

CRYSTALLIZATION MECHANISM AND KINETIC PARAMETERS IN $\text{Ge}_2\text{Sb}_2\text{Te}_5$ THIN FILMS FOR THE PHASE CHANGE MEMORY APPLICATION

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Thermal properties, mechanism and kinetics of crystallization for $\text{Ge}_2\text{Sb}_2\text{Te}_5$ thin films were investigated. The parameters of amorphous-crystalline phase transition for $\text{Ge}_2\text{Sb}_2\text{Te}_5$ thin films were determined. Kinetic triplet (effective activation energy, pre-exponential factor and reaction model) for the crystallization process of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ thin films was established. The model of GST film crystallization was proposed. Obtained kinetic parameters for $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films allowed predicting data processing and storage times of the phase change memory cell. It was found that $\text{Ge}_2\text{Sb}_2\text{Te}_5$ thin film can provide the data processing time of the phase change memory cell about nanoseconds, which is comparable with that of the random access memory.

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1. Introduction

Currently active investigations of phase change memory (PCM) are carried out. PCM is considered to be one of the most promising candidates for the next generation of memories due to non-volatility, low power consumption, fast operation speed, high endurance, extended scalability.

The PCM concept is based on the electronic switching effect in chalcogenide glassy semiconductors, which was discovered for the $\text{TlAsSe}(\text{Te})$ compound at the Ioffe Physical-Technical Institute in 1963 by B.T. Kolomiets, and E.A. Lebedev [1], and the reversible switching and memory effect, which was reported in the late 1960s by S.R. Ovshinsky [2]. Ovshinsky used these effects and demonstrated the possibility of electrical and optical ways to store information using devices on the basis of chalcogenide glassy semiconductors [3, 4]. However, nearly 30 years passed from the first generation of PCM with not exciting parameters till the appearance of commercially successful discs of different formats, such as DVD+RW and Blu-Ray.

Noticeable progress was achieved last years in the development of PCM. However, despite the success electrical PCM does not become widespread technology. This is explained by the existence of quite specific requirements to the phase-change materials, which greatly complicate improvement of the technology. Some of these requirements are contradictory and quite difficult to be achieved. In this case, improving of PCM technology requires effective methods for controlling the properties of PCM materials, and possibility to predict the behavior of the materials at different temperatures.

For this reason only few materials are actually useful for PCM application. At the beginning of PCM technology main problems were connected with the slow crystallization rate, limited cyclability, and spontaneous crystallization at room temperature. A breakthrough was reached by the discovery of fast switching stable compositions on the quasi-binary line between

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GeTe and Sb_2Te_3 by Yamada and coauthors [5]. This discovery led to the commercial success of DVD+RW, and Blu-Ray discs.

Three compounds exist on this quasi-binary line: $\text{Ge}_2\text{Sb}_2\text{Te}_5$, GeSb_2Te_4 and GeSb_4Te_7 . The most promising among them is considered to be $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST225) due to the complex of properties (appreciable stability at room temperature, high crystallization rate and good reversibility between amorphous and crystalline phases).

One of the problems of the PCM technology is connected with the necessity of decreasing the data processing time (write time is 100 ns [6]) to the level comparable with that of the random access memory RAM (~10–50 ns [7]).

Three operations can determine the data processing time of the PCM memory: reading, recording, and erasing operations (Fig. 1). Reading operation is fast enough – from 1 to 10 ns. Recording operation or RESET is connected with the transition to the high resistance amorphous state, while erasing operation or SET - with the transition to the low resistance crystalline state.

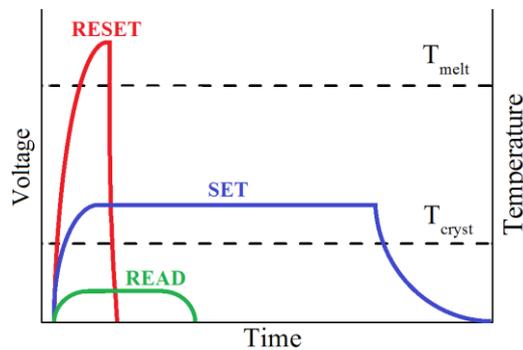


Fig. 1. Operations determining the work of PCM devices

Crystallization kinetics is sufficiently at least on the order of magnitude slower than formation of amorphous state [7]. So, exactly crystallization process it means SET operation determines data processing rate of the PCM cell, which strongly motivates investigation of the kinetics and mechanism of crystallization.

Requirements for the PCM materials with high crystallization rate are summarized in the Table 1.

As can be seen it is just a complex of requirements. The main of them is minimization of diffusion processes, because these are slow processes. Phase separation due to the crystallization must be excluded in PCM materials.

Compounds on the quasi-binary line GeTe- Sb_2Te_3 forms homologous series and have similar phase diagrams [8]. They crystallize in the metastable NaCl type structure, which is highly symmetric and isotropic [9, 10]. Large oscillations of atoms [8] and high concentration of vacancies [11-13] causes disordering of the structure, which becomes close to large extent to the amorphous. In this case atoms do not need large displacements and diffusion to take their places in the crystal structure, which explain rapid crystallization [14]. Small difference of the volumes of amorphous and crystalline phases leads to small stresses due to the phase transition [8, 15]. Together with the absence of phase separation this characteristic features determines high cyclability of the materials [8]. In addition, crystalline phase allows modification of composition [8] and doping [16-20], which is necessary for controlling the properties. From these points of view alloys on the quasi-binary line GeTe- Sb_2Te_3 are the most promising PCM materials. These compositions in addition can be useful for the fabrication of the components of sensors measuring physical parameters (namely MEMS and MOEMS). In particular, using the modes of conductivity switching (or regulation), it is possible to realize self-calibration process of the MEMS device.

So, the main aim of this study is to investigate the thermal properties, mechanism and kinetics of crystallization for GST225 thin films.

Table 1. Requirements for the PCM materials with high crystallization rate

Requirements	Reasons
Diffusionless phase transition.	Do not require large displacements of atoms.
Absence of phase separation caused by the phase transition.	Small migration of atoms.
Composition corresponding to the compound.	Formation of one phase upon crystallization
Congruent melting.	Absence of the composition changes.
Compounds with not strong covalent bonds of atoms. Existence of weak bonds in the structure.	Possibility of selective and rapid bonds breaking.
Similarity of the distribution of atoms in amorphous and crystalline states.	Lower energy barrier for the transition between amorphous and crystalline states.
High symmetry of the crystal structure (simple cubic and fcc structures).	Isotropic distribution of atoms close to the amorphous state. Small migration of atoms.
Significant thermal oscillations of atoms.	Noticeable displacements, increasing of random distribution of atoms in crystalline state.
Small change of volume due to the phase transition.	Small mechanical stresses and displacements of atoms.
Absence of phase separation in wide range of compositions.	Possibility to modify properties by changing of the composition.
Optimally high activation energy of crystallization.	Wide range of crystallization rates.
High mobility of atoms in amorphous and supercooled states. Low viscosity.	Rapid displacements of atoms.

2. Experimental

GST225 was prepared with using of quenching technique, which was proposed in [21], and modified in [22]. The mixture of elements (99.99% purity) in the predetermined amounts was synthesized in evacuated ($5 \cdot 10^{-3}$ Pa) quartz ampoules by step-wise gradual heating up to 800 °C in a rocking furnace to ensure homogeneity of the melt with annealing at this temperature during some hours. Then, the melt was quenched to the room temperature, and after solidification the alloy was annealed during 12 hours at 500°C.

Thin films were prepared by thermal evaporation of the synthesized material in vacuum, with the substrate temperature during evaporation did not exceeding 50°C. AFM and scanning electron microscopy (SEM, Carl Zeiss NVision 40) were used for the investigation of the characteristic features of the film morphology.

For the elemental analysis of the thin films we used Rutherford backscattering spectroscopy (RBS, $E_d=1.0$ and $E_d=2.7$ MeV at 135° scattering angle) and Energy Dispersive X-Ray Analysis (EDX, CAMEBAX, Cameca). RBS allowed to determine only ratios Ge/(Sb + Te) due to the overlapping of Sb and Te peaks on the spectra caused by their neighbor position in the Periodic table, while EDX permitted to determine the ratio of the Sb and Te atoms of the thin films. Results of the RBS and EDX measurements are quite close (Table 2), and shows that deposited thin films have composition of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ with accuracy of $\pm 5\%$.

Table 2. Results of elemental analysis for GST225 thin films

Method	Ge, at. %	Sb, at. %	Te, at. %	Sb+Te, at. %
RBS	22.5			77.5
EDX	23.8	21.1	55.1	76.2
Calculation	22.2	22.2	55.6	77.8

The structures of the synthesized GST225 and thin films on its basis (Fig. 2) were checked by X-ray diffraction (D8 Advance Bruker, $\text{CuK}_{\alpha 1}$ radiation, 0.15418 nm). XRD showed that synthesized material was polycrystalline and has a trigonal phase of $\text{Ge}_2\text{Sb}_2\text{Te}_5$. As-deposited thin

films were amorphous, and annealing at temperatures above 150°C led to the crystallization of the films with the appearance of cubic (rock-salt) and trigonal modifications of GST225.

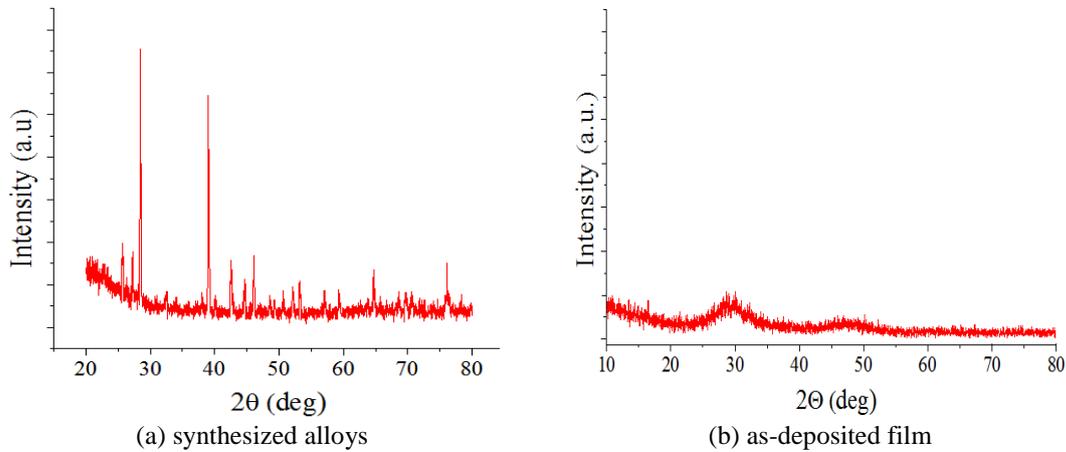


Fig. 2. Results of XRD measurements

Investigation of thermal properties, thermally induced transformations, and kinetics of the crystallization for GST225 thin films were carried out in non-isothermal conditions with using of differential scanning calorimetry (DSC-50, Shimadzu). The use of non-isothermal measurements allows to overcome a major problem of the isothermal experiments, which is connected with the loss of data at the beginning of heating due to the requirement of some time to reach the necessary temperature. However, a typical solid state process has a maximum reaction rate at the beginning of the transformation. In the case of non-isothermal experiments this problem is absent. Therefore this technique is widely used. But the advantages of the non-isothermal technique are at least partially reduced by computational difficulties associated with the kinetic analysis. The proposed approach allows a better understanding of the physical and chemical characteristics of solids.

DSC measurements were performed at 8 different heating rates (from 5 to 90°C/min) in a nitrogen flow (20 ml/min). Thin films were scraped off from c-Si wafers with sapphire spatula. Dispersity of the powder was estimated by the optical microscopy and was in the range of 1.5 – 30 μm. The powder samples had masses of a few milligrams and were pressed in Al pans. Empty Al pans were used as references. Temperature calibration was checked with In, Sn, Pb, Cd and Zn for all used heating rates.

3. Results and Methods of Calculations

DSC scans of as-deposited GST225 thin films are presented in Fig. 3. Exothermic peak in the range 130-190 °C is due to the crystallization of amorphous phase, which shifts to the higher temperatures with the increase of the heating rate [23]. The parameters of amorphous-crystalline phase transition for the GST225 thin films are presented in Table 3. In the case of heat effects overlapping, resolution with using of Gaussians was carried out. This fitting procedure allowed us to estimate characteristics of the peaks.

Table 3. Thermal properties of GST225 thin films

Crystallization			
Temperature, °C			Heat effect, J/g
Onset	Peak	Endset	
139.4	145.1	151.0	4.49

For non-isothermal conditions with constant heating rate $\beta = dT/dt$, as in our case, transformation kinetics can be described by the following equation [24]:

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt} \frac{1}{\beta} = \frac{A}{\beta} \exp\left(\frac{-E_a}{RT}\right) f(\alpha),$$

where α is the fraction of crystallites (conversion), $f(\alpha)$ is the reaction (crystallization) model. Integral form of the reaction model can be obtained by integrating

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(\frac{-E_a}{RT}\right) dT = \frac{A}{\beta} I(E, T) = \frac{A}{\beta} \frac{E_a}{R} p(x)$$

where T_0 is the initial temperature; $I(E, T)$ is the temperature integral, which has no analytic solution; $p(x) = \int_x^\infty (e^{-x} / x^2) dx$, where $x = E_a/RT$, is the exponential integral, which can be found in mathematical tables.

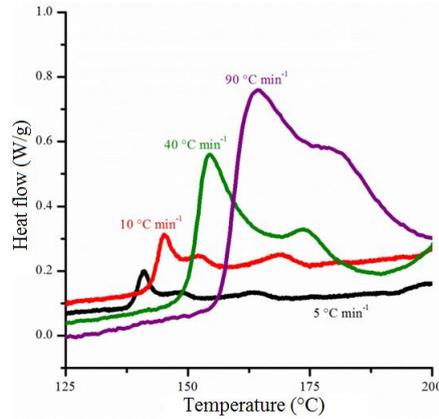


Fig. 3. DSC scans of as-deposited GST225 thin films for four heating rates

The dependencies of conversions on temperature were calculated from the experimental DSC curves for all heating rates assuming that the entire area of the phase transition peak corresponds to the fully passed reaction. The dependences of conversion on temperature are presented in Fig. 4.

Then, for the determination of kinetic triplet (effective activation energy, pre-exponential factor and reaction model) for crystallization process of GST225 thin films we used model-free Ozawa-Flynn-Wall (OFW) and model-fitting Coates-Redfern (CR) methods [24]. Joint application of these methods allowed us to estimate effective activation energies and pre-exponential factors as functions of conversion (Fig. 5), and establish reaction (crystallization) model (Table 4). It was found that crystallization process most adequately can be described by the second-order reaction, which is characteristic for spontaneous nucleation with further growth without overlapping [25].

The main advantage of this approach is that kinetic triplet enables to obtain information about mechanism of solid state reactions. It should be noted that Arrhenius parameters of solid state reactions are difficult to interpret in the terms of the transition state theory. Therefore, computed Arrhenius parameters are effective constants.

4. Discussions

Fig. 6 shows temperature dependencies of α and $d\alpha/dt$ for GST225 thin films. All temperature dependencies of conversion have S-shapes. It is known that the shape of such dependence is connected with the character of crystallization process in solid state [26]. In the given case shapes of the curves indicate that crystallization of GST films is a complex process consisting of at least two stages. For crystallization process the most obvious stages are nucleation and crystal growth.

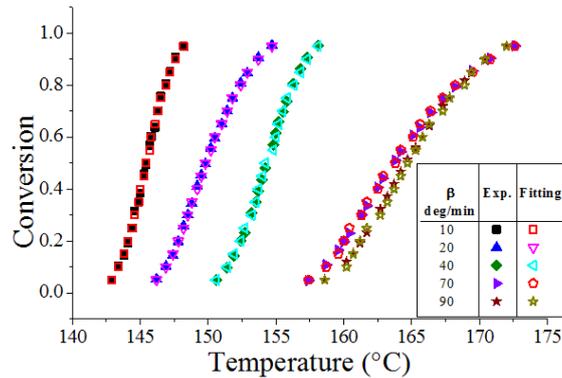


Fig. 4. Temperature dependences of conversion for crystallization of thin films

The initial range of curves corresponds to the induction period. This time is necessary for the nucleus to exceed critical size, after which probability of its growth became higher than dissociation. Induction period is followed by the acceleration period, when nucleuses begin growing. Decrease of the growth rate begins, when growing crystallites come into contact. This leads to the decrease of the surface of transformation front due to the conjunction of crystallites, and leads to the absorption of potential nucleation sites.

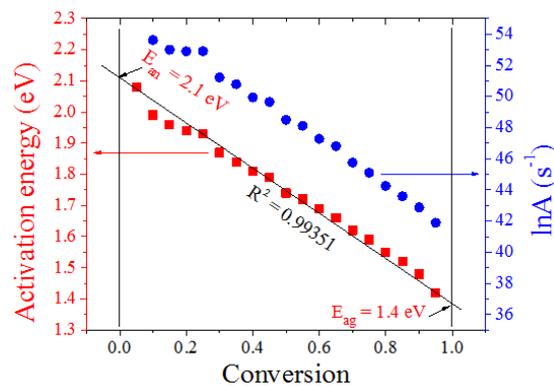


Fig. 5. Effective activation energy of crystallization (E_a) as a function of conversion

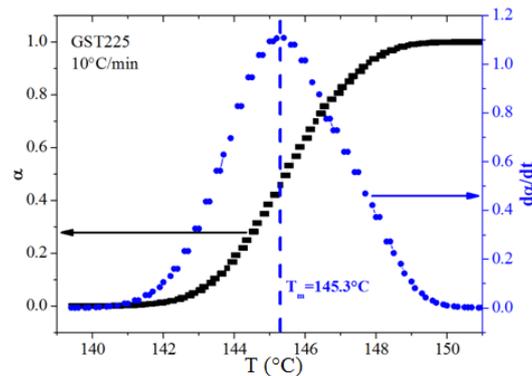


Fig. 6. Temperature dependencies of α and $d\alpha/dt$ for crystallization of thin films

As can be seen from the Fig. 5 effective activation energy gradually decreases with the increase of conversion. This result agrees with the assumption that crystallization of GST thin film is determined by two parallel processes – nucleation and crystalline growth. Contribution of the first process gradually decreases, while of the second increases. In this case, activation energy in the initial moment corresponds to the activation energy of nucleation rate E_{an} , while in the end – to the activation energy of crystalline growth rate E_{ag} . The dependence of effective activation energy on conversion was approximated by linear function with using of least square method ($R^2 = 0.99351$), which allowed us to estimate E_{an} and E_{ag} (Fig. 5 and Table 4).

In the classical theory of nucleation and crystalline growth the difference between the activation energies of nucleation and crystalline growth rates corresponds to the energy barrier for the formation of nucleus with critical size $\Delta G^* = E_{an} - E_{ag}$. For the investigated materials this barrier is less, than 1 eV (see Table 4). Such a low value indicates on the sufficient role of the heterogeneous nucleation on the interfaces [27].

Table 4. Crystallization model, activation energies of nucleation and growth rates, and the energy barrier for the formation of nuclei with critical size for the crystallization process of GST225 thin films

Model	Differential form, $f(\alpha)$	Integral form, $g(\alpha)$	E_{an} , eV	E_{ag} , eV	ΔG^* , eV
Second-order reaction	$(1-\alpha)^2$	$[1/(1-\alpha)]-1$	2.1	1.4	0.7

Earlier we have shown [23] that as-deposited GST225 thin films have island-like structure. It follows from the AFM scans that the diameters of islands from one to two orders of magnitude larger than their height. Taking into account results of crystallization kinetics investigations, which indicate on the sufficient role of the heterogeneous nucleation on the interfaces, we suppose that island-like structure promote nucleation on the film surface, which is due to the lower energy formation of nucleus on the boundary surface than in the bulk material.

According to AFM (Fig.7) crystallization of the film at 150 °C is accompanied by the increase of mean height of islands nearly on the order of magnitude [23]. In our case, growing crystallites at the beginning are extended in the plane of the substrate. Even more sufficient modification of the morphology was observed after the heating above 330 °C. Significant increase of the sizes of islands and of their heights was observed. It can be due to the conjunction of growing crystallites, and their growth in the volume of the film. Proposed model of GST225 film crystallization is presented in Fig. 7. Our results and proposed model correlates with [28]. It was shown in this study that nucleation of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ thin films begins at the surface of the film and further proceeds by the growth of the grains through the thickness of the film, which is accompanied by the coalescence of the grains leading to the increase of the grain size.

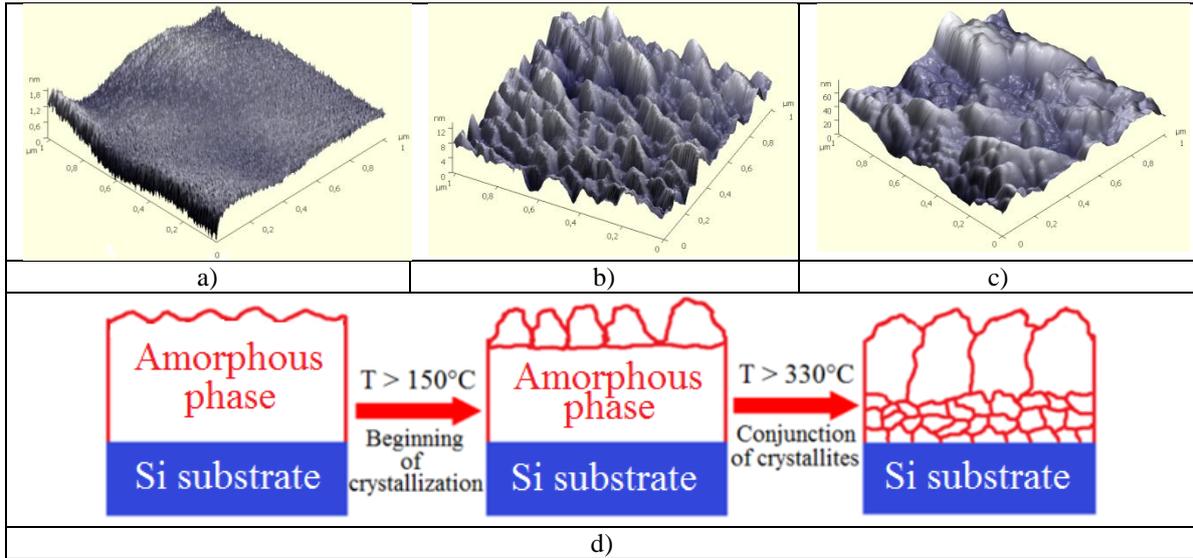


Fig. 7. AFM scans for GST225 thin films and proposed model of film crystallization:
 a) - as-deposited film; b) - annealed at 150 °C; c) - annealed at 415 °C;
 d) - model of film crystallization

Determined kinetic triplet was used to calculate the times of crystallization, which allowed us to estimate the possible processing and storage times in PCM cells on the basis of investigated material. We assumed that “0” and “1” states of the PCM cells differs in the value of conductivity not less, than by 1-2 orders of magnitude. Then, taking into consideration that crystallization of investigated films is accompanied by a change of conductivity by 3-4 orders of magnitude [19], we estimated conversion, which corresponds to the transition between the “0” and “1” states of the PCM cell by the equation [29]

$$\alpha = (\ln \sigma - \ln \sigma_a) / (\ln \sigma_c - \ln \sigma_a),$$

where σ_a and σ_c are the conductivities of completely amorphous and completely crystalline materials, respectively, and σ is the conductivity of the material with the crystalline fraction α . The calculations showed that transition between logical “0” and “1” states occurs at $\alpha=0.45$, which correlates with the data of work [30]. By using of this value of conversion possible storage times of PCM cells on the basis of investigated material were calculated as transition time between amorphous and crystalline states at room temperature. Data processing times of PCM cells were estimated at different temperatures above crystallization temperature. For calculations we used following equation [25]:

$$t = \frac{g(\alpha)}{A \cdot \exp(-E/RT)},$$

where $g(\alpha)$ is integral form of the found reaction model, A is the pre-exponential factor.

Calculated storage times (transition time at room temperature) and data processing times (transition times) for different temperatures in the range of 200-500 °C for PCM cells on the basis of GST225 are shown in Fig. 8.

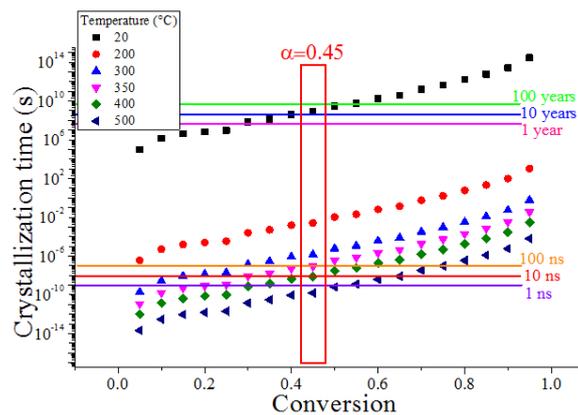


Fig. 8. Estimated crystallization times for investigated thin film

As can be seen, crystallization time sufficiently decreases with the temperature. At crystallization temperatures higher than 350 °C SET operation is predicted lower than ~50 ns, which is comparable with the data processing time of the random access memory.

At the temperatures higher than 400 °C extremely low values of crystallization time less than 10^{-9} s can be calculated, which is quite doubtful.

From the above mentioned, it follows that induction period plays important role in the crystallization process of GST materials. So, calculations of crystallization time must have lower limit, which is determined by the time comparable with the induction period, because in this period nucleation, but not crystalline growth plays dominating role and Arrhenius dependence fails. According to the existing information it is difficult to achieve crystallization rate of PCM material faster than 1 ns, which can be accepted as lower limit for calculations by the method.

On the other hand, crystallization time at room temperature, which determines probability of spontaneous crystallization and data storage time, exceeds 10 year. Such large range of crystallization rates between the low and high temperatures is determined by the high value of activation energy of crystallization.

5. Conclusions

Thus, in this study thermal properties, mechanism and kinetics of crystallization for GST225 thin films in non-isothermal conditions with using of differential scanning calorimetry were investigated.

The joint application of model-free Ozawa-Flynn-Wall and model-fitting Coates-Redfern methods allowed to estimate kinetic triplet for crystallization process of GST225 thin films, i.e. effective activation energies and pre-exponential factors as the functions of conversion, and establish crystallization model. Obtained kinetic triplet permits adequately describe non-isothermal crystallization of GST225 films, and predict data processing and storage times of the phase change memory cell on the basis of this material. It was found that $\text{Ge}_2\text{Sb}_2\text{Te}_5$ can provide the data processing time of the PCM cell lower than ~50 ns, which is comparable with that of the random access memory. Meanwhile, storage time at room temperature exceeds 10 years.

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