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Structure and electronic properties of amorphous $\text{As}_{40}\text{Se}_{30}\text{S}_{30}$ films prepared by ion-plasma sputtering method

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The atomic and local structure, as well as the electrical, optical, photoelectrical properties and drift mobility of charge carriers in amorphous $\text{As}_{40}\text{Se}_{30}\text{S}_{30}$ films, prepared by the method of RF ion-plasma sputtering (RF-films), were studied in comparison with those of the films, prepared by the method of thermal vacuum evaporation (TE-films). These two methods differ significantly in the conditions of substance vaporization and condensation of atoms on a substrate.

It was found that the films fabricated by the different methods have differences in structure and electronic parameters. The essential differences in photoconductivity and transport phenomena are observed, too.

It was concluded that RF $\text{As}_{40}\text{Se}_{30}\text{S}_{30}$ films have a modified structure. This leads to changes in the spectrum of extended and localized electronic states in these films, which, in its turn, causes differences in their electronic properties.

Key words: ion-plasma sputtering, RF-films, photoconductivity.

PACS numbers: 68.55.-a, 73.61.-r

1 Introduction

It was shown earlier that electronic properties of amorphous As_2Se_3 and As_2S_3 films, arsenic containing chalcogenide glassy semiconductors (ChGS) of binary composition, are strongly influenced by structure modification as a result of their preparation by ion-plasma sputtering method [1, 2]. Redistribution in electron energy spectrum in these modified films be assumed in the first place is due to As atoms presence in composition of the films. As a consequence it is of interest to study the films preparation technique influence on electronic properties of amorphous $\text{As}_{40}\text{Se}_{30}\text{S}_{30}$ films, arsenic containing ChGS of triple composition.

In this work the results of complex investigation of atomic and local structure, electrical, optical and photoelectrical properties as well as carrier drift mobility in $\text{As}_{40}\text{Se}_{30}\text{S}_{30}$ amorphous films, prepared by the methods of RF sputtering (RF films) in comparison to the results of the films prepared by thermal vacuum evaporation (TE films) are described.

2 Experimental

For the films fabricated by sputtering of a bulk ChGS target of the initial composition, the process was carried out in argon atmosphere at a frequency of 13.56 MHz and a pressure ~ 1 Pa. Fabrication of the films by evaporation was carried out in a vacuum of $\sim 4 \cdot 10^{-3}$ Pa on substrates kept at a room temperature. In the both methods The preparation parameters were selected so as to produce amorphous films with composition corresponding to that of the starting ChGS and having the maximum possible carrier drift mobility. The latter parameter is known to be one of the most structure-sensitive for semiconductor materials [3, 4]. The thickness of the obtained films was varied from 0.5 to 5 μm .

To stabilize the structure and properties as-prepared films were annealed at temperature close to glass transition temperature of $\text{As}_{40}\text{Se}_{30}\text{S}_{30}$ 440 K for 30 min. The composition, morphology and amorphicity of the prepared films were determined by scanning electron microscope Quanta 3D 200i

using energy-dispersive analysis and x-ray diffraction analyses, respectively.

The atomic structure of the amorphous films (the short- and medium range order in the atomic arrangement) was studied by x-ray diffraction analysis using $\text{CuK}\alpha$ radiation ($\lambda=1.5418\text{\AA}$). The x-ray grazing angle was constant and equal to 4.52° . The intensity of reflected x-rays was recorded in the range of diffraction angles 2θ from 5° to 140° . The results were reproducible within 2%.

The local structure of the films was analyzed by means of Raman spectroscopy. The Raman spectra were recorded at room temperature on T64000 (Horiba Jobin Yvon) spectrometer using light of DPY Nd:YAG laser (532 nm). Vertically polarized light of lasers were used in the backscattering (at an angle of 180°) mode. The number of accumulations was the same at all measurements and equal to 25. The measurement error was $\pm 1 \text{ cm}^{-1}$.

The temperature dependence of the films conductivity was measured in the range from 300 to 430 K. The planar structure samples were used. The optical gap E_g of the films was found from spectral characteristics of absorption according to Tauc relation $(ahv)^{1/2} \sim (hv - E_g)$ (where $h\nu$ is the photon energy), at absorption coefficient α corresponding to the fundamental absorption edge.

Charge carrier transport was studied at a room temperature using time-of-flight technique [3-5], with carriers injected into a sample by a 10 ns pulse of strongly absorbed light ($0.337 \mu\text{m}$). Films photoconductivity was studied using standard technique.

3 Results and discussion

Figures 1 and 2 show the chemical composition and morphology of amorphous RF and TE $\text{As}_{40}\text{Se}_{30}\text{S}_{30}$ films.

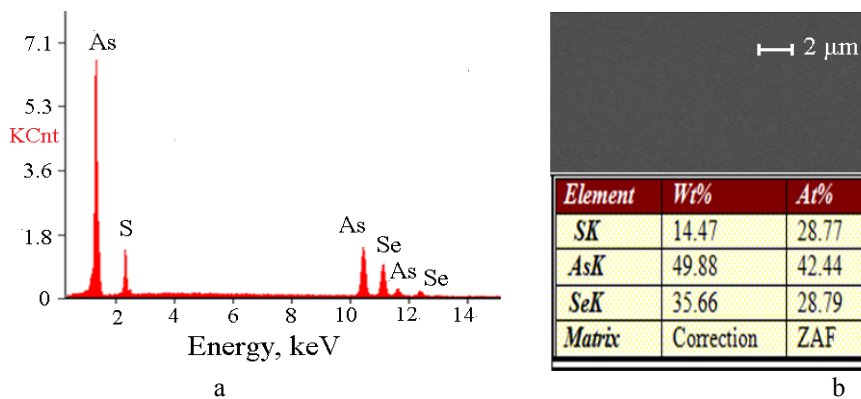


Figure 1 – Energy-dispersive spectrum (a) and morphology (b) of RF $\text{a-As}_{40}\text{Se}_{30}\text{S}_{30}$ film

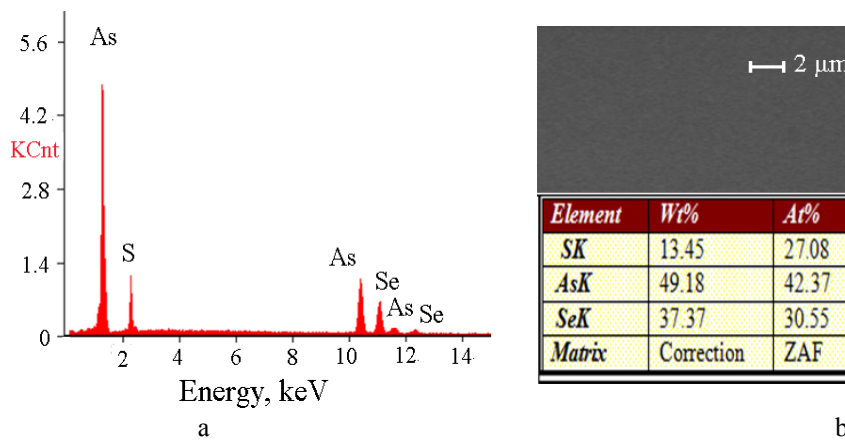


Figure 2 – Energy-dispersive spectrum (a) and morphology (b) of TE $\text{a-As}_{40}\text{Se}_{30}\text{S}_{30}$ film

The results show that the $\text{a-As}_{40}\text{Se}_{30}\text{S}_{30}$ films prepared by both methods are continuous, and there are no unintentional impurities and the submicron sized defects in these films.

The composition of the films differed from that

of initial material by less than 3% regardless of the preparing method.

Figure 3 (a, b) shows angular dependences of the x-ray diffraction intensity $I(2\theta)$ for RF and TE $\text{a-As}_{40}\text{S}_{30}\text{Se}_{30}$ films.

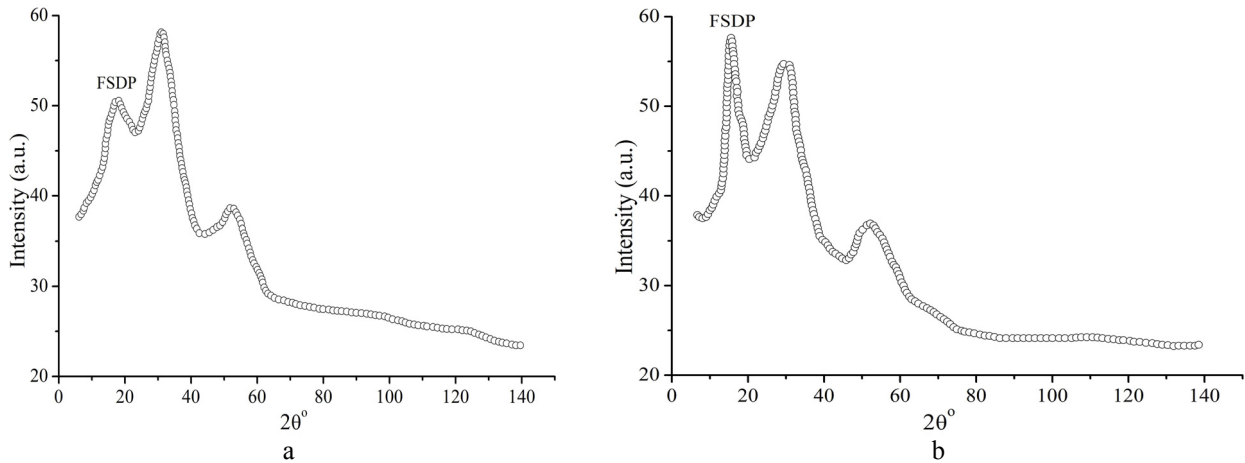


Figure 3 – X-ray diffraction patterns for RF (a) and TE (b) $\text{a-As}_{40}\text{S}_{30}\text{Se}_{30}$ films

It can be seen, that there are three distinct peaks on $I(2\theta)$ curves for films prepared by both methods. However, the diffraction peak amplitudes and peak half-widths differ for RF and TE films. These distinctions are particularly well seen for the first sharp diffraction peak (FSDP) in the curves. The FSDP curves made it possible to determine the wave factor S , at which the FSDP maximum is observed ($S = 4\pi \cdot \sin(\theta_{max1})/\lambda$, where θ_{max1} is the angle of the FSDP maximum; λ is the x-ray wavelength). FSDP on $I(2\theta)$ curves for RF and TE films are situated at $2\theta = 16.5^\circ$, and $S=1.17 \text{ \AA}^{-1}$. Linear dimensions of the local structural order regions (medium-range order), characterized by the parameter $L = 0.9 \cdot \lambda / [B(2\theta) \cos(\theta_{max1})]$, where $B(2\theta)$ is the FSDP half-widths in radians, were estimated using the Scherrer's formula [6]. Medium range order parameter has been estimated to be 15 \AA and 24 \AA for RF and TE films, respectively. The 'quasi-period' d of the structure, whose existence within a certain correlation region gives rise to FSDP, was estimated using an approximate expression $d \approx 2\pi/S_{\text{FSDP}}$. For RF and TE films studied, d is 5.2 and 5.5 \AA , respectively.

It should be noted that the difference in the short-range order structural parameters of RF and TE films is far from being as significant as the difference in the medium range order parameter L .

The shorter dimension of the medium-range order region for RF films indicates that the structure of these films is more disordered. Besides, the photostructural changes in RF films are less obvious. It follows that the structure of these films is more rigid than that of the TE films.

Figure 4 shows the Raman spectra of RF and TE films. It can be seen that the spectrum of RF films as well as that of TE films have two general broad bands corresponding to vibrations of pyramidal structure units $\text{AsSe}_{3/2}$ (in the range from 200 to 300 cm^{-1}) and $\text{AsS}_{3/2}$ (in the range from 300 to 400 cm^{-1}). It follows that these pyramidal structure units are general units in the network of studied films. The peaks that modulate the contour of the bands and the frequencies of the peaks point on the presence of a great number of homopolar bonds such as As-As, Se-S, Se-Se and S-S in the network of the RF and TE films [7-9]. However the spectra of both RF and TE films have significant differences in the shape and intensity above mentioned general bands. In the spectra of RF films one can see a great number of clear recorded additional peaks that modulate the contour of the bands. Thus in RF films one can see the peaks with low intensity at frequencies $114, 167, 183, 202, 211, 218 \text{ cm}^{-1}$ on the slope of the band (from 200 to 300 cm^{-1}) at low frequency region. These peaks

correspond to different types of As-As and As-Se bond vibrations in structural molecular units such as $AsSe_{4/2}$, As_4Se_4 and As_4Se_3 . These structural units can be present in the network of triple composition As-Se-S films because of their

presence in the structure of the binary stoichiometric composition As_2Se_3 and As_2S_3 films [8-9]. The revealed differences in Raman spectra show significant differences in local structure of RF and TE films.

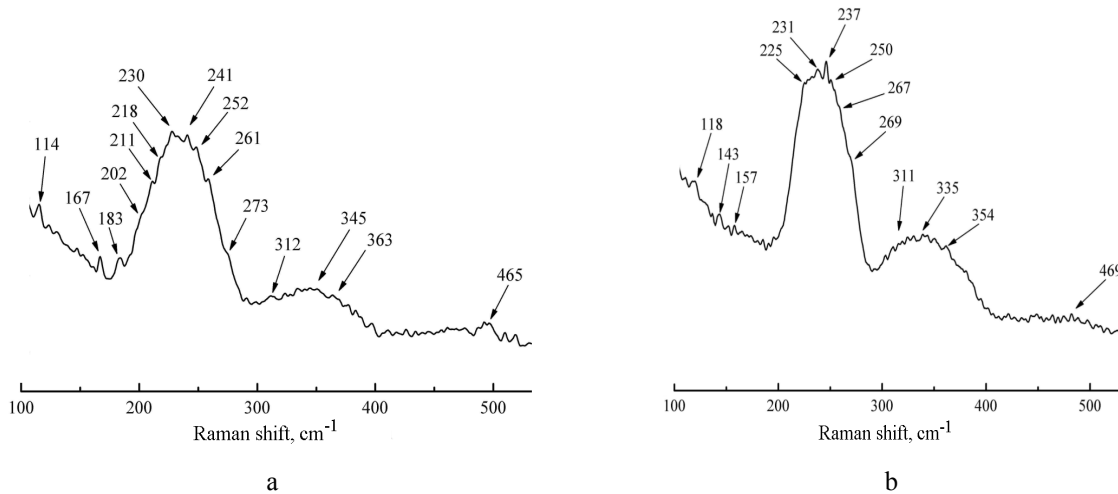


Figure 4 – Raman spectra of a- $As_{40}S_{30}Se_{30}$ films: (a) RF film and (b) TE film

The results we obtained in studying the electrical and optical properties of amorphous RF and TE films were used to determine the following parameters of the films: conductivity σ at $T= 300 K$; activation energy of conductivity E_{σ} and optical band gap E_g as well as ΔE_F (shift

of Fermi level with respect to the midgap) (Table). The error in these parameters, resulting from data scatter from sample to sample, are about half an order of magnitude for σ , $\Delta E_{\sigma} = \pm 0.02 eV$ and $\Delta E_g = \pm 0.01 eV$ for the activation energy and optical gap.

Table – Electronic parameters of amorphous RF and TE $As_{40}S_{30}Se_{30}$ films

Films	$\sigma(T=300 K)$, $Ohm^{-1}\cdot cm^{-1}$	E_{σ} , eV	C , $Ohm^{-1}\cdot cm^{-1}$	E_g , eV	$\Delta E_F = E_g/2 - E_{\sigma}/2$, eV
RF	$6 \cdot 10^{-16}$	1.02	$3 \cdot 10^3$	1,89	- 0.08
TE	$1 \cdot 10^{-15}$	0.96	$4 \cdot 10^3$	2,08	0.08

One can see from the Table that the parameters of the RF and TE films are different. The RF films are characterized by lower conductivity, higher activation energy of conductivity and narrower optical gap. The contradiction between lower conductivity at narrow band gap can be accounted for by invoking concepts of the physics of amorphous semiconductors, concerning the antiparallel energy fluctuations of the band gap [3].

The spectral dependence of photoconductivity of the amorphous RF and TE films was measured in

longitudinal regime at electric field strength ranging from 10^2 to $10^4 V/cm$ [10]. The “sandwich” structure samples were studied. It was found that the dependences for the RF and TE films have significant difference in short wavelength region (Figure 5). It is seen from Figure 5, that in TE films the photorectification takes place. On the contrary, the spectral characteristics of RF films don’t depend on the voltage polarity on illuminated electrode that is the evidence in favor of bipolar photoconductivity in these films.

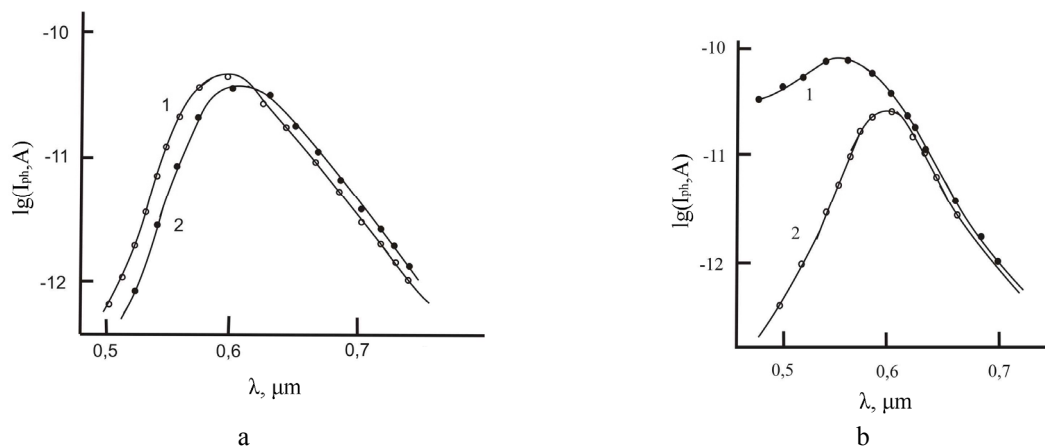


Figure 5 – Spectral dependence of longitudinal photocurrent in RF (a) and TE (b) $\text{a-As}_{40}\text{S}_{30}\text{Se}_{30}$ films: 1 – positive and 2 – negative voltage polarity on illuminated electrode

Significant differences can be seen in charge carrier drift mobility μ studying for TE and RF films ($E=10^5$ V/cm, $T=300$ K) (Figure 6). The mobile charge carrier in TE films are the holes only ($\mu_p \approx 10^{-6}$ cm²/(V·s)), but in RF films both electrons and holes are mobile ($\mu_p \approx \mu_n \approx 10^{-6}$ cm²/(V·s)), that is the bipolar charge carrier transport occur.

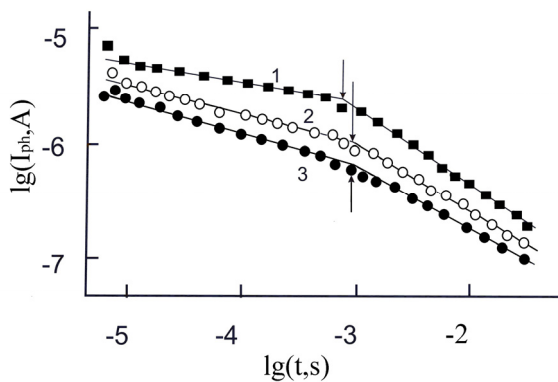


Figure 6 – Transient hole (1, 2) and electron (3) photocurrents in $\text{a-As}_{40}\text{S}_{30}\text{Se}_{30}$ TE (1) and RF(2, 3) films

The results of our photoconductivity and charge carrier drift mobility study are indicative of considerable redistribution in localized electron states controlling electron transport in RF films.

It should be noted that observed features in the differences of structure and electronic properties of RF and TE $\text{a-As}_{40}\text{S}_{30}\text{Se}_{30}$ films are similar to those for RF and TE As_2Se_3 and As_2S_3 films [1, 2, 11], that is the evidence in favor of important role of arsenic atoms in structure modification of RF films of arsenic containing lower coordinated ChGS.

4 Conclusion

Thus, the use of RF ion-plasma sputtering method for preparation of amorphous $\text{As}_{40}\text{Se}_{30}\text{S}_{30}$ films makes it possible to modify electronic properties of the films by changing their structure and opens new opportunities for controlling the electronic properties of amorphous films of arsenic containing chalcogenide glassy semiconductors.

Acknowledgments

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