Influence of Bi doping on electrical and optical properties of phase change material $Ge_2Sb_2Te_5$

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In this paper, we studied the electrical and optical properties of $Ge_2Sb_2Te_5$ thin films and the influence of Bi impurity on the key parameters of phase change cell operation – resistivity and optical constants (*n*, *k*). Bi was chosen as impurity due to its isomorphism with one of the main material component - Sb. The Bi doping led to the shift of phase transformation temperature to the lower one, which can be related to the modification of chemical bonding parameters. A decrease in activation energy of conductivity for amorphous thin films from 0.36 eV ($Ge_2Sb_2Te_5$) to 0.22 eV ($Bi_{0.14}Ge_2Sb_2Te_5$) was observed. A regular decrease of refractive index *(n)* and a general increase in the extinction coefficient *(k)* with the increasing of Bi concentration was observed.

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1. Introduction

Thin films of materials based on chalcogenide semiconductor Ge-Sb-Te (GST) system with a stoichiometry composition on the pseudo-binary line GeTe - Sb_2Te_3 are currently intensively studied due to their possible applications in devices of phase change memory (PCM), particularly in optical disks with different formats (CD-R, DVD-RW, Blu-Ray) and nonvolatile memory cells of PCRAM type [1-4]. The work of such devices is based on rapid reversible phase transformations between amorphous and crystalline state, which take place in nanovolume of material under low-energy external influences. These phase transformations are accompanied by abrupt changes in optical and electrical properties of the materials [5-6].

Doping and modification of the structural matrix by dopants are used as one of the effective methods of control to achieve changes in electrical and optical properties of amorphous semiconductor materials. However, it's well known that most chalcogenide glasses are insensitive to the doping due to high density of intrinsic defects pinning the Fermi level near the center of the band gap [7]. In this case, controlling the electrical and optical properties of the PCM material is a complex problem. Therefore, it is necessary to find alloying elements which have a positive influence on the properties of amorphous and crystalline phases, as well as on the parameters and performance of PCM devices in general.

The choice of the dopant was based on the assumption 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. One of such promising dopants is bismuth. It is known that Bi is one of the elements that can change the type of conductivity in glassy chalcogenide semiconductors (GCS) [8]. In addition, it was shown [9] that Bi doping in $Ge_2Sb_2Te_5$ (GST225) led to about 30% decrease in crystallization time comparing to that of the undoped one. However, the influence of Bi doping on the properties of GST225 thin films is not well investigated yet. Therefore, the aim of this work is to study the influence of Bi doping on electrical and optical properties of $Ge_2Sb_2Te_5$ thin films.

2. Experimental

The initial doped $Ge_2Sb_2Te_5$ alloys with different amounts of Bi (0.5, 1 and 3 wt.%) were prepared using quenching technique [10]. The materials (99.99% purity) were sealed in evacuated ($5\cdot10^{-3}$ Pa) quartz ampoules then step by step heated to 800^0C in a rocking furnace to ensure the melt was homogeneous. Thin films were prepared by thermal evaporation of the doped, synthesized GST225 in vacuum. Residual pressure in the chamber was 10^{-4} Pa. The maximum temperature during evaporation was kept under 630^0C.

The thicknesses of the films were determined using AFM (NT-MDT SolverPro) scan; they were in the range from 35 to 200 nm. The morphology of the films was studied by SEM (Carl Zeiss NVision 40).

Rutherford backscattering (RBS) method was used to study the composition of the thin films; the data are presented in Table 1. The results of RBS thin films studying showed that Bi had been successfully incorporated into the deposited layers, and the amount of bismuth in the thin films was calculated with accuracy about ± 10%.

Table 1. Results of RBS studying.

Original polycrystalline compound	$Ge_2Sb_2Te_5$	$Ge_2Sb_2Te_5$+0.5 wt.% Bi	$Ge_2Sb_2Te_5$+1.0 wt.% Bi	$Ge_2Sb_2Te_5$+3.0 wt.% Bi
Composition of thin films [at.%]	$Ge_2Sb_2Te_5$	$Bi_{0.024}Ge_2Sb_2Te_5$	$Bi_{0.053}Ge_2Sb_2Te_5$	$Bi_{0.14}Ge_2Sb_2Te_5$

The set-up on the basis of KEITHLEY 6486 and a voltage control unit NI6008 was used for the investigation of the temperature dependences of resistivity of thin films. Planar structures containing Al electrodes with fixed interelectrode distances (1, 5, 10 μm), and deposited upon them GST thin film were fabricated on oxidized c-Si substrates. The samples were heated from room temperature to 300^0C at the rate of 1^0C/min.

A spectroscopic ellipsometer (ELLIPSE-1881A) was used to measure the optical constants - extinction coefficient *(k)* and refractive index *(n)* in the 380 and 1050 nm range with wavelength steps of 10 nm at two different incident angles 60^0 and 70^0.

3. Results and discussions

3.1 Temperature dependence of resistivity

The temperature dependences of resistivity for $Ge_2Sb_2Te_5$ and Bi-doped $Ge_2Sb_2Te_5$ compositions are shown in Fig. 1.

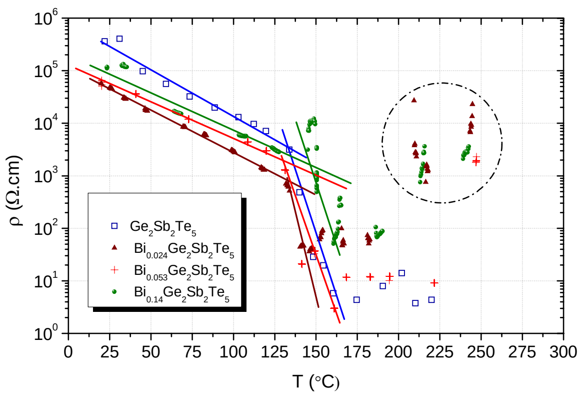


Fig. 1. (Color online) Temperature dependences of resistivity for $Ge_2Sb_2Te_5$ and Bi-doped $Ge_2Sb_2Te_5$ compositions.

Exponential temperature dependences in the range from room temperature to 120^0C for all compounds were observed. Sharp drops in resistivity for all investigated material were observed in the range from 120 to 170^0C, which corresponded to a phase transformation from amorphous to crystalline state. Further heating above the transformation temperature revealed increased resistivity values with unsystematic changes within the orders of magnitude for all measured samples.

Activation energies of conductivity were calculated for thin amorphous films of materials $Ge_2Sb_2Te_5$, $Bi_{0.024}Ge_2Sb_2Te_5$, $Bi_{0.053}Ge_2Sb_2Te_5$, and $Bi_{0.14}Ge_2Sb_2Te_5$ (Fig. 2). The Bi doping led to a decrease in the activation energy of amorphous thin films from 0.36 eV ($Ge_2Sb_2Te_5$) to 0.22 eV ($Bi_{0.14}Ge_2Sb_2Te_5$). It may be associated both with the decrease of the band gap width and the shift of the Fermi level toward the top of the valence band.

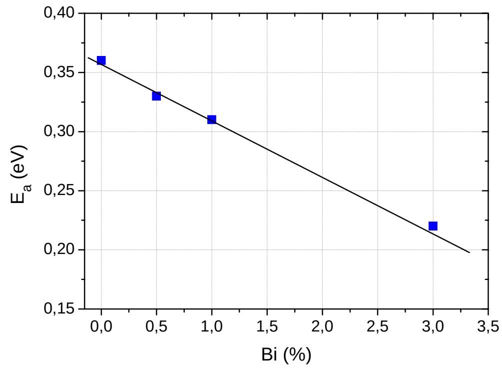
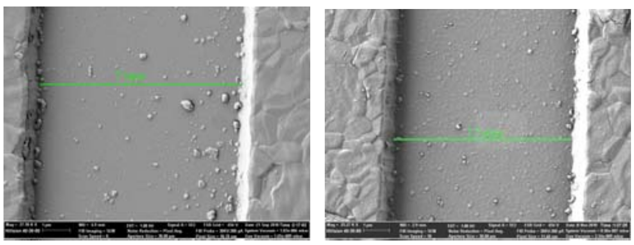


Fig. 2. (Color online) Dependence of activation energy of conductivity on Bi (wt.%) content

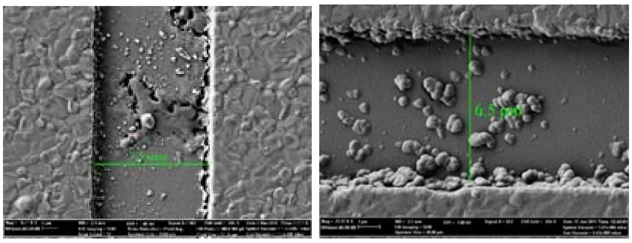
The unsystematic increases in resistivity of the samples beyond the transformation temperature from amorphous to crystalline state might be related to the changes in the structure and surface morphology of the thin films. Therefore, we studied the surface of measured samples before and after annealing by SEM. According to the SEM data (Fig. 3), we found that deposited Ge-Sb-Te and Ge-Sb-Te-Bi films before heat treatment had similar surface morphologies.



(a) *(b)*

Fig. 3. (Color online) SEM pictures of samples: (a) $Ge_2Sb_2Te_5$; (b) $Bi_{0.14}Ge_2Sb_2Te_5$

The study of sample surfaces after heat treatment up to a temperature of 350^0C by SEM (Fig. 4a) showed significant changes in the morphology of thin films. After heating, there was a large number of cracks on the surface of the films with a number of discontinuity areas, as well as the flaking of the film GCS away from the electrode contact boundary. In order to study the possibilities of reducing changes of the surface morphology with the accompanying unsystematic resistivity changes, a silicon dioxide thin film with 200 nm thickness was deposited using electron-beam evaporation on top of the GST film.



(a) (b)

Fig. 4. (Color online) SEM pictures of $Bi_{0.14}Ge_2Sb_2Te_5$ samples without (a) and with (b) a covering film after heating up to 350 ^0C

As we can see from Fig. 5, a pronounced step on the temperature resistivity of dependence, and significant reduction of unsystematic changes at high temperature were observed for GST225 sample with SiO_2 covering.

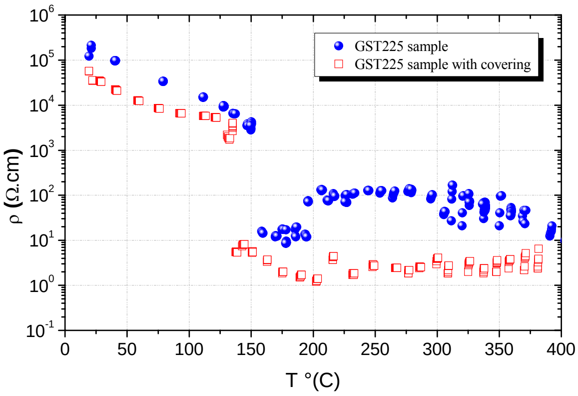


Fig. 5. (Color line) Temperature dependences of resistivity for $Ge_2Sb_2Te_5$ thin films

The transformation temperature from amorphous to crystalline state for GST225 sample with SiO_2 covering correlates with that of the thin film with the same composition but without the covering. In addition, SEM pictures showed no changes on the surface morphology of the samples with the covering after heat treatment up to a temperature of 350^{0}C compared to thin films without the covering (see Fig. 4b). Thus, the formation of structures with a covering prevents the formation of cracks and breaks in the film during heat treatment.

Based on the results, all following measurements of temperature dependence of resistivity of $Ge_2Sb_2Te_5$ thin films doped with different amounts of Bi (0.5, 3 wt.%) were carried out on structures with a SiO_2 covering on the surface. The main results are presented in Table 2, where T_x – on-set of transformation range, and T_y – ending of transformation range.

Table 2. Properties of GST thin films with SiO_2 covering.

Sample	Dopant, wt. %	Transformation range, ^oC		ρ_R, Ω·cm
		T_x	T_y	
$Ge_2Sb_2Te_5$	-	132	139.4	$5.7*10^4$
$Ge_2Sb_2Te_5$	0.5% Bi	126.3	138.6	$1.2*10^5$
$Ge_2Sb_2Te_5$	3% Bi	166	194.1	$1.1*10^6$

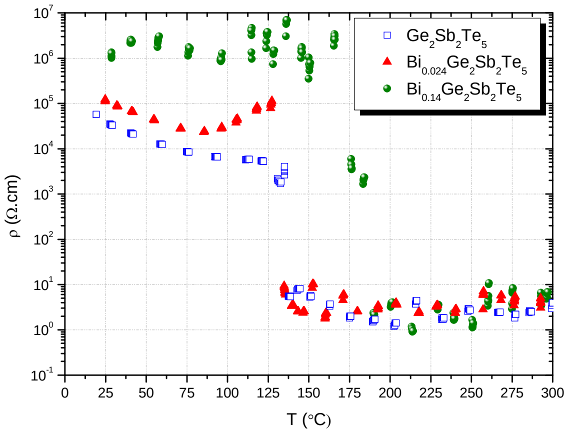


Fig. 6. (Color online) Temperature resistivity dependences of $Ge_2Sb_2Te_5$ doped by Bi with covering.

The obtained data (Fig. 1, 6, and Table 2) showed that the introduction of a small amount of bismuth into GST225 material (up to 1 wt.%) led to a deacrease in transformation temperature from amorphous to crystalline state compare to the undoped GST225, which is consistent with the data of [9, 11]. The decrease in transformation temperature can be associated with a decrease of the binding energy between atoms in the material with the introduction of the Bi dopant. According to reference data [12], the binding energy of Sb-Te is 277.4 kJ/mol, while the Bi-Te bonding - 232.3 kJ/mol. At the same time the adding of Bi with 3 wt.% in GST225 gives a significant increase in the on-set crystallization temperature.

3.2 Optical properties

The experimental spectra of the compounds are monotonic curves without oscillations. With the help of a theoretical modeling method, the spectral dependences of the refractive index *(n)* and extinction coefficient *(k)* were calculated for undoped thin films GST225 and films doped with different contents of Bi (0.5, 1 and 3 wt.%, respectively).

In our calculations, we used a two-layer model of the films. The first layer was a pure GST with thickness from 150 to 160 nm, and the second layer was a mixture of GST (95%) and voids (5%). Its thickness is from 4 to 6 nm. The use of the second layer in the film modeling allowed us to take into consideration the surface roughness of thin films. Results of the simulation correlated with the AFM data for the films.

According to the obtained spectra, the values of the refractive index *(n)* (see Fig. 7) for all compounds are in the range from 2.0 to 4.5, which are typical for amorphous chalcogenide thin films [13].

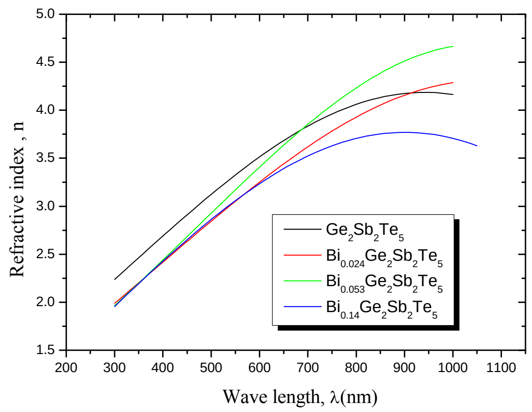


Fig. 7. (Color online) Spectra of refractive index (n).

With the increasing concentration of Bi, a regular decrease of reflection coefficient (*n)* was noticed, which was also observed earlier for the GST thin films doped with B [14]. Typically, in the wavelength range of 300-600 nm, when our thin films are nontransparent, the spectra of refractive index *(n)* are either the same or slightly different from each other. When *λ>600* nm, the difference for *(n)* becomes more noticeable, and we can assume that in the near-infrared region, it will increase more. The increase in refractive index in amorphous thin films gave us more interest to study their crystalline state in the future. It also showed a promising increase in optical contrast for such compounds, which will be necessary for materials used in optical disks.

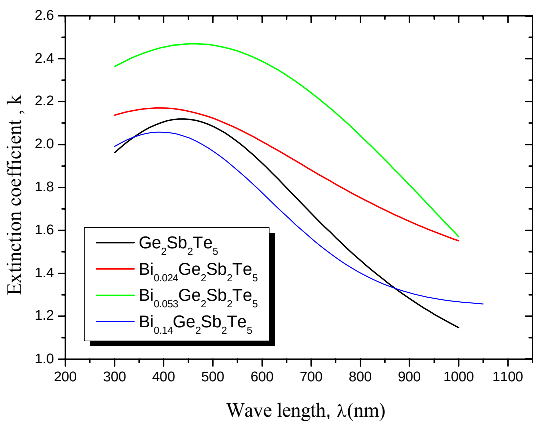


Fig. 8. (Color online) Spectra of extinction coefficient (k).

A general increase in the extinction coefficient *(k)* with the incorporation of Bi can be noted (Fig. 8), although its dependence on the concentration of Bi and can be hardly formulated.

To explain the observed dependencies, we should consider possible changes in the structure of $Ge_2Sb_2Te_5$, due to the changes in the parameters of the chemical bonds with the substitution of Sb for Bi. With the isomorphic substitution of Sb for Bi, an increase in the lattice parameters (short-range ordering) occurs because of the increased covalent radius of the atom (from 1.40 Å to 1.51 Å), in addition, we also had the decreasing energy of chemical Bi-Te bond in comparison with the Sb-Te one [12].

4. Conclusion

We obtained a deacrease in transformation temperature from amorphous to crystalline state for Bi-doped GST225 in comparison with the undoped one. A decrease of the activation energy of conductivity for amorphous thin films from 0.36 eV ($Ge_2Sb_2Te_5$) to 0.22 eV ($Bi_{0.14}Ge_2Sb_2Te_5$) was observed. The changes in the structure and surface morphology of the thin films caused the unsystematic increases in resistivity of the thin films after the transformation temperature from amorphous to crystalline state. This effect was eliminated with the help of a SiO_2 covering thin film. The behaviour of optical constants depends on the wavelength range. The increasing in refractive index of the thin films comparing to the updoped GST225 was noticeable starting after 600nm. The increasing in extinction coefficient was obtained with the incorporation of Bi in $Ge_2Sb_2Te_5$.

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