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Phase-change transition of chalcogenide system $Ge_8Sb_{2-x}Bi_xTe_{11}$ thin film using single femtosecond laser pulses

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The phase transformation amorphous to crystalline of thin films $Ge_8Sb_{2-x}Bi_xTe_{11}$ system (where x = 0; 1; 2) deposited by the Flash Thermal Evaporation (FE). Phase transformation were induced by ultra-fast (40 fs) femtosecond single laser pulse irradiation, and were compared in structure, optical properties and topography. The obtained results demonstrate, that single fs pulse laser irradiation appears to be effective in inducing crystallization of $Ge_8Sb_{2-x}Bi_xTe_{11}$ thin films and enabling the attainment of a higher speed data set/reset. The substitution of bismuth for antimony leads to a change in optical, electrical and thermal properties depending on the Bi concentration for the studied materials. The high optical contrast makes the studied $Ge_8Sb_{2-x}Bi_xTe_{11}$ samples promising for PRAM memories.

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Keywords: Phase transition, Thin films, Chalcogenide glass, Femtosecond laser, Crystallization

1. Introduction

From the time of computers invention and different computers devices to the our day, where is rapid growth of global networking, data storage capacity is an eternal problem. The perfect type of storage capacity is characterized by excellent all-round capabilities, such as long cycling life, nonvolatility, fast read/write processes, fast read/write processes, multilevel storage, 3D integration, low power consumption, and affordability of the final product. According to the above listed criteria one of the most promising technology of data storage is phase-change materials (PCMs) [1-3], which based on the reversible transformation between the amorphous and crystalline states of PCMs induced by local heating/cooling either by electrical or laser pulses.

The earliest research on the field of PCMs was published in 1968 by Ovshinsky [4], and considerable studies have been made on the topic of chalcogenides for data storage. The investigated of chalcogenide material system in PCM based memory technology were started at the beginning of 1970's, particularly the Ge-Sb-Te system, in the $Ge_2Sb_2Te_5$ (GST) [5, 6]

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composition was widely populer. However, despite commercial success of GST, further research must be carried out to improve PCM technology. For this need, the effective methods for controled of thermal, electrical, physical properties, and stability of PCM materials are required. However, maintaining control over the properties is a tough problem owing to the insensitivity of most chalcogenide glassy semiconductors to doping because of Fermi level pinning.

One of method for the control chalcogenide properties is to dope these materials with isomorphic elements, that was used in our work. For GST materials, Bi is an example of such an element, because it is in the same group as Sb, but have a larger atomic radius. By replacing Sb atoms with Bi was observed the binding energy will decrease from 277.4 kJ mol^{-1} for the Sb–Te bond to 232 kJ mol^{-1} for that of Bi–Te [7]. In addition,were conducted several experiment for the influence of Bi on PCM materials. Lee et al. [8] reported that the substitution of Sb by Bi in $Ge_4Sb_1Te_5$ can lower the crystallization temperature from 227 °C to 202 °C and crystallization energy from 4.03 eV to 2.70 eV, while Wang et al. [9] reported that for a $Ge_2Sb_2Te_5$ alloy doped with 3% Bi, two transition temperatures were observed in the temperature dependent sheet resistance measurements at 136 °C and 236 °C. Compared with pure $Ge_2Sb_2Te_5$, lower transition temperatures were demonstrated because of Bi doping [10]. In our previous work, we investigated the effect of the introduction of Bi on the thermal, electrical and optical properties of thin films of the system of chalcogenide rocks $Ge_8Sb_{2-x}Bi_xTe_{11}$, [11,12]. Due to the latest trends in the study of PCM recording using ultrashort laser pulses, in this paper we present our results of phase change transition in new chalcogenide materials of the $Ge_8Sb_{2-x}Bi_xTe_{11}$ system using individual femtosecond laser pulses.

2. Experimental conditions and methods

The $Ge_8Sb_{2-x}Bi_xTe_{11}$ (where x = 0, 1, 2) alloy were prepared by the melt-quenching technique from high-purity (5N) elements (Ge, Sb, Bi, Te). The bulk glass was synthesized by weighing out suitable proportions for the required composition and mixing them in an evacuated sealed silica ampoule (vacuum $1 \cdot 10^{-3}$ Pa). For the cleaning of ampoules were used aqua regia. Ampoules were placed into aqua regia (mixture of nitric acid HNO_3 and hydrochloric acid HCl, optimally in a molar ratio of 1 : 3) for 10 - 12 hours, and for thorough washing was used distilled water and isopropanol, then were heat treated (at ~127 °C) for twelve hours in order to remove adsorbed water and other contaminants.

The weighed elements were heated gradually in steps at a 1 °C min^{-1} heating rate to the 980 °C in a rocking furnace. The rocked motion ensures that a complete mixing of the materials takes place. To assure complete chemical reactions between the constituents, the furnace temperature program was adjusted at 980 °C for 24 hours. The melt was quenched in cold water. The thin films are prepared by deposition techniques: Flash Thermal Evaporation (FE).

The thin films of $Ge_8Sb_{2-x}Bi_xTe_{11}$ were fabricated by FE technique on commercial glass. The Si (100) was used as substrate for test samples. For the main experiment were prepared several samples of thin films of the Ge-Sb-Bi-Te system (limited in size and quantity) on the substrate of non-diffraction wafer. Before use the substrates were placed into aqua regia (mixture of nitric acid HNO_3 and hydrochloric acid HCl, optimally in a molar ratio of 1: 3) for 5 hours and for thorough washing was used distilled water. After this the substrates were thoroughly cleaned manual by soap-free detergent and then iteratively rinsing in distilled water and isopropanol to remove the traces of detergent.

The vacuum chamber before evaporation was pumped to a base pressure of $2 \cdot 10^{-4}$ Pa. Schematic view of the rapid evaporation unit is presented in Figure 1. The starting material was bulk crystalline $Ge_8Sb_{2-x}Bi_xTe_{11}$, which was crushed to a powder particle size of 50-150 µm, and then placed inside the dispenser. The distribution of $Ge_8Sb_{2-x}Bi_xTe_{11}$ particles from the dispenser to the molybdenum flash exchanger was performed using a screw dispenser (Figure 1). The number of $Ge_8Sb_{2-x}Bi_xTe_{11}$ particles entering the heat exchanger flash was the speed of rotation of the feeder, i.e. 1 rpm, evaporation rate ~ 0.3 nm · s^{-1}.

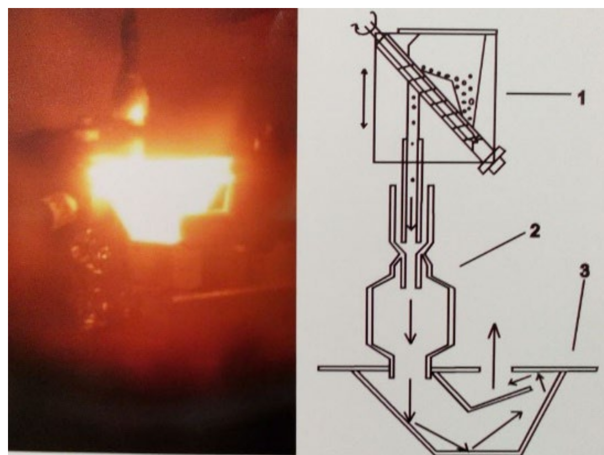

Fig. 1. Schematic representation of the Flash Thermal Evaporation (FE) experimental setup. 1) screw dispenser, 2) adapter, 3) molybdenum flash exchanger.

The evaporation process is controlled through the chamber window. The particle distribution of $Ge_8Sb_{2-x}Bi_xTe_{11}$ was started after heating the flash exchanger to a temperature of 980 °C, suitable for evaporation of $Ge_8Sb_{2-x}Bi_xTe_{11}$ powder. The distance between the flash and the substrate was about 25 cm. The film thickness (100 nm) was monitored using a quartz crystal microbalance (QCM). The $Ge_8Sb_{2-x}Bi_xTe_{11}$ films were deposited at a substrate temperature of 25 °C.

Ti-sapphire laser with a wavelength of 795 nm with a pulse duration of 40 fs, with a repetition rate of 10 Hz was used for the laser irradiation of thin film. The system had ability to manually control the modulator for allocate single pulse. The laser fluency energy was F □ 2.2 mJ · cm^{-2}. An electro-optical modulator was used to extract a single pulse. The laser beam was focused by a convex lens (1.4 diopter) on the surface of the deposited thin films. The experiment setup of the static femtosecond (fs) pulse laser irradiation is shown in Figure 2 .

Experimental determination of the average fluence is estimated as the laser energy divided by the spot size. The laser fluence was varied between 20 and 190 mJ · cm^{-2} for the fs pulse laser irradiation (S_0 - area of the output laser beam, L_0 - focal length of the convex lens, L_f - position of sample in lens focus, S_s - theoretically calculated sample irradiation area). It is summarized in Table 1.

Table 1. The laser fluence of different irradiated place.

Marks of irradiated place	L_f (mm)	L_0 (mm)	S_0 (mm^2)	S_s (cm^2)	F/S_s (mJ · cm^{-2})
1	160	650	19	0.0115	191.1
2	185			0.0154	142.9
3	210			0.0198	110.9
4	235			0.0248	88.5
5	260			0.0304	72.3
6	285			0.0365	60.2
7	310			0.0432	50.9
8	335			0.0505	43.6
9	360			0.0583	37.7
10	385			0.0667	33
11	410			0.0756	29.1
12	435			0.0851	25.8
13	460			0.0952	23.1
14	485			0.1058	20.8

The phase transition of $Ge_8Sb_{2-x}Bi_xTe_{11}$ (where x = 0, 1, 2) thin films from the amorphous phase into the crystalline phase was induced by single femtosecond pulses. During the laser irradiation the thin film with thickness 100 nm prepared by Flash Thermal Evaporation (FE) deposition process was placed in box (see Figure 2.) with inert atmosphere (Ar) to avoid the possible oxidation of the surface.

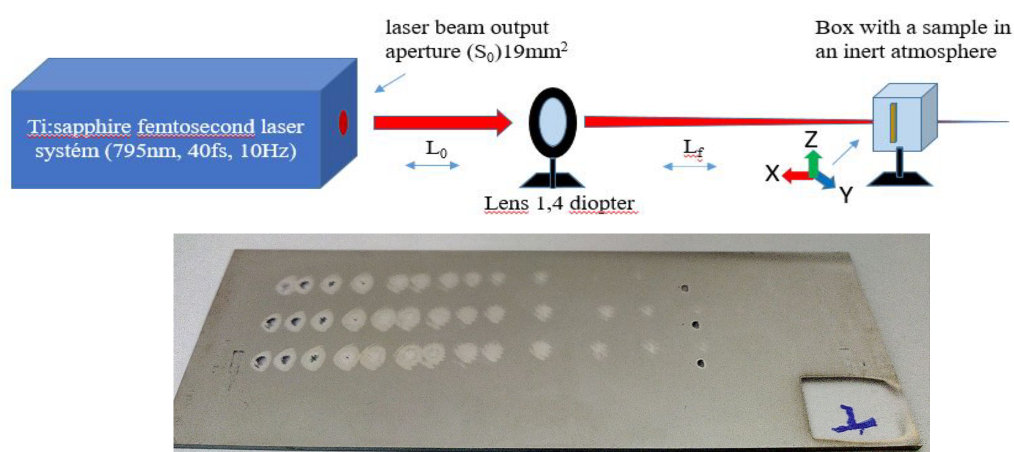

Fig. 2. The experiment setup and box with inert atmosphere to avoid the possible oxidation of the surface and $Ge_8Sb_{2-x}Bi_xTe_{11}$ thin film after laser irradiation.

3. Characterization methods

The bulk samples were analyzed by X-ray powder diffraction (XRPD) employing the Bruker D8-Advance diffractometer (Bruker AXS, Germany) using CuKα radiation with secondary graphite monochromator. The diffraction patterns were measured from 10° to 80° in 0.02° steps with a counting time of 10 s per step.

The samples of thin films were analyzed by X-raz powder micro-diffraction (μ-XRPD). Diffraction patterns were collected with a PANalytical X´Pert PRO diffractometer equipped with a conventional X-ray tube (CoKα radiation, 40 kV, 30 mA, point focus), an X-ray mono-capillary with a diameter of 0.1 mm, and a multichannel detector X'Celerator with an anti-scatter shield. A sample holder for single crystal XRD measurement was adopted by adding z-(vertical) axis adjustment (Huber 1005 goniometer head). The diffraction patterns were taken between 10 and 70° 2Θ with a step of 0.0334° and 1900 s counting time per step that produces total counting time of about 7 hours 45 minutes.

We used two different diffractometers with two different radiations (Cu and Co tubes), therefore all figures that display results of (μ-)XRPD analyses are presented in d values (interplanar distances).

Atomic Force Microscopy (AFM) is used to obtain the topography of the $Ge_8Sb_{2-x}Bi_xTe_{11}$ (where x = 0, 1, 2) films at the nanoscale (grain density and magnitude of the grain), as well as their local phase transformation behavior.

Contactless surface topography measurements using a scanning microscope for white light interferometry (New-View 7200; Zygo Corp.) were used to further verify the surface of the samples in areas irradiated with a femtosecond laser pulse. The microscope vertically scans the test area to generate a digital 3-D topographical map of the surface with a vertical resolution of up to 0.1 nm, a value well below the surface roughness. The sufaces were measured using a 5X interferometric objective with a lateral resolution of 140 μm by 105 μm. The field of view of CCD camera array of 640 by 480 pixels, yielding up to 306 710 data points per measurement with. The

scan length 10 micrometer bipolar (2 sec.), and extended scan length 2000 microns. The areal surface roughness, expressed as the arithmetic average Ra, was computed after correcting for geometry, typically a cylinder or a plane. The topography data were otherwise unfiltered.

Optical microscopes are the most commonly used type of surface analysis of test specimens. Reflectivity and surface were examined using an AXIO ZEISS optical microscope (ZEN).

Since ellipsometry is measuring the ratio of two complex values (rather than the absolute value as, for example, reflectance), it is very accurate (can achieve angstrom resolution) and reproducible. The ellipsometry data were recorded in the spectral region 400 - 1800 nm by variable angle spectroscopic ellipsometry (WASE®, J. A. Woollam Co., Inc.) for incidence angles of 50°, 60° and 70°. Nearly normal reflectivity (18°) were carried out by the same instrument. Microspot was employed to focuse light beam to 200 μm^2 area on the sample surface. Experimental data were treated by WASE32 software considering single layer model. Dielectric function of the GS(B)T films was parameterized by a sum of Lorentz oscillators [13].

4. Results and Discussion

The application of phase-change materials for data storage relies on the fast reversible transformation between the disordered amorphous and ordered crystalline states, which can be achieved by local heating - cooling at high rates, either with a laser beam or electrical pulses. It is known that the data transfer rate is limited by the duration of the laser pulses used, which is a few tens of nanoseconds (ns) for triggering phase transitions in state-of-the-art products. Currently, use of ultrashort laser pulses available only at laboratory level and for performing switching operations would allow surpassing current benchmarks by several orders of magnitude. In the nineties, first experiment was done for proof-of-concept of ultrafast reversible phase in GeSb films using picosecond (ps) and femtosecond (fs) pulses. Later, the reversible phase change in $Ge_2Sb_2Te_5$, which is the standard composition used in most phase change optical disks (PCODs), was demonstrated. In a related composition within the GeTe-Sb_2Te_3 pseudobinary system, $Ge_1Sb_4Te_7$, both amorphization and crystallization have been achieved using single sub-ps laser pulses. It is important to remark that the amorphization process is straightforward to trigger with ultra-short laser pulses in phase-change materials since it normally requires ultrafast melting and quenching, which is inherent to the use of ultra-short pulses. Recent studies provide evidence that there is an alternative pathway for amorphization without passing through the molten phase, in the form of a photo-assisted process generating sufficiently high carrier densities to trigger the phase transition. In contrast, crystallization is more difficult to achieve with ultra-short pulses, due to the existence of a minimum time required for stable crystalline nuclei to form and grow [14].

Based on the existing research trend we present our results of the phase transition study in thin films of relatively new chalcogenide materials with the $Ge_8Sb_{2-x}Bi_xTe_{11}$ system. In this work, the primary concern was to determine the optimal value of the laser fluence (in the range from 20 to 190 mJ · cm^{-2}) while observing the irradiated places upon single femtosecond laser pulse using an optical microscope .

Our previous experiments for the test samples showed, that the process of phase change from amorphous to crystalline phase by single femtosecond laser pulse begins at a fluency energy from 25 mJ · cm^{-2} to 70 mJ · cm^{-2} (From 25 mJ · cm^{-2} to 50 mJ · cm^{-2} was observed the partial phase change on the irradiation position. From 50 mJ · cm^{-2} to 70 mJ · cm^{-2} was observed the complete phase change with partial damage of surface in the irradiation position. At higher energy as 70 mJ · cm^{-2} was observed ablation of thin films.).

At a further increase of the fluence energy the evaporation (ablation) of the materials was observed. In our case, the optimal value of a single femtosecond laser pulse with a fluency energy of 50 mJ · cm^{-2} was determined. It was used in subsequent (the main experiment) experiments to change the phase in the thin films of the studied material deposited on a substrate of non-diffraction wafer.

4.1. Structure analysis

XRD measurements were used to investigate the phase transition of $Ge_8Sb_{2-x}Bi_xTe_{11}$ thin films (where x = 0, 1, 2) from the amorphous phase into the crystalline phase upon single femtosecond laser irradiation. For the investigation, as-deposited films with 100 nm thickness prepared by flash thermal evaporation (FE) were used. Figure 3. shows the XRD patterns of bulk samples, amorphous thin films prepared by FE, thin films after thermal treatment and as-deposited films after irradiation by a single pulse. The laser fluence was 50 mJ · cm^{-2} for a single fs pulse.

To compare the phase transition in different composition, part of the thin films was thermally annealed for 30 min in an inert argon atmosphere at a temperature above the crystallization temperature at 20 ° C of the amorphous phase T_c (determined by DSC). Also, in all samples the chemical composition were controlled by using EDX, where the difference between the measured and the theoretically calculated composition was a minimum of 1 - 3 at. %, that is within the limits of acceptable in terms of sensitivity methods.

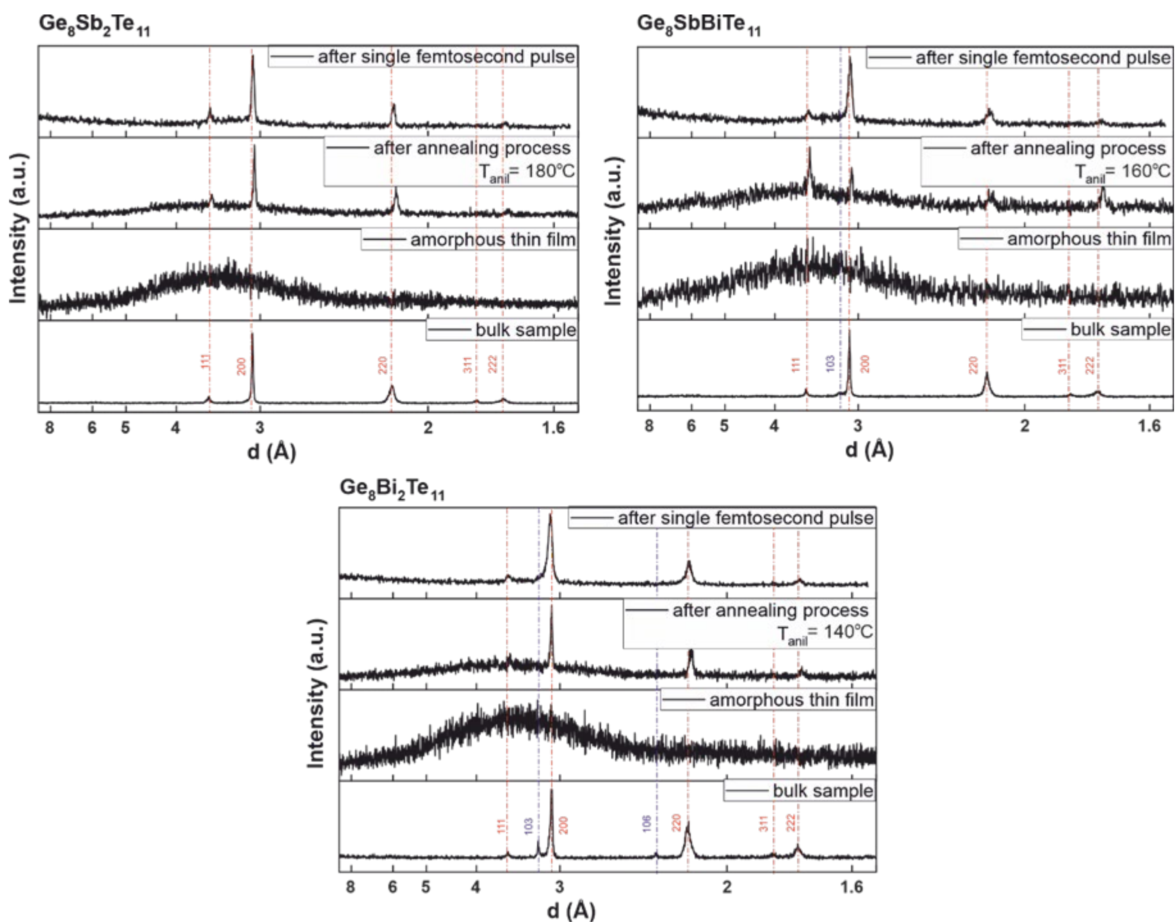

Fig. 3. XRD patterns of bulk samples, amorphous thin films prepared by FE, thin films after thermal treatment, as-deposited films after irradiation by single pulse [12].

Results of XRD showed that all bulk samples presented a cubic structure of Fm-3m, in the case of bulk samples of $Ge_8SbBiTe_{11}$ and $Ge_8Bi_2Te_{11}$, the rhombohedral phase R-3m and the hexagonal R-3m1 phase were observed as well. The amorphous state was confirmed in all freshly prepared thin films. The as-deposited thin films after thermal annealing and laser irradiation showed only a cubic structure for all cases.

A comparison of the XRD curves shows that thin films irradiated with a single femtosecond laser pulse with a fluence energy of 50 mJ · cm^{-2} are sufficient for the transition from

the amorphous to the crystalline phase in the volume of thin films with lattice parameters in Table 2.

Table 2. Latice parameters (a, c) for bulk samples of the $Ge_8Sb_{2-x}Bi_xTe_{11}$ system, after annealing thin film and for thin films after single femtosecond pulse [12].

Sample	Crystalline phases	Bulk			Annealling thin film / Induced thin film by single fs pulse
		Cubic	Hexagonal		Cubic
		a (Å)	a (Å)	c (Å)	a (Å)
$Ge_8Sb_2Te_{11}$	Cubic Fm-3m (225)	5.980	-	-	5.950 / 5.956
$Ge_8SbBiTe_{11}$	Cubic Fm-3m (225)	5.996	4.383	16.105	5.973 / 5.979
	Rhombo. H. axes R3m (166)				
$Ge_8Bi_2Te_{11}$	Cubic Fm-3m (225)	6.005	4.289	17.327	5.981 / 5.988
	Hexagonal P-3m1 (164)				

4.2. Optical properties of $Ge_8Sb_{2-x}Bi_xTe_{11}$ (where x = 0, 1, 2) thin films

As already mentioned, the irradiated thin films of chalcogenide glass of the $Ge_8Sb_{2-x}Bi_xTe_{11}$ system (where x = 0, 1, 2) were first examined with an optical microscope. The results of the research are shown in Figure 4 - 6., where we can clearly observe the optical reflectivity of thin films in the region of the amorphous to crystalline phase transition after a single (as well as two single) femtosecond pulse irradiation with a fluence energy of 50 mJ · cm^{-2}.

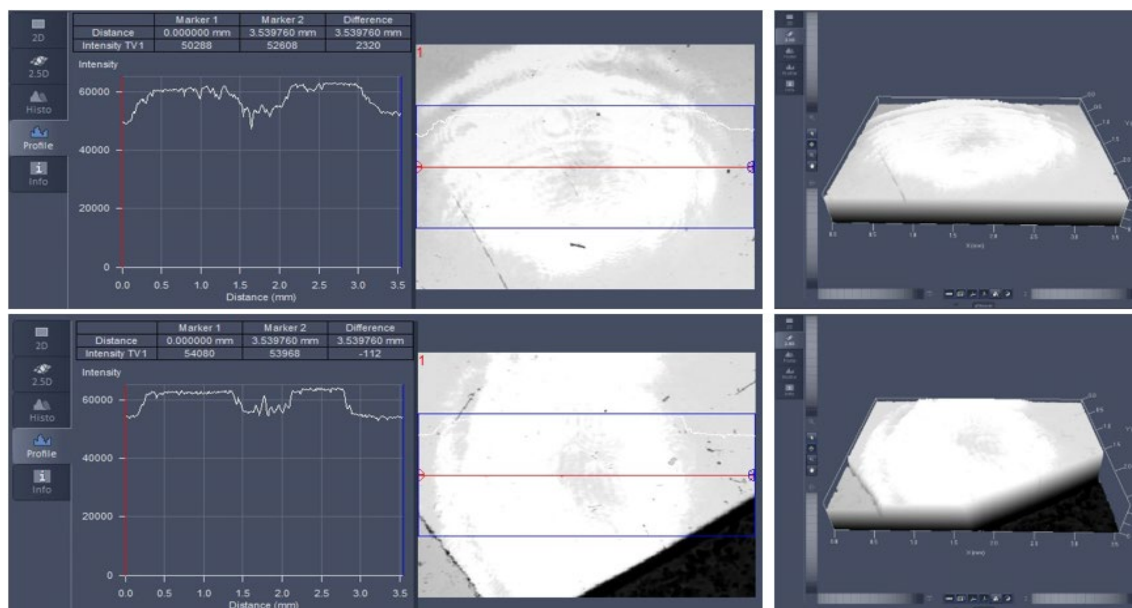

Fig. 4. Reflection analysis of $Ge_8Sb_2Te_{11}$ under optical microscope AXIO ZEISS after single (up) and two single (down) pulses.

As can be seen from the results of $Ge_8Sb_2Te_{11}$ thin films, single femtosecond pulse is enough for change the amorphous phase to crystalline. In the centers of the irradiated spot, there is a decrease in reflectivity, which corresponds to the parameters of the amorphous thin film, which indicates the reamorphized area of the material. This reamorphization effect is a consequence of the reflected part of the energy of the laser beam from the substrate of the material, namely at its maximum photon density (gaussian profil). The undesirable effects of light interference were also observed in the security box window, which as a result were copied into the irradiated spot. After two single femtosecond pulses, the crystalline phase of the irradiated position was expressed.

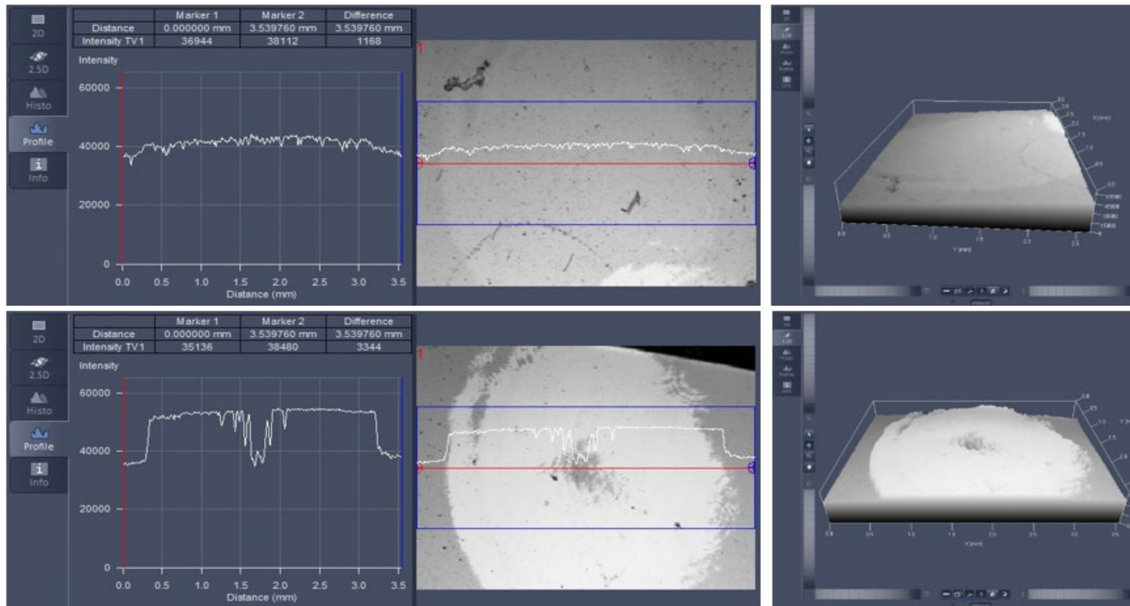

Fig. 5. Reflection analysis of $Ge_8SbBiTe_{11}$ under optical microscope AXIO ZEISS after single (up) and two single (down) pulses.

In contrast to $Ge_8Sb_2Te_{11}$ thin films, a small change in reflectivity was observed in the $Ge_8SbBiTe_{11}$ thin films in the position irradiated with a single femtosecond pulse, that is, a partially crystallized phase, which may indicate a lack of energy for complete crystallization. This is also due to the thermal properties that we proved in previous works [11,12] for chalcogenide materials with the $Ge_8Sb_{2-x}Bi_xTe_{11}$ system, where it was found that thin films of $Ge_8SbBiTe_{11}$ have a higher activation energy of crystallization compared to $Ge_8Sb_2Te_{11}$ and $Ge_8Bi_2Te_{11}$. It should also be noted that there is a process of laser operation, where there could be an uncontrolled process of reducing the laser energy by 15 % – 25 %. In the case of using two single femtosecond pulses was detected a clear change in the reflectivity in the irradiated position with a reamorphized part in the center of the spot.

In the thin films of the $Ge_8Bi_2Te_{11}$, after both the single and two single femtosecond pulses with an energy of 50 mJ $\cdot$ cm^{-2} the reflectivity of the crystalline phase was observed in the irradiation region, but at this case was not observed the reverse process of reamortization as in $Ge_8Sb_2Te_{11}$ and $Ge_8SbBiTe_{11}$. In previous works were investigated the thermal properties by DSC.

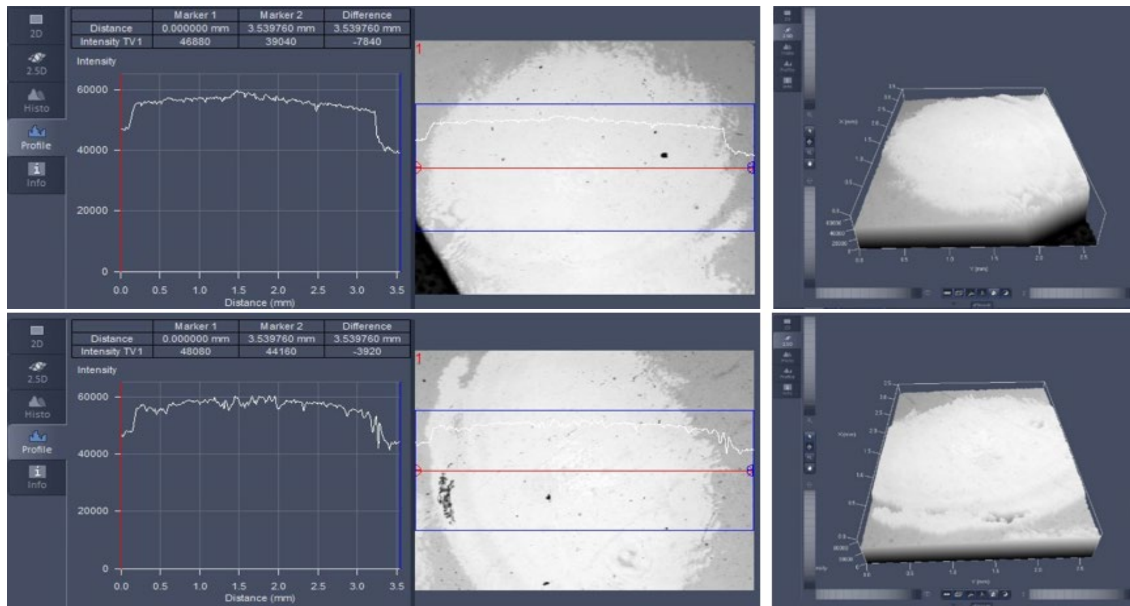

Fig. 6. Reflection analysis of $Ge_8Bi_2Te_{11}$ under optical microscope AXIO ZEISS after single (up) and two single (down) pulses.

The activation energy of the primary phase-change crystallization process decreases with the Bi content . This may again be related to the looser packing of the amorphous and crystalline phases based on Bi (due to the presence of larger Bi atoms), where the Ge atoms have lower steric restrictions when undergoing the order-disorder transition (the phase change is based on the umbrellaflip of Ge atoms from an octahedral position to a tetrahedral position without rupture of the strong covalent bond [11,12]).

The activation energy of crystallization had the lowest value in $Ge_8Bi_2Te_{11}$ thin films as other samples, which means that we need to provide slightly more energy to obtain the reverse reamorphization process.

4.3. Topography

As the optical record of data is based on reflectivity of material at the PCM reading of data, accordingly the topology of surface also plays the important role. For better understanding of the development of topography and roughness in the surface on thin films of the chalcogenide system $Ge_8Sb_{2-x}Bi_xTe_{11}$ (where x = 0, 1, 2) in positions irradiated with single and two single pulses with an energy of 50 mJ · cm^{-2} were conducted with the help of AFM to determine the density and size of the crystals in Table 3. Calculation was performed in Gwyddion software [15]. In our experiment, the area of the laser irradiated is quite large □ 2 mm^2 compared to similar types of experiment conducted by many other researchers. Therefore, for a broader representation of the surface and microroughness in the central and extreme positions of the spot irradiated by femtosecond laser pulse, the WLI method (white light interferometry) was used for additionally analysis with a larger study area of 105 ×140 µm, compared with AFM, where area is 5 × 5 µm. From WLI is seen that the topography and roughness of amorphous thin films before and after laser irradiation are not very different as we can see in Figures 7 - 8. Attempts were made to study the samples by SEM, but there was no clear boundary between the amorphous phase and the crystalline phase after a single femtosecond laser pulse. In addition, when the composition was checked using EDX SEM, no deviations in the composition of the thin films were detected.

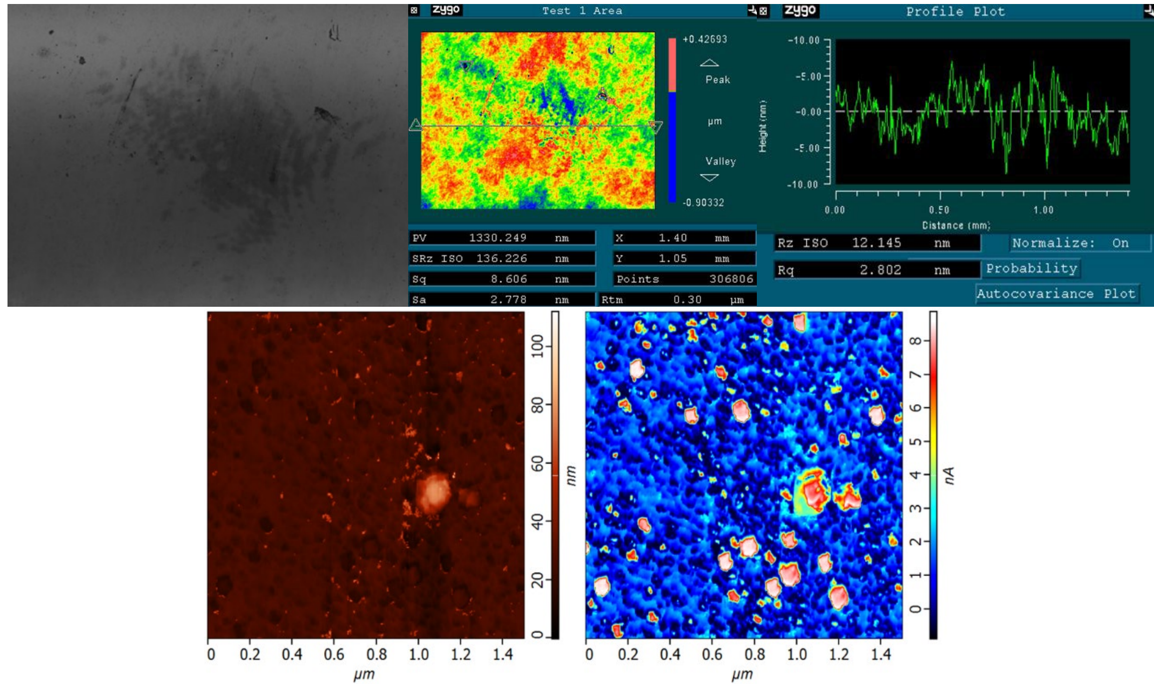

Fig. 7. Measurements micro-roughness using WLI (top) and AFM (down) on thin layers of $Ge_8SbBiTe_{11}$ of middle irradiation point after two single femtosecond laser pulses.

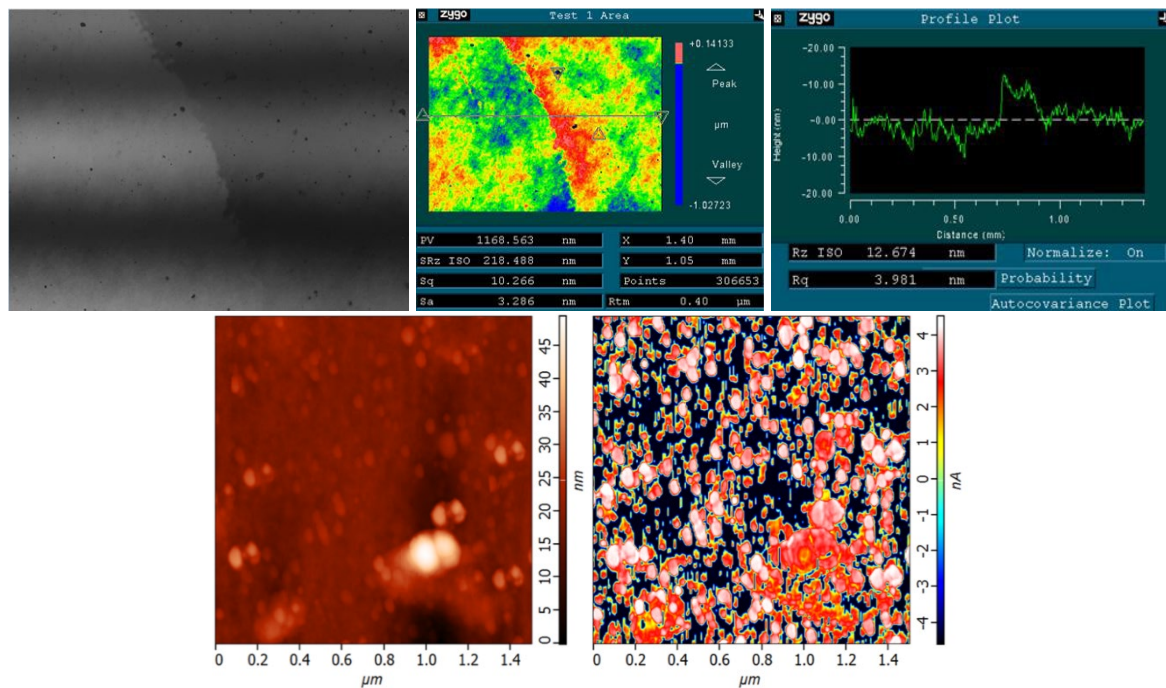

Fig. 8. Measurements micro-roughness using WLI (top) and AFM (down) on thin layers of $Ge_8SbBiTe_{11}$ of edge irradiation point after two single femtosecond laser pulses.

The WLI and AFM measurements was used for determined Average rougness (Sa) in the center of irradiated region (as shown in Table 3.). From results of WLI measurements we can see that the values of Sa in the center of the irradiated region does not differ much from the amorphous region. This means that the material is not removed during irradiation, which may be a characteristic phenomenon when using high laser energies. The roughness is slightly greater at the

edge of the irradiated part. From results of AFM measurements we can see that the values of Sa somewhat different, this may be related to the position and area of the analysis. It should be noted that the studied of roughness and surface structure differed slightly depending on the position of the analysis. This is due to the large size of the spot as well as the accompanying effects during the experiment, such as the interference of a focused femtosecond laser pulse on quartz glass, which served as a window for a protective housing with a thin film. In our case, this effect of interferometric decomposition of the laser beam in some cases manifested itself in thin films as an image of the changed / unchanged phase.

Table 3. Grain density and magnitude of the grain before and after laser irradiation of $Ge_8Sb_{2-x}Bi_xTe_{11}$ (where x = 0, 1, 2) films.

Materials	Regions	WLI	AFM		
		S_a (nm)	S_a (nm)	Grain density (grain · μm^{-2})	Magnitude of the grain (nm)
$Ge_8Sb_2Te_{11}$	Amorphous region	3.38	1.57	116	19
	Center of the irradiated region single laser pulses	4.01	11.09	46	88
	Center of the irradiated region two single laser pulses	3.16	2.85	15	56
$Ge_8SbBiTe_{11}$	Amorphous region	3.32	1.84	17	31
	Center of the irradiated region single laser pulses	3.32	7.94	20	68
	Center of the irradiated region two single laser pulses	2.77	30.21	180	38
$Ge_8Bi_2Te_{11}$	Amorphous region	2.2	2.32	204	40
	Center of the irradiated region single laser pulses	3.84	9.18	16	71
	Center of the irradiated region two single laser pulses	4.25	3.38	8	95

The values of roughness and topography of the clear transition crossed each other at the boundary between the amorphous and crystalline phases, due to the manifestation of this effect.

In the process of changing the phase from amorphous to crystalline, there is a tendency for crystals to grow in the material. The number and size of crystalline grains were also investigated using AFM and summarized in Table 3.

From AFM analysis, we can see some interesting trend in the obtained results of the number and size of crystals on thin films of chalcogenide materials with the $Ge_8Sb_{2-x}Bi_xTe_{11}$ system (where x = 0, 1, 2) at the irradiation sites by single femtosecond laser pulse.

In the amorphous state of $Ge_8Sb_2Te_{11}$ materials we obtain a sufficiently large number of grains with a size of almost 20 nm. After irradiation by a single laser pulse, the density of grains decreased, due to which their size increased. It is a classic principle of crystal growth. The density and size of the crystals are reduced after using two single laser pulses with a time interval between pulses of a few seconds (manual control). This behavior may be associated with partial reamorphization in the center of the irradiated spot, as shown by the reflective ability of thin films, which was examined by an optical microscope. The number of grains (almost twice) and their size are twice as large in the case of thin films of $Ge_8Bi_2Te_{11}$, which is due to the presence of bismuth. Also, when irradiated by a single laser pulse, pronounced decrease in the density of the crystallization centers was observed in comparison with thin films of $Ge_8Sb_2Te_{11}$ and also a less pronounced change in the size of the crystals.After irradiation of two single pulses, in contrast to

thin $Ge_8Sb_2Te_{11}$ films, further growth of crystals is observed in $Ge_8Bi_2Te_{11}$ films, which is consistent with observations by optical microscope.

A rather interesting trend was observed with regard to thin films of $Ge_8SbBiTe_{11}$. In the amorphous film, the number of crystal grains is quite low compared to that of other films, their size is intermediate between $Ge_8Sb_2Te_{11}$ and $Ge_8Bi_2Te_{11}$, which may be due to the stoichiometry of these materials. An interesting effect is that after irradiation by a single femtosecond laser pulse, in the irradiation region from observations under an optical microscope, has low reflectivity, this may be due to the lack of energy of the laser pulse fluence, which is manifested as partial crystallization of the irradiated position. At the same time, the amount of grain increased slightly, and the size of the crystals doubled. After irradiation of thin films by two laser pulses, the number of crystals has a large value of 180 (grain · μm^{-2}), but their size may correspond to the size of the crystals in the amorphous film. This trend is most probably associated with the formation of chemical bonds related to the total amount of the (Sb_2Te_3 + Bi_2Te_3) phase. The effect is quite interesting in terms of properties and bulk compactness. At present, such behavior is still under investigation because there is a need to conduct a systematic quantitative and qualitative analysis of this behavior. Despite this, the replacement of bismuth with antimony showed quite interesting results and has a great potential in this field of research and use in recording media.

4.4. Optical properties

Although it was used an optical microscope to observe the reflectivity of studied samples, the detailed parameters of the reflectivity in the studied materials was determined by spectral ellipsometry.

WASE ellipsometer was used to determine the refraction index, extinction coefficient and reflectivity of $Ge_8Sb_{2-x}Bi_xTe_{11}$ (where x = 0, 1, 2) thin films after a single and two single pulses. The optical functions (refractive indices and extinction coefficients) obtained by ellipsometric data for amorphous and crystalline (after single and two single pulse) phases are compared in Figure 9 and Table 4.

Table 4. Refractive index and extinction coefficient of $Ge_8Sb_{2-x}Bi_xTe_{11}$ (where x = 0, 1, 2) thin films after single pulses at 405 nm, 650 nm and 780 nm wavelength.

Thin films	Position of measurement	405 nm		650 nm		780 nm	
		n	k	n	k	n	k
$Ge_8Sb_2Te_{11}$	amorphous	2,79	2,24	3,88	1,64	4,03	1,44
	1 fs pulse	1,45	2,87	3,14	3,89	3,69	3,97
	2 fs pulse	1,43	2,9	3,12	4	3,67	4,11
$Ge_8SbBiTe_{11}$	amorphous	2,68	2,04	3,7	1,54	3,85	1,35
	1 fs pulse	2,18	2,18	3,43	1,98	3,64	1,83
	2 fs pulse	1,47	2,81	3,18	3,76	3,69	3,82
$Ge_8Bi_2Te_{11}$	amorphous	2,7	2,29	4,05	1,54	4,19	1,19
	1 fs pulse	1,12	2,27	2,32	3,24	2,97	3,47
	2 fs pulse	1,31	2,42	2,69	3,45	3,43	3,63

It is well known that the Cauchy dispersion relation is able to describe optical functions correctly in the non-absorbing region of the amorphous chalcogenide materials, which is confirmed by good agreement between optical functions obtained by all the models. On the other hand, a simple Cauchy model is not appropriate in the case of the Ge-Sb-Te cubic phase. Lorentz and Tauc-Lorentz models were used for the fits.

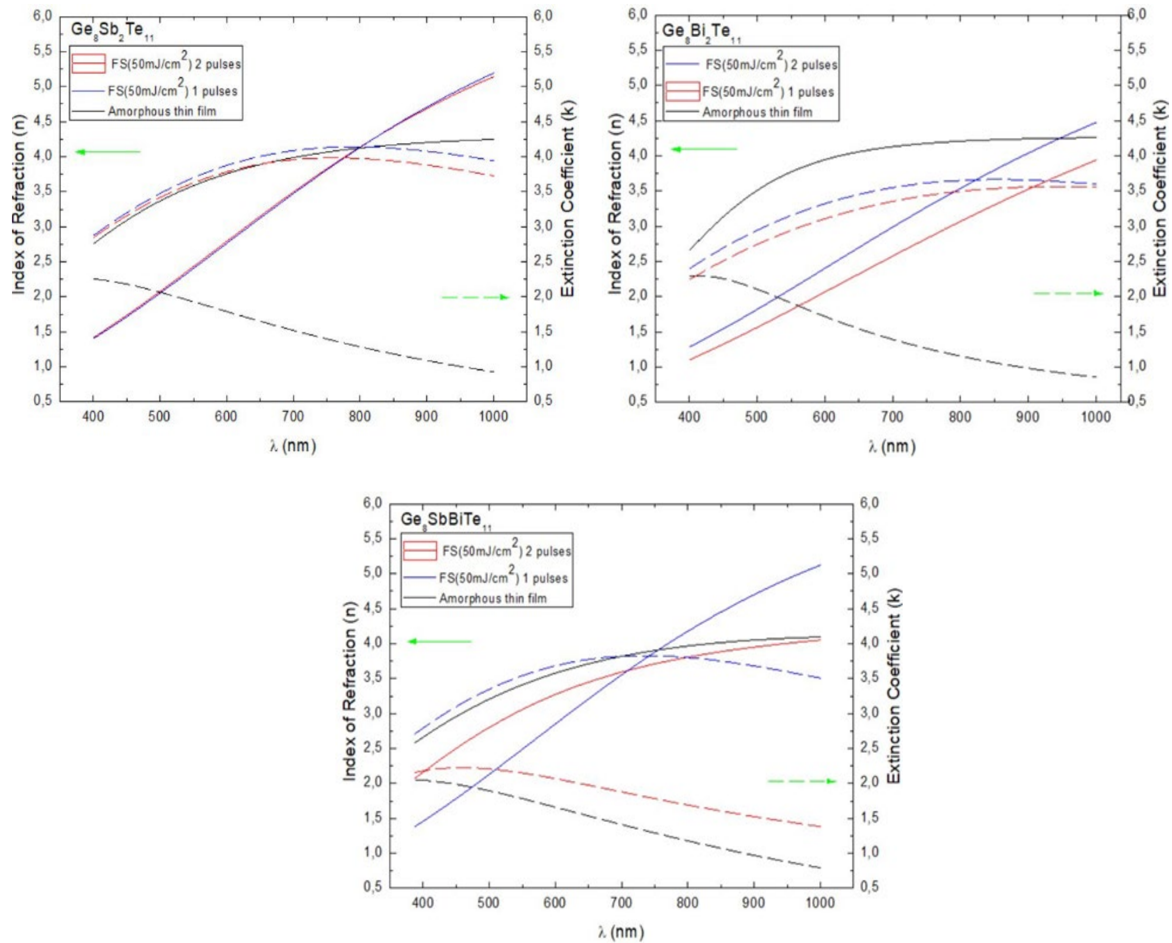

Fig. 9. Refractive index and extinction coefficient of $Ge_8Sb_{2-x}Bi_xTe_{11}$ (where x = 0, 1, 2) thin films after single and two single pulse (red and blue lines) compared with amorphous phase (black lines).

The reflectivity study of the prepared samples was also performed using the ellipsometer. Although this method is considered an indirect method of studying the reflectivity, but despite this, experimentally recorded spectra of reflectivity areconsistent with the results obtained from Ocean Optics Spectrometers.

In Figure 10. shows the reflectivity curve obtained at room temperature from direct evaluation of ellipsometry data.

It is well known that the optical recording of information is based on the reflectivity of the material between the amorphous and crystalline states. Therefore, in the analysis, an important parameter for PCM materials is the optical contrast. From the reflectivity was determined optical contrast, and summarized in Table 5. at 405 nm, 650 nm and 780 nm.

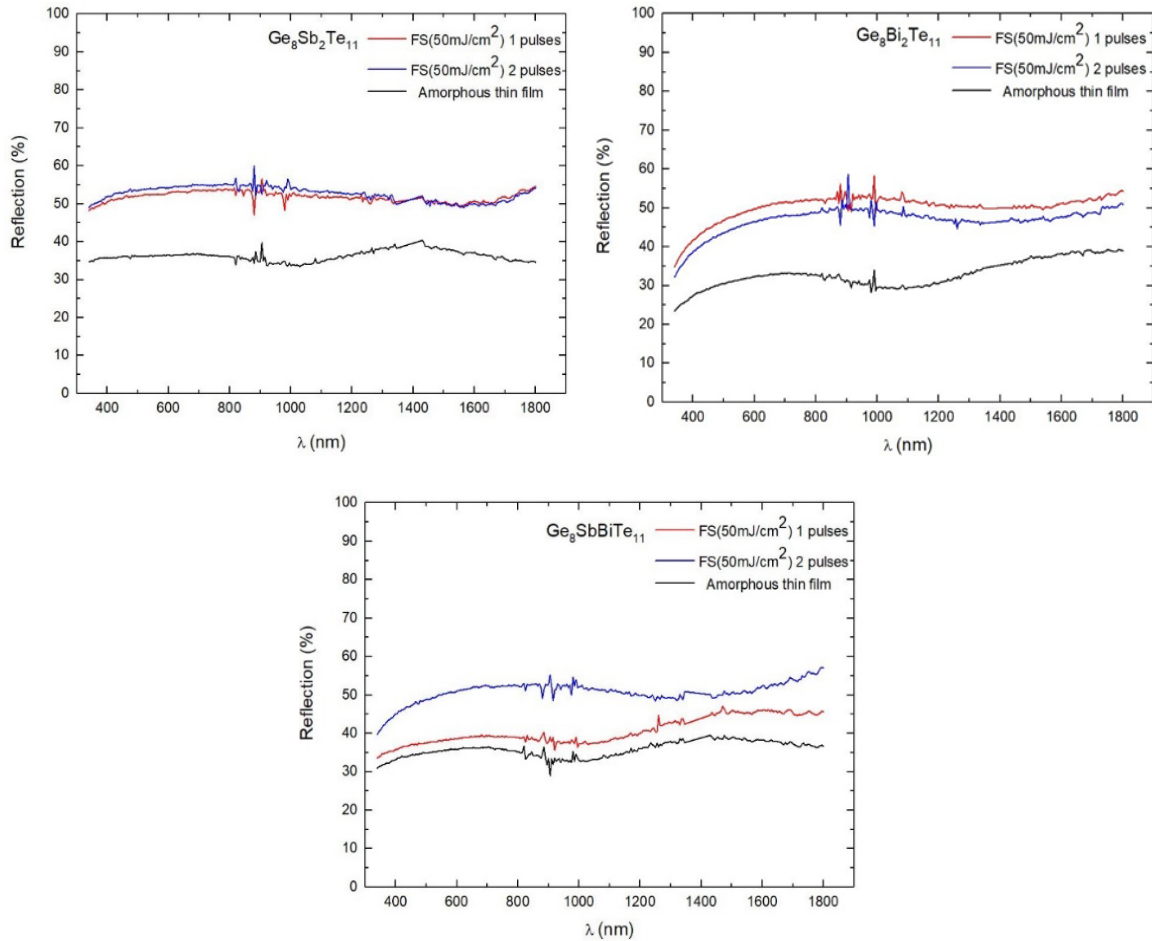

Fig. 10. Reflectivity of $Ge_8Sb_{2-x}Bi_xTe_{11}$ (where x = 0, 1, 2) thin films after single and two single pulse (red and bluelines) compared with amorphous phase (black lines).

The values of optical contrast of the prepared films are given by equation

$$C = (Rc - Ra)/Rc \cdot 100\% \quad (2)$$

where R_c is the reflectivity of crystalline film and R_a is the reflectivity of amorphous film.

Table 5. Calculated optical contrast C (%) at the given wavelengths between as-deposited and crystallized by laser pulses thin films.

Thin film	C (%)		
	λ = 405 nm	λ = 650 nm	λ = 780 nm
$Ge_8Sb_2Te_{11}$	30	31	32
$Ge_8SbBiTe_{11}$	26	30	32
$Ge_8Bi_2Te_{11}$	34	35	37

The results show that the optical contrast difference between the amorphous and crystalline state is 26 - 37%, which is a good indicator that makes the material suitable for phase change recording.

In the works of S. Kozyukhin and P. Lazarenko performed a similar study of the effect by nanosecond single laser irradiation in $Ge_2Sb_2Te_5$ thin film. After irradiation by a nanosecond laser pulse at sufficient energy, as well as in our work, was observed the phase change from amorphous to crystalline, and the reamorphization was observed after several pulses and confirmed by the Raman analysis [16,17]. In work Xinxing Sun [18] was compared the phase changes in $Ge_2Sb_2Te_5$ films used a nanoscond and femtosecond laser pulse.

Currently, there are many unanswered questions about what mechanisms prevail that will lead to phase changes when using ultra-short femtosecond pulses. The author of this work concluded that regarding the physical process of laser-induced phase transition, on the one hand ns laser pulse irradiation can be considered as a thermal process, while upon excitation with ultrashort pulses (fs) non-thermal effects are probable to be involved in the phase transition process [18]. Depending on the type and conditions of such experiments may be dominated by thermal or non-thermal processes of the phase change, it is also possible that both processes are present to one degree or another, which may be accompanied together. The model of non-thermal processes in phase change materials is supported by Makino and Hase [19, 20]. Solis and Afonso [21] conducted experiments and discussions using similar materials ($Ge_2Sb_2Te_5$). In the case of femtosecond pulses, it has been shown that the applicability of the material as a recording medium is connected to the presence of an ultrafast non-thermal phase transition occurring in the hundreds of fs timescale. The non-thermal transformation process in semiconductors using femtosecond pulses is also mentioned in the work of Rousse and also Sundaram and Mazur [22, 23]. On the other hand, according to Liu [24] the process of transformation in femtosecond laser irradiation is accompanied by thermal processes. Liu shows a simplified, one-dimensional model that accounts for optical absorption, thermal transport and thermally activated crystallization provides values of the optical reflectivity and mark area that are in very good quantitative agreement with the experimental data to justifying the one-dimensional heat flow assumption.

5. Conclusion

Despite some uniqueness of the experiments we were able to show the following.

The X-ray diffraction pattern confirmed the crystalline state with the cubic phase for all thin films of the chalcogenide system $Ge_8Sb_{2-x}Bi_xTe_{11}$ (where x = 0, 1, 2) after irradiation by single femtosecond pulses with 50 $mJ \cdot cm^{-2}$ energy. This indicates the ability of the studied materials to change the phase in the ultra-short time interval of 40 femtoseconds. The topography was observed and the growth of crystals was confirmed for thin films of the studied materials in the positions of the phase changed in the region of irradiation by single femtosecond laser pulses.

For all compositions the observations under an optical microscope showed good reflectivity in the irradiation area of thin films.

The reflectivity studies by ellipsometry showed a clear difference between the amorphous and the crystalline phase after a single / two single femtosecond pulses in thin films of the $Ge_8Sb_{2-x}Bi_xTe_{11}$ system (where x = 0, 1, 2). The high values from 26 to 37% of the optical contrast was presented at phase change for all study materials, which indicates sufficient potential for use in optical recording of information. In this study, the effect of bismuth concentration in the structure of films played a very important role in the reverse process of reamorphization and in growth and size of crystal in the irradiation region by a femtosecond laser pulse of thin films with the $Ge_8Sb_{2-x}Bi_xTe_{11}$ system (where x = 0, 1, 2). The substitution of bismuth for antimony leads to a change in optical, electricity and thermal properties depending on the concentration for the studied materials of system $Ge_8Sb_{2-x}Bi_xTe_{11}$ (where x = 0, 1, 2). This trend makes bismuth one of the best materials for doping or substitution for PCM.

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