



Influence of bismuth on optical and electrical properties of thin $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films prepared by DC ion plasma sputtering

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ARTICLE INFO

Keywords:

$\text{Ge}_2\text{Sb}_2\text{Te}_5$ Films
Impurity
DC Ion-plasma sputtering
Bismuth nanoclusters
Atomic structure
Electronic properties

ABSTRACT

The structure of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ thin films doped with Bi has been studied using TEM, Raman spectroscopy, and Optical Transmission Spectroscopy. Thin films were obtained by direct current (DC) ion-plasma sputtering with thicknesses from 60 to 200 nm. TEM images revealed an amorphous film structure with bismuth nanocrystallites with a size of ~ 1 to ~ 20 nm. A shift in the Raman peaks of Bi-doped $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films compared to undoped samples was observed. A shift of the fundamental absorption edge to the long wavelength region of the spectrum along with an increase in the concentration of bismuth were detected in the optical transmission spectra of the films. A decrease in the optical band gap of bismuth-doped films was found. It has been shown that with increasing bismuth content in the films, their conductivity also increases. It has been found from studies of the current-voltage film characteristics reversible switching effect takes place.

1. Introduction

For the upcoming generation of non-volatile memory devices, the chalcogenide glassy semiconductor (CGS) ternary system Ge-Sb-Te, namely GeSb_4Te_7 , GeSb_2Te_4 , and $\text{Ge}_2\text{Sb}_2\text{Te}_5$, has been considered the most promising [1]. Currently, research efforts were concentrated on the enhancement of switching parameters and information recording in phase change memory (PCM) devices. $\text{Ge}_2\text{Sb}_2\text{Te}_5$ is the compound that interests us the most due to its combination of important properties [2]. The materials of this system are capable of both amorphous and crystalline states at room temperature. The amorphous phase is metastable in this instance, and crystallization takes tens of years. But, when the temperature rises, the rate of crystallization increases more rapidly, and at a temperature of roughly 500°C , the crystallization time is reduced to a few tens of nanoseconds. It is simple to discern between the respective states because there are several orders of magnitude between the resistivities of the amorphous and crystalline phases. Moreover, the Ge-Sb-Te system's materials have a high optical contrast, allowing for their usage in rewritable optical discs. The Ge-Sb-Te system's materials can withstand 10^{12} write-erase cycles [3]. The unique properties of

CGSs, including Ge-Sb-Te, are associated with structural features of these materials. It is generally accepted that, for most CGSs, the amorphous phase retains the short-range order of the crystalline phase; therefore, the properties of the amorphous phase are in many respects like those of the crystal [4]. However, in the materials of the Ge-Sb-Te system, the arrangement of atoms in the amorphous and crystalline phases differs significantly. It is believed that the difference in the length and type of bonds is the reason for the significant difference in resistivity and the large optical contrast [5,6]. Due to the presence of defects in their structure, CGS exhibit properties specific to this class of materials, such as photostructural transformations, photodoping, transparency in the IR region, and the switching effect [7]. Despite recent technological advancements, it is still necessary to tune specific material properties and PCM performance. By altering the phase transition temperature or the optical and electrical contrast, it is possible to boost writing speed and cut power consumption while maintaining phase memory performance.

One of the most efficient ways to modify a material's electrical characteristics is by adding dopants [8–13]. Due to their poor sensitivity to doping, modifying the properties of chalcogenide glasses is a

Abbreviation: CGS, Chalcogenide Glassy Semiconductor; PCM, Phase Change Memory; CVC, Current-Voltage Characteristic; DC, Direct Current; SEM, Scanning Electron Microscopy; EDXA, Energy Dispersive X-ray Analysis; TEM, Transmission Electron Microscopy; SPM, Scanning Probe Microscopy; UV, Ultraviolet.

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<https://doi.org/10.1016/j.jnoncrysol.2023.122544>

Received 13 April 2023; Received in revised form 4 July 2023; Accepted 29 July 2023

Available online 9 August 2023

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challenging task, thus appropriate impurities must be selected. In a previous study [14], we demonstrated that Bi doping significantly affects the electrical and optical characteristics of CGS films. According to ref. [15], the addition of bismuth to $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films significantly altered their current-voltage characteristics, resistivity, mobility gap, Urbach energy, distribution density of localized states, and activation energy of conduction. For $\text{Ge}_2\text{Sb}_2\text{Te}_5$ alloyed with 0.5 wt.% bismuth, the most pronounced alteration of the current-voltage characteristic (CVC) of thin films was reported. The effect of bismuth ion implantation on the temperature dependence of the resistivity of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ thin films was studied in Ref. [16]. This paper reports that the implantation of bismuth ions into $\text{Ge}_2\text{Sb}_2\text{Te}_5$ thin films results in a decrease in the crystallization temperature and a transformation from cubic to hexagonal structure. According to [17–19], adding bismuth to Ge–Sb–Te compositions reduces its crystallization time by 30% and changes their type of conductivity.

To control the electronic properties of CGS, two approaches based on structural and impurity modification were developed. Ion implantation, magnetron sputtering, and thermal evaporation are a few techniques that can be used to produce doped $\text{Ge}_2\text{Sb}_2\text{Te}_5$ thin films. Each approach has benefits and drawbacks. Ion-plasma sputtering allows for the insertion of relatively high quantities of metal impurities while preventing crystallization in the material matrix. The resultant films' stoichiometry and homogeneity of thickness are simultaneously maintained. The purpose of this research was to examine the impact of bismuth doping on the composition and electrical characteristics of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ amorphous thin films.

2. Experimental

2.1. Thin films synthesis

Bismuth-doped $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films were obtained by DC ion-plasma magnetron sputtering. A monolithic polycrystalline $\text{Ge}_2\text{Sb}_2\text{Te}_5$ target from AciAlloys (USA) with a diameter of 2.00 inches and a thickness of 0.125 inches was utilized for sputtering. Its chemical purity was 99.995%. Metal pieces were uniformly positioned on the chalcogenide target in the sputtering zone to produce a $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film doped with bismuth. By adjusting the ratio of the surface areas of the metal and chalcogenide targets, the concentration of metal impurities in the films could be changed. The utilized bismuth had a purity of 99.99%. The films were prepared using an accelerating voltage of 300 V, a discharge current of 12 mA, and an operating pressure of 1 Pa in an argon atmosphere. As substrates, quartz, glass, single-crystal silicon, and "Kapton" polyamide film were all employed.

2.2. Characterization and measurements

The surface morphology and composition of the films were investigated using scanning electron microscopy (SEM), Quanta-3D 200i, and energy dispersive X-ray (EDX) analysis. For TEM studies, the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film was deposited on a fresh KBr monocrystals cleavage. The $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film was transferred onto a copper TEM grid with a mesh size of 100 μm according to the following procedure. The copper TEM grid was placed in advance in a Petri dish, which was then filled with distilled water. The $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film-coated KBr monocrystal was placed onto the distilled water ($\text{Ge}_2\text{Sb}_2\text{Te}_5$ film side up) allowing the KBr monocrystal to be etched. Following the complete dissolution of KBr monocrystal, only a $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film remained on the surface of the distilled water. The deposition of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film onto copper TEM grid was performed by carefully removing water via a syringe from the Petri dish. During this step, the copper TEM grid was placed directly under the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film to obtain a copper TEM grid– $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film system. Transmission electron microscopy (TEM) investigations on FEI Titan were performed to investigate the structural peculiarities of the Bi-doped $\text{Ge}_2\text{Sb}_2\text{Te}_5$. The experiments used a 2 nA beam current and a 300 kV electron beam

accelerating voltage. On a Ntegra Thermo Scanning Probe Microscopy (SPM), the contact approach was used to analyze the morphology of thin films. The Raman spectra were captured using an NT-MDT Solver-Spectrum 600/600 spectrometer. Radiation from a He–Ne laser with a wavelength of 633 nm was employed as the excitation source. The range of the applied power was 0.63 to 2.0 mW. The spot diameter was $\sim 1 \mu\text{m}$. The spectra were recorded with an accuracy of $\pm 1 \text{ cm}^{-1}$. With a Shimadzu UV3600 spectrophotometer, optical transmission $T(\lambda)$ and reflection $R(\lambda)$ spectra of Bi-doped $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films were captured at room temperature in the wavelength range of 300 to 2000 nm. A Keithley-6485 picoammeter was used to measure the temperature dependences of electrical conductivity of the films in the region of 300 to 400 K at direct current and an electric field strength of 10^2 V/cm . 2°C/min was the sample heating rate. A copper-constantan thermocouple was used to measure the temperature of the sample.

3. Results

The studied films contained bismuth impurities in amounts of 5.57 and 12.54 at.% (see Supplementary Materials 1–3). It was found that the studied films do not contain uncontrolled impurities and the maximum deviation from the formula component ratio is less than 5 at.%. SEM was also used to control the morphology of the films and measure their thickness. The morphology of the prepared films was homogenous and smooth, with a typical roughness of about 20 nm, according to surface analysis. It was found that the film thicknesses ranged from ~ 60 to $\sim 200 \text{ nm}$.

Fig. 1 shows typical electron diffraction pattern and TEM images of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films containing $\sim 12 \text{ at.}\%$ bismuth.

The TEM images in Fig. 1(A–C) were obtained in the dark field mode, i.e., areas with high density in the TEM image are darker. It follows from Figs. 1(A, B) that the films have an amorphous cellular structure with a short-range order. The high-resolution TEM image (Fig. 1(C)) shows crystalline nanoregions (nanocrystallites) with a size of ~ 1 to $\sim 20 \text{ nm}$, separated from each other by transition regions with an amorphous structure. Crystalline nanoregions are quite uniformly distributed in the amorphous matrix. If we assume that the crystalline nanoregion occupies the entire area of the cells (Fig. 2(a)), then by processing such a TEM image using the ImageJ program, one can obtain the size distribution of these cells (nanocrystallites) (Figs. 2(b) and 3).

Distribution of nanocrystallites in the film $\text{Ge}_2\text{Sb}_2\text{Te}_5 < 12 \text{ at.}\% \text{ Bi}$ are shown in Table 1.

It was feasible to determine from analysis of the electron diffraction pattern depicted in Fig. 1(D) that the nanocrystalline regions are formed by nanocrystalline bismuth (Fig. 4).

Raman spectra of bismuth-modified $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films are shown in Figs. 5 and 6.

The peak positions differ noticeably from those of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films without any bismuth impurities in their composition. Two peaks define the spectra's shape, which is typical of the films' amorphous nature. In tetrahedral GeTe_4 and pyramidal SbTe_3 , the heteropolar bond's vibrations are thought to be responsible for the peak in the region 117–126 cm^{-1} [20]. Sb–Sb bond vibrations in $(\text{Te}_2)\text{Sb}(\text{Te}_2)$, in which Sb atoms are coupled to four Te atoms, are responsible for the peak that may be found in the range of 135–145 cm^{-1} [21,22]. The location of the vibrational modes in Bi_2Te_3 crystals at 133 cm^{-1} was demonstrated in [23,24,25]. It appears that the formation of Bi_2Te_3 and Sb_2Te_3 fragments, as well as the substitution of Bi atoms for Sb atoms, occur because of bismuth doping of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films. The germanium telluride sublattice exists alongside the antimony telluride sublattice in the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ structure, and the isomorphic substitution of tellurium for antimony should similarly induce vibrational alterations in the $\text{GeTe}_{4-n}\text{Gen}$ ($n = 1, 2$) germanium tetrahedra. If we suppose that, for example, a rise in the proportion of $n = 2$ tetrahedra causes these structural units to become less symmetrical and twisted with the introduction of bismuth, this should result in a shift of vibrations to the

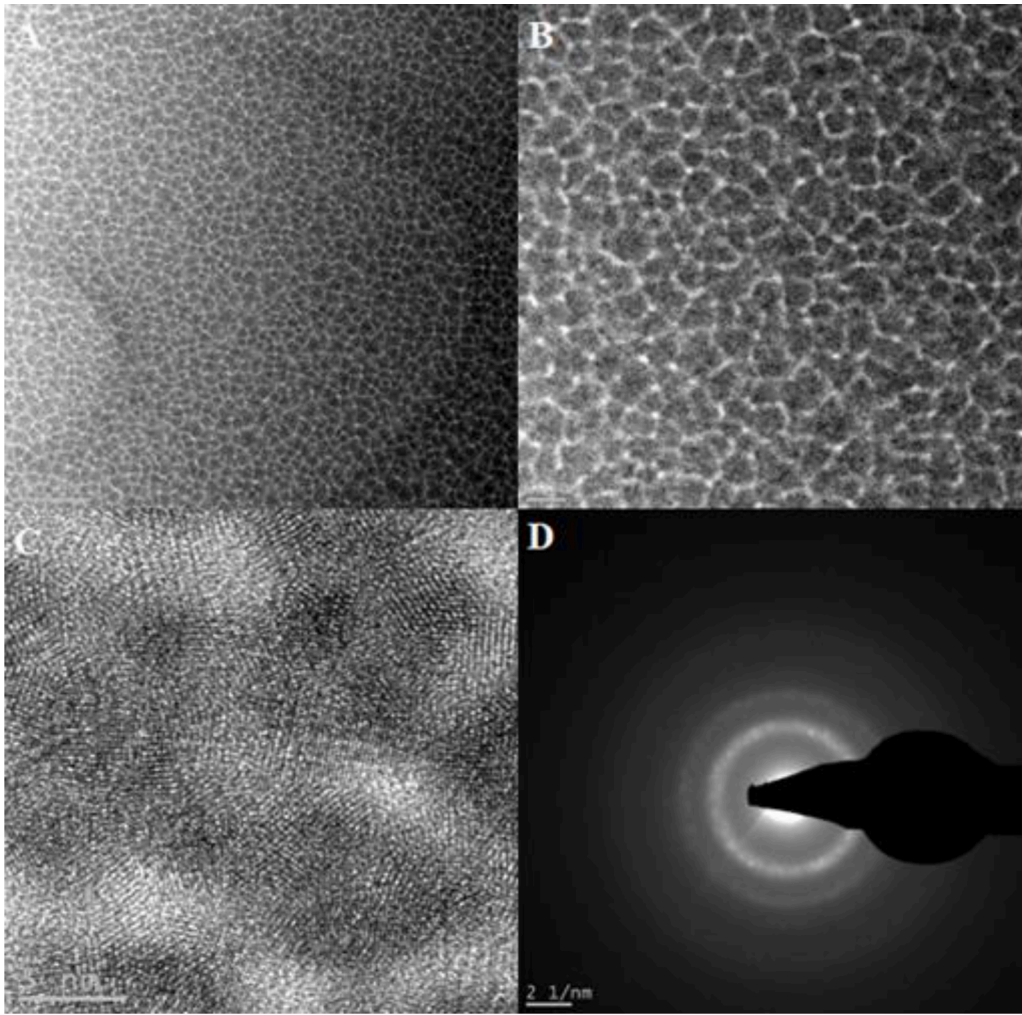


Fig. 1. TEM images of Ge₂Sb₂Te₅<12 at.% Bi> film on a TEM grid with a mesh size of 100 μ m: (A) – 100 nm; (B) – 20 nm; (C) – 5 nm; (D) – typical electron diffraction pattern.

high-frequency region [26]. Bismuth atoms can fill up positions in lattice interstices as an interstitial impurity or swap places with germanium atoms when bismuth concentration rises, however this mechanism appears to be energetically unfavorable.

CGSs are interesting for developing novel optical devices in the near- and mid-IR regions because they exhibit high optical transparency throughout a broad wavelength range ($\lambda = 0.5\text{--}20\ \mu\text{m}$). At the same time, optical research techniques offer significant information on the characteristics of electronic and vibrational excitations in a disordered medium and are highly sensitive to the nature of the atomic and electronic structure of the material. Electronic states and optical transitions are most affected by structure disorder in the region of the spectrum that corresponds to the fundamental absorption edge: "tails" of localized states and localized states of defects arise, and the nature of optical transitions alters. The CGS fundamental absorption band is mostly found in the UV part of the spectrum, except for the long-wavelength edge that corresponds to the visible range. Overall, this band resembles the fundamental absorption bands found in crystalline semiconductors: its width is $\geq 10\ \text{eV}$ and characteristic absorption coefficient values of $\alpha \sim 10^6\ \text{cm}^{-1}$. The same time, the spectra of glass are substantially smoothed, as evidenced by a detailed comparison of the spectra of the imaginary part of the permittivity $\epsilon_2(\hbar\omega) \equiv (nc/\omega) \alpha(\hbar\omega)$, there n – extinction coefficient, c – light velocity) for amorphous CGS and their crystalline analog [27]. Since K is a poor quantum number in the absence of structural periodicity, the smoothness of the spectra in CGS

results from the noncrystalline semiconductors' compliance with the selection rule for the quasi-momentum K during optical transitions. Only the law of energy conservation is satisfied. The energy difference between the final (f) and initial (i) states must therefore match the energy of the absorbed photon.

$$E_f - E_i = \hbar\omega \quad (1)$$

Then the spectrum ϵ_2 or α is determined by the density of occupied (initial) and free (final) states $g_i(E)$ and $g_f(E)$ and the probability of the corresponding transition, which is proportional to the square of the matrix element $|D_E|^2$ [28]. For the transition between the states of the valence band (v) and the conduction band (c), the expression for ϵ_2 has the form:

$$\epsilon_2 = 2(2\pi e\hbar/m\omega)^2 \Omega \int |D_E|^2 g_v(E) g_c(E + \hbar\omega) dE \quad (2)$$

where e and m – electron charge and mass, Ω – system volume, the integral is taken over all pairs of states in the valence and conduction bands. If we assume, as is usually done, that the matrix element does not depend on energy and, moreover, is the same for transitions between nonlocalized states and nonlocalized and localized states of the "tails" of the bands, then ϵ_2 is determined only by convolution of the densities of states:

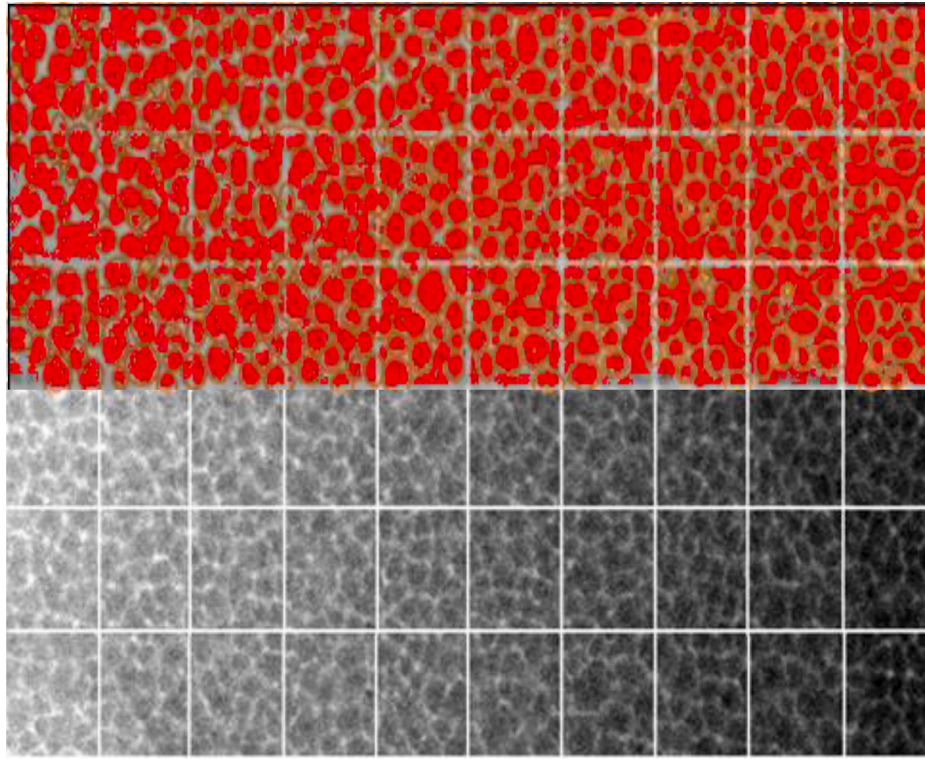


Fig. 2. TEM image of a 500×300 nm $\text{Ge}_2\text{Sb}_2\text{Te}_5<12 \text{ at. \% Bi}>$ film for processing using the ImageJ program.

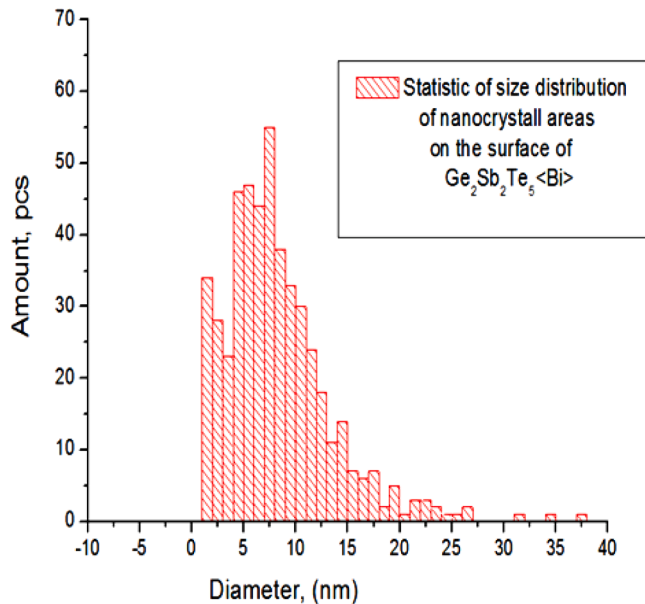


Fig. 3. Size distribution of nanocrystallites of $\text{Ge}_2\text{Sb}_2\text{Te}_5<12 \text{ at. \% Bi}>$ films.

$$\varepsilon_2 = A \int g_v(E) g_c(E + \hbar\omega) dE \quad (3)$$

The factor A can be estimated using the Mott estimate for D_E :

$$D_E = D_{av} \sim (a/\Omega)^{1/2} \quad (4)$$

where a - average interatomic distance. Then $A \sim 2(2\pi e\hbar/m\omega)^2 a$.

Note that for transitions between localized states it is usually assumed that $D_{av} = 0$. Thus, the spectra $\varepsilon_2(\hbar\omega)$ are mainly determined by the shape of the density of states.

The spectrum $\varepsilon_2(\hbar\omega)$ near the long-wavelength absorption edge can be modeled using expression 3 by making certain assumptions about the shape of the density of states near the edges of the valence and conduction bands. Assuming the parabolic shape of the zones:

$$g_c(E) \sim (E - E_g)^{1/2} \quad (5)$$

$$g_v(E) \sim (-E)^{1/2} \quad (6)$$

It turns out that

$$(\hbar\omega)^2 \varepsilon_2(\hbar\omega) \sim (\hbar\omega - E_g)^2 \quad (7)$$

where E_g - optical band gap. The spectral dependence was first obtained by Tauc [29]. Such a dependence was observed experimentally in CGS and other disordered semiconductors in the range of absorption coefficients of $\alpha \sim 5 \cdot 10^3 - 10^5 \text{ cm}^{-1}$ and is still used to determine the optical gap E_g . Since at $\hbar\omega = E_g$ the values of ε_2 and α do not vanish, the value of E_g is usually found by extrapolating the dependence to the abscissa axis.

It should be noted that in [30], it was demonstrated that the Tauc methodology is valid for measuring the optical band gap of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films of nanoscale thickness.

Glass, single-crystal silicon, and "Kapton" polyimide sheets were all employed as substrates in our investigation. The substrates were first treated chemically and thermally to prevent contamination. On polished glass substrates, $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films were deposited in order to examine their optical characteristics. On samples with both planar and

Table 1
Distribution of nanocrystallites in the film $\text{Ge}_2\text{Sb}_2\text{Te}_5<12 \text{ at. \% Bi}>$.

Value	d, nm
d_{mean}	8.3
d_{min}	1.1
d_{max}	37.0
σ	2.1

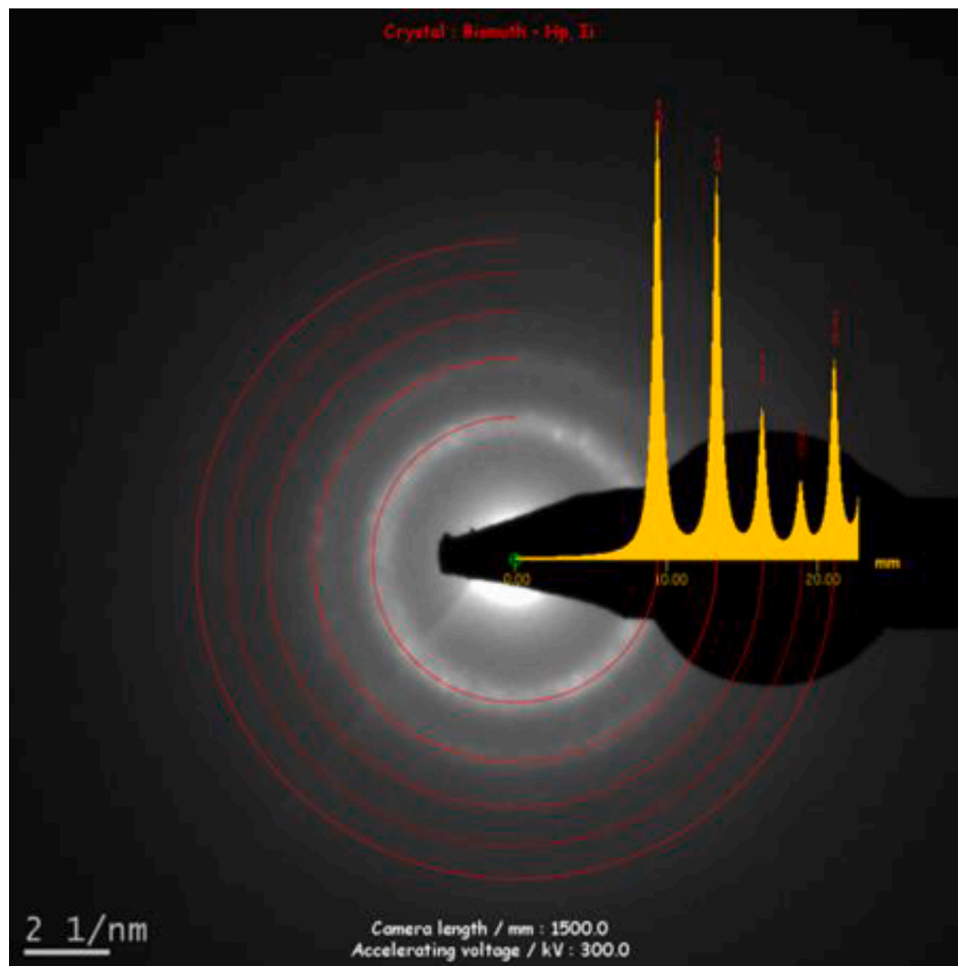


Fig. 4. Analysis of the electron diffraction pattern of nanocrystalline regions of $\text{Ge}_2\text{Sb}_2\text{Te}_5<12 \text{ at. \% Bi}>$ films.

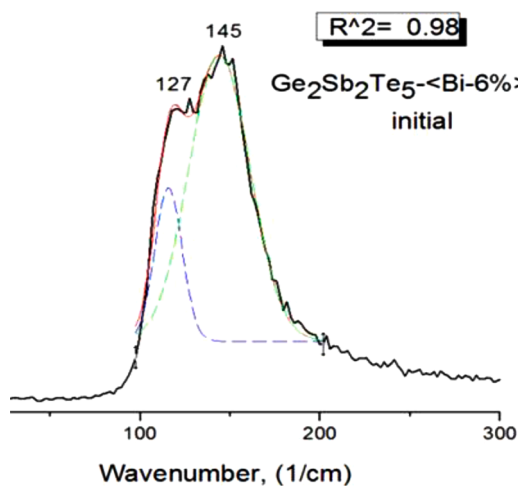


Fig. 5. Raman spectra of $\text{Ge}_2\text{Sb}_2\text{Te}_5<6 \text{ at. \% Bi}>$ films.

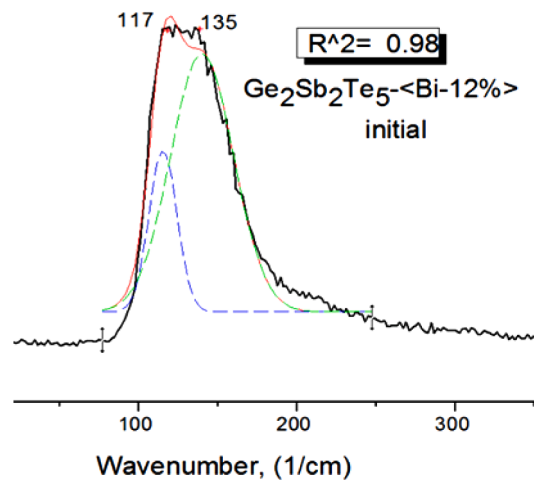


Fig. 6. Raman spectra of $\text{Ge}_2\text{Sb}_2\text{Te}_5<12 \text{ at. \% Bi}>$ films.

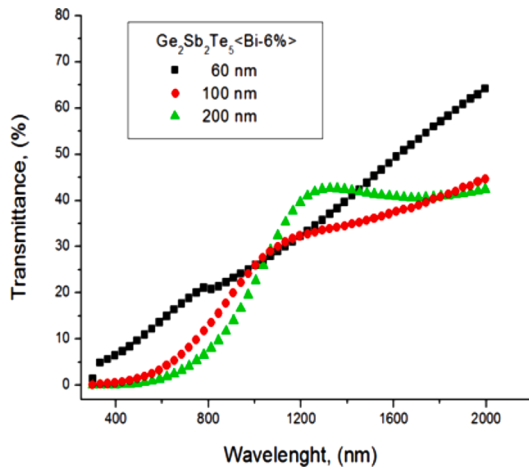
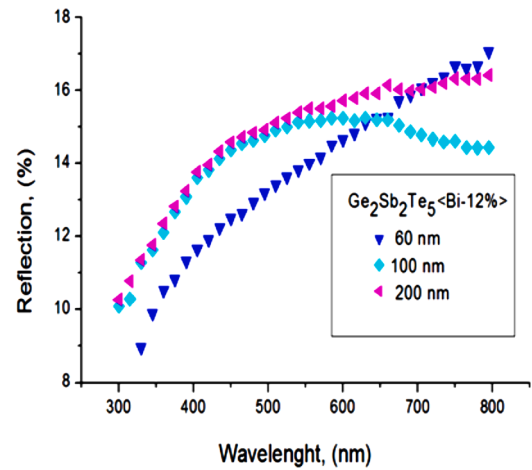
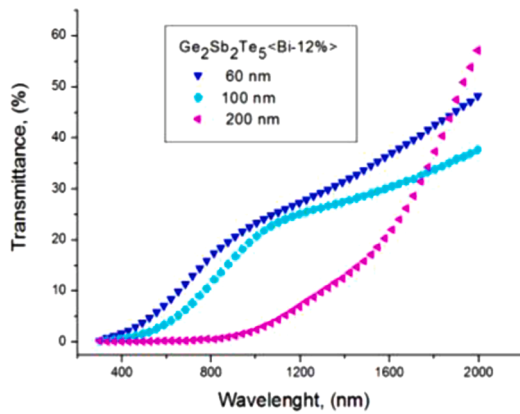
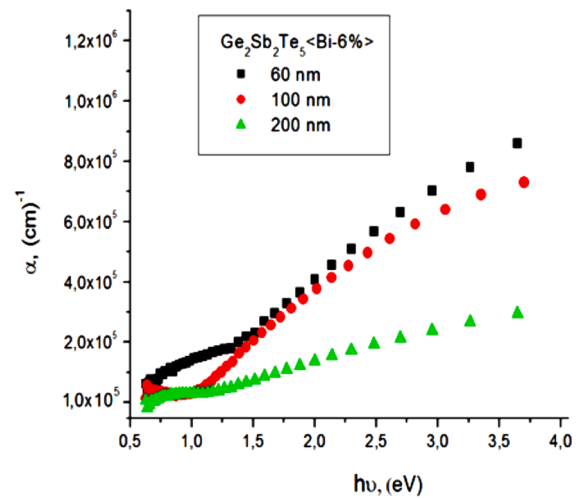
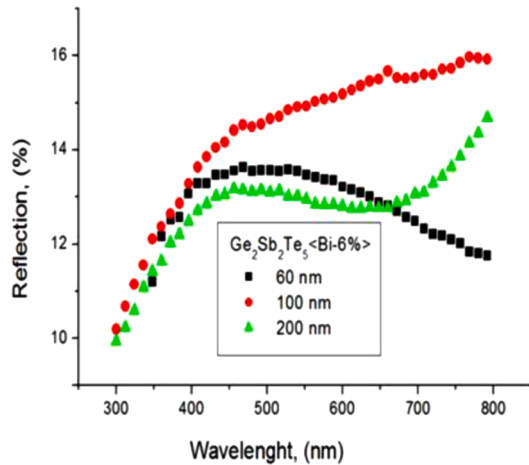
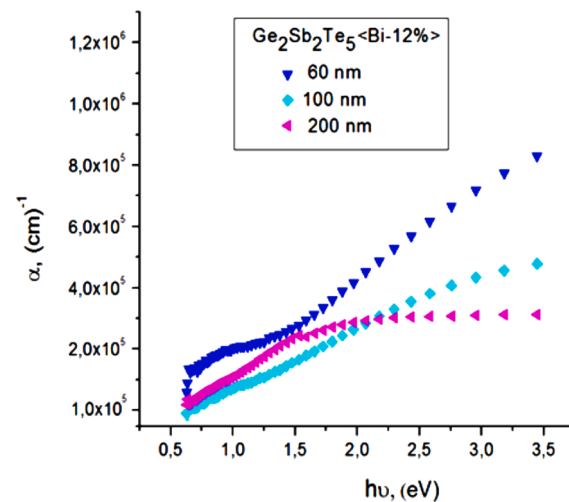
"sandwich" configurations made on polyimide sheet "Kapton" with a resistivity of 1017 Ohm-cm, the electrical characteristics of the films were examined.

The optical transmission spectra of $\text{Ge}_2\text{Sb}_2\text{Te}_5<6 \text{ at. \% Bi}>$ and $\text{Ge}_2\text{Sb}_2\text{Te}_5<12 \text{ at. \% Bi}>$ films with thicknesses $\sim 60, 100$, and 200 nm are shown in Figs. 7 and 8.

According to a comparison of the optical transmission spectra of the

films, the fundamental absorption edge of the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films shifts to the long wavelength region of the spectrum when bismuth content rises (transmission range: 0 to 15%). Similar outcomes were seen before in the references [31,32]. The optical reflection spectra $R(\lambda)$ and the spectral dependences of the absorption coefficient on the photon energy $\alpha(h\nu)$ are shown in Figs. 9–12.

The absorption coefficient α was determined according to the formula:

Fig. 7. Optical transmission spectra of $\text{Ge}_2\text{Sb}_2\text{Te}_5<6 \text{ at. \% Bi}>$ films.Fig. 10. Optical reflection spectra of $\text{Ge}_2\text{Sb}_2\text{Te}_5<12 \text{ at. \% Bi}>$ films.Fig. 8. Optical transmission spectra of $\text{Ge}_2\text{Sb}_2\text{Te}_5<12 \text{ at. \% Bi}>$ films.Fig. 11. Spectral dependences of the $\text{Ge}_2\text{Sb}_2\text{Te}_5<6 \text{ at. \% Bi}>$ film absorption coefficient on the photon energy.Fig. 9. Optical reflection spectra of $\text{Ge}_2\text{Sb}_2\text{Te}_5<6 \text{ at. \% Bi}>$ films.Fig. 12. Spectral dependences of the $\text{Ge}_2\text{Sb}_2\text{Te}_5<6 \text{ at. \% Bi}>$ film absorption coefficient on the photon energy.

$$\alpha(\lambda) = (1/l) \ln\{T(\lambda)/(1-R(\lambda))\}$$

Here, l – the film thicknesses, $T(\lambda)$ – transmission coefficients and $R(\lambda)$ – reflection coefficients.

The Tauc quadratic absorption law $(\alpha h\nu)^{1/2} \sim (h\nu - E_g)$ was found to be effectively satisfied for $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films in the region of the absorption coefficient $\alpha \geq 10^3 \text{ cm}^{-1}$ [31,32]. By extrapolating the experimental dependences $(\alpha h\nu)^{1/2} = f(h\nu)$ onto the energy axis, the optical band gap E_g was calculated from the spectral dependences of the absorption

coefficient (Fig. 11,12) at the region corresponding to the edge of the fundamental absorption band (Figs. 13 and 14). The measurement error for E_g was 0.01 eV.

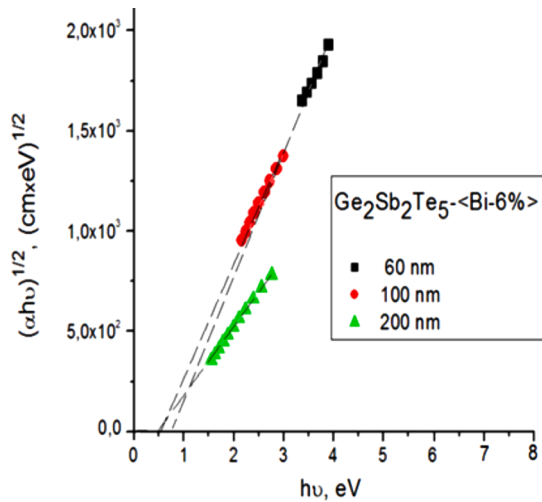


Fig. 13. Spectral dependence of the optical absorption edge of $\text{Ge}_2\text{Sb}_2\text{Te}_5<6 \text{ at. \% Bi}>$ films.

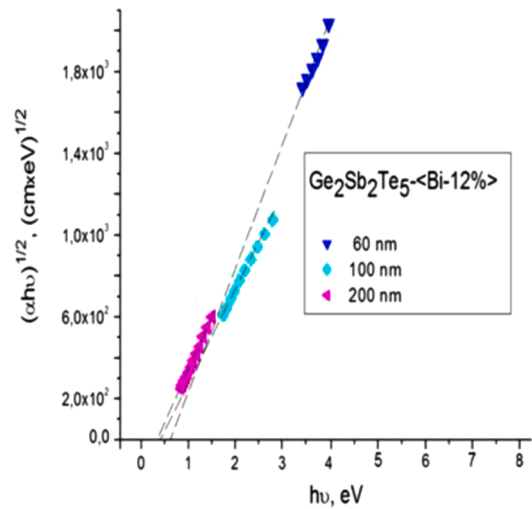


Fig. 14. Spectral dependence of the optical absorption edge of $\text{Ge}_2\text{Sb}_2\text{Te}_5<12 \text{ at. \% Bi}>$ films.

Fig. 15 shows the dependences of the optical band gap on their thickness.

As can be seen, the optical band gap of the films decreases as they are doped with bismuth and increases as the thickness is reduced.

In the region of linearity of the current-voltage characteristic, the temperature dependences of the films' electrical conductivity were investigated between 300 and 400 K at direct current and an electric field strength of 10^2 V/cm .

Figs. 16 and 17 show the temperature dependences of electrical conductivity for $\text{Ge}_2\text{Sb}_2\text{Te}_5<6 \text{ at. \% Bi}>$ and $\text{Ge}_2\text{Sb}_2\text{Te}_5<12 \text{ at. \% Bi}>$ films. The figures show that for the studied concentrations and temperatures, all $\sigma(T)$ graphs follow the exponential law of conductivity change with temperature well: $\sigma(T) = C \exp(-E_g/kT)$ with a fixed activation energy for the concentration of bismuth impurities in films and their thicknesses.

An increase in conductivity, a shift in the Fermi level ΔE_F and activation energy E_g is observed with an increase in the film thickness from 60 to 200 nm.

With an increase in the composition's bismuth content, $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films' optical band gap E_g is observed to decrease, and the edge of the transmission band shifts to the long-wavelength region. This is since as bismuth concentration rises in the films, the concentration of Bi-Te bonds in the CGS composition also rises. In bismuth-doped $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films, the value of E_g is decreased by the presence of such bonds.

Table 2 shows the results for the effect of film thickness and impurity concentration on the main semiconductor characteristics.

4. Discussion

Numerous investigations [33–39] have demonstrated the significant impact of the preparation techniques and conditions on the electrical and optical characteristics of $\text{Ge}_2\text{Sb}_2\text{Te}_5$. The performance improvement of the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ thin film transistor on a flexible plastic substrate was demonstrated by reducing its thickness to 5 nm [40]. It should be noted that the DC magnetron sputtering method makes it possible to deposit $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films of uniform thickness with a uniform distribution of elements and a composition close to that of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ [41]. However, Ref. [42] described the columnar structure of amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films that were deposited on silicon nitride substrates and had lateral cell sizes of 10–15 nm. A sputter-deposited $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film 30 nm thick, consisting of isolated islands with a bimodal distribution of average sizes 15 nm and 25 nm and an average distance between islands of 5 nm, was observed in Ref. [43]. The uniformity of the film thickness, as well as the uniformity of the composition of our samples, was confirmed by

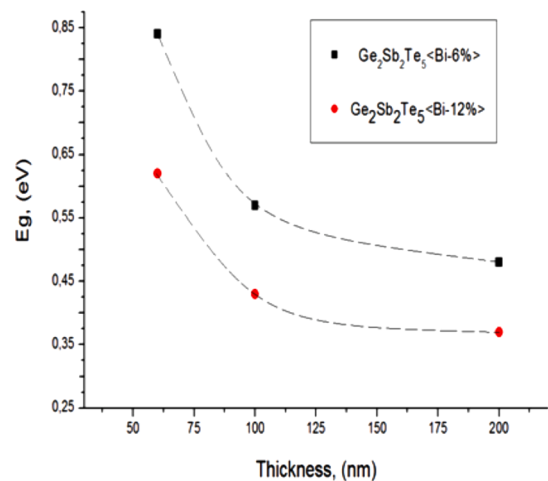


Fig. 15. Dependence of the optical band gap of Bi-doped $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films on their thickness.

scanning electron microscopy.

Impurity and defect electronic states in CGSs became the subject of intense research almost immediately after the discovery in 1955 of the semiconductor properties of chalcogenide glasses. In works [44,45] devoted to CGS doped with 3d metals by the synthesis method, the appearance of microinhomogeneous regions enriched in 3d metals was shown using magnetic susceptibility measurements, differential thermal analysis, and EPR methods. In this connection, a model was proposed in [45, p. 51–52] that relates the increase in conductivity in CGS doped with 3d metals to the overlap of space-charge regions arising at the matrix-microregion interface. However, within the framework of this model, it is difficult to explain the huge effect of impurities on conductivity starting from concentrations of the order of $\sim 1 \text{ at. \%}$.

A microinhomogeneous model was developed in [45, p. 53–55] based on the study of a significant number of experimental results on impurity doping and modification of CGS. CGSs are characterized by the presence of electrons that do not participate in covalent bonds (electrons of lone pairs). These structural features are due to the low coordination of the constituent atoms of CGS - the average coordination number in typical CGS does not exceed 2.5–2.8 [46]. The binary composition GeTe has less tendency to be in the amorphous state because its coordination number is 3. On the other hand, the coordination number of another binary composition, Sb_2Te_3 , is about 2.4. In most cases, the introduction

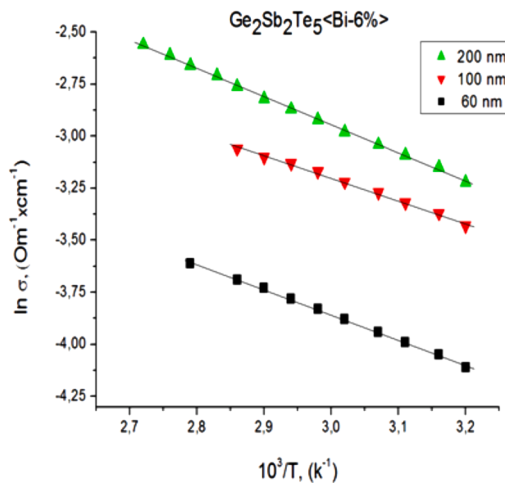


Fig. 16. Temperature dependence of electrical conductivity of $\text{Ge}_2\text{Sb}_2\text{Te}_5<6 \text{ at. \% Bi}>$ films.

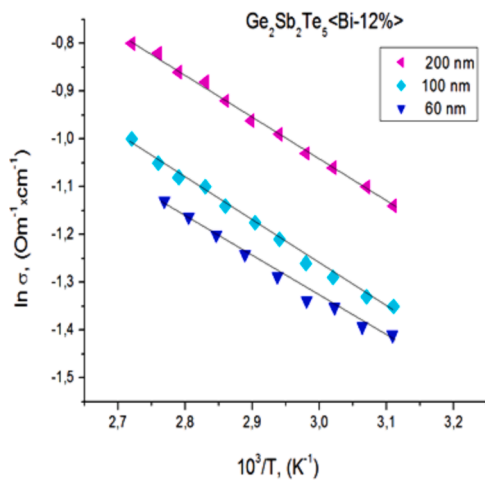


Fig. 17. Temperature dependence of electrical conductivity of $\text{Ge}_2\text{Sb}_2\text{Te}_5<12 \text{ at. \% Bi}>$ films.

of an impurity into such a low-coordinated structure leads to a slight local displacement of the atoms of the initial CGS and saturation of the valence bonds of the impurity atom due to lone pair electrons. For the appearance of an electrically active impurity center, the existence of microregions with increased coordination of atoms is necessary. At a sufficient size of the microregion, structural rearrangement near the impurity atom becomes impossible, and the impurity will behave as in a crystal. This means that the donor or acceptor character of the impurity center will be determined by the atomic structure of the microregion, and not by the initial matrix.

The presence of rigid microregions occupying a relatively small volume and playing the role of "large electrically active centers" is the main reason for the occurrence of impurity conduction in doped CGSs in the model. It is normal to expect that rigid microregions with a high

coordination number will appear upon the introduction of elements that form compounds with the CGS components, which are characterized by an increased crystallization ability. Indeed, impurity conduction in CGS is usually observed upon doping with 3d metals. A small amount of 3d metals causes the appearance in the CGS of microregions with an increased coordination number, and an increase in their concentration ultimately always leads to the appearance of a crystalline phase.

Since the shift of the Fermi level is negligible in our case, E_F 0.1 eV, we think that the increase in conductivity of $\text{Ge}_2\text{Sb}_2\text{Te}_5<\text{Bi}>$ films in the range of impurity concentrations under study is caused by a decrease in E_g . According to this instance, the incorporation of impurities leads to the formation of solid solutions based on the narrow-gap semiconductors Bi_2Te_3 , which results in a reduction in the optical band gap of the CGS.

In a theoretical papers [47,48], the molecular dynamics approach was used to investigate the impact of the bismuth impurity on the spectrum of electronic states of the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ composition. According to the research, as the concentration of bismuth in the films rises, the antibonding states of the 6p electrons in bismuth atoms cause the energy edge of the conduction band to form, as well as a reduction in the band gap and a switch from p-type to n-type conductivity.

High-resolution TEM images in Fig. 1C show that bismuth nano-cluster relative volume in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films is quite considerable (approximately 50%), allowing for percolation-controlled conduction over nanoclusters. However, additional investigation is required in order to develop such explanations for our experimental results. We hope that this issue will be addressed in our future research.

Numerous experimental experiments and modeling techniques have been used to study percolation in chalcogenide glasses [49–52]. The compositional dependencies of Ge-Bi-Se and Ge-Bi-S glasses' resistivity have been studied and discussed in Ref. [49] from the perspective of percolation-controlled conductivity in these materials. The authors conclude that the appearance of n-type conductivity started in the vicinity of the percolation threshold, where these components were dominant, taking into account that the binary chalcogenide glasses Bi_2S_3 and Bi_2Se_3 have strong n-type semiconductor materials and assuming that inhomogeneous transport plays a significant role in the Ge-Bi-Se and Ge-Bi-S systems.

5. Conclusions

We have demonstrated that the amorphous matrix of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films can cluster crystalline bismuth when they are doped with bismuth using DC ion-plasma sputtering. The key semiconductor characteristics of the films vary significantly in this instance. We think that the outcomes of our research can be useful for developing phase-change memory devices.

Funding

This research was funded by the Ministry of Science and Higher Education of the Republic of Kazakhstan grant number AP13268877, "Development of manufacturing technology for radiation-resistant electronic components of artificial Earth satellites", Astana IT University.

Table 2

The main semiconductor parameters of the films.

Samples	Thickness, nm	E_g , eV	σ , $(\Omega \cdot \text{cm})^{-1}$	E_σ , eV	$\Delta E_F = (E_g/2) - E_\sigma$, eV
$\text{Ge}_2\text{Sb}_2\text{Te}_5$ <6 at. % Bi>	60	0.84	1.15×10^{-2}	0.25	0.17
	100	0.57	3.21×10^{-2}	0.22	0.07
	200	0.48	4.01×10^{-2}	0.27	-0.03
$\text{Ge}_2\text{Sb}_2\text{Te}_5$ <12 at. % Bi>	60	0.62	1.82×10^{-1}	0.17	0.14
	100	0.43	2.21×10^{-1}	0.19	0.03
	200	0.37	2.81×10^{-1}	0.11	0.08

CRediT authorship contribution statement

Sanzhar Sultanbekov: Investigation, Writing – original draft. **Oleg Prikhodko:** Conceptualization, Methodology. **Dauren Muratov:** Investigation. **Nurlan Almas:** Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Acknowledgements

We acknowledge Dr. Andrei Sazonov from the University of Waterloo for his guidance and assistance with the TEM measurements and analysis. Also, we would like to express our sincere gratitude to Mr. Nazim Guseinov from the Al-Farabi Kazakh National University for his assistance with the SEM measurement and Ms. Renata Nemkayeva from the same institution for her assistance with the Raman spectroscopic measurement.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:[10.1016/j.jnoncrysol.2023.122544](https://doi.org/10.1016/j.jnoncrysol.2023.122544).

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