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STRUCTURE AND ELECTRONIC PROPERTIES OF MODIFIED BISMUTH FILMS$Ge_2Sb_2Te_5$

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This article shows the study results of optical transmission spectra investigation and temperature dependencies of conductivity of virgin and modified by bismuth $Ge_2Sb_2Te_5$ thin films, obtained by the method ion-plasma sputtering. It has been estimated that electronic properties of bismuth modified films significantly changes. Particularly, reducing of the optical energy gap and activation energy are estimated. While the conductivity at the room temperature increases. Decreasing of the optical energy gap can be interpreted that bismuth doping forms the chemical bonds with elements of the ChG matrix and forms inside the film well known narrow gap semiconductors compounds Bi_2Te_3, etc. In this case Fermi energy is still fixed in the middle of energy gap, decreasing of the activation energy of conductivity and increasing the conductivity as a consequence of decreasing of the optical energy gap.

Keywords: flashmemory, structure, transmission electron microscopy, Raman spectroscopy, $Ge_2Sb_2Te_5$, modification, conductivity

Introduction

Thin films of complex chalcogenide semiconductors compounds of Ge-Sb-Te (GST) intensively studied of the last time. Successful application of GST in the optical devices as DVD-RW, Blu-Raycan allow to use it in nonvolatile memory devices of new generation as PC-RAM (Phase Change Random Access Memory) [1].

Work principle of PCRAM based on ultra-fast, reversible phase transitions “amorphous↔crystalline” state occurring in nanosized chalcogenide films under the external influence of low-energy interaction of light or electric pulse accompanying with significantly change in the optical and electrical characteristics. Despite on the relatively simple phenomenon of phase transition on GST its nature is currently the subject of debate. On the basis of phase transition (PT) under the electric pulse there is the switching effect that opened in chalcogenide glassy semiconductors (CGS) in the 60s of the last century [2] and described in [3] which provides details of different models of this phenomenon. There is a variety of models that describe the processes of recording and erasing information on the optical disk by the laser radiation. For example, in [4] for an explanation of the strong changes in the optical constants of GST proposed structural model, which is based on the reversible "jumping" of germanium atoms in the tetrahedral to octahedral coordination by laser irradiation.

Further improvement of the functional materials on PT are providing speed, a large number of cycles of recording, erasing and lowest energy consumption during programming operations, reading and erasing of information. These factors are the important scientific and practical problems.

One of the common ways of purposeful change of optical and electrical properties of semiconductor materials is structural and impurity modification. However, in the majority of CGS observed insensitivity to the dopant due to the high density of intrinsic defects that fixing the Fermi level near the middle of the energy gap [5]. So controlling the characteristics of GST materials are challenge for PCRAM devices. By the method of impurity modification is required an individual approach to the features of chemical composition and structure of chalcogenide material.

In this work, studied chalcogenide composition of $Ge_2Sb_2Te_5$ (GST225) which lies on the quasi-binary line GeTe- Sb_2Te_3. Selecting of embedded bismuth dopant for this composition is due to the fact that this element is isovalent and isomorphic with one of the main components (Te, Sb) will allow for the replacement mechanism for doping. Bismuth concentration was 1.08 at %.

Experimental results and discussion

Preparation of the films was carried out on ion-plasma sputtering method. The sputtering target of $Ge_2Sb_2Te_5$ has monolith polycrystalline structure with 99.999% chemical purity and has been casted in Aci Alloys - Company (USA). The spraying process was implemented with cosputtering of GST and Bi in argon atmosphere at 1 Pa pressure value. The accelerating voltage was 400 V and the rate of film deposition was approximately equal to 0.3 nm/s. The films were deposited on quartz and silicon substrates, which have previously been undergone to chemical and thermal treatment. The films composition were controlled by scanning electron microscopy with energy-dispersive analysis (EDS) on scanning electron microscope Quanta 3D 200i. Detection of studied films was performed under the influence of the electron beam with energy 30 keV. In Figure 1a, b, respectively, shows the energy spectra of virgin and bismuth modified$Ge_2Sb_2Te_5$films. The elemental composition of the films are shown in Table 1.

Table1.Elemental composition of $Ge_2Sb_2Te_5$ (a) and modified by bismuth$Ge_2Sb_2Te_5$<Bi>film (b).

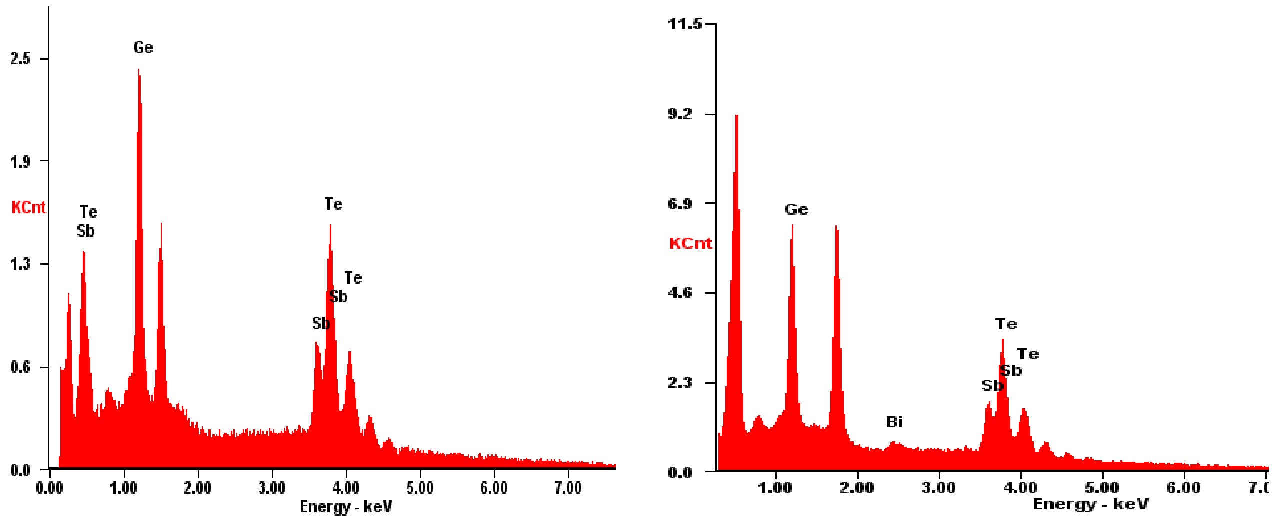
Element	*Wt%*	*At%*
GeL	13.85	21.79
SbL	25.60	24.02
TeL	60.55	54.20

a)

Element	*Wt%*	*At%*
GeL	14.79	23.25
BiM	1.47	0.80
SbL	24.34	22.81
TeL	59.40	53.13

b)

Notification: Wt% -weight percent; At% - atomic percent



a) b)

Fig.1. Energy dispersion spectra of virgin (a) and Bi modified (b) films $Ge_2Sb_2Te_5$

The film's thickness was determined by scanning electron beam on cleavage structure of crystalline silicon and $Ge_2Sb_2Te_5$ film and was 140 nm (Figure 2).

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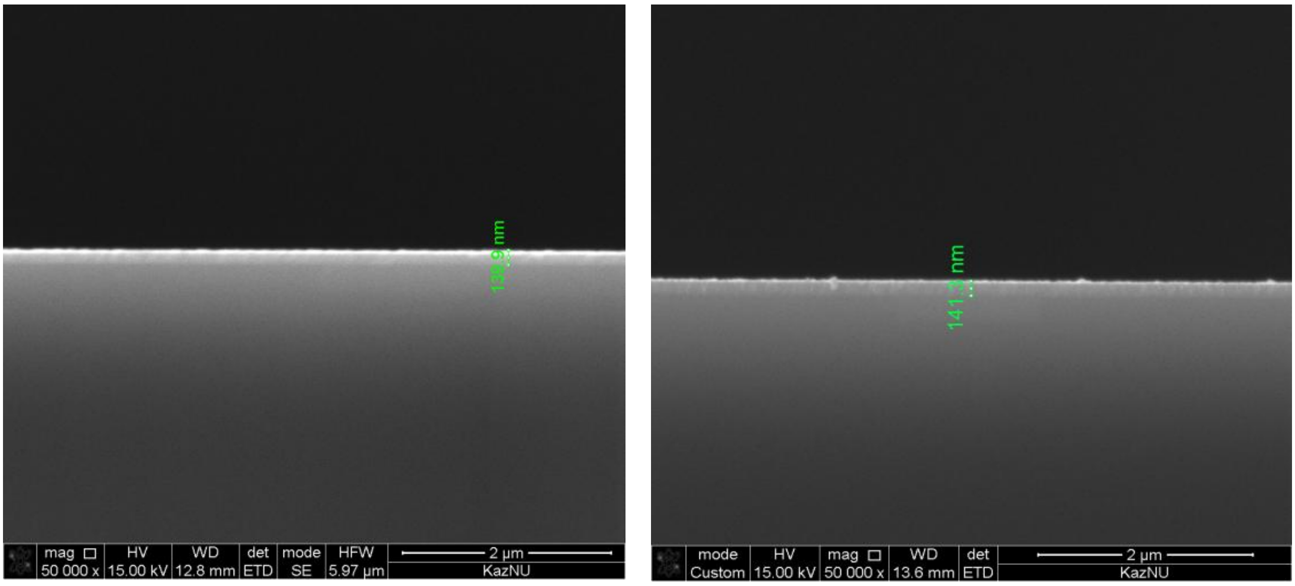
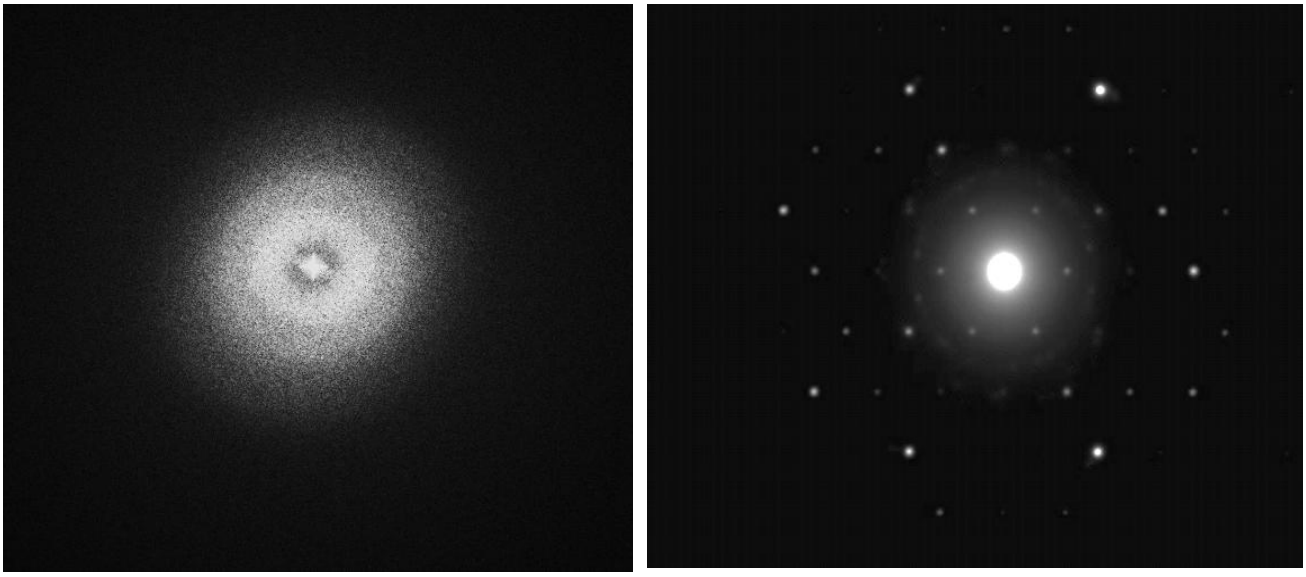


a) b)

Fig.2. Thickness of virgin (a) and Bi modified (b) films $Ge_2Sb_2Te_5$

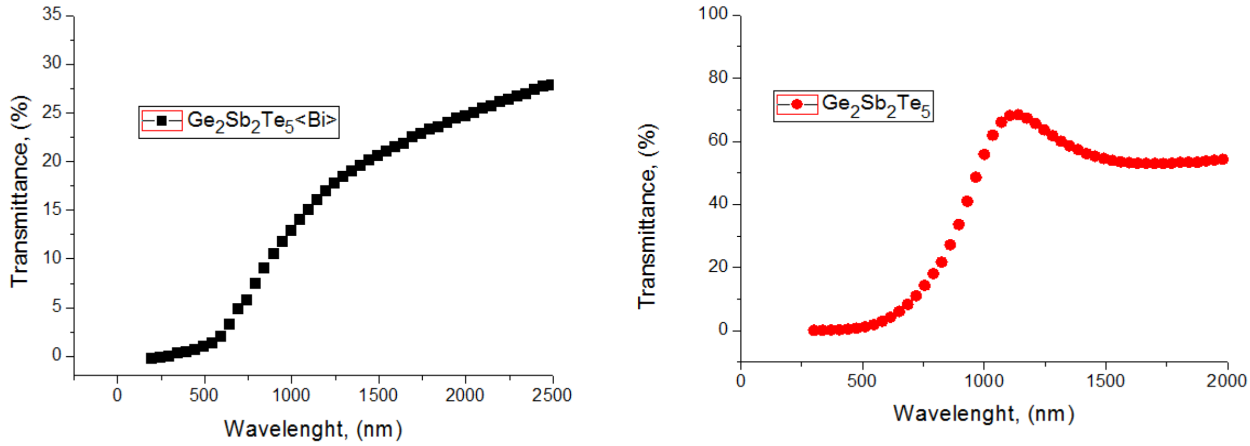
The films structure was studied by transmission electron microscopy using the high resolution imaging (HRTEM) on Titan equipment of FEI-company. Scanning carried out at an accelerating voltage of 300 kV and beam current of 2 nA electrons (picture 3). Figure 3 shows a typical micrograph and electron diffraction pattern of $Ge_2Sb_2Te_5$ film. From the figure 3 could be seen that the investigated film possesses a typical amorphous structure without crystalline nanoregions. It should be noted that such structure was typical for all investigated films for different thicknesses.



a) b)

Fig. 3. HR-TEM of virgin (a) and Bi modified (b) films $Ge_2Sb_2Te_5$

Spectrum of optical transmittance can be calculated from dependency - $T(\lambda)$ of films of $Ge_2Sb_2Te_5$ and introduced on picture 4. Registration at room temperature in wavelength range from 300 nm to 2000 nm on spectrophotometer Shimadzu UV3600.



a) b)

Fig.4.Spectra of optical transmittance of virgin (a) and Bi modified (b) films $Ge_2Sb_2Te_5$

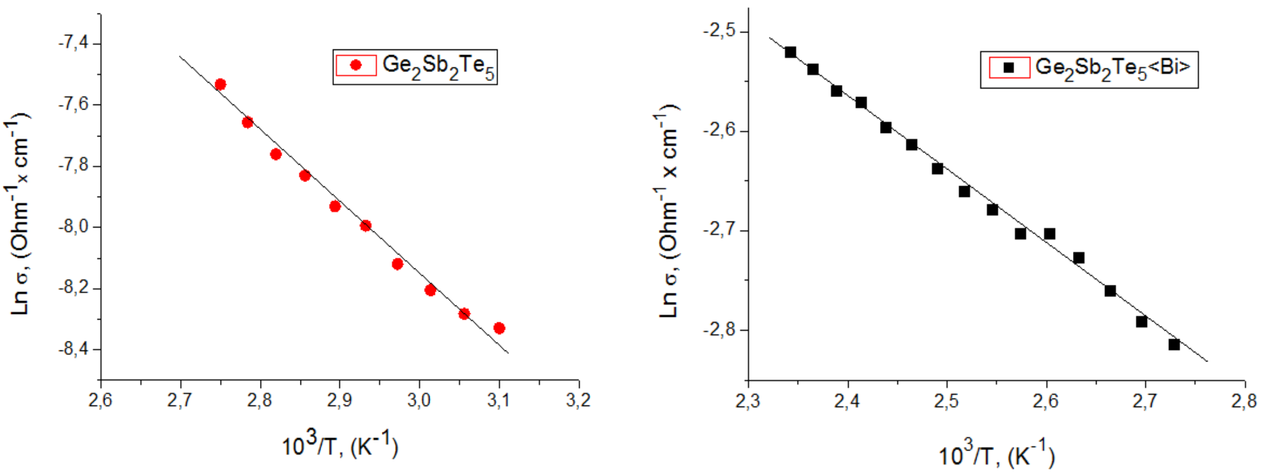
On estimated value of l, transmittance $T(\lambda)$ and reflectivity of the light $R(\lambda)$ its absorption coefficient $\alpha$is calculated:

$$\alpha(\lambda) = (1/l)\cdot\ln\{T(\lambda)/(1-R(\lambda)^2\}. \quad (1)$$

It has been estimated, that in range of absorption coefficient area$\alpha \geq 10^3$см$^{-1}$ for investigated films, the Tauc method is used:

$$(\alpha h\upsilon)^{1/2} \sim (h\upsilon - E_g). \quad (2)$$

The optical band gap E_g area was determined from the spectral dependences of the absorption coefficient α in the area, the appropriate to edge of the fundamental absorption band, by extrapolation of experimental dependences $(\alpha h\upsilon)^{1/2} = f(h\upsilon)$ on the energy axis (Figure 5).



a) b)

Fig.5. Temperature dependence of electrical conductivity of virgin (a) and Bi modified (b) films $Ge_2Sb_2Te_5$

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For the $Ge_2Sb_2Te_5$ and $Ge_2Sb_2Te_5$<Bi> films optical energy band gap E_g were 0.67 and 0.59eV, respectively. The error in the determination was ± 0,01EgeV. Temperature dependence of electrical conductivity of $Ge_2Sb_2Te_5$ thin films were investigated on picoammeter Keithley-6485 at temperature range from 300 to 400 K. The direct current applied in electric field strength about 10^2 V/cm in the linear region of the volt-ampere characteristics. The samples have planar arrangement of electrodes with size of the gap about 100 μm. The heating rate of the samples was 2° per minute.

Figure 5 shows the temperature dependence of electrical conductivity σ(*T*) with different thickness and constructed in the coordinates *lg*(σ) - *1/T*. The figure 5 illustrates that σ(*T*) for films with different thickness are well described by an exponential law:

$$\sigma(T)=C\exp(-E_\sigma/\kappa T). \quad (3)$$

From dependencies σ(*T*) were determined the main semiconductor parameters of the films: electrical conductivity at room temperature (300 K) σ_r, activation energy E_σ. For $Ge_2Sb_2Te_5$ and $Ge_2Sb_2Te_5$<Bi> values σ_r and E_σ are $4.84*10^{-3}(Ohm*cm)^{-1}$and 0.45 eV and $2.82*10^{-1}$ $(Ohm*cm)^{-1}$ and 0.12 eV respectively. Error estimation of σ_r and E_σ don't exceed $\Delta\sigma_r$ ±0.2 for value ΔE_σ= ±0.02эВ. For explanation of the mechanism for the effect of impurities on the electronic properties of bismuth films can turn to model concepts proposed in [6]. For these model representations of the bismuth atoms in the modification form chemical bonds with the atoms of the matrix Bi-Te, Bi-Ge, Bi-Sb and are not electrically active. Among the chemical bonds dominate Bi connection with Te, since the energy of this connection has a minimum value and a stable compound known Bi2Te3. Since the chemical elements bismuth compounds matrix films are narrow-gap semiconductors, and this leads to a decrease in the optical band gap. Since the Fermi level is fixed approximately in the middle of the band gap, due to the decrease of Eg, decreases conductivity activation energy and, consequently, increased electrical conductivity.

Conclusion

In this work presented the influence of bismuth impurity on $Ge_2Sb_2Te_5$ films. The structure and electronic properties of GST<Bi> significantly changes with increasing of doping concentration. Changes in optical spectra can provide the possibility to use GST<Bi> films for optical storage devices. Thus, this study found that the method of ion-plasma sputtering is effective to control the electronic properties of the films$Ge_2Sb_2Te_5$in wide range.

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