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UDC 539

OPTICAL PARAMETERS OF As-DEPOSITED AND ANNEALED $(Ga_{0.3}In_{0.7})_2Se_3$ THIN FILMS

The $(Ga_{0.3}In_{0.7})_2Se_3$ *films deposited by the thermal evaporation technique are annealed in the inert atmosphere (argon) for 1 h at temperatures of 50, 100, and 150 °C. The spectral ellipsometry is applied for measuring the spectral dependences of the refractive and extinction coefficients of as-deposited and annealed* $(Ga_{0.3}In_{0.7})_2Se_3$ *films. The optical transmission spectra, as well as the optical absorption spectra of* $(Ga_{0.3}In_{0.7})_2Se_3$ *films, are studied depending on the annealing temperature. The optical absorption edge for annealed* $(Ga_{0.3}In_{0.7})_2Se_3$ *films is shifted to the short-wavelength region and broadens, as the annealing temperature increases. Parameters of the Urbach absorption edge are determined for as-deposited and annealed* $(Ga_{0.3}In_{0.7})_2Se_3$ *films. The spectral dependences of the refractive index are analyzed in the framework of the Wemple–DiDomenico model. The nonlinear increase of the energy pseudogap, Urbach energy, and refractive index with the annealing temperature are revealed.*

Keywords: thin film, spectral ellipsometry, transmission spectra, refractive index, energy pseudogap, Urbach energy.

1. Introduction

Semiconducting $(Ga_xIn_{1-x})_2Se_3$ solid solutions with $0.02 < x < 0.55$ belong to the defect wurtzite structure with the hexagonal symmetry [1]. They are characterized by a high concentration of vacancies that can form spirals along the optical axis c of the crystal [2]. The alternation of cations and vacancies results in random fluctuations of the lattice electric potential which, in turn, affects physical properties of the above-mentioned semiconductors. The optical absorption edge in γ_1-$(Ga_xIn_{1-x})_2Se_3$ solid solutions at low absorption levels is shown to be formed by indirect interband optical transitions [3], the temperature effect on the absorption edge being studied in Ref. [4]. At high absorption levels in the range of direct interband optical transitions, the absorption edge in γ_1-$(Ga_xIn_{1-x})_2Se_3$ solid solutions for the $\boldsymbol{E} \parallel c$ polarization has the Urbach shape, while, for the $\boldsymbol{E} \perp c$ polarization, the absorption edge is not described by the Urbach law [4]. The interrelation between photoluminescence and optical absorption spectra was investigated in Ref. [5]. Refractometric, birefringent and gyrotropic properties of γ_1-$(Ga_xIn_{1-x})_2Se_3$ mixed crystals were studied in Refs. [6–8] the. It should be noted that γ_1-$(Ga_xIn_{1-x})_2Se_3$ mixed crystals are characterized by a high optical activity along the optical axis and are promising materials for acousto-optical modulators [9].

In recent years, the studies for preparing of $(Ga_xIn_{1-x})_2Se_3$ solid solutions in the form of thin films were performed for their effective practical application [10]. In Ref. [10], the refractive index and extinction coefficient dispersions were measured by spectral ellipsometry, and the temperature behavior of the Urbach absorption edge and the temperature dependences of the optical parameters were studied. The influence of X-ray irradiation on such optical parameters of $(Ga_xIn_{1-x})_2Se_3$ films as the energy

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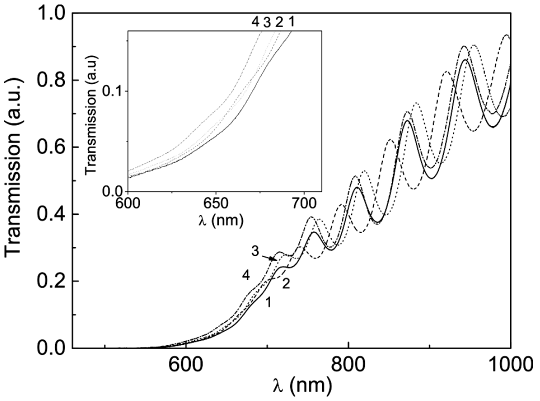

Fig. 1. Optical transmission spectra of as-deposited (*1*) and annealed $(Ga_{0.3}In_{0.7})_2Se_3$ films at various temperatures: 323 (*2*), 373 (*3*), and 423 K (*4*). The insert shows the short-wavelength region of the transmission spectra

pseudogap, Urbach energy, and refractive index have been investigated in [11, 12].

In the present paper, we report on the ellipsometric studies of the refractive and extinction coefficients, effect of the annealing temperature on the optical transmission and absorption spectra, Urbach absorption edge parameters, and refractive indices in $(Ga_{0.3}In_{0.7})_2Se_3$ films.

2. Experimental

$(Ga_{0.3}In_{0.7})_2Se_3$ crystals were obtained by the Bridgman technique. The investigated thin films were sputtered onto a quartz glass substrate by the thermal evaporation, their thickness being 1.5 mcm. The structure of the deposited films was analyzed by X-ray diffraction; the diffraction spectra show the films to be amorphous. The composition of the thin films was determined by EDX on a Hitachi S4300 SEM.

The annealing was performed the in inert atmosphere (argon) during 1 h at different temperatures (323, 373, and 423 K). A spectroscopic ellipsometer Horiba Smart SE was used for the measurements of the optical constants of $(Ga_{0.3}In_{0.7})_2Se_3$ thin films. Measurements were carried out in the spectral region from 440 nm to 1000 nm at an incident angle of 70°. Optical transmission spectra of $(Ga_{0.3}In_{0.7})_2Se_3$ film were measured by using a LOMO KSVU-23 grating monochromator. In many applications, the spectral dependences of the absorption coefficient were often derived from the interference transmission spectra by the Swanepoel method [13]. In our case, based on the refractive index values, the absorption coefficient values α were calculated using the experimental values of the transmission coefficient T and the reflectivity coefficient R as [14]

$$\alpha = \frac{1}{d}\ln\left[\frac{(1-R_1)(1-R_2)(1-R_3)}{T}\right], \qquad (1)$$

where d is the sample thickness; R_1, R_2, and R_3 are the reflectivity coefficients of "air–thin film", "thin film–substrate", and "substrate–air" interfaces, respectively.

3. Results and Discussion

Figure 1 presents the optical transmission spectra at various annealing temperatures for $(Ga_{0.3}In_{0.7})_2Se_3$ films. With an increase in the annealing temperature, a shift of the transmission spectra to the short-wavelength region of the spectrum is observed.

Dispersion dependences of the refractive index obtained by the spectral ellipsometry for the annealed $(Ga_{0.3}In_{0.7})_2Se_3$ films at various annealing temperatures are presented in Fig. 2. In the transparency region, a slight dispersion of the refractive index for $(Ga_{0.3}In_{0.7})_2Se_3$ films is observed, which is increasing with approaching the optical absorption edge. As the annealing temperature increases, the nonlinear increase of the refractive index in annealed $(Ga_{0.3}In_{0.7})_2Se_3$ films is revealed (refractive index increases from 2.461 to 2.522 at $\lambda = 1\ \mu$m).

Now, let us describe the experimental refractive index dispersion for as-deposited and annealed $(Ga_{0.3}In_{0.7})_2Se_3$ films. A lot of various models (from purely empirical to semiempirical) are widely used for the theoretical description of the refractive index dispersion [15]. Among them, the most widely used was the Wemple and DiDomenico (WD) model, which described the refractive index dispersion based on the relationship between the refractive index and the energy gap [16]. In the above- mentioned model, the refractive index dispersion in the transparency region below the gap can be described by the relation [16]

$$n^2(E) - 1 = \frac{E_d^{\mathrm{WD}}\, E_0^{\mathrm{WD}}}{(E_d^{\mathrm{WD}})^2 - E^2}, \qquad (2)$$

where E_0^{WD} is the single-oscillator energy, and E_d^{WD} is the dispersion energy. The dispersion energy E_d^{WD}

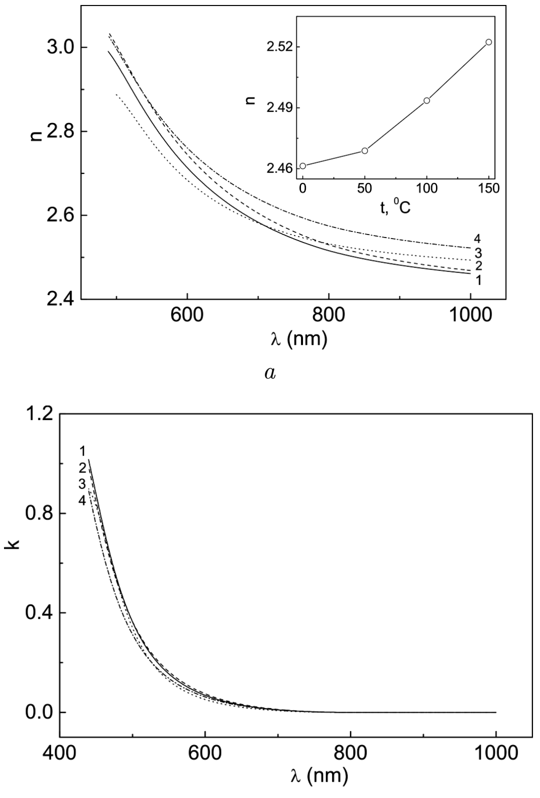

Fig. 2. Spectral dependences of the refractive indices n (*a*) and the extinction coefficient k (*b*) for as-deposited (*1*) and annealed $(\mathrm{Ga_{0.3}In_{0.7}})_2\mathrm{Se_3}$ films at various temperatures: 323 (*2*), 373 (*3*), and 423 K (*4*). The inset shows the dependence of the refractive index on the annealing temperature

characterizes the average strength of interband optical transitions and relates to the changes in the structural ordering of the material (ionicity, anion valency, and coordination number of the material). It is shown that, with the increase of annealing temperature, the single-oscillator energy E_0^{WD} and dispersion energy nonlinearly increase (Fig. 3).

Spectral dependences of the absorption coefficient in the range of their exponential behavior and in the Tauc region at various annealing temperatures for $(\mathrm{Ga_{0.3}In_{0.7}})_2\mathrm{Se_3}$ films are shown in Fig. 4. In Ref. [4], it is shown that the optical absorption edge for $(\mathrm{Ga_{0.3}In_{0.7}})_2\mathrm{Se_3}$ crystal in the region of its exponential behavior is described by the Urbach rule

$$\alpha(h\nu, T) = \alpha_0 \exp\left[\frac{h\nu - E_0}{E_U(T)}\right], \tag{3}$$

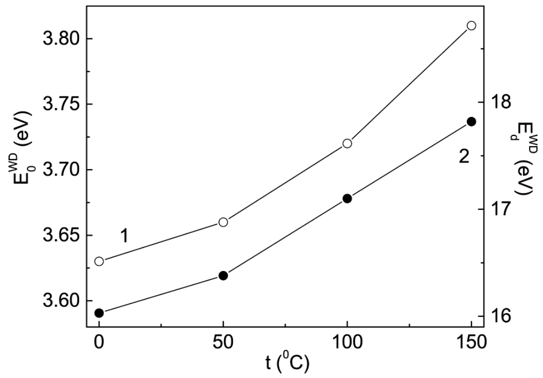

Fig. 3. The dependences of the single-oscillator energy E_0^{WD} (*1*) and dispersion energy E_d^{WD} (*2*) on the annealing temperature for $(\mathrm{Ga_{0.3}In_{0.7}})_2\mathrm{Se_3}$ films

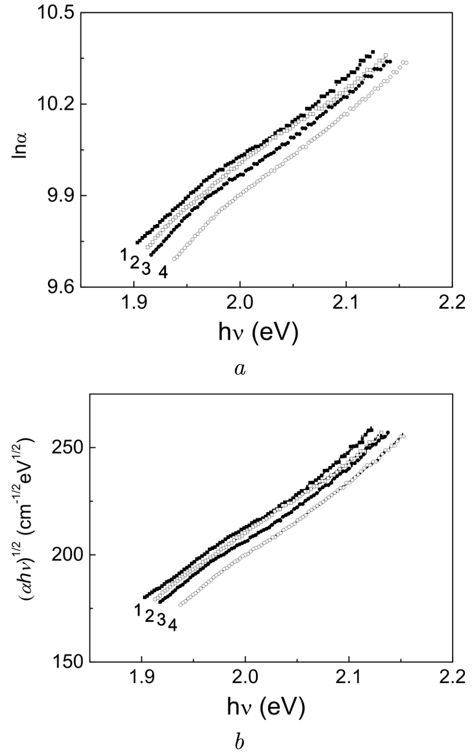

Fig. 4. Spectral dependences of $ln\alpha$ (*a*) and $(\alpha \cdot h\nu)^{1/2}$ (*b*) for as-deposited (*1*) and annealed $(\mathrm{Ga_{0.3}In_{0.7}})_2\mathrm{Se_3}$ films at various temperatures: 323 (*2*), 373 (*3*), and 423 K (*4*)

where $E_U(T)$ is the Urbach energy, α_0 and E_0 are the coordinates of the convergence point of the Urbach "bundle", $h\nu$ and T are the photon energy and temperature, respectively. In annealed $(\mathrm{Ga_{0.3}In_{0.7}})_2\mathrm{Se_3}$ films, we also observed the Urbach shape of the optical absorption edge (Fig. 4, *a*). It

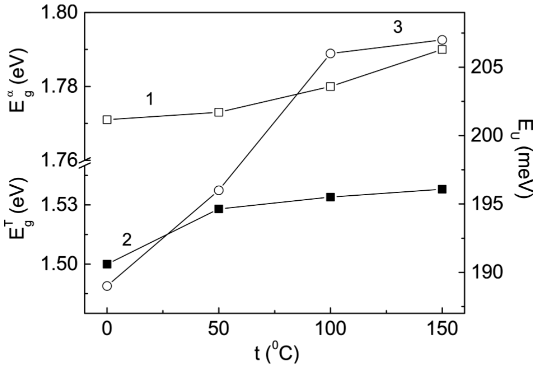

Fig. 5. Dependences of the energy pseudogap E_g^α (*1*), Tauc energy E_g^T (*2*), and Urbach energy E_U (*3*) on the annealing temperature for $(Ga_{0.3}In_{0.7})_2Se_3$ films

should be noted that the optical absorption edge for annealed $(Ga_{0.3}In_{0.7})_2Se_3$ films is shifted to the short-wavelength region, as the annealing temperature increases.

For the characterization of a spectral position of the absorption edge, such parameter as the energy pseudogap E_g^α (E_g^α is the energy position of the exponential absorption edge) at a fixed absorption coefficient value was determined. We used the E_g^α values taken at $\alpha = 10^4$ cm^{-1} for as-deposited and annealed $(Ga_{0.3}In_{0.7})_2Se_3$ films. The observed variation of the optical absorption edge shows that the E_g^α and E_U values increase with the annealing temperature (from 1.771 to 1.790 eV and from 189 to 207 meV, respectively). The increase of E_U and E_g^α with the annealing temperature (Fig. 5) can be attributed to the increase of the degree of disorder that results in an increase of the band tailing, and, consequently, an increase of the band gap. The dependences of E_U and E_g^α for annealed $(Ga_{0.3}In_{0.7})_2Se_3$ films on the annealing temperature are presented in Fig. 5.

In the Tauc region, the value can be determined from the Tauc relation [16]:

$$\alpha(h\nu) = \frac{B(h\nu - E_g^T)^2}{h\nu}, \tag{4}$$

which is valid within the range of high energies, when the absorption coefficient has values $\alpha \geq 10^4$ cm^{-1}. In Eq. (4), B is the constant that depends on the film material and characterizes the slope of the Tauc absorption edge. The Tauc energy E_g^T values for as-deposited and annealed $(Ga_{0.3}In_{0.7})_2Se_3$ films were determined by the extrapolation of the dependences $[\alpha(h\nu)\cdot h\nu]^{1/2} \sim f(h\nu)$ down to $\alpha(h\nu) = 0$ (Fig. 4). It is shown that E_g^T value increases with the annealing temperature from 1.500 eV to 1.538 eV.

It is well known that the Urbach energy E_U is characterized by the disordering level of the investigated system and, in solid solutions, is described by the relation [17, 18]

$$E_U = (E_U)_T + (E_U)_X + (E_U)_C =$$
$$= (E_U)_T + (E_U)_{X+C}, \tag{5}$$

where $(E_U)_T$, $(E_U)_X$ and $(E_U)_C$ are the contributions of temperature, structural and compositional disordering to E_U, respectively. Structural disordering in crystalline $(Ga_{0.3}In_{0.7})_2Se_3$ solid solutions is of intrinsic nature, being determined by a high concentration of disordered vacancies in the cation sublattice, while the compositional disordering arises due to the cation substitution of In atoms by Ga. It is shown in Ref. [4] that, with the increase of the gallium concentration in crystalline $(Ga_{0.3}In_{0.7})_2Se_3$ solid solutions, the contributions of $(E_U)_X$ and $(E_U)_C$ increase, while that of $(E_U)_T$ remains unchanged. It should be noted that the compositional contribution is predominant and, by a factor of more than 3, exceeds the contribution of a structural disordering [4]. In amorphous $(Ga_{0.3}In_{0.7})_2Se_3$ films, the structural disordering can also be determined by the absence of a long-range ordering of atoms, presence of pores, defects, and others structural inhomogeneities. In annealed $(Ga_{0.3}In_{0.7})_2Se_3$ films, the Urbach energy E_U is increasing by 10%, that is the evidence of that the structural disordering increases due to the annealing of films (Fig. 5).

4. Conclusions

$(Ga_{0.3}In_{0.7})_2Se_3$ films deposited by the thermal evaporation technique were annealed at different temperatures. The spectral dependences of the refractive index and extinction coefficient were measured by the spectral ellipsometry technique in the range from 440 nm to 1000 nm, while the absorption coefficient was derived from the spectrometric studies of interference transmission spectra. It is shown that the optical absorption edge for the as-deposited and annealed $(Ga_{0.3}In_{0.7})_2Se_3$ films has an exponential form, shifts to the high-energy region, and is broadening, as the annealing temperature increases. The influence of the annealing temperature on optical parameters of $(Ga_{0.3}In_{0.7})_2Se_3$ films has been investigated. With the annealing temperature increase, the increase of the energy pseudogap, as well as the increase of the Urbach energy and the refractive index, have been observed. In addition, the increase of the Urbach energy is the evidence of an increase of the structural disordering contribution, which is caused by the annealing of films.

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ОПТИЧНІ ПАРАМЕТРИ СВІЖОПРИГОТОВАНИХ ТА ВІДПАЛЕНИХ ТОНКИХ ПЛІВОК $(Ga_{0,3}In_{0,7})_2Se_3$

Напилену методом термічного випаровування плівку $(Ga_{0,3}In_{0,7})_2Se_3$ відпалювали в інертній атмосфері (аргон) протягом 1 год при температурах 323, 373 і 423 К. Методом спектральної еліпсометрії досліджено спектральні залежності показника заломлення та коефіцієнта екстинкції свіжоприготованої та відпаленої плівки $(Ga_{0,3}In_{0,7})_2Se_3$. Досліджено спектри оптичного пропускання та поглинання плівки $(Ga_{0,3}In_{0,7})_2Se_3$ залежно від температури відпалу. Показано, що край оптичного поглинання для відпаленої плівки $(Ga_{0,3}In_{0,7})_2Se_3$ зміщується в короткохвильову область і розширюється зі збільшенням температури відпалу. Визначено параметри урбахівського краю поглинання для свіжоприготованої та відпаленої плівки $(Ga_{0,3}In_{0,7})_2Se_3$. Спектральні залежності показника заломлення проаналізовано в рамках моделі Уемпла–ДіДомініко. Виявлено нелінійне збільшення ширини псевдозабороненої зони, урбахівської енергії та показника заломлення зі збільшенням температури відпалу.

Ключові слова: тонка плівка, спектральна еліпсометрія, спектри пропускання, показник заломлення, енергія псевдощілини, енергія Урбаха.