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## Optical studies of X-ray irradiated $(\text{Ga}_{0.4}\text{In}_{0.6})_2\text{Se}_3$ films

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**Abstract.** As-deposited  $(\text{Ga}_{0.4}\text{In}_{0.6})_2\text{Se}_3$  films are irradiated using a wide-band radiation of Cu-anode X-ray tube during different exposure times. The spectral dependences of refractive index and extinction coefficient are measured with a spectral ellipsometric technique. The optical transmission spectra of X-ray irradiated  $(\text{Ga}_{0.4}\text{In}_{0.6})_2\text{Se}_3$  films are studied depending on the irradiation time. The parameters of Urbach absorption edge for those films are determined. The spectral dependences of refractive indices for both non-irradiated and irradiated  $(\text{Ga}_{0.4}\text{In}_{0.6})_2\text{Se}_3$  films are described in the framework of Wemple–DiDomenico model.

**Keywords:** thin films, spectral ellipsometry, optical transmission spectra, X-ray irradiation, refractive index, pseudogap

**UDC:** 535.3; 539.21

### 1. Introduction

$(\text{Ga}_x\text{In}_{1-x})_2\text{Se}_3$  mixed crystals with the concentrations  $0.02 < x < 0.55$  belong to a defect wurtzite structure with hexagonal symmetry (space group  $P6_1$  or  $P6_5$ ) [1]. The main feature of these semiconductors is high concentration of the vacancies which can form spirals along the optic axis  $c$  of crystal [2]. Alternation of cations and vacancies results in random fluctuations of lattice electric potential which, in their turn, affect different physical processes in the above materials.

The optical absorption edge in mixed  $\gamma_1$ - $(\text{Ga}_x\text{In}_{1-x})_2\text{Se}_3$  crystals at low absorption levels has been shown to be formed by indirect interband optical transitions [3]. The effect of temperature on the absorption edge has been studied in Ref. [4]. Interrelations between the photoluminescence and the optical absorption spectra have been elucidated in Ref. [5]. The optical refraction, birefringent and gyrotropic properties of the  $\gamma_1$ - $(\text{Ga}_x\text{In}_{1-x})_2\text{Se}_3$  crystals have been examined in detail in Refs. [6–8]. It should be noted that  $\gamma_1$ - $(\text{Ga}_x\text{In}_{1-x})_2\text{Se}_3$  is characterized by high enough optical activity along the optic axis and, moreover, it represents a promising material for acousto-optical modulators [9].

Recently a number of studies of thin films  $(\text{Ga}_x\text{In}_{1-x})_2\text{Se}_3$  have been performed, with the emphasis at their efficient applications [10, 11]. In particular, the refractive index and extinction coefficient dispersions have been measured for the  $(\text{Ga}_{0.4}\text{In}_{0.6})_2\text{Se}_3$  film using spectral ellipsometry and the optical absorption edge has been examined in Ref. [11]. The works concerned with the influence of irradiations of different types (in particular, X-ray irradiation) on the physical parameters of thin films have been concentrated on their applications in large-area, flexible and light-weight radiation detectors [12]. It worthwhile that the influence of X-ray irradiation on the optical properties of thin films of different types (e.g., those based upon  $\text{MgPc}$ ,  $\text{CoMTPP}$ ,  $\text{Bi}_2\text{Te}_3$ ,  $\text{a-Se}_{1-x}\text{As}_x$  and  $\text{Cu}_6\text{PS}_5\text{I}$ ) has earlier been studied in Refs. [13–18].

In the present paper, we report on the ellipsometric studies of optical constants for the case of X-ray irradiated  $(\text{Ga}_{0.4}\text{In}_{0.6})_2\text{Se}_3$  films. Moreover, we analyze the influence of X-ray irradiation on their optical transmission spectra, Urbach-like absorption-edge parameters and refractive indices.

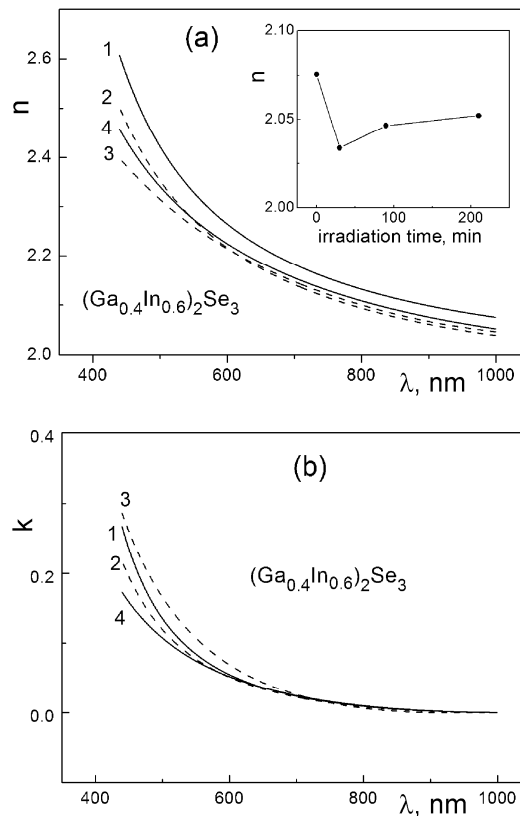
## 2. Experimental

(Ga<sub>0.4</sub>In<sub>0.6</sub>)<sub>2</sub>Se<sub>3</sub> films with the thickness 2.8 μm were deposited onto quartz glass substrates using a thermal evaporation technique. The structure of deposited films was analyzed with X-ray diffraction; the diffraction spectra demonstrated amorphous structure of the films.

The films were X-ray irradiated for different exposure times (30, 60 and 120 min), using a wide-band radiation of Cu-anode X-ray tube (the power ~ 400 W; 33 kV and 13 mA). Spectroscopic ellipsometer Horiba Smart SE was used to measure the optical constants of our (Ga<sub>0.4</sub>In<sub>0.6</sub>)<sub>2</sub>Se<sub>3</sub> films. The measurements were carried out in the spectrum region 440–1000 nm at the incident angle 70°. Optical transmission spectra of the (Ga<sub>0.4</sub>In<sub>0.6</sub>)<sub>2</sub>Se<sub>3</sub> films were detected using a LOMO KSVU-23 grating monochromator.

## 3. Results and discussion

Dispersion dependences of the refractive index for the (Ga<sub>0.4</sub>In<sub>0.6</sub>)<sub>2</sub>Se<sub>3</sub> films X-ray irradiated for different irradiation times are presented in Fig. 1. In the transparency region, a slight dispersion of the refractive index is observed, which increases with approaching the optical-absorption edge. When the irradiation time increases, the refractive index for the irradiated (Ga<sub>0.4</sub>In<sub>0.6</sub>)<sub>2</sub>Se<sub>3</sub> films changes in a non-monotonic manner (see inset in Fig. 1a). Namely, the refractive index at the light wavelength  $\lambda = 1 \mu\text{m}$  decreases from 2.076 to 2.034 due to initial X-ray irradiation during 30 min, while it increases nonlinearly up to the value of 2.052 with further increase of the irradiation time.

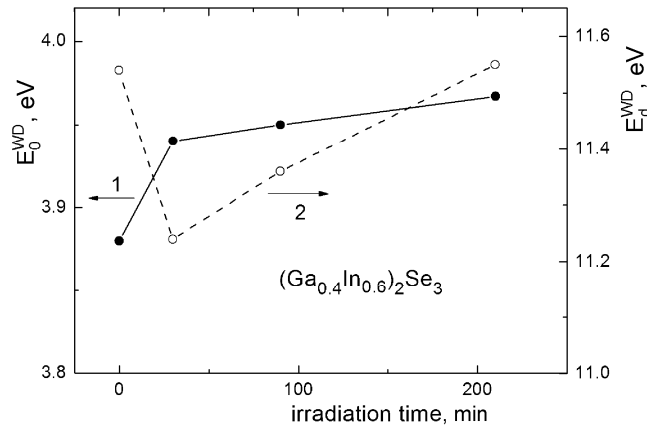


**Fig. 1.** Spectral dependences of refractive indices  $n$  (a) and extinction coefficients  $k$  (b) measured for non-irradiated (1) and X-ray irradiated (Ga<sub>0.4</sub>In<sub>0.6</sub>)<sub>2</sub>Se<sub>3</sub> films. Curves (2), (3) and (4) correspond respectively to irradiation times 30, 90 and 210 min. The inset shows dependence of the refractive index measured at  $\lambda = 1 \mu\text{m}$  on the X-ray irradiation time.

A great variety of theoretical models can be used to describe the refractive-index dispersion [19]. The most commonly used models are those suggested by Cauchy, Drude, Sellmeier, Lorentz, and Wemple–DiDomenico (WD) [19]. Further on, we adopt a well-known WD model which describes the refractive-index dispersion as [20]

$$n^2(E) - 1 = [E_d^{\text{WD}} \times E_0^{\text{WD}}] / [(E_0^{\text{WD}})^2 - E^2]. \quad (1)$$

Here  $E_0^{\text{WD}}$  is the single-oscillator energy and  $E_d^{\text{WD}}$  the dispersion energy. The latter parameter characterizes the average strength of interband optical transitions and can be associated with the changes in structural ordering of material (ionicity, anion valency and coordination number of the material). We have determined the  $E_0^{\text{WD}}$  and  $E_d^{\text{WD}}$  parameters, using the experimental dependences  $(n^2 - 1)^{-1}$  on  $E^2$  and Eq. (1). These parameters of the WD model are listed in Table 1 for the both non-irradiated and X-ray irradiated  $(\text{Ga}_{0.4}\text{In}_{0.6})_2\text{Se}_3$  films. It is obvious that the single-oscillator energy  $E_0^{\text{WD}}$  increases nonlinearly with increasing irradiation time. On the other hand, the dispersion energy  $E_d^{\text{WD}}$  decreases for the small X-ray irradiation times less than 30 min. After that,  $E_d^{\text{WD}}$  increases with increasing irradiation time (see Fig. 2). According to the relation  $E_0^{\text{WD}} \approx 2E_g^{\text{opt}}$  [21], the optical bandgap value  $E_g^{\text{opt}}$  can be estimated (see Table 1).



**Fig. 2.** Dependences of WD model parameters calculated for non-irradiated and X-ray irradiated  $(\text{Ga}_{0.4}\text{In}_{0.6})_2\text{Se}_3$  films: single-oscillator energy  $E_0^{\text{WD}}$  (1) and dispersion energy  $E_d^{\text{WD}}$  (2).

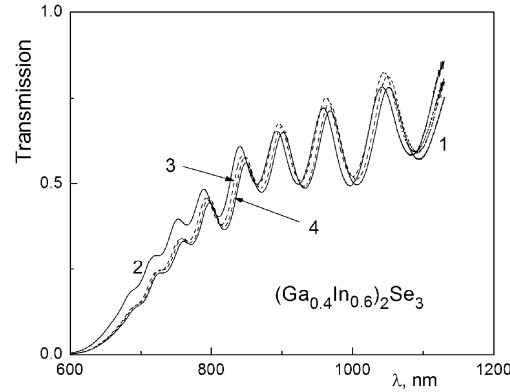
Table 1. Parameters of WD model, optical bandgap, static refractive index and ionicity calculated for the non-irradiated and X-ray irradiated  $(\text{Ga}_{0.4}\text{In}_{0.6})_2\text{Se}_3$  thin films.

Thin film	$E_0^{\text{WD}}$ , eV	$E_d^{\text{WD}}$ , eV	$E_g^{\text{opt}}$ , eV	$n_0^{\text{WD}}$	$f_i^{\text{WD}}$
Non-irradiated	3.88	11.54	1.94	1.990	0.58
X-ray irradiated for 30 min	3.94	11.24	1.97	1.963	0.59
X-ray irradiated for 90 min	3.95	11.36	1.98	1.969	0.59
X-ray irradiated for 210 min	3.97	11.55	1.99	1.978	0.59

The other parameters of the WD model, such as the static refractive index ( $n_0^{\text{WD}} = [1 + E_d^{\text{WD}}/E_0^{\text{WD}}]^{1/2}$ ) and the ionicity ( $f_i^{\text{WD}} = [E_0^{\text{WD}}/E_d^{\text{WD}}]^{1/2}$ ), are also displayed in Table 1. The data shows that the static refractive index  $n_0^{\text{WD}}$  of the  $(\text{Ga}_{0.4}\text{In}_{0.6})_2\text{Se}_3$  films nonlinearly increases and the ionicity remains unchanged with increasing X-ray irradiation time.

Fig. 3 displays the optical transmission spectra for the  $(\text{Ga}_{0.4}\text{In}_{0.6})_2\text{Se}_3$  films detected at different irradiation times and the room temperature. During the first stage (30 min) of irradiation, a blue shift of the short-wavelength part of the transmission spectra is observed. When the

irradiation time increases up to 90 min, the short-wavelength part of the transmission spectra demonstrates a low-energy shift. Finally, we have a further small shift towards the high-energy region (see Fig. 3).



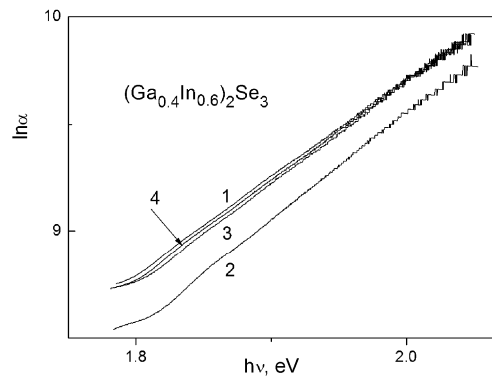
**Fig. 3.** Optical transmission spectra measured for non-irradiated (1) and X-ray irradiated  $(\text{Ga}_{0.4}\text{In}_{0.6})_2\text{Se}_3$  films. Curves (2), (3) and (4) correspond respectively to irradiation times 30, 90 and 210 min.

Note that the spectral dependences of the absorption coefficient can be derived from the interference transmission spectra [22]. Fig. 4 shows the spectral dependences of absorption coefficient for the  $(\text{Ga}_{0.4}\text{In}_{0.6})_2\text{Se}_3$  films measured in the region of their exponential behaviour for different irradiation times. It has been shown in Refs. [4, 11] that the optical-absorption edge for the  $(\text{Ga}_{0.4}\text{In}_{0.6})_2\text{Se}_3$  crystals and films is successfully described by a known Urbach rule in the region of its exponential behaviour:

$$\alpha(h\nu, T) = \alpha_0 \cdot \exp \left[ \frac{h\nu - E_0}{E_U(T)} \right]. \quad (2)$$

In Eq. (2),  $E_U(T)$  denotes the Urbach energy,  $\alpha_0$  and  $E_0$  are the coordinates of convergence point of the Urbach bundle, and  $h\nu$  and  $T$  imply respectively the photon energy and the temperature.

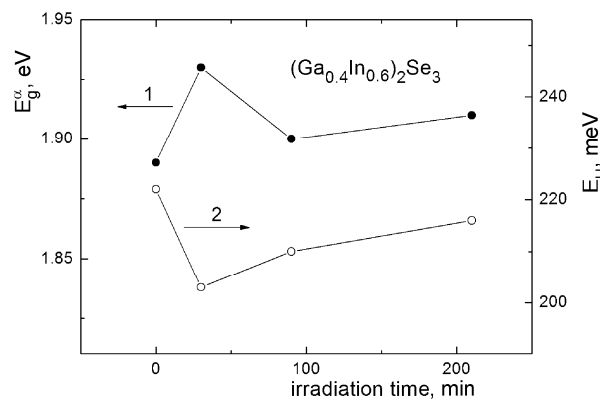
As seen from Fig. 4, the X-ray irradiated  $(\text{Ga}_{0.4}\text{In}_{0.6})_2\text{Se}_3$  films also reveal the Urbach shape of their optical-absorption edge. Notice that the behaviour of optical absorption edge for the irradiated  $(\text{Ga}_{0.4}\text{In}_{0.6})_2\text{Se}_3$  films follows the behaviour of the short-wavelength part of their transmission spectra (see Fig. 3).



**Fig. 4.** Spectral dependences of  $\ln \alpha$  for non-irradiated (1) and X-ray irradiated  $(\text{Ga}_{0.4}\text{In}_{0.6})_2\text{Se}_3$  films. Curves (2), (3) and (4) correspond respectively to irradiation times 30, 90 and 210 min.

To characterize the spectral position of the absorption edge, one can find a so-called

pseudogap  $E_g^\alpha$  at a fixed absorption coefficient value  $\alpha$ , with  $E_g^\alpha$  representing the energy position of the exponential absorption edge. In the case of our X-ray irradiated  $(\text{Ga}_{0.4}\text{In}_{0.6})_2\text{Se}_3$  thin films, we have used the  $E_g^\alpha$  values taken at  $\alpha = 10^4 \text{ cm}^{-1}$ . We have revealed that the energy pseudogap  $E_g^\alpha$  increases from 1.891 to 1.932 eV at the exposure times less than 30 min. The  $E_g^\alpha$  parameter decreases from 1.932 to 1.902 eV with increasing irradiation time up to 90 min. After that, one witnesses a further small increase from 1.902 to 1.910 eV. At the same time, the  $E_U$  value decreases from 222 to 203 meV when the X-ray irradiation time increases to 30 min, whereupon it increases nonlinearly from 203 to 216 meV with further irradiation time increase. The dependences of the  $E_g^\alpha$  and  $E_U$  parameters on the irradiation time are represented in Fig. 5. It is important that the  $E_g^\alpha$  values obtained from the WD model for our irradiated  $(\text{Ga}_{0.4}\text{In}_{0.6})_2\text{Se}_3$  films differ less than 4%.



**Fig. 5.** Dependences of pseudogap  $E_g^\alpha$  (1) and Urbach energy  $E_U$  (2) on the X-ray irradiation time for  $(\text{Ga}_{0.4}\text{In}_{0.6})_2\text{Se}_3$  films.

It is well-known that the Urbach energy  $E_U$  characterizes disordering level of a system under study. It is given by the relation [23]

$$E_U = (E_U)_T + (E_U)_X = (E_U)_T + (E_U)_{X,stat} + (E_U)_{X,dyn}, \quad (3)$$

where  $(E_U)_T$  and  $(E_U)_X$  are respectively the contributions of temperature-related and structural disorderings, whereas  $(E_U)_{X,stat}$  and  $(E_U)_{X,dyn}$  denote respectively the contributions of static and dynamic structural disorderings. According to Eq. (3), the irradiation-imposed changes in the Urbach energy  $E_U$  (see Fig. 5) are caused by changing contribution of the static disordering associated with the irradiation. Hence, structural ordering of the film is observed on the initial stage of irradiation (up to 30 min), thus leading to decreasing  $E_U$  parameter. With further increase in the irradiation time (up to 210 min), structural ordering occurs, which corresponds to the  $E_U$  increase).

#### 4. Conclusions

The  $(\text{Ga}_{0.4}\text{In}_{0.6})_2\text{Se}_3$  films deposited with the thermal evaporation technique are irradiated during different exposition times, using a wide-band radiation of Cu-anode X-ray tube. The spectral dependences of the refractive index and the extinction coefficient are measured in the range 440–1000 nm, using the spectral ellipsometry technique. The absorption coefficient is derived from spectrometric studies of the interference transmission spectra. The dispersion of the refractive

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indices for the non-irradiated and X-ray irradiated  $(\text{Ga}_{0.4}\text{In}_{0.6})_2\text{Se}_3$  films in the transparency region is described using the standard WD dispersion relation.

We show that the optical-absorption edge for the both non-irradiated and X-ray irradiated  $(\text{Ga}_{0.4}\text{In}_{0.6})_2\text{Se}_3$  films has an exponential shape. The influence of irradiation on the optical parameters of our films is analyzed. During the first 30 min of irradiation, one observes increasing energy pseudogap and decreasing Urbach energy and refractive index. With further increase of the irradiation time, a nonlinear increase in the Urbach energy and the refractive index occur. The dependence of the pseudogap for our X-ray irradiated  $(\text{Ga}_{0.4}\text{In}_{0.6})_2\text{Se}_3$  films on the irradiation time turns out to be more complex: the  $E_g^\alpha$  parameter decreases when the irradiation time increases up to 90 min, although a small  $E_g^\alpha$  increase is observed for longer irradiation times.

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**Анотація.** Свіжовисаджені плівки (Ga<sub>0.4</sub>In<sub>0.6</sub>)<sub>2</sub>Se<sub>3</sub> опромінено протягом різних часів експозиції ширококутовим випромінюванням рентгенівської трубки з Си-анодом. Спектральні залежності показника заломлення та коефіцієнта екстинкції знайдено за допомогою спектральної еліпсометричної методики. Вивчено спектри оптичного пропускання опромінених плівок (Ga<sub>0.4</sub>In<sub>0.6</sub>)<sub>2</sub>Se<sub>3</sub> залежно від часу опромінення. Визначено параметри краю поглинання Урбаха для цих плівок. Спектральні залежності показників заломлення для неопромінених і опромінених плівок (Ga<sub>0.4</sub>In<sub>0.6</sub>)<sub>2</sub>Se<sub>3</sub> описано в рамках моделі Вемпля–ДіДоменіко.