

Crystallization process in thin stoichiometric GeSbTe films

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The crystallization kinetics of $\text{Ge}_1\text{Sb}_2\text{Te}_4$ and $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films has been analyzed using results of impedance measurements, in which Bruggerman's effective medium approximation was employed, considering that the amorphous matrix contained inclusions of two different crystalline phases. To validate the predictions from analytical model, we compared those with experimental results obtained for $\text{Ge}_1\text{Sb}_2\text{Te}_4$ and $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films. The proposed analytical model allows us to simulate similar transformation curves as those obtained from the experiments in different materials.

Кинетика процессов кристаллизации в пленках $\text{Ge}_1\text{Sb}_2\text{Te}_4$ и $\text{Ge}_2\text{Sb}_2\text{Te}_5$ проанализирована с помощью измерений импеданса с использованием приближения Бруггермана, учитывающего наличие включений двух различных кристаллических фаз в аморфной матрице. Предсказания аналитической модели сравнены с экспериментальными результатами для $\text{Ge}_1\text{Sb}_2\text{Te}_4$ и $\text{Ge}_2\text{Sb}_2\text{Te}_5$. Предложенная аналитическая модель позволяет моделировать кривые фазовых превращений, подобные полученным экспериментально для различных материалов.

GeSbTe stoichiometric compound semiconductors are under extensive studied due to their applications in optical and electrical memory devices. The electrical and optical properties of these semiconductors depend on the microstructure changes that occur during crystallization. It is known that upon annealing, amorphous layers of this material first undergo the amorphous-to-crystalline (fcc) transition in the range of 140–180°C and at higher temperatures (at about 230°C), the crystal (fcc)-to-crystal (hex) transition occurs. In recent years, extensive experimental studies have been conducted to understand the crystallization phenomena in these materials [1–7]. One of the main concerns is to study the incubation time necessary to form the critical nuclei previous to the crystallization of the amorphous phase [1]. This is important because it limits the fast-action of the devices. The nature of these nuclei is not well known so

far. The aim of this work is to investigate the crystallization kinetics during isokinetic and isothermal annealing.

GeSbTe thin films of the stoichiometric $\text{Ge}_2\text{Sb}_2\text{Te}_5$ ($\text{Ge}_{22}\text{Sb}_{22}\text{Te}_{56}$) and $\text{Ge}_1\text{Sb}_2\text{Te}_4$ ($\text{Ge}_{14}\text{Sb}_{29}\text{Te}_{57}$) compositions and of 30 to 500 nm thickness were prepared by DC magnetron reactive sputtering and vacuum evaporation of the bulk alloy onto unheated glass and Si substrates. The film composition was determined by electron dispersion spectroscopy (EDS) and it was found that the deviation from the stoichiometry was not exceed 2 %, for every element. The samples were heated using a resistance cartridge heater and the temperature was controlled by a controller programmed to produce a constant heating rate of 5°C/min. in isokinetic measurements. In the isothermal measurements, the temperature controller was programmed to maintain a constant heating rate of 3°C/min to reach the specified

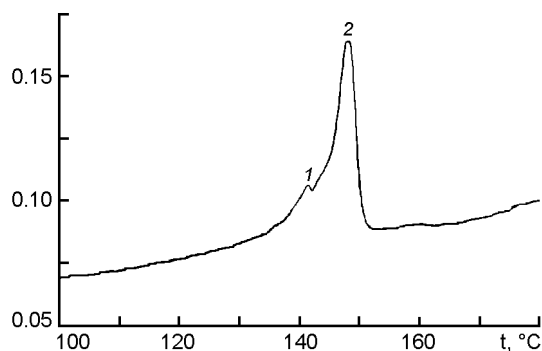


Fig. 1. DSC curve obtained for a $\text{Ge}_2\text{Sb}_2\text{Te}_5$ compound at the heating rate of $5^\circ\text{C}/\text{min}$.

isothermal annealing point. The kinetics of the amorphous-to-crystalline phase transformation in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and $\text{Ge}_1\text{Sb}_2\text{Te}_4$ thin films was investigated using electrical impedance, X-ray diffraction (XRD), and differential scanning calorimetry (DSC) measurements.

In situ impedance measurements were carried out in the frequency range of 40 Hz to 110 MHz using an Agilent Precision Impedance Analyzer 4294A. The X-ray measurements were carried out at room temperature on samples previously heated to different temperatures.

Isokinetic measurements. The DSC curve for a $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film shown in Fig. 1 indicates that the crystallization process involves two exothermic reactions that, in combination with XRD measurements (Fig. 2), allow us to conclude what follows. At temperatures below 100°C , the sample shows only wide bands which are characteristic of the amorphous material (Fig. 2, curve 1). The first exothermic peak in the DSC measurements can be associated with the appearance of metastable nucleation centers embedded in the amorphous matrix. The X-ray data indicate that these nuclei have a nanometric size of about 12 nm and an fcc $\text{Ge}_1\text{Sb}_4\text{Te}_7$ composition (Fig. 2, curve 2). The second (large) exothermic peak in the DSC measurements, which is observed at a higher temperature, corresponds to the transformation of these nucleation centers into an fcc stoichiometric crystalline phase ($\text{Ge}_2\text{Sb}_2\text{Te}_5$ or $\text{Ge}_1\text{Sb}_2\text{Te}_4$), which covers the whole volume of the film (Fig. 2, curve 3). A size range of the crystallites between 22 and 30 nm was determined from the peak width. The results from the isokinetic experiments have shown that during the amorphous-to-crystalline phase transformation in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and $\text{Ge}_1\text{Sb}_2\text{Te}_4$ compound

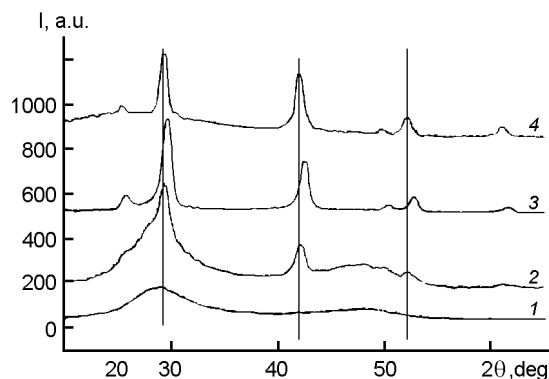


Fig. 2. X-ray diffraction patterns for $\text{Ge}_2\text{Sb}_2\text{Te}_5$ samples measured on films heated at temperatures ($^\circ\text{C}$): 100 (1), 140 (2), 180 (3). Pattern 4 corresponds to a $\text{Ge}_1\text{Sb}_4\text{Te}_7$ sample annealed at 180°C .

semiconductors, a stable fcc phase and a metastable one coexist during crystallization within a certain temperature range.

Isothermal measurements. Fig. 3 shows the evolution of the total volume fraction ($1 - f_a$, where f_a is the volume fraction of amorphous phase) of low-resistivity crystalline phases (nuclei of $\text{Ge}_1\text{Sb}_4\text{Te}_7$ and $\text{Ge}_2\text{Sb}_2\text{Te}_5$) for $\text{Ge}_2\text{Sb}_2\text{Te}_5$ samples, calculated from impedance measurements for films isothermally annealed at 115°C (black circles) using Maxwell-Wagner model [8]. This model assumes that conductive spheres are distributed in a continuous amorphous medium and that the impedance spectrum can be fitted by two RC equivalent circuits in series [8]. The volume fraction of the metastable nuclei estimated from impedance measurements and using Bruggerman effective medium approximation [9, 10] can be expressed as

$$f_a \frac{\varepsilon_a - \varepsilon}{\varepsilon_a + 2\varepsilon} + (1 - f_a - f_x) \frac{\varepsilon_c - \varepsilon}{\varepsilon_c + 2\varepsilon} + f_x \frac{\varepsilon_x - \varepsilon}{\varepsilon_x + 2\varepsilon} = 0, \quad (1)$$

where ε_a , ε_c and ε_x are dielectric constants of the amorphous (matrix), crystalline, and nuclei phases ($\text{Ge}_1\text{Sb}_4\text{Te}_7$), respectively; f_a , $(1 - f_a - f_x)$ and f_x , are the corresponding volume fractions, and ε is the static effective dielectric constant. The value of ε can be estimated experimentally fitting the impedance data to one RC circuit [7]. From Maxwell-Wagner model, f_a can be estimated. The values of ε_c and ε_x have been measured directly on crystalline samples of

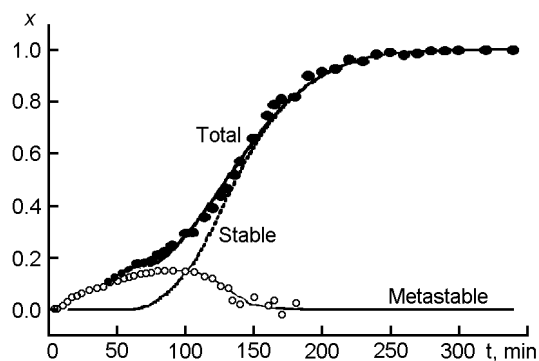


Fig. 3. Time evolution of the volume fraction calculated for a $\text{Ge}_2\text{Sb}_2\text{Te}_5$ sample annealed at 115°C from impedance measurements (black circles). Open circles: the volume fraction of the metastable nuclei estimated from impedance measurements using Bruggeman approximation. Solid lines: results from the analytical model.

$\text{Ge}_2\text{Sb}_2\text{Te}_5$ and $\text{Ge}_1\text{Sb}_4\text{Te}_7$. From the equation above, we obtain the values for f_x shown in Fig. 3 (open circles). The volume fraction of nuclei measured in sample is seen to increase in the time range between 0 and 100 minutes and then to decrease in time, thus being in accordance with X-ray measurements (Fig. 5), indicating that the nuclei of $\text{Ge}_1\text{Sb}_4\text{Te}_7$ phase are transformed gradually into the main $\text{Ge}_2\text{Sb}_2\text{Te}_5$ material. Fig. 4 shows a plot of $\ln[-\ln(1-x)]$ vs $\ln(t)$ for a $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film. According to the Kolmogorov-Mehl-Avrami-Johnson (JMAK) theory [11–13], this dependence should be linear in materials with random nucleation and isotropic growth in an infinite specimen. As is seen, the linear relation between $\ln[-\ln(1-x)]$ and $\ln(t)$ appears only after some incubation time (i.e., time required for the appearance of critical nuclei).

Fig. 5 shows the X-ray diffraction spectra for a $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film taken at room temperature after isothermal annealing during 30, 60, 120, and 300 min at 110°C . Note that the crystallization temperature (T_c) for this material is about 135°C . In this figure, the diffraction patterns are shown corresponding to the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (pattern 2) and $\text{Ge}_1\text{Sb}_4\text{Te}_7$ (pattern 1) materials, fully crystallized at 180°C . The positions of the $\text{Ge}_1\text{Sb}_4\text{Te}_7$ peaks is indicated by vertical lines. The same X-ray diffraction spectra have been observed in $\text{Ge}_1\text{Sb}_2\text{Te}_4$ films.

To try to explain deviations from the well-known KJMA kinetics theory, we have

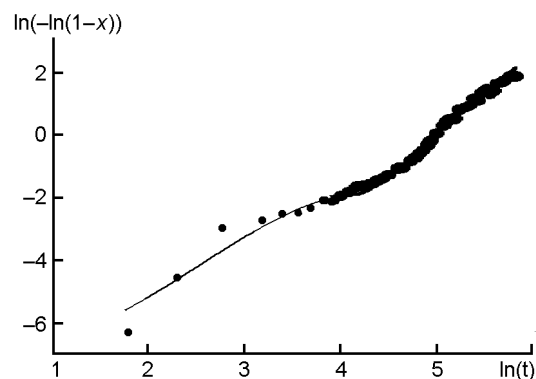


Fig. 4. Dependences of $\ln[-\ln(1-x)]$ vs $\ln(t)$ for a $\text{Ge}_2\text{Sb}_2\text{Te}_5$ sample isothermally annealed 115°C . Black circles: results calculated from impedance measurements. Solid line: results of the simulation using the analytical model.

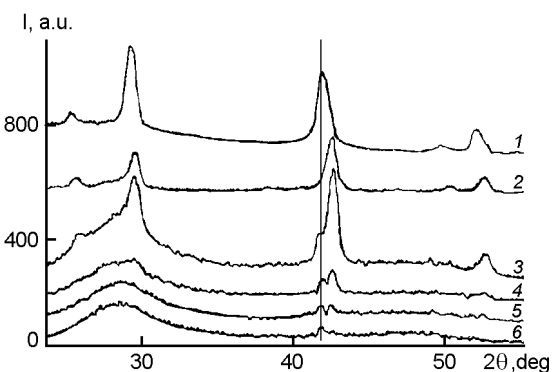


Fig. 5. X-ray diffraction spectra for a $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film taken at room temperature after isothermal annealing during 30 (pattern 6), 60 (pattern 5), 120 (pattern 4), and 300 (pattern 3) min at 110°C .

developed an analytical model. In the model, we have assumed that the metastable phase grows up to a certain fraction (due to external parameters, such as temperature, concentration variations, etc.) and then stops growing when the stable phase that has nucleated therein overpasses the metastable grain boundaries. Thus, a sigmoid curve represents the first stage of transformation from amorphous phase to metastable one. The second stage consists of nucleation and growth of the stable phase within the metastable one, until the grain boundaries are reached. The third and last stage deals with the classical nucleation and growth of the stable phase within the amorphous one (another sigmoid). In all cases, the total volume fraction of crystalline phases equals the sum of the metastable, the stable in

amorphous, and the stable in metastable ones.

The metastable phase can be represented by a KJMA-type equation with subtraction of f_{sm} to take into account the growth of the stable phase inside the metastable grains, expressed as:

$$f_m(t) = f_{\max}(1 - \exp(-K_m t^{n_m})) - f_{sm}(t), \quad (2)$$

where f_m and f_{sm} represent the overall transformed fractions of the metastable phase and that of the stable in metastable one, respectively; f_{\max} is the maximum transformed fraction of metastable phase, and K_m and n_m are the two classical KJMA parameters. The kinetic behavior of the stable phase in the metastable one, even though it is assumed as a martensite type, can be represented by a classical KJMA formula, changing the K_m and n_m parameters accordingly and considering t_{sm} as the induction time for the nucleation of the stable phase in the metastable one:

$$f_{sm}(t) = f_{\max}(1 - \exp(-K_{sm}(t - t_{sm})^{n_{sm}})) \quad (3)$$

for $t \geq t_{sm}$ and $f_{sm}(t) = 0$ for $t < t_{sm}$.

The stable phase transformation kinetics in amorphous fraction is a KJMA sigmoid with its specific parameters:

$$f_{sa}(t) = (1 - f_{\max})(1 - \exp(-K_{sa}(t - t_{sa})^{n_{sa}})) \quad (4)$$

for $t \geq t_{sa}$ and $f_{sa}(t) = 0$ for $t < t_{sa}$,

where f_{sa} is the volume fraction of stable phase in amorphous (from 0 to $1 - f_{\max}$), and K_{sa} and n_{sa} are the KJMA parameters.

The total fraction of transformed material is given by the equation:

$$f_{total}(t) = f_m(t) + f_{sm}(t) + f_{sa}(t). \quad (5)$$

This two-stage transformation allows us to simulate transformation curves similar to the experimental ones (Fig. 3 and Fig. 4, solid lines). It should be noted that the model is capable of predicting the three slopes shown clearly in the JMAK plot of Fig. 4, corresponding to three distinguishable stages in the crystallization process. The first slope is related to the metastable phase formation, the second one (very insignificant), to the transition between the metastable and stable phases, and the last one, to the stable phase nucleation and growth. It is quite evident from the experimental results that the first slope of the JMAK

plot can be related with the kinetic behavior of the metastable phase.

It is to note that the simulation results have shown that without the appearance of the stable phase in the metastable one, it is impossible to obtain the step in the total volume fraction vs time curve (Fig. 3), nor the two slopes in the JMAK plot (Fig. 4). From X-ray measurements, we can conclude that the metastable phase represents the crystalline fcc $\text{Ge}_1\text{Sb}_4\text{Te}_7$ material. It is supposed that the appearance of some nanocrystalline nuclei of the $\text{Ge}_1\text{Sb}_4\text{Te}_7$ composition could be related to local fluctuations in the film composition, since the crystallization temperature of this nanocrystalline nuclei is lower than that of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ or $\text{Ge}_1\text{Sb}_2\text{Te}_4$ alloys.

The results of this investigation have shown that during the process of amorphous-to-crystalline phase transformation (for isokinetic as well as for isothermal) in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and $\text{Ge}_1\text{Sb}_2\text{Te}_4$ compound semiconductors, a stable fcc phase and a metastable one coexist within a certain temperature (or time) range in the course of crystallization. Perhaps the appearance of some nanocrystalline nuclei of the $\text{Ge}_1\text{Sb}_4\text{Te}_7$ composition could be related to local fluctuations in the film composition. In addition, the Kolmogorov, Johnson, Mehl and Avrami model cannot be applicable directly in the case of GeSbTe alloys, since the transformation kinetics includes two stages. The analytical model proposed in this work can represent the kinetic behavior observed in experiment.

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Процес кристалізації у тонких стехіометричних плівках GeSbTe

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Кінетику процесів кристалізації у плівках $\text{Ge}_1\text{Sb}_2\text{Te}_4$ і $\text{Ge}_2\text{Sb}_2\text{Te}_5$ проаналізовано за допомогою вимірювань імпедансу з використанням наближення Бруггермана, яке бере до уваги наявність включень двох різних кристалічних фаз в аморфній матриці. Прогнози аналітичної моделі зіставлено з експериментальними результатами для $\text{Ge}_1\text{Sb}_2\text{Te}_4$ та $\text{Ge}_2\text{Sb}_2\text{Te}_5$. Запропонована аналітична модель дозволяє моделювати криві фазових перетворень, аналогічні одержаним експериментально для різних матеріалів.