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Isothermal and CW laser crystallization of amorphous Ge₂Sb₂Te₅ 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 Ge₂Sb₂Te₅ (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 presynthesized 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: $\Delta T = 150-220$ °C, $\Delta t = 15-180$ 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) \times 2 monochromator (CuK_{a1} 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 thinwindow 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 ($\lambda = 532$ 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 asdeposited 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 ± 0.1}Sb_{22.8 ± 0.1}Te_{54.9 ± 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 (Sb₂Te₃). 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 P3m1) contain one nine-layer packet, and one twelve-layer packet consisting of one fivelayer 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; Sb₂Te₃ compound has a rhombohedral lattice (space group R3m) 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 $P\overline{3}m1$) 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



Fig. 2. TEM image of the film after influence of CW laser illumination. The separate crystalline areas are highlighted (a). HRTEM image of crystalline film (b).

crystallization is widely used for various materials including GST225 PCM material [7]. However, in the case of finite geometry this model tends to give inaccurate predictions because effect of boundaries on crystallization eliminated from calculations. Various approaches to describe the influence of boundaries in finite volumes were performed including both analytical [20,22–24] and numerical [25,26]. Most of the models deal with spherical geometry of crystallized volume and utilize simplified view on crystallization process.

In the present study we introduce the description of amorphous thin films crystallization based on widely recognised Kolmogorov's one [21].

4.1. Modelling of thin film crystallization

We have chosen the modelling geometry to be an infinite slab with regular thickness d, which is common for the thin films and could approximately describe any sample with high lateral-dimension-to-thickness ratio. In general, two ways of nucleation are possible in that case: i) homogeneous nucleation in the bulk and i) heterogeneous nucleation at both film boundaries. However, TEM results (Figs. 1 and 2) shown that the surface driven crystallization dominated in our experiments. Moreover, the homogeneously nucleated clusters were not observed in the study. Consequently, we took into account only heterogeneous nucleation mechanism. It should be noted, however, that the absence of homogeneous nucleation in the described case is not the general behaviour of finite systems; both nucleation mechanisms may lead to the

crystallization simultaneously [27].

In the case of heterogeneous nucleation, a nucleus always emerges at the film boundary. Let the nucleation rate $I (\text{cm}^{-2} \text{s}^{-1})$ in that case be constant, which is attributed to steady-state isothermal conditions [28]. It can be inferred [20,29] that a heterogeneous nucleus is a spherical cap described by its wetting angle θ (Fig. S3 in Supplementary Material). TEM microphotograph of surface nucleated grains shown in Fig. 4 also facilitates this assumption. Let the cap grows by increasing radius of its sphere *r* with constant velocity *c* while holding its wetting angle $\theta = const$. The first assumption is again attributed to isothermal conditions [28]. The second one is stated on the basis that the wetting angle is determined by properties of boundary only [29], *i.e.* material properties, not size of a nucleus. Crystallization process starts at time t = 0. We are looking for the probability *p* of arbitrary point *P* in the prescribed volume to belong to crystalline fraction at time *t*.

Our evaluations (see Supplementary Material) gave the desired probability p as:

$$p = \begin{cases} p & , p > 0, \\ 0 & , p \le 0, \end{cases}$$
(1a)

$$p_{-} = 1 - \exp\left[-\frac{\pi I c^2 t^3}{3} - \frac{\pi I}{3c \cos \theta} (z^3 - (z + ct \cos \theta)^3)\right].$$
 (1b)

4.2. Results of numerical simulation

Eqs. (1a) and (1b) allow one to determine the time dependence of crystallization probability distribution p(z) in the case of time-independent crystallization parameters: nucleation rate *I*, growth rate *c*, and wetting angle θ .

The wetting angle value cannot be determined undoubtedly from our TEM studies, which is why we have chosen $\theta = 90^{\circ}$ for the simulation purposes as the mean of possible values. Similar assumptions have been made by other authors [30]. For instance, in [7] the authors determined the wetting angle for *Si*-GST225 interface as 94° and for SiN-GST225 interface as 87° from comparison of simulation and experiment results. The values of nucleation rate and growth rate were estimated to fit experimental data with the proposed model (Eqs. (1a) and (1b)).

For the case of isothermal annealing, experimental data are the mean thickness of crystalline layer (39 nm from the TEM microphotograph, Fig. 3) and the average size of crystalline grains (14 nm from the evaluation of XRD data).

Recalling TEM image Fig. 2, it is noticeable that the surface layer of the laser-irradiated film is not entirely covered with crystalline fraction so that the crystalline grains appear separated. We estimated the surface layer coverage of about p(z = 0) = 90% from our TEM



Fig. 3. Results of numerical simulation for thin film crystallization during isothermal annealing according to Eqs. (1a) and (1b).

Table 1

Parameters of simulation of crystallization during isothermal annealing and laser illumination.

Crystallization parameter	Isothermal annealing	Laser illumination
Nucleation rate <i>I</i> Growth rate <i>c</i>	$\begin{array}{c} 1.66 \times 10^{13}\text{m}^{-2}\text{s}^{-1} \\ 3.77 \times 10^{-11}\text{m}\text{s}^{-1} \end{array}$	$\frac{2.67 \times 10^{16} \text{ m}^{-2} \text{ s}^{-1}}{2.13 \times 10^{-7} \text{ m s}^{-1}}$

observations. The regime of crystallization during laser scanning is strongly non-isothermal. Nevertheless, it seems possible to describe the crystallization process in such cases with still time-independent parameters *I* and *c*, which have the meaning of average values. Thus, we can again determine the parameters of crystallization for our experiments according to the developed model (Eqs. (1a) and (1b)). Recent research [31] indicates that the Kolmogorov's approach holds its validity in both isothermal and non-isothermal conditions. Numerous research [10,32,33] indicate that crystallization of GST225 compound is proceeded effectively for temperature above approximately 150 °C. We used the solution of El-Adawi [34] to estimate the time when the film material is heated above 150 °C and the mean temperature in that time interval. The calculated values are $\Delta t_{150} = 122 \text{ ms}$ and $T_m = 236 \text{ }^\circ\text{C}$ (see Supplementary Material). Experimental data that we aimed to fit in the case of CW laser illumination were the surface coverage p(z = 0)and the peak thickness of crystalline layer h_{peak} (about 15 nm accordingly to Fig. 2) caused by crystallization during Δt_{150} .

Estimated crystallization parameters are shown in Table 1 for the case of isothermal annealing and CW laser illumination; results of simulation are depicted in Figs. 3 and 4.

5. Discussion

The quantity *p* in Eqs. (1a) and (1b) defines the probability of the point located at distance z from the nearest boundary of the film to be inside the crystalline fraction at time *t*. Thus, p = 1 for the arbitrary plane (points equidistant with the boundary) inside the film means that this layer must belongs to crystalline material, while values of p < 1suggest that such layer only partly crystalline; the p value has the meaning of fraction of crystalline material in such case.

From the general point of view, in the case of heterogeneous nucleation the crystallization of material may be described by growing of crystalline layer from the boundary inside the bulk. Simulation results in Fig. 3 support that consideration. It is reasonable to suppose that there are two consequent stages of crystallization.

At the initial stage (t < 10 min in Fig. 3 and all the charts in Fig. 4) of crystallization p(z = 0) < 1 which implies that the surface layer of the film is not entirely covered by crystalline material. The p(z)



Fig. 4. Results of numerical simulation for thin film crystallization during CW laser illumination according to Eqs. (1a) and (1b).

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Fig. 5. Nucleation rates of GST225 as a function of reciprocal temperature, determined in [35,36] using in situ TEM, in [37] using ex situ TEM, and the ones calculated in this study.

relationships are gradual at this stage; this means that there is no distinct crystalline layer boundary. TEM microphotograph in Fig. 4 illustrates this early stage of crystallization. It seems probable that the nucleation process dominates this stage of crystallization.

Eventually the surface layer becomes entirely covered by the crystalline material and the second stage (t > 10 min in Fig. 3) of crystallization starts. Almost step-like form of p(z) relationships at this stage suggests that there is a distinct continuous crystalline layer at the film boundary. During crystallization, this layer grows; its front becomes smoother. That is why a steepness of the p(z) characteristics is increased during time; eventually the characteristic becomes almost square at t = 30 min in Fig. 3. As a result, crystallization leads to continuous smooth crystalline layer (Fig. 3). This stage of crystallization process may well be growth-dominated because the boundary is covered fully by crystalline material so there is no possibility for heterogeneous nucleation.

Figs. 5 and 6 show the values of nucleation rate and growth rate determined in this study with those being published elsewhere. We used the obtained by heating effect simulation value of temperature 236 °C for CW laser-induced crystallization. Ruitenberg et al. [35] and Privitera et al. [36] used in situ TEM to obtain their results while Kalb et al. [37,38] used ex situ TEM and AFM to get theirs. Both charts have been presented in Arrhenius coordinates. Straight line is the result of regression of experimental values from [35-38]. In response to the Arrhenius behaviour of corresponded quantities, two points are enough to establish a correlation between the data obtained in this work and the



Fig. 6. Crystal growth rates of GST225 as a function of reciprocal temperature, determined in [35,36] using in situ TEM, in [38] using ex situ AFM, and the ones calculated in this study.

reference data.

Fig. 5 demonstrates that our results for nucleation rate are in remarkably good agreement with reference values.

Growth rate values calculated in this study (Fig. 6) are consistent with regression line relatively good, especially in comparison with reference data scatter.

Despite the good conformity of our results with those being published by the other authors [35–38], it should be emphasized that our approach is based on the theory-experiment comparison, not the direct measurements. Our model neglects transient crystallization effects, such as induction time [39–41], and is valid only for isothermal conditions when nucleation and growth rates are both constants. However, even under isothermal conditions the growth rate could be considered size- and, therefore, time-dependent [42]. Constant nucleation, assumed in this study, is also not strictly valid for all cases. Presence of inclusions and pre-existent crystalline clusters may lead to instantaneous nucleation behaviour [20]. Future work will attribute these limitations.

6. Conclusions

Obtained TEM results indicated that the crystallization process in amorphous GST225 thin films after thermal annealing and CW laser illumination was driven by heterogeneous nucleation mechanism. This result allowed us to develop the simplified model of amorphous thin films crystallization based on the Kolmogorov's formalism [21] [21]. Results of the simulation fitted TEM data with sufficient accuracy. The fitting variables (nucleation rate and growth rate) are in reasonable agreement with the data being published by the other authors. The developed model may be useful for the simulation of phase change materials crystallization in the PCM devices.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.jnoncrysol.2017.07.014.

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