ФИЗИКА КОНДЕНСИРОВАННОГО СОСТОЯНИЯ И ПРОБЛЕМЫ МАТЕРИАЛОВЕДЕНИЯ

EFFECT OF THERMAL AND LIGHT IRRADIATIONS ON OPTICAL PROPERTIES AND SHORT- AND MEDIUM-RANGE ORDER IN ATOMIC STRUCTURE OF AMORPHOUS CHALCOGENIDE FILMS PREPARED BY DIFFERENT METHODS

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The changes in optical properties and atomic structure of as-prepared amorphous As_2Se_3 and As_2S_3 films upon annealing and light irradiation have been studied. The films were prepared by the methods of thermal evaporation in a vacuum and radio frequency ion plasma sputtering. It was found that after the thermal and light irradiations the optical transmission edge of the films is shifted and there are some changes in atomic film structure. The most essential changes in atomic structure and optical properties as well as a correlation between the changes in the medium-range order of the atomic structure and the optical band gap have been revealed in the TE films7.

1. Introduction

The effect of short- and medium-range order of atomic structure in the non-crystalline materials on their electrical properties is one of the main problems in non-crystalline solid physics [1-3]. It is more actual for the chalcogenide glassy semiconductors (ChGSs) with structural lability due to low coordination of their atoms [1-6]. One can change, to some extent, ChGS films structure using external influences (such as light irradiation and annealing [2-6]) and different methods of preparation [2, 7, 8]. Changes in films atomic structure lead to modification of their thermodynamic, electrical and optical properties [3-6]. In particular, some changes in the position of absorption band edge, which is determined by its energy gap, are observed. Most of investigations deal with TE films of As_2Se_3 and As_2S_3 stoichiometric composition, which are the model object for ChGSs properties investigation.

This study is devoted to the results of comparative investigations of the thermal and light irradiation effect on optical properties and short- and medium range order in atomic structure of amorphous As_2Se_3 and As_2S_3 films obtained by different methods. ChGS films were prepared by thermal evaporation in a vacuum (TE films) and RF ion plasma sputtering (RF films) – two techniques differ essentially in the conditions of substance vaporization and condensation of atoms and molecules on a substrate.

2. Experimental procedures

The technique of amorphous As_2Se_3 and As_2S_3 preparation by TE and RF methods is described in [7, 8]. The films were deposited onto polished glass substrates, and their thickness was varied between 4 and 12 μm. As-prepared films were annealed for an hour. The annealing temperature was 150^{o}C and 165^{o}C for a-As_2Se_3 and a-As_2S_3, respectively. Light irradiation of the films was carried out by a lamp of 150 W with tungsten filament. The focusing lens, IR-cut and optical filters were used as well. The light filters were chosen so that it could transmit the light photons with the energy corresponding to the fundamental absorption band. The exposure time was 4 hours.

Spectral characteristics of the films optical transmission were measured in the wavelength range from 0.4 to 0.75 μm at T=300 K. The optical gap E_g was determined from spectral transmission characteristics at absorption coefficients corresponding to the fundamental absorption edge by extrapolating the dependence $(\alpha h\nu)^{1/2} = f(h\nu)$ to the axis of energy. The measurement error was ± 0.01 eV.

The parameters of short- and medium-range order in the atomic structure of amorphous films were determined by x-ray diffraction analysis. The intensities of the reflected x-rays were recorded at the constant grazing angle of 4.52°. The wavelength λ of X-ray monochromatic radiation was 1.5418 Å. The error in the coordination sphere radii was $\Delta R = \pm 0.01$ Å, and in the number of nearest neighbors - $\Delta Z = \pm 0.1$.

3. Results and discussion

Figures 1-4 show the effect of the thermal and light irradiation on optical transmission spectra for amorphous As_2Se_3 and As_2S_3 films. It is seen that annealing and irradiation shift the optical transmission edge of TE films towards long wavelength region of the spectrum. On the contrary, the optical transmission edge of RF films shifts towards shorter wavelengths during the annealing process. The following irradiation leads to the shift of the transmission spectrum to the longer wavelength region both for RF films and TE films. Table 1 shows thermal and light irradiations influence on the optical band gap of the films.

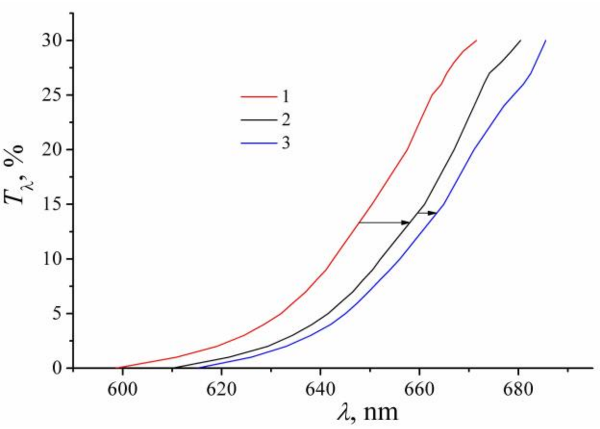


Fig. 1. Spectral transmission characteristics of as-prepared (1), annealed (2) and irradiated (3) TE a-As_2Se_3 films

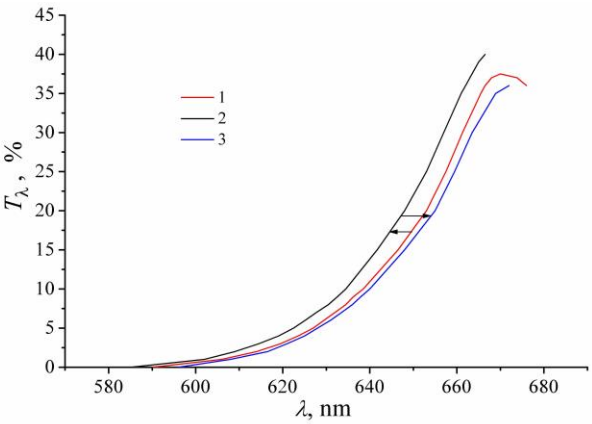


Fig. 2. Spectral transmission characteristics of as-prepared (1), annealed (2) and irradiated (3) RF a-As_2Se_3 films

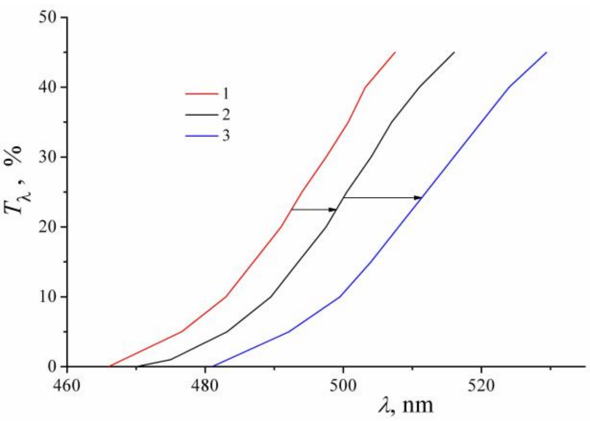


Fig. 3. Spectral transmission characteristics of as-prepared (1), annealed (2) and irradiated (3) TE a-As_2S_3 films

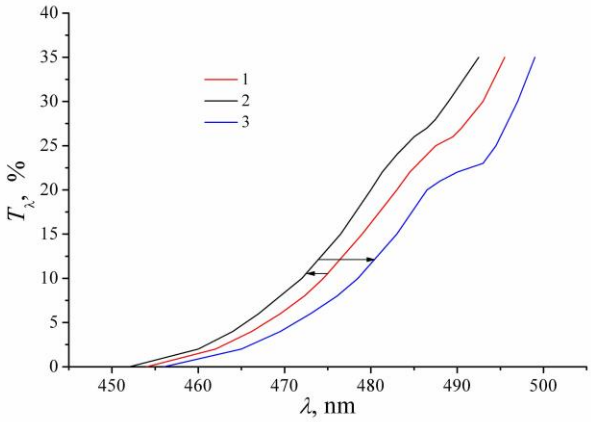


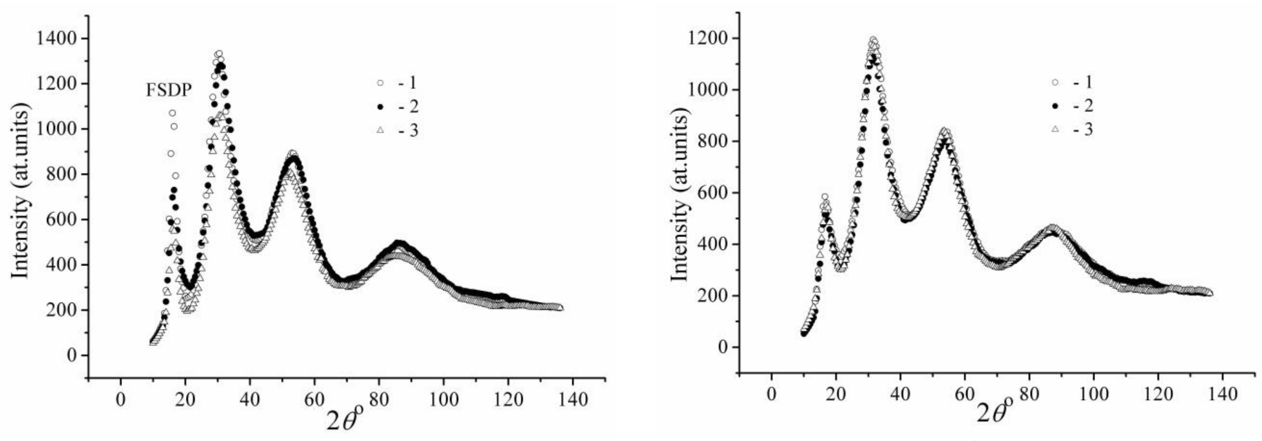
Fig. 4. Spectral transmission characteristics of as-prepared (1), annealed (2) and irradiated (3) RF a-As_2S_3 films

It should be noted that thermal and light irradiations have more influence on the optical properties of TE-films than those of RF-films.

Table 1. Optical band gap E_g of as-prepared, annealed and irradiated TE and RF a-As_2Se_3 and a-As_2S_3 films

Composition		As_2Se_3		As_2S_3	
Films		TE	RF	TE	RF
E_g, эВ	as-prepared	1.81	1.75	2.43	2.25
	Annealed	1.78	1.76	2.38	2.28
	irradiated	1.73	1.74	2.33	2.24

The effect of annealing and light irradiation on x-ray diffraction patterns *I (2θ)* for as-prepared TE- and RF a- As_2Se_3 and As_2S_3 films is presented in figures 5-8. Figure 5a shows that annealing of TE-films leads to essential decrease of the first sharp diffraction peak (FSDP) and slight decline of the second diffraction peak. The other part of diffraction spectrum is not changed. Light irradiation reduces the intensity and half-width of the peaks.



a) b)

Fig. 5. X-ray diffraction intensity versus diffraction angle for TE- (a) and RF- (b) a-As_2Se_3 films: 1- as-prepared, 2- annealed and 3-irradiated

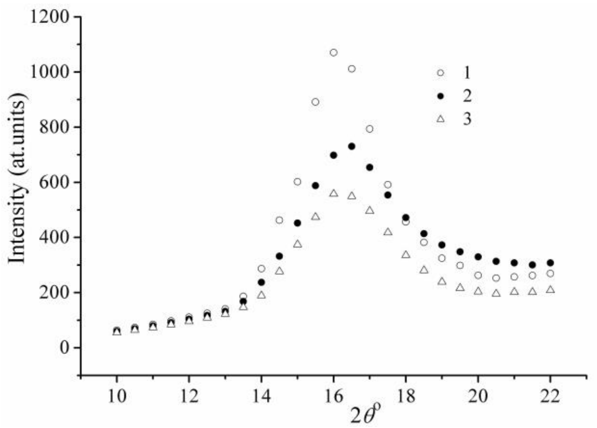
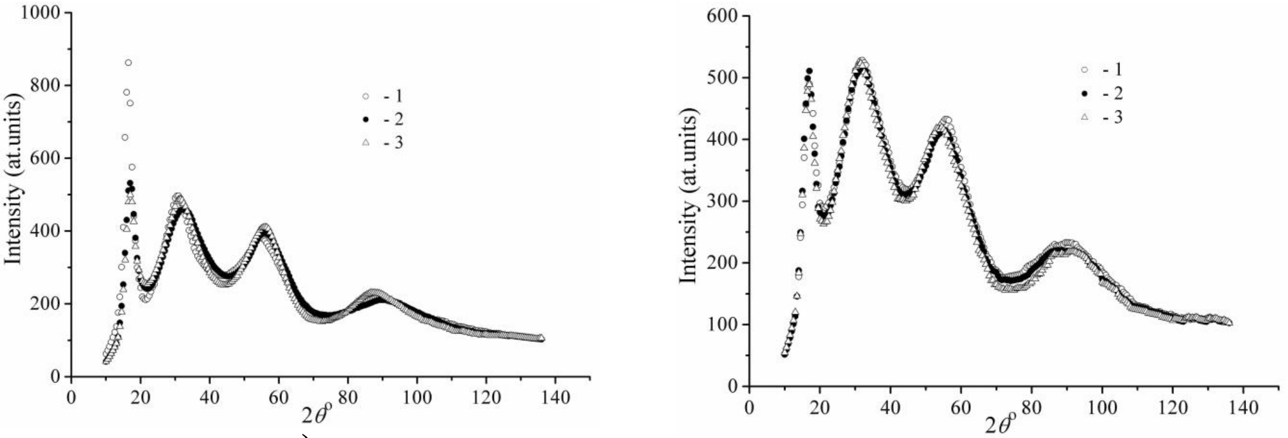


Figure 6. FSDP of as-prepared (1), annealed (2) and irradiated (3) TE a-As_2Se_3 films

The influence of annealing and light irradiation on the FSDP of the films in more detail is shown in Figure 6. After annealing the FSDP intensity for as-prepared TE films is 30 % less and the intensity maximum shifts to the greater diffraction angles. The further irradiation decreases the FSDP intensity by ~ 18 % and the maximum shifts practically to its original position. For as-prepared, annealed and irradiated TE films the *2θ* angles of FSDP maxima are 16.1°, 16.4° and 16.2°, respectively.

The dependence $I(2\theta)$ for as-prepared, annealed and irradiated RF a-As_2Se_3 films is shown on figure 5b. It can be seen the slight influence of annealing and irradiation on curves $I(2\theta)$. Slight distinctions are observed in the region of FSDP at 2θ scattering angles exceeding 100^o.



a) b)

Figure 7. X-ray diffraction intensity versus diffraction angle for TE- (a) and RF- (b) a-As_2S_3 films: 1 - as-prepared, 2 - annealed и 3 - irradiated

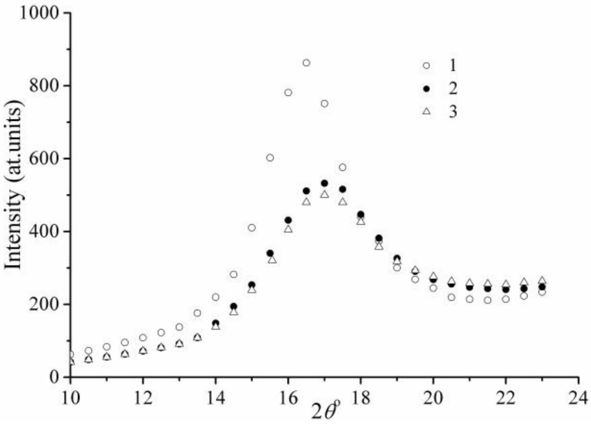


Figure 8. FSDP of as-prepared (1), annealed (2) and irradiated (3) TE a-As_2S_3 films

The $I(2\theta)$ curves were used to calculate the atomic radial distribution functions (RDF) and the short-range order parameters for amorphous TE and RF As_2Se_3 films, namely, the radii of the first r_1 and the second r_2 coordination spheres, the number of the nearest neighbours of arsenic Z_{As} and selenium Z_{Se} atoms in the first coordination sphere as well as the valence angles between the bonds φ and their change $\Delta\varphi$. Linear dimensions of the regions of local structural order, i. e. medium-range order is characterized by parameter $L=0.9\lambda/[\beta(2\theta)\cos(\theta_{\mathrm{maxFSDP}})]$, where $\beta(2\theta)$ is the FSDP half-width in radians and $2\theta_{\max}$ is the angle of the FSDP maximum , were estimated using FSDP curves by Scherrer's formula.

Using an approximate relation $d\approx 2\pi/S$, where $S=4\pi\sin\theta_{\mathrm{maxFSDP}}/\lambda$, the estimation of "quasi-period" d of the structure was carried out.

It can be seen from the Table 2 that annealing and irradiation cause insignificant variations in short- and medium-range parameters for RF As_2Se_3 films in comparison with TE-films.

The results of thermal and light irradiations effect on $I(2\theta)$ for as-prepared TE and RF a-As_2S_3 are presented in figures 7,8. Figure 7a shows significant difference in the first diffraction peak for as-prepared TE-films due to annealing and irradiation. The FSDP is sharper in as-prepared films (Figure 8) rather than in annealed and irradiated films. Besides, the FSDP intensity is far higher for as-prepared films (by ~ 38 % and ~ 44 %) comparing with annealed and irradiated samples, respectively. The angle (2θ) of FSDP maximum for as-prepared films comes to 16.5°. Annealing and irradiation shift slightly (by ~0.5°) the FSDP maximum towards the greater angles.

The effect of annealing and irradiation on $I(2\theta)$ is insignificant for RF a-As_2S_3 films in contrast with TE films (Figure 7b). The obtained short and medium range order parameters for TE and RF As_2S_3 films are listed in Table 3. The data indicate that annealing and light irradiation have a pronounced effect on TE films atomic structure parameters and, mainly, on medium-range order parameter L of atomic structure.

Table 2. Parameters of short- and medium-range order of the atomic structure for as-prepared, annealed and irradiated TE and RF a-As_2Se_3 films

Films	TE			RF		
External influence	as-prepared	annealing	irradiation	as-prepared	annealing	irradiation
Z_{As}	3.4	3.3	3.5	3.2	3.2	3.2
Z_{Se}	2.3	2.2	2.4	2.1	2.1	2.1
R_1, Å	2.35	2.40	2.45	2.40	2.39	2.42
R_2, Å	3.71	3.70	3.67	3.65	3.67	3.66
$\varphi \pm \Delta\varphi$	102°±27°	101°±25°	97°±22°	99°±26°	100°±25°	95°±23°
L, Å	31	22	19	13	12	14
d, Å	5.5	5.5	5.4	5.4	5.2	5.2

Table 3. Parameters of short- and medium-range order of the atomic structure for as-prepared, annealed and irradiated TE and RF a-As_2S_3 films

Films	TE			RF		
External influence	as-prepared	annealing	irradiation	as-prepared	annealing	irradiation
Z_{As}	3.8	3.6	3.9	4.0	3.9	3.8
Z_S	2.5	2.4	2.6	2.7	2.6	2.5
R_1, Å	2.30	2.29	2.36	2.34	2.35	2.35
R_2, Å	3.58	3.52	3.59	3.54	3.54	3.53
$\varphi \pm \Delta\varphi$	103°±28°	100°±26°	96°±23°	98°±23°	97°±24°	99°±27°
L, Å	38	21	18	14	17	15
d, Å	5.4	5.2	5.2	5.2	5.3	5.2

It can be concluded that annealing and light irradiation mainly effect on the parameters of atomic structure of TE a-As_2Se_3 and a-As_2S_3 films, and the essential changes occur in medium-range order parameter L.

Let us analyze the change of E_g and L parameters in TE films. These parameters decrease markedly during annealing of as-prepared TE a-As_2Se_3 and a-As_2S_3 films. The further irradiation leads to substantial decrease of E_g and L parameters as well. Thus, change in the medium-range order of the atomic structure is correlated with change in the optical gap of these films.

It should be noted that medium range order parameter L, which characterizes linear dimensions of the regions of local structural order, has much lower value for RF films in comparison with that of TE films. That is the evidence that the RF films structure at the medium-range order level is more disordered than in TE films. Note that while investigating the local structures of the films by Raman spectroscopy we found that RF films have much complicated local structure, i.e. RF film matrix contain, along with the structural units common to TE films, other structural units with As-As bonds predominance.

4. Conclusion

The results of annealing and irradiation effect on optical properties and atomic structure of a-As_2Se_3 and a-As_2S_3 films show that the films prepared by radio frequency ion-plasma sputtering have more rigid structure compared with the films prepared by thermal evaporation in a vacuum.

Changes in medium-range order of the atomic structure in TE films are correlated with changes in the optical gap of these films under annealing and irradiation processes.

Differences in atomic structure of TE and RF films seem to be caused by essentially different conditions of substance vaporization and condensation of atoms and molecules on a substance in two techniques.

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ӘРТҮРЛІ ӘДІСТЕРІМЕН ДАЙЫНДАЛҒАН БОСҚЫЛ ХАЛЬКОГЕНИДТІ ҚАБЫРШАҚТАРЫНЫҢ АТОМДЫҚ ҚҰРЫЛЫМНЫҢ ЖАҚЫН ЖӘНЕ ОРТАША РЕТТЕРІНДЕГІ ҚАСИЕТТЕРІНЕ ЖӘНЕ ПАРАМЕТРЛЕРІНЕ ЖЫЛУЛЫҚ ЖӘНЕ ЖАРЫҚ СӘУЛЕЛЕНДІРУДІҢ ТҮСІРЕТІН ЫҚПАЛЫ

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Жарықпен сәулелендірудің және қыздырудың әсерінен жаңадан дайындалған As_2Se_3 және As_2S_3 босқыл қабыршақтардың оптикалық қасиеттерінің және атомдық құрылымның өзгеруі зерттелген. Қабыршақтар вакуумдағы термиялық булану және жоғары жиілікті иондық-плазмалық шашырау әдістерімен алынған. Жылулық және жарықтық сәулелендірудің әсерінен қабыршақтардың оптикалық жұтудың шеті ығысатыны және қабыршақтардың атомдық құрылымында өзгерістер пайда болатыны анықталған. Атомдық құрылымында және оптикалық қасиеттеріндегі көптеген өзгерістер және атомдық құрылымның орташа ретіндегі өзгерістерімен және тыйым салынған зонаның оптикалық еніндегі арасындағы корреляция термиялық булану әдісімен алынған қабыршақтарда пайда болатыны байқалған.

ВЛИЯНИЕ ТЕПЛОВОГО И СВЕТОВОГО ОБЛУЧЕНИЯ НА ОПТИЧЕСКИЕ СВОЙСТВА И ПАРАМЕТРЫ БЛИЖНЕГО И СРЕДНЕГО ПОРЯДКОВ АТОМНОЙ СТРУКТУРЫ АМОРФНЫХ ХАЛЬКОГЕНИДНЫХ ПЛЕНОК, ПРИГОТОВЛЕНННЫХ РАЗНЫМИ МЕТОДАМИ

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Исследованы изменения оптических свойств и атомной структуры свежеприготовленных аморфных пленок As_2Se_3 и As_2S_3 при отжиге и облучении светом. Пленки приготавливались методами термического испарения в вакууме и высокочастотного ионно-плазменного распыления. Установлено, что после теплового и светового облучений край оптического поглощения пленок сдвигается, и имеют место изменения в атомной структуре пленок. Наибольшие изменения в атомной структуре и оптических свойствах, а также корреляция между изменениями в среднем порядке атомной структуры и оптической шириной запрещенной зоны были обнаружены у пленок, полученных методом термического испарения.