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BISMUTH IMPURITY INFLUENCE ON ELECTRONIC PROPERTIES OF AMORPHOUS $As_{40}Se_{30}S_{30}$ FILMS ♣

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Influence of Bi impurity on the structure and electrical, photoelectrical and optical properties of amorphous $As_{40}Se_{30}S_{30}$ films have been studied. Bismuth concentration in the films was changed up to 20 at.%. Amorphous $As_{40}Se_{30}S_{30}$ films modified by Bi (a-$As_{40}Se_{30}S_{30}$<Bi> films) were prepared by RF sputtering of combined target glassy $As_{40}Se_{30}S_{30}$ and Bi. Electronic parameters of a-$As_{40}Se_{30}S_{30}$<Bi> films have essential differences from these of pure films, and the differences increase with Bi content in the films. Amorphous $As_{40}Se_{30}S_{30}$<Bi> films show significant increase of the photoconductivity under illumination. The results are well explained by a microheterogenious doping model of ChGS.

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1. Introduction

It is well known that one of the way of chalcogenide glasses semiconductors (ChGS) electronic properties effective control is the “cold” doping with metal impurity (Ovshinsky method) [1]. Impurity modification of ChGS represents a great interest both for non-crystalline semiconductor physics and for practice, by opening up possibilities of various amorphous-crystalline and amorphous semiconductor homo- and heterostructures fabrication [2].

Up to now the study of the impurity modification was carried out, mainly, for ChGS with binary stoichiometric compositions [3, 4]. The modification of a-$As_{40}Se_{30}S_{30}$ films, which have great possibilities of application in optical devices, was not accomplished.

This report presents the results of the study of Bi impurity influence on electronic properties of amorphous $As_{40}Se_{30}S_{30}$ films (a-$As_{40}Se_{30}S_{30}$<Bi> films). Bismuth was chosen as impurity because of his ability for changing of conductivity type in binary ChGS [3, 4].

2. Experimental technique

Amorphous $As_{40}Se_{30}S_{30}$ films modified by Bi were prepared by ion plasma RF sputtering of the combined ChGS-Bi target in the argon atmosphere at pressure ≈ 1 Pa. The Bi concentration in the films was dependent on the ratio of glassy $As_{40}Se_{30}S_{30}$ and Bi target areas and was changed up to 20 at.%.

The a-$As_{40}Se_{30}S_{30}$<Bi> films composition and morphology was monitored by the method of energy dispersive analysis on QUANTA 3D 200i electron scanning microscope.

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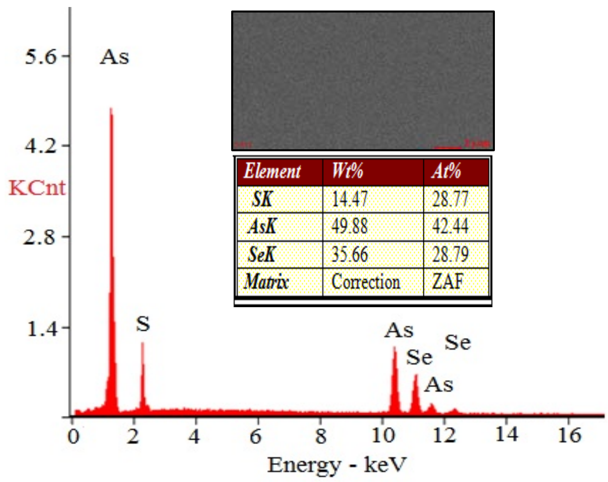
To stabilize a structure and electronic properties as-prepared films were annealed at temperature 440 K for 40 min. Study of the films composition and morphology was carried out on monocrystal Si substrates. For study of electrical and optical properties the films were deposited onto polyimide “Kapton” and polished glass substrates, respectively.

The electrical properties of the films were studied on samples with planar geometry. Aluminium was used as electrode material. Temperature dependences of conductivity were measured in the range from 300 to 440 K. Optical transmission spectra were obtained by SF-2000 spectrophotometer in the range from 300 to 1100 nm. These data were used to determine the optical absorption coefficient α with account of the film thickness. The optical gap of the studied films was determined from spectra of optical absorption at α corresponding to the fundamental absorption edge [5].

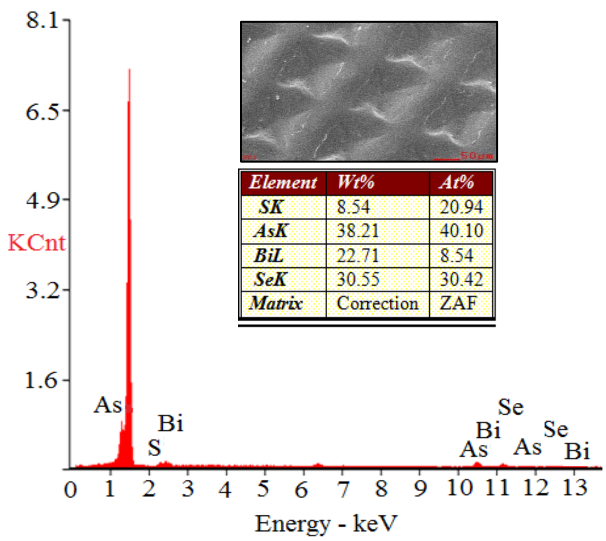
3. Results and discussion

Figs. 1 and 2 show the chemical composition and morphology of pure and Bi containing $As_{40}Se_{30}S_{30}$ films.



Element	Wt%	At%
SK	14.47	28.77
AsK	49.88	42.44
SeK	35.66	28.79
Matrix	Correction	ZAF

Fig. 1. Composition and morphology of pure $As_{40}Se_{30}S_{30}$ film



Element	Wt%	At%
SK	8.54	20.94
AsK	38.21	40.10
BiL	22.71	8.54
SeK	30.55	30.42
Matrix	Correction	ZAF

Fig. 2. Composition and morphology of $As_{40}Se_{30}S_{30}$ <8.54 at.%) Bi> film

It can be seen that the $As_{40}Se_{30}S_{30}$ <8.54 at.% Bi> film has sufficiently complicated surface. In pure film the deviation from stoichiometric composition is negligible and less than 2 at.%.

Temperature dependence of the dark dc conductivity and transmission spectra of a-$As_{40}Se_{30}S_{30}$<Bi> films were studied, and the room temperature conductivity σ_k (T=300 K), conductivity activation energy E_σ and optical gap E_g as well as ΔE_F (shift of Fermi level with respect to the midgap) were found. The obtained data for the films with various Bi content show in Fig. 3 and in the table.

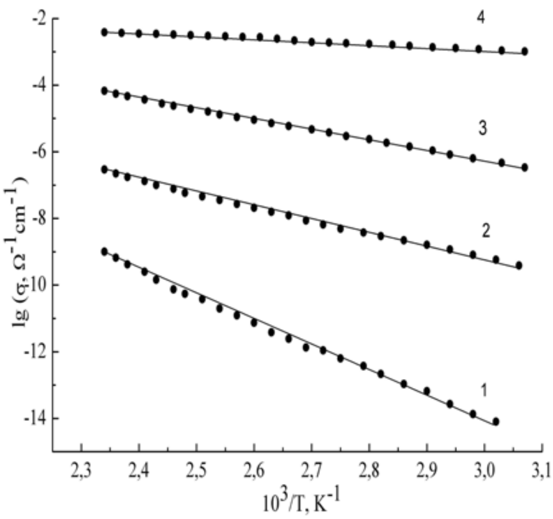


Fig. 3. Temperature dependence of dark conductivity for pure (1) and Bi containing $As_{40}Se_{30}S_{30}$ films: 2 –2.54 at.%, 3 –8.54 at.%, 4 - 19.78 at.%

One can see from figure 3 that $\sigma(T)$ dependence is described by relation $\sigma = C\cdot exp(-E/kT)$ [4, 5] with alone slope independently of Bi content in the films. It follows from data of the Table that electronic parameters of a-$As_{40}Se_{30}S_{30}$<Bi> films significantly differ from these of pure film, and the differences increase with Bi content in the films. Incorporation of Bi in a-$As_{40}Se_{30}S_{30}$ films result in essential increase of the films conductivity at room temperature (up to 14 order of magnitude) (figure 4) and decrease of energy activation of conductivity and optical band gap (figure 5). It should be noted that Bi impurity in the films don't leads to shifting of Fermi level with respect to the midgap. The negative sign of ΔE_F shows evidence for antiparallel fluctuations of allowed bands edges.

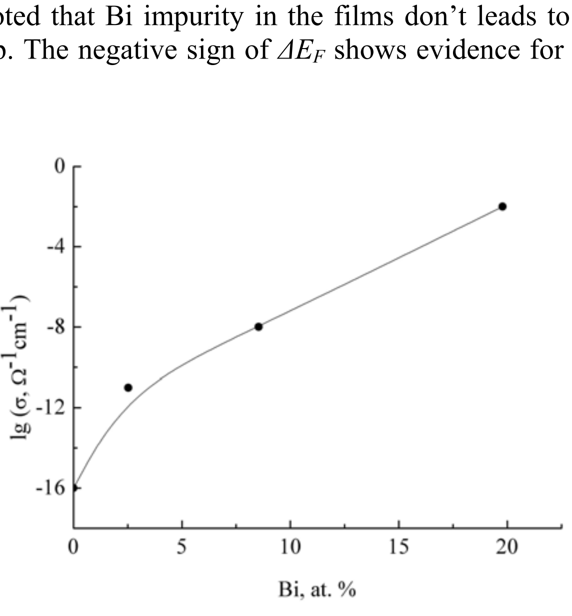


Fig. 4. Concentration dependence of conductivity at room temperature for a-$As_{40}Se_{30}S_{30}$<Bi> films

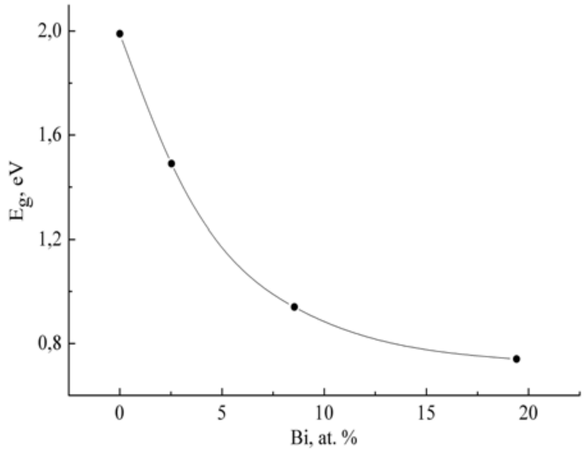


Fig. 5. Concentration dependence of optical band gap for a-$As_{40}Se_{30}S_{30}$<Bi> films

The increase of a-$As_{40}Se_{30}S_{30}$<Bi> films conductivity can be explained by E_g decrease so far as the shift of Fermi level with respect to the midgap is negligible. Optical band gap decrease in the films may be due to formation of solid solutions on the base of Bi impurity and S and Se atoms. It is known that these solid solutions are narrow gap semiconductors [6].

Table. The electronic parameters of a-$As_{40}Se_{30}S_{30}$<Bi> films with different Bi concentration

Bi concentration, at.%	$\sigma_к$, $(\Omega\cdot см)^{-1}$	E_σ, eV	E_g, eV	$\Delta E_F=E_g/2-E_\sigma$, eV
0	$1{,}04\cdot10^{-16}$	1,27	1,99	-0,27
2,53	$2{,}98\cdot10^{-11}$	0,78	1,49	-0,03
8,54	$5{,}38\cdot10^{-8}$	0,61	0,94	-0,14
19,78	$6{,}08\cdot10^{-2}$	0,41	0,74	-0,04

In the spectral region from 460 to 830 nm photoconductivity $\Delta\sigma_{ph}(\lambda)$ of a-$As_{40}Se_{30}S_{30}$<Bi> films at room temperature was measured (figure 6). The geometry of the samples was planar.

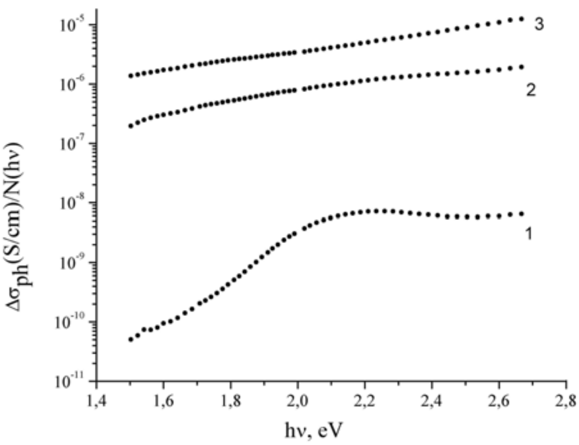


Fig. 6. Spectral dependence of photoconductivity for a-$As_{40}Se_{30}S_{30}$<Bi> films with different Bi content: 1 - 0 am.%, 2 - 2,54 am.%, 3 - 8,54 am.%

It can be seen that Bi incorporation in a-$As_{40}Se_{30}S_{30}$ films leads to essential rise of spectral response of photoconductivity (for example, up to 10^4 times for the films with 8.54 at. % Bi at 2 eV), and it is more pronounced in low energy region of the spectrum. It should be noted that linear type of $\Delta\sigma_{ph}(\lambda)$ dependences for a-$As_{40}Se_{30}S_{30}$<Bi> films is not typical of the most ChGS, and this peculiarity needs in further study. High photoconductivity a-$As_{40}Se_{30}S_{30}$ films modified by Bi with respect to that of pure films may be due to high charge carrier mobility in the modified films.

Similar patterns in change of the electronic properties as a result of the modification by bismuth were observed for As_2Se_3 films in [3, 4], and they are explained on the basis of microheterogeneous doping model of ChGS [4, 7]. According to this model we suggest that a-$As_{40}Se_{30}S_{30}$<Bi> films are heterogeneous and consist of amorphous matrix of ChGS that is depleted of bismuth and amorphous clusters of solid solutions of Bi, Se and S atoms.

4. Conclusion

Incorporation of Bi atoms in a-$As_{40}Se_{30}S_{30}$ films by the method of RF ion-plasma sputtering and variation of their concentration leads to significant change of the films electronic parameters in the wide range. These results open up the ways for the fabrication of various semiconductor homo- and heterostructures.

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References

[1] S.R. Ovshinsky. In: Proc. 7th Internat, Conf. on amorph. and liquid semiconductors.- Edinburgh, 519 (1977).

[2] Sh. Sh. Sarsembinov., O.Yu. Prikhodko V.L., Averyanov, S.Ya. Maksimova S.A. Dzakelov. J. Non-Cryst. Sol. **97-98**, 987 (1987).

[3] V.L. Averyanov, B.L. Gelmont, B.T. Kolomiets, V.M. Lyubin, O.Yu Prikhodko, K.D. Tsendin. J. Non-Cryst. Sol. **64,** 279 (1984).

[4] Ed. by K.D. Tsendin. Electronic phenomena in chalcogenide glasses semiconductors. St.Petersburg:. 486 p. (1996).

[5] N.F. Mott and E.A. Davis. Electron Processes in Non-Crystalline Materials. Oxford. 660 p. (1979)

[6] T.E. Manjulalli, T. Balasubramanian, D. Nataraj. Chalcogen. Lett. **5**, 297 (2008).

[7] N.Zh. Almasov, O.Yu. Prikhodko, K.D. Tsendin. Semicond. **46**, 1296 (2012).