam and subsequent quenching. The bits can be erased due to crystallization of the amorphous spots employing moderate laser powers. The issues of vital importance for the improving of PCM devices are high data transfer rates, *i.e.*, fast processes to read, write, and erase bits of information. Since writing, *i.e.* amorphisation, is an inherently fast process for chalcogenide films [3], and pronounced difference of optical properties makes possible fast its reading, erasure is considered as the time limiting step which, hence, governs the maximum data transfer rate obtainable.

A considerable number of previous studies have therefore already focused on the crystallization process of PCM materials. These studies have determined the activation energy for crystallization [4], measured the kinetic exponent (Avrami coefficient) [5,6], and discussed the crystallization mechanism [7–11]. However, the general theory of crystallization of PCM materials, which includes laser crystallization, is in progress. We suppose that it is related with several factors. Among the key factors may be noted such ones as *i*) strong non-equilibrium processes; *ii*) the complexity of the separation of surface and volume driven crystallization in the thin film; *iii*) the complexity of size effect consideration in the process simulation, and so on.

The present study focuses on transmission electron microscopy (TEM) examinations of amorphous GST225 thin films crystallized by isothermal annealing and CW laser illumination, and comparison of experimental results with a theoretical model of crystallization, which we have developed for the case of thin films.

2. Experimental

Thin films were prepared by the vacuum thermal evaporation of pre-synthesized polycrystalline material of GST225 composition on the c-Si substrates. The mix of GST225 and quartz powder was placed in molybdenum heating element of boat type through which a large current flowed. In this study we used an evaporant with a mass of 40 mg, which made it possible to prepare thin films having a thickness in the range of 85–100 nm. The film thickness was estimated with using of TEM facility. The maximum temperature of boat during evaporation was kept below 700 °C, the substrate temperature during deposition was no higher than 50 °C. Residual pressure in the chamber was 10^{-4} Pa. According to our estimates, the deposition rate was approximately 10 nm/s.

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The isothermal crystallization of thin films was carried out at varying time-temperature regimes: ΔT = 150–220 °C, Δt = 15–180 min including the heating time. The period of non-isothermal heating from room temperature (RT) was 1.5–2 min depending on the annealing temperature for all samples, which corresponds to the heating rate of 85–90°/min.

We used the combination of X-ray diffraction (XRD) and TEM to determine the evolution of the amorphous thin films after annealing. XRD studies of thin films were performed using Rigaku Smart Lab diffractometer equipped with the X-ray generator with rotating copper anode. 2θ-scans measurements were made in parallel beam geometry with a Ge(220) × 2 monochromator ($CuK_{\alpha 1}$ radiation). For the TEM analyses, we used *in-situ* lift-out method of sample preparation. The cross-sections of the samples were prepared using Focused Ion Beam (FIB) milling technique in a Helios NanoLab 600i (FEI) scanning electron/ion microscope system, a FIB/SEM dual beam system equipped with C and Pt gas injection system (GIS) and micromanipulator (Omniprobe) [12]. All specimens were studied using a transmission/scanning electron microscope (TEM/STEM) Titan 80–300 (FEI) equipped with a spherical aberration (Cs) corrector, a high angle annular dark field (HAADF) detector (Fischine), and atmospheric thin-window energy dispersive X-ray (EDX) spectrometer (Phoenix System, EDAX). The TEM analyses were performed at 300 kV. High resolution TEM (HRTEM) procedure was used to determine interplanar distances in the crystalline areas by direct measurements using micrographs as well as indirect measurements through Fourier transformation. We also used a liquid nitrogen-cooling holder (Gatan 636 Double Tilt, Gatan) to prevent potential sample decomposition and/or amorphisation during the study.

We performed CW laser illumination of the amorphous films at RT for their crystallization using green laser (λ = 532 nm, the corresponding photon energy E_{ph} = 2.33 eV, $P \approx$ 1.3 mW) with NTEGRA Spectra setup (NT-MDT). The diameter of the focused laser spot was about of 5 μm. The irradiation area was formed on the initial film surface by scanning with laser beam.

Both isothermal annealing and laser illumination experiments were carried out at atmosphere conditions. It was shown in [13] that kinetic model of crystallization of chalcogenide glasses is not affected by the presence of oxygen so we leave the thermal oxidation effect out of consideration.

3. Experimental results

As is known [14] that an amorphous structure should exhibit: no discernible microstructure > 10 Å; rapid onset of crystallization at a well-defined temperature *via* random nucleation centres; release of heat of transformation; crystallization of high resistivity materials by spherulitic and dendritic growth. We have performed a study of as-deposited films using XRD, TEM, SEM, and direct current (*dc*) conduction measurements (see Fig. S1 in Supplementary Material) which indicate that an as-deposited films were amorphous. We have carried out an element mapping of the film using EDX spectrometer also, and these results indicated that composition of films corresponds to $Ge_{22.3 \pm 0.1}Sb_{22.8 \pm 0.1}Te_{54.9 \pm 0.1}$.

Isothermal annealing of amorphous film at 180 °C in the duration of 30 min (this regime corresponds crystallization of thin film in accordance with [11]) leads to crystallization of amorphous phase that is reflected in TEM image (Fig. 1). Platinum layer on the top of the film is due to sample preparation technique for the TEM study. Crystalline material appears darker in the TEM microphotographs. The XRD results allowed us to estimate average grain size of polycrystalline material about 14 nm (see Fig. S2 in Supplementary Material) using the Scherrer equation [15] and assuming that GST225 film after isothermal annealing comprised of monocrystalline grains with random orientations.

One can see that the structure of the thin film becomes ordered in these annealing conditions, but not completely. A characteristic feature of the process is the total crystallization for top layer of about 40 nm

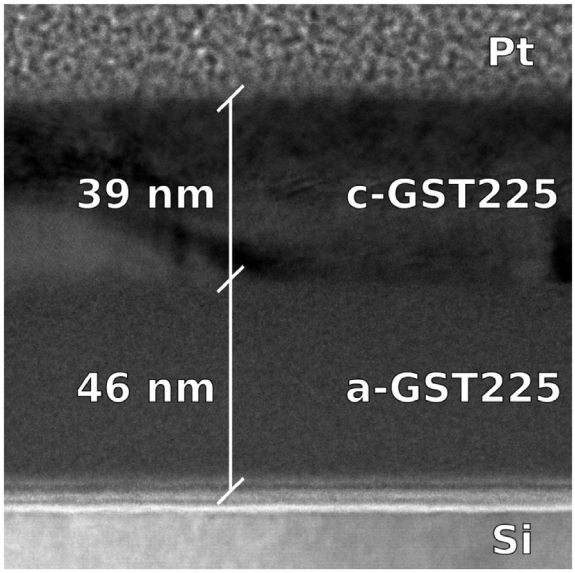

Fig. 1. TEM image for thin film after isothermal annealing.

thickness only, but the film layer at the interface with the silicon substrate (bottom layer) remains amorphous. This result will be considered in section Discussion. We carried out HRTEM study of crystalline area also, and this result is shown in Fig. S3. Analysis has shown that top layer contains disoriented relative to each other crystallites with close lattice parameters. One type of a crystallites had a trigonal lattice with parameters close to GST225 composition one [16], while the other kind of crystallites had a trigonal symmetry also, but lattice parameters slightly differ. We assume that this is due to the possible diffusion of elements during crystallization process, and the formation of regions, the chemical composition of which is different from initial GST225. Our studies using EDX spectroscopy showed that excess antimony and, respectively, deficiency of germanium compared to initial film have been observed in the top layer. It should be noted that the diffusion of certain element such as tellurium during crystallization has been previously described in [9,17,18]. We assume that other kind of crystallites have crystal structure either GST147 or even antimony telluride (Sb_2Te_3). Both compositions are characterised by trigonal symmetry with the lattice parameters close to ones of GST225 composition. For example, the GST225 and GST147 unit cells (space group $P\bar{3}m1$) contain one nine-layer packet, and one twelve-layer packet consisting of one five-layer and one seven-layer stack, respectively. The lattice parameters are given below: GST225: a = 0.420(2) nm; c = 1.696(6) nm; GST147: a = 0.421(2) nm; c = 2.365(8) nm; Sb_2Te_3 compound has a rhombohedral lattice (space group $R\bar{3}m$) with following lattice parameters in the hexagonal configuration: a = 0.4264 nm, c = 3.0458 nm [19].

TEM image for GST225 thin films after treatment of CW laser illumination is shown in Fig. 2. One can see that there is a relatively thin top layer, which consists of separated crystalline clusters (highlighted in the Fig. 2a). However, the main part of the film remains amorphous. High resolution lattice TEM image for crystals in laser irradiated sample is shown in Fig. 2b, also Fourier transformation is presented in Fig. S4 for this crystalline area. On the basis of these results, we concluded that the crystallized area corresponds to the structure characterised by trigonal symmetry (space group $P\bar{3}m1$) with the lattice parameters close to ones of GST225 composition.

4. Theory and numerical simulation

It is well known [20] that crystallization can be described as a consequence of two simultaneous processes. Those are (i) emerging of nuclei (nucleation) and (ii) increasing of nuclei sizes (growth). In the case of infinite geometry the KJMA [21] approach to describe overall