Influence of indium doping on the electrical properties of $Ge_2Sb_2Te_5$ thin films for nonvolatile phase change memory devices

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Abstract. In this article the influence of different amounts of In (0, 0.5, 1 and 3 wt. %) on the thermal and electrical properties of $Ge_2Sb_2Te_5$ thin films for nonvolatile phase change memory devices is investigated. Crystallization temperature, resistivity, width of the optical band gap, Urbach energy, activation energy and type of conductivity are estimated for all investigated compounds. Storage and data processing times of the PCM cells on the basis of investigated materials were calculated. Nonmonotonic concentration dependences of properties were observed.

1. Introduction

Memory devices based on the flash technology are the most widespread today. However, flash technology has a number of drawbacks [1]. In this regard, development of new types of memory is quite essential. Promising memory types at this moment are magneto-resistive (MRAM), ferroelectric (FRAM), resistive (RRAM) and phase change (PCM) memories [1–3].

In this paper we investigated the materials for phase change memory application. Principle of operation of the PCM is based on the rapid reversible phase transformation between amorphous and crystalline states, which takes place in PCM materials under low-energy external influences. The material of $Ge_2Sb_2Te_5$ (GST225) is considered to be the most promising for use in PCM devices. It should be noted that some applications (for example in cosmic units) impose specific requirements on the properties of PCM materials. So, we must be able to control the properties of PCM materials. However, maintaining control of the properties is a tough problem due to the insensitivity of most chalcogenide glassy semiconductors to the doping because of Fermi level pinning.

One of the possible effective ways for the modification of the properties of materials is using substitutional doping [4,5]. Indium is in the same period of the Periodic table as antimony and has a close atomic radius (0.159 nm for Sb and 0.166 nm for In). By replacing antimony atoms with indium, the binding energy decreases from 277 kJ/mol for the Sb–Te bond to 218 kJ/mol for that of In–Te [6]. In this case, it is a good reason to believe that indium can substitute antimony. It was shown [7] that incorporation of indium into GST225 shifts peaks of Raman spectra to lower frequencies that can be caused by the incorporation of indium atoms into both germanium telluride and antimony telluride

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sublattices. Indium is also a good choice because recently it was reported that the introduction of indium into GST225 increased an optical contrast and changed the crystallization speed [8].

However, the influence of indium doping on the electrical properties of GST225 is not well understood. Thus, in this study we investigated the influence of indium doping on the electrical properties of $Ge_2Sb_2Te_5$ thin films, which are critical for the operation of PCM devices.

2. Experimental setup and samples

The initial $Ge_2Sb_2Te_5$ alloys doped with different amounts of In [0 wt. % (alloy #1), 0.5 wt. % (alloy #2), 1 wt. % (alloy #3) and 3 wt. % (alloy #4)] were synthesized with using of quenching technique [9]. The materials (99.99% purity) were sealed in evacuated ($5 \cdot 10^{-3}$ Pa) quartz ampoules then step by step heated to 800 °C in a rocking furnace to ensure homogeneous melt. The melt was quenched to the air.

Thin films were prepared by thermal evaporation of the synthesized GST225 in vacuum. Residual pressure in the chamber was 10^{-3} Pa. The substrate temperature during evaporation did not exceed 50°C.

The films thicknesses were determined by atomic force microscopy (AFM, NT-MDT SolverPro). The structure of obtained thin films was determined by X-Ray diffraction (XRD, Rigaku D/MAX). According to XRD, as-deposited films have the amorphous structures.

X-Ray Microanalysis (CAMEBAX) was used to determine thin films compositions. Results of composition analysis are presented in table 1. Analysis revealed agreement between compositions of the initial bulk alloys and respective deposited thin films.

Table 1. Results of composition analysis of deposited thin films

Initial bulk alloy	Thin film composition according to X-Ray microanalysis (at. un.), accuracy ±5%				Indium content in thin films (wt.%, calculation)
	Ge	Sb	Te	In	
# 2	0.2236	0.2234	0.5483	0.0046	0.45
# 3	0.1984	0.2649	0.5280	0.0087	0.96
# 4	0.1910	0.2673	0.5064	0.0353	3.80

The planar structures containing Al electrodes with a fixed interelectrode distance and the investigated thin films deposited upon them were fabricated on oxidized c-Si substrates to study their electrical properties. Interelectrode distances were formed by the photolithography method and were equal to 7 mcm. Planar structures were mounted in the glass-to-metal package.

Measurements of current-voltage characteristics (I-V characteristics or CVC) were carried out in the isothermal regime at the temperature range from room temperature to 70 °C with a step of 10 °C and voltage range from 0.1 to 10 V with a step of 0.1 V. Temperature dependences of resistivity of planar samples were measured in the heat-up regime in the temperature range from room temperature to 300 °C with a step of 0.1 °C and a heating rate of 1 °C.

The set-up on the basis of a multimeter HP 34401A-01 and a power supply Agilent E3674 was used for the investigation of thermopower and determination of the type of conductivity for the investigated films. The samples containing Al electrodes and the investigated thin films deposited upon them were fabricated on pyroceramics substrates. The distances between electrodes were 5 mm, and temperature gradient was 5 °C.

Differential scanning calorimetry (DSC-50, Shimadzu) at 8 different heating rates from 1 to 90 deg/min in a nitrogen flow (20 ml/min) was used to examine the thermal properties, activation energies and times of crystallization of investigated materials. Thin films were scraped off from c-Si wafers and pressed into Al pans. The samples had masses of few milligrams. Empty Al pans were used as references.

3. Experimental results

Ohmic regions at low electric field strength ($E \leq 10^3$ V/cm) were observed for all investigated compounds by I-V measurements. This was a reason why the value of electrical strength of 10^3 V/cm was chosen for measurements of temperature dependences of resistivity (figure 1).

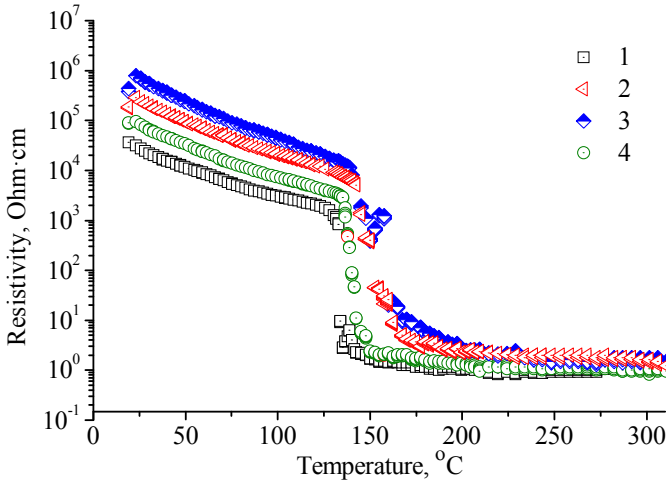

Figure 1. Temperature dependencies of resistivity for the thin films of GST225 with different contents of In: 1 – 0 wt. % In; 2 – 0.5 wt. % In; 3 – 1 wt. % In; 4 – 3 wt. % In.

Exponential temperature dependences in the range from room temperature to 120 °C were observed for all compounds. The temperature dependence of the conductivity of amorphous semiconductor typically shows an exponential behavior [10]. This allows to get the information on the activation energy of conductivity:

$$\sigma = \sigma_0 \, exp\left(-\frac{E_a}{kT}\right), \tag{1}$$

where σ is the conductivity, σ_0 is a constant, E_a is the activation energy of conductivity, k is the Boltzmann constant, and T is the absolute temperature.

Results of the activation energies calculations are presented in table 2. A width of optical band gap (E_g) and Urbach energy (E_0) were estimated by means of spectrophotometry and ellipsometry and are also shown in the table.

Table 2. Energy parameters for GST225 + In thin films

In, wt. %	E_g, eV	E_0, eV	E_a, eV
0	0.61	0.13	0.29
0.5	0.67	0.17	0.29
1	0.62	0.18	0.32
3	0.64	0.15	0.30

Results of thermopower measurements showed that holes are the majority carriers in the investigated thin films. According to the dual-channel model proposed by P. Nagels [11], p-type conductivity in chalcogenide glassy semiconductors is formed by the charge carrier transport via the delocalized states of the valence band, and localized states of the valence band tail. As the values of E_a

of the investigated thin films are close to the half of the optical band gap width, the main contribution in the conductivity is introduced by the transport of charge carriers via the delocalized states. It should be noted that the incorporation of indium into $Ge_2Sb_2Te_5$ leads to the increase of Urbach tails, which pointed out to the growth of the structure disorder.

Sharp drops in resistivity for all investigated materials were observed in the range from 120 to 170 °C. Taking into account literature data [12] and our results obtained from DSC (see figure 2) and XRD measurements, this sharp drops can be attributed to the phase transitions from amorphous to metastable fcc (NaCl type) crystalline state.

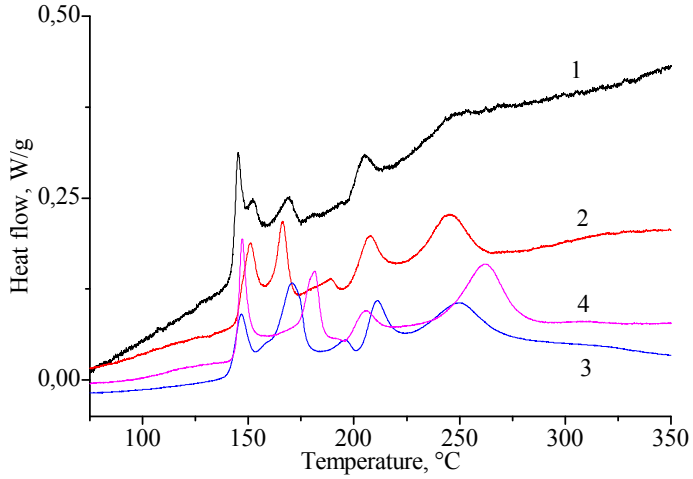

Figure 2. DSC scans of as-deposited GST225 thin films with different contents of In: 1 – 0 wt. % In; 2 – 0.5 wt. % In; 3 – 1 wt. % In; 4 – 3 wt. % In.

The onset crystallization temperatures determined from temperature dependencies of resistivity (T_{on} is the temperature of the beginning of sharp drop) for compounds with different In content (table 3) adequately correlate with those found by DSC. Discrepancies can be attributed to the difference in the heating rates, which were lower in the case of resistivity measurements.

Table 3. Energy parameters for GST225 + In thin films

In, wt. %	ρ vs T				DSC
	T_{on}, °C	ρ_{25}, Ohm·cm	ρ_{200}, Ohm·cm	ρ_{25}/ρ_{200}	T_{on}, °C
0	132	$1.6 \cdot 10^4$	1.6	$1 \cdot 10^4$	141
0.5	136	$4.8 \cdot 10^4$	1.9	$2.5 \cdot 10^4$	145
1	143	$2 \cdot 10^5$	1.7	$1.2 \cdot 10^5$	150
3	140	$6 \cdot 10^4$	2.9	$2.1 \cdot 10^4$	152

Incorporation of In leads to the increase of resistivity of amorphous films and of the difference in the resistivity values for amorphous and crystalline states (see table 3), which is important for the reliable work of PCM cells. Except for the thin film of alloy #4, the contrasts of resistivities are not very different from the undoped GST225. The symbols ρ_{25} and ρ_{200} in table 3 represent resistivities of the amorphous films at 25 °C and crystalline films at 200 °C, respectively.

Understanding the kinetics of phase transition allows predicting the behavior of materials under certain temperature conditions, which is important for the development and optimization of

technology. In particular, the kinetics of crystallization determines the performance and stability of the phase change memory cell. Parameters determining crystallization kinetics of the investigated films, the so called kinetic triplet (effective activation energy E_{ac}, pre-exponential factor A, and reaction model) were estimated by using the previously proposed procedure [13] and are presented in table 4.

Table 4. Determined kinetic parameters of crystallization process for GST225 + In thin films

In, wt. %	E_{ac}, eV			ln$A$, c^{-1}			Model
	α=0.05	α=0.95	Average values	α=0.05	α=0.95	Average values	
0	2.08	1.42	1.75	55.50	41.89	48.61	2nd and 3rd order reaction models
0.5	1.93	1.64	1.87	50.73	33.43	42.78	
1	1.63	1.21	1.52	51.14	33.85	43.21	
3	1.76	1.58	1.80	46.13	45.89	49.72	

Determined kinetic triplets were used to predict the possible storage and data processing times of PCM cells on the basis of the investigated materials with crystallization at room temperature and at 400 °C, respectively. We used the procedure proposed in the work [13]. The calculated data on processing and storage times for PCM cells on the basis of investigated materials are presented in figure 3. As can be seen, the compositions with 0.5 and 3 wt. % In allow to increase sufficiently a storage time in comparison with the undoped material (figure 3). On the other hand, crystallization time at 400 °C decreases nearly by an order of magnitude for the thin film of alloy #3 in comparison with that of the undoped GST225.

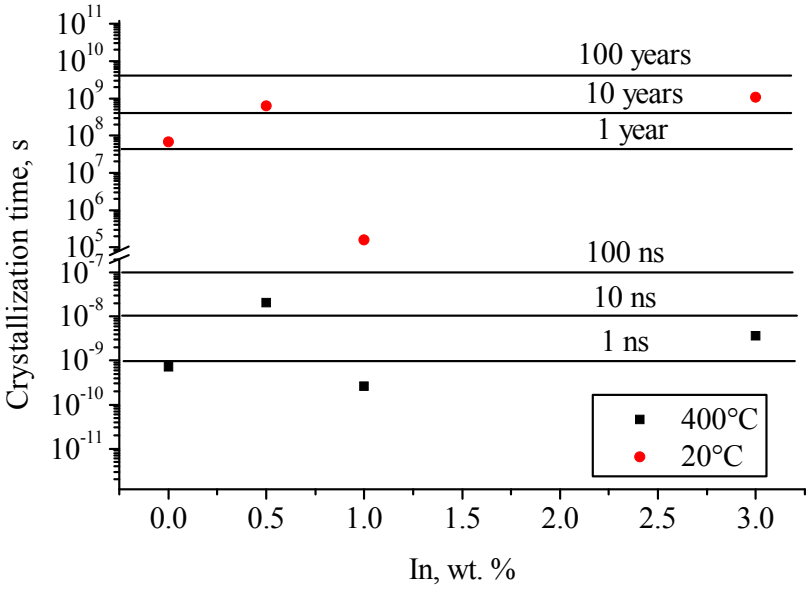

Figure 3. The dependencies of crystallization time on concentration of In in GST225 thin films. Calculations were carried out for two temperatures (20 and 400 °C).

It should be noted, that deviations from monotonous concentration dependences for thermal and electrical parameters were observed consisting in the appearance of extremes on these dependences.

This effect can be explained by using the percolation theory according to which the formation of an infinite cluster is accompanied by critical phenomena [5].

4. Conclusion

The influence of In doping on the properties of $Ge_2Sb_2Te_5$ thin films was investigated. Introduction of low concentrations of In (upon 3 wt. %) in $Ge_2Sb_2Te_5$ thin films is accompanied by the changes of crystallization temperature, resistivity, optical band gap width, Urbach energy, the activation energy of conductivity, storage and data processing times. Introduction of In to $Ge_2Sb_2Te_5$ allows to control the properties of materials for the phase change memory application, which is important for the optimization of PCM technology.

Acknowledgments

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