

Investigation of the crystallization kinetics in Ge-Sb-Te-Bi and Ge-Sb-Te-In phase-change memory materials

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In this work crystallization kinetics for thin films on the basis of Ge-Sb-Te-Bi and Ge-Sb-Te-In perspective for phase change memory application were investigated. Possible data processing and storage times of the PCM cell were estimated. Introduction of Bi and In influences the thermal properties and crystallization process of $\text{Ge}_2\text{Sb}_2\text{Te}_5$, and its kinetic parameters can be varied in wide range. It was shown that PCM cell based on $\text{Ge}_2\text{Sb}_2\text{Te}_5+0.5$ wt. % Bi can have minimum data processing and maximum data storage times in comparison with the other investigated materials.

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1. Introduction

Nowadays phase change memory (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, low manufacturing cost. Transition from the use of NOR flash memory to PCM in mobile phones will enable a reduction of 30% in energy consumption and 40% of occupied space [1].

Two main types of PCM memory devices exist now - optical and electrical phase-change memories. The work of both types of devices is based on rapid reversible amorphous-to-crystalline phase transitions, which can be initiated by laser or electrical pulses, respectively. These phase transformations are accompanied by the abrupt changes in optical and electrical properties, which allows to distinguish “zero” and “unit” logical states.

During the last years thin films of chalcogenide semiconductors were intensively studied due to their possible application in PCM devices. At present the most widely investigated and used PCM materials have compositions along the $\text{GeTe-Sb}_2\text{Te}_3$ quasi-binary line due to the rapid crystallization [2]. Three intermetallic 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 of them is $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST225), which exhibits appreciable stability at room temperature, high crystallization rate and good reversibility between amorphous and crystalline phases.

Noticeable progress was achieved last years in the development of phase change memory. However, despite of successful commercial application of optical PCM as optical recording discs with different formats (CD-RW,

DVD-RW, DVD-RAM, and Blu-ray) electrical PCM technology does not become widespread, and is needed to be improved. One of the problems is connected with the need of decreasing the data processing time of PCM to the level comparable with that of the random access memory (~10–50 ns). For this purpose increasing of crystallization rate and effective methods for controlling thermal properties of PCM materials are required. Bi and In are considered to be promising dopants for the modification of properties including thermal characteristics of $\text{Ge}_2\text{Sb}_2\text{Te}_5$. The choice of the dopants is explained by their isomorphism with the main components. In addition it was assumed that the isovalent elements with covalent atomic radius close to that of the elements in GST will give the least strain in the matrix structure of the material. However, crystallization kinetics of doped $\text{Ge}_2\text{Sb}_2\text{Te}_5$ is needed to be elucidated.

So, the aim of the work was investigation of the crystallization kinetics in Ge-Sb-Te-Bi and Ge-Sb-Te-In thin films.

2. Experimental

The GST225 alloys with different amounts of Bi (from 0 to 5 wt. %) and In (from 0 to 3 wt. %) were prepared by the quenching technique [3]. The materials (99.99 % purity) were sealed in evacuated ($5 \cdot 10^{-3}$ Pa) quartz ampoules and synthesized at the temperature of 800°C in a rocking furnace to ensure the melt was homogeneous. Thin films were prepared by thermal evaporation of the synthesized materials in vacuum.

Substrate temperature during the deposition did not exceed 50°C.

Structure of the synthesized materials was examined by X-ray diffraction (Rigaku D/MAX, Cu Ka $k = 0.15481$ nm), while elemental analysis of the thin films was studied by Rutherford backscattering (RBS, $E_d=1.0$ and $E_a=2.7$ MeV at 135° scattering angle) and Energy Dispersive X-Ray Analysis (EDXRA, Inka-Sight). Morphology of the films was investigated by AFM (NT-MDT SolverPro) and SEM (Carl Zeiss NVision 40).

Differential scanning calorimetry (DSC-50, Shimadzu) was used for the investigation of thermal properties. Measurements were carried out at 8 different heating rates (from 1 to 90°C/min).

3. Results and discussion

3.1 Compositions and structure

According to X-ray diffraction synthesized materials were polycrystalline and has a trigonal phase of $\text{Ge}_2\text{Sb}_2\text{Te}_5$. Introduction of Bi leads to the appearance of trigonal modification of $\text{Bi}_2\text{Ge}_2\text{Te}_5$ [4], which indicates on the replacement of Sb by Bi. As-deposited thin films were amorphous up to 3 % of dopants. Higher concentrations of Bi led to the appearance of crystalline phases.

RBS and EDXRA showed that the compositions of films were close to those of synthesized materials (Tables 1 and 2).

Table 1. Results of elemental analysis by RBS for GST225+Bi thin films

Initial compounds (bulk polycrystalline)	Thin film compositions, at. un., accuracy $\pm 5\%$				Bi content for thin film (calculation), wt. %
	Ge	Sb+Te	Bi	Oxygen	
GST 225	2	7			
GST225+0.5 wt.% Bi	2	6.80 \pm 0.20	0.024 \pm 0.010	<(0.12 \pm 0.04)	0.48
GST225+1 wt.% Bi	2	6.86 \pm 0.20	0.053 \pm 0.010	<(0.20 \pm 0.06)	1.07
GST225+3 wt.% Bi	2	6.90 \pm 0.20	0.14 \pm 0.010	<(0.10 \pm 0.04)	2.75

Table 2. Results of elemental analysis by EDXRA for GST225+In thin films

Initial compounds (bulk polycrystalline)	Thin film compositions, at. un.				In content for thin film (calculation), wt. %
	Ge	Sb	Te	In	
GST225+0.5 wt. %In	0.224	0.222	0.547	0.00463	0.45
GST225+1 wt. %In	0.197	0.263	0.527	0.00866	0.96
GST225+3 wt. %In	0.191	0.268	0.505	0.0353	3.80

3.2 Thermal properties

Differential scanning calorimetry of the as-deposited amorphous films revealed a number of heat effects with crystallization peak for all compositions laying in the temperature range of 135-220°C (Fig. 1, 2).

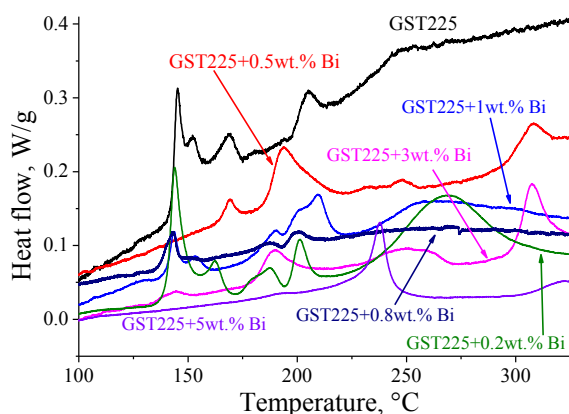


Fig. 1. DSC scans of as-deposited GST225+Bi thin films for heating rate of 10 °C/min

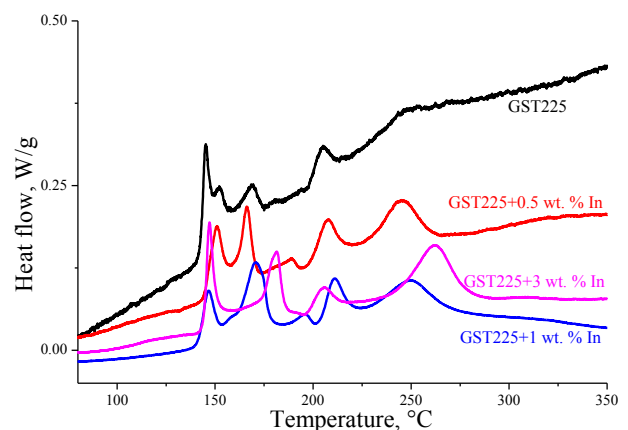


Fig. 2. DSC scans of as-deposited GST225+In thin films for heating rate of 10 °C/min

Crystallization temperatures for all investigated materials were estimated as onset temperature of the crystallization exothermic peak, and are presented in the Table 3.

Table 3. Crystallization temperature for GST225+Bi and GST225+In thin films.

Parameter	Composition									
	GST225	Bi content wt. %						In content wt. %		
		0.2	0.5	0.8	1	3	5	0.5	1	3
Crystallization temperature, °C	139.4	140.2	161.8	153.5	138.7	173.8	222.8	142.0	138.5	170.7

Differential scanning calorimetry showed that introduction of dopants affect crystallization temperature with greater influence of Bi. Crystallization temperatures increases with dopant concentration higher than 1wt. %. At lower concentrations dependencies are not monotonous with the largest deviation for GST225+0.5 wt. % Bi.

3.3 Crystallization kinetics

Knowledge of the crystallization kinetics of PCM materials allows predicting behavior of the materials at different temperatures, which is quite necessary for the optimization of PCM technology, increasing of

crystallization rate, and so data processing time of PCM cell.

Kinetic parameters of crystallization processes were determined by combination of isoconversional model-free Ozawa-Flynn-Wall method (OFW) [5], and Coates-Redfern model-fitting method [5]. Methodic was proposed in our work [6]. Such joint use of model-free and model-fitting methods allowed us to determine kinetic triplet (effective activation energy of crystallization, pre-exponential factor, crystallization model) for crystallization process of GST thin films. Results of kinetic triplet determination are presented in Table 4.

Table 4. Crystallization kinetics parameters

Composition	E_a , eV			$\ln A$, [s ⁻¹]			Model
	$\alpha=0.05$	$\alpha=0.95$	Average values of α	$\alpha=0.05$	$\alpha=0.95$	Average values of α	
GST 225	2.08	1.42	1.75	55.50	41.89	48.61	Second order
GST225+0.2 wt.% Bi	2.27	1.78	2.11	61.90	54.66	58.28	Third order
GST225+0.5 wt.% Bi	3.92	2.90	3.67	102.59	82.02	98.41	Second order
GST225+0.8 wt.% Bi	1.10	1.13	1.18	26.60	33.14	29.08	Second order
GST225+1 wt.% Bi	2.04	1.67	1.90	54.47	49.36	53.09	Second order
GST225+3 wt.% Bi	1.92	1.14	1.56	46.19	29.75	38.71	Third order
GST225+5 wt.% Bi	1.85	1.88	1.86	42.03	27.68	34.86	Second order
GST225+7.7 wt.% Bi	-						
GST225+0.5 wt.% In	1.93	1.64	1.87	50.73	33.43	42.78	Second order
GST225+1 wt. %In	1.63	1.21	1.52	51.14	33.85	43.21	Second order
GST225+3 wt. %In	1.76	1.58	1.80	46.13	45.89	49.72	Third order

According to the obtained results activation energy for the investigated materials decreases with the increase of conversion. It was discovered that the crystallization processes in investigated materials are most likely described by second and third-order reaction models, which are characteristic for spontaneous nucleation with further growth without overlapping [7].

Determined kinetic triplets were used to predict the possible transition and storage times of the PCM cells on

the basis of investigated materials. We supposed that logical “zero” and “unit” states in the PCM cell differs by the values of conductivity not less, than by 1-2 orders of magnitude. This allowed us to estimate conversion at which transition between “0” and “1” logical states of the PCM cell occurs. For this purpose we used following equation [8]

$$\alpha = (\ln \sigma - \ln \sigma_a) / (\ln \sigma_c - \ln \sigma_a), \quad (1)$$

where σ_a is the conductivity of a completely amorphous material, σ_c is the conductivity of a completely crystalline material, and σ is the conductivity of the material with the crystalline fraction α .

The calculations showed that the transition between “0” and “1” occurs at $\alpha=0.45$. By using this value of conversion we estimated possible storage times of PCM cells on the basis of investigated materials as crystallization time at room temperature. Data processing times of PCM cells were estimated at different temperatures above crystallization temperature. For calculations we used following equation [7]:

$$t = g(\alpha) / [A \exp (E_a / (RT))], \quad (2)$$

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

Calculated dependencies of crystallization times for $\alpha=0.45$ on crystallization temperatures for all investigated materials are shown in Fig. 3 and 4.

As can be seen from the figures, crystallization time significantly decreases with the temperature. Sufficiently higher temperature dependence is observed for GST with 0.5 wt. % of Bi. This result can be explained by the highest value of activation energy of crystallization for this material, which provides greater sensitivity of crystallization rate to the temperature, and large range of crystallization rates between the low and high temperatures. On the one hand, GST225 + 0.5 wt. % Bi has the largest crystallization time at room temperature, which indicates on the largest storage time of the PCM cell. On the other hand, crystallization time for this composition become smallest at the temperatures higher than 180°C.

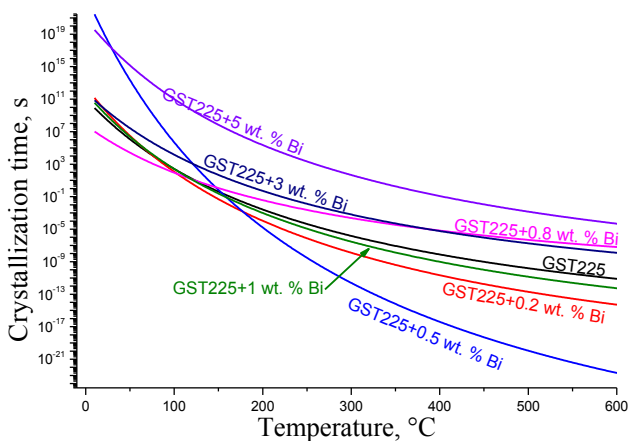


Fig. 3. Estimation of crystallization time for GST225 with different Bi content

At the crystallization temperatures higher than 300 °C SET operation of PCM cell (determined by the transition from high resistive amorphous to low resistive crystalline

phases, logical “zero” and “unit” states, respectively) on the basis of $\text{Ge}_2\text{Sb}_2\text{Te}_5+0.5$ wt. % Bi is predicted to be lower than ~50 ns, which is comparable with the data processing time of the random access memory.

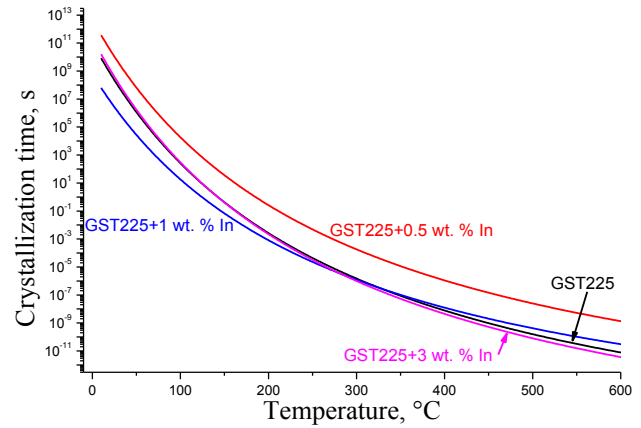


Fig. 4. Estimation of crystallization time for GST225 with different In content

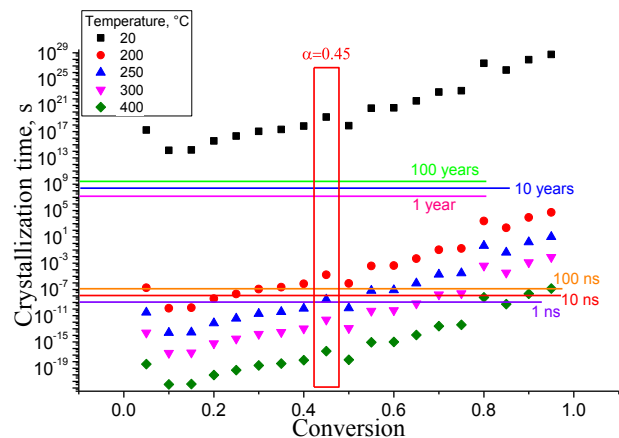


Fig. 5. Dependencies of crystallization times on conversion for GST225 + 0.5 wt. Bi

So, it was found that PCM cells on the basis of $\text{Ge}_2\text{Sb}_2\text{Te}_5+0.5$ wt. % Bi can have the best recording and storage times in comparison with the rest compositions.

4. Conclusions

Thus, in this work crystallization kinetics of thin films on the basis of GST225 doped by Bi and In was investigated. It was shown that introduction of Bi and In influences the thermal properties and crystallization process in materials, and their kinetic parameters can be varied in wide range. The possible transition and storage times of the phase-change memory cells on the basis of investigated materials were evaluated. It was shown that GST225 +0.5 wt. % Bi thin films have the most promising kinetic characteristics among the investigated materials.

Acknowledgements

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