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# MATERIALS FOR OPTICAL SENSORS OF X-RAY IRRADIATION BASED ON $(Ga_xIn_{1-x})_2Se_3$ FILMS

*$(Ga_xIn_{1-x})_2Se_3$ films with $0.1 \leq x \leq 0.4$ were deposited by the thermal evaporation technique. As-deposited $(Ga_xIn_{1-x})_2Se_3$ films were irradiated using the wideband radiation of a Cu-anode X-ray tube at different exposure times. The spectral dependences of the refractive index and extinction coefficient are measured by the spectral ellipsometry technique. The optical transmission spectra of X-ray irradiated $(Ga_xIn_{1-x})_2Se_3$ films are studied for various irradiation times. Parameters of the Urbach absorption edge for X-ray-irradiated $(Ga_xIn_{1-x})_2Se_3$ thin films are determined and compared with those of non-irradiated films. The spectral dependences of the refractive indices of non-irradiated and X-ray-irradiated $(Ga_xIn_{1-x})_2Se_3$ films are described in the framework of the model developed by Cauchy, Sellmeier, Wemple, and DiDomenico, as well as by the optical-refractometric relation. The detailed variation of the parameters of the Wemple–DiDomenico model for non-irradiated and X-ray-irradiated $(Ga_xIn_{1-x})_2Se_3$ films has been analyzed. The perspective of applications of $(Ga_xIn_{1-x})_2Se_3$ films as the materials for optical sensors of X-rays is discussed.*

*K e y w o r d s*: film, spectral ellipsometry, transmission spectra, X-ray irradiation, energy pseudogap, refractive index.

## 1. Introduction

Compounds of the type $A_2^{III}C_3^{VI}$–$B_2^{III}C_3^{VI}$ are semiconductor materials that are promising for the use in optoelectronics due to the relatively wide area of transparency in the IR region of the spectrum, in nonlinear optics, electrooptics, and acoustic optics [1, 2]. X-ray diffraction studies in the $Ga_2Se_3$-$In_2Se_3$ system showed that, in $0 \leq x \leq 1$ concentration interval, four types of $(Ga_xIn_{1-x})_2Se_3$ solid solutions are composed and are stable at room temperature [1]. Crystals of $\gamma_1$-$(Ga_xIn_{1-x})_2Se_3$ ($\gamma_1$-phase) with $0.02 < x < 0.55$ have hexagonal symmetry ($P6_1$ or $P6_5$ space group) of the defect wurtzite. A characteristic feature of this structure is the high concentration of vacancies, since a one third of positions in the cationic sublattice is unfilled. These vacancies are internal defects of the crystal lattice capable of forming spirals along the axis c [3]. The alternation of cations with vacancies provides a disordered distribution of vacancies, which causes chaotic fluctuations of the electric potential of the crystal lattice, which, in turn, affects the course of physical processes in these materials.

Electrical studies conducted on polycrystalline samples indicate the low electrical conductivity for all phases which varies from $10^{-10}$ S/cm to $10^{-6}$ S/cm [1]. Photoconductivity in the $\gamma_1$-phase (the largest for $x = 0.4$) is almost three orders of magnitude higher than for other phases. Optical absorption edge

in $\gamma_1$-$(Ga_xIn_{1-x})_2Se_3$ mixed crystals at low values of the absorption coefficient is shown to be formed by indirect interband optical transitions [4], temperature behavior of the absorption edge being studied in Ref. [5]. The interrelation between photoluminescence and optical absorption spectra was investigated in Ref. [6]. Refractometric, birefringent, and gyrotropic properties of $\gamma_1$-$(Ga_xIn_{1-x})_2Se_3$ mixed crystals were studied in detail in Refs. [7–9]. It should be noted that $\gamma_1$-$(Ga_xIn_{1-x})_2Se_3$ mixed crystals are characterized by the high optical activity along the optical axis and are promising materials for acousto-optical modulators [10].

In recent years, the studies of the preparation of $(Ga_xIn_{1-x})_2Se_3$ mixed crystals in the form of films were performed for their effective practical application [11–13]. In Refs. [11–13], the refractive index and extinction coefficient dispersions were measured by spectral ellipsometry, as well as the temperature behavior of the Urbach absorption edge and the temperature dependences of the optical parameters were studied. Investigations of the influence of the different types of irradiation (in particular, X-ray irradiation) on physical parameters of thin films were determined by their application to the development of large-area, flexible, and light-weight radiation detectors [14]. It should be noted that the influence of X-ray irradiation on optical properties of thin films was studied in Refs. [15–21]. It was shown that, in MgPc thin films, the X-ray irradiation leads to an increase in the energy gap from 2.735 eV to 2.81 eV and in the refractive index [15]. In CoMTPP thin films after X-ray irradiation, the refractive index decreases, and the fundamental gap increases [16]. For $Bi_2Te_3$ thin films, the optical gap and refractive index appeared to decrease corresponding to increasing the X-ray radiation energy [17]. For chalcogenide $As_2S_3$ thin film, an increase in the refractive index and a decrease in the film thickness (increase in the density) as a result of the X-ray irradiation are obtained, which confirms that the changes in $n$ stem occur primarily due to the changes in the film density as expected from the Clasius–Mossotti equation [18]. It should be noted that the influence of X-ray irradiation was recently studied for argyrodite-based superionic thin films [19, 20]. As the irradiation time increases, the decreases in the energy position of the absorption edge, as well as the increase in the Urbach energy and refractive index for an $Cu_{5.56}P_{1.66}S_{4.93}I_{0.85}$ thin film were observed [19]. For $Cu_{5.5}P_{1.2}Se_{5.0}I_{1.3}$ thin films, the nonlinear increase in the energy pseudogap and Urbach energy, as well as the nonlinear decrease in the refractive index with an increase in the X-ray irradiation time were revealed [20]. In Ref. [21], the optical transmission spectra, absorption edge, and the dispersion of refractive indices in the X-ray-irradiated $(Ga_{0.4}In_{0.6})_2Se_3$ films were investigated.

In the present paper, we report on the ellipsometric studies of optical constants, the influence of X-ray irradiation on the optical transmission spectra, Urbach absorption edge parameters, and refractive indices in $(Ga_xIn_{1-x})_2Se_3$ films with $0.1 \leq x \leq 0.4$ which can be used to create X-ray radiation detectors on their basis.

## 2. Methodology of Experiment

Synthesis of $(Ga_xIn_{1-x})_2Se_3$ solid solutions with $0.1 \leq x \leq 0.4$ was conducted from simple substances: indium (99.999%), gallium (99.999%), and selenium (99.9999%) taken in stoichiometric ratios in quartz ampoules evacuated to 0.13 Pa. The synthesis mode included the step heating to 873 K at a rate of 100 K/h (exposure during 24 hours), further increasing the temperature to 1340 K (∼50 K above the melting one of $Ga_2Se_3$) at a rate of 50 K/h and the exposure at this temperature during 24 hours. Cooling was carried out in the oven-off mode.

Growing crystals of $(Ga_xIn_{1-x})_2Se_3$ solid solutions with $0.1 \leq x \leq 0.4$ was performed by the vertical zone crystallization method from the solution-melt. The process was carried out in a two-zone tubular resistance furnace (melt zone temperature 1163 K, annealing zone – 833 K) using a quartz container of a special configuration. In order to homogenize the melt, a 24-hour exposure of the ampoule was performed in the melt zone. The cultivation of a single crystal consists of the formation of a nucleus in the lower conical part of the container by the method of collective recrystallization for 24 hours and the growth of the crystal on the formed seed. The optimal rate of crystallization front movement was 0.4–0.5 mm/h, annealing temperature – 833 K (120 hours), the rate of cooling to room temperature – 5 K/h. This method was used to obtain dark-red crystals of $(Ga_xIn_{1-x})_2Se_3$ solid solutions with $0.1 \leq x \leq 0.4$. The length of the crystals constituted 30–40 mm, and the diameter was 20 mm.

$(Ga_xIn_{1-x})_2Se_3$ films with $0.1 \leq x \leq 0.4$ were deposited onto a quartz glass substrate by the thermal

evaporation, their thickness being 2.0–2.8 $\mu$m. The structure of the deposited films was analyzed by X-ray diffraction; the diffraction spectra show the films to be amorphous. X-ray irradiation was performed for the different exposure times (30, 60, and 120 min) using the wideband radiation of a Cu-anode X-ray tube with the applied power of about 400 W (33 kV, 13 mA).

A spectroscopic ellipsometer Horiba Smart SE was used for the measurements of the optical constants of $(Ga_xIn_{1-x})_2Se_3$ films with $0.1 \le x \le 0.4$. Measurements of $\Psi$ and $\Delta$ ellipsometric angles were carried out in the spectrum region from 440 nm to 1000 nm at an incident angle of $\varphi_0 = 700$. The main ellipsometric equation was solved for every set of $\varphi_0$, $\Psi$, $\Delta$ values [22]:

$$\rho = \frac{R_p}{R_s} = \operatorname{tg}\Psi\, e^{i\Delta}, \tag{1}$$

where

$$R_p = \frac{r_{01}^p + r_{12}^p\, e^{-i2\beta}}{1 + r_{01}^p\, r_{12}^p\, e^{-i2\beta}}$$

and

$$R_p = \frac{R_{01}^s + r_{12}^s\, e^{-i2\beta}}{1 + r_{01}^s\, r_{12}^s\, e^{-i2\beta}}$$

respectively are the reflection coefficients for $p$ and $s$ polarizations, which are manifested through Fresnel coefficients on the interfaces of media as

$$\begin{aligned} r_{01}^p &= \frac{N_1\cos\varphi_0 - N_0\cos^*\varphi_1}{N_1\cos\varphi_0 + N_0\cos^*\varphi_1},\\ r_{12}^p &= \frac{N_2\cos^*\varphi_1 - N_0\cos^*\varphi_2}{N_2\cos^*\varphi_1 + N_0\cos^*\varphi_2},\\ r_{01}^s &= \frac{N_0\cos\varphi_0 - N_1\cos^*\varphi_1}{N_1\cos\varphi_0 + N_0\cos^*\varphi_1},\\ r_{12}^s &= \frac{N_1\cos^*\varphi_1 - N_1\cos^*\varphi_1}{N_2\cos^*\varphi_1 + N_2\cos^*\varphi_2}, \end{aligned} \tag{2}$$

$\varphi_2$ and $\varphi_1$ angles are complex values that agree well with the Snell's law

$$N_0\sin\varphi_0 = N_1\sin^*\varphi_1 = N_2\sin^*\varphi_2, \tag{3}$$

and $\beta = \frac{2\pi}{\lambda} d N_1\cos^*\varphi_1$ is the phase thickness of the film, $N_2 = n_2 - ik_2$ is the complex refractive index of the substrate, $N_1 = n_1 - ik_1$ is the complex refractive index of the film, and $N_0$ is the refractive index of the dielectric environment that surrounds the film-substrate system. Obtained experimental spectral dependences of $\Psi$ and $\Delta$ ellipsometric angles were analyzed using the $\Delta\Psi_2$ software and corresponding models, which allowed determining the dispersion of the refractive index $n$ and extinction coefficient $k$.

Optical transmission spectra of $(Ga_xIn_{1-x})_2Se_3$ films with $0.1 \le x \le 0.4$ were measured by using a LOMO KSVU-23 grating monochromator. Based on the refractive index values, the absorption coefficient values $\alpha$ were calculated using the experimental values of transmission coefficient $T$ and reflectivity coefficient $R$ as [23]

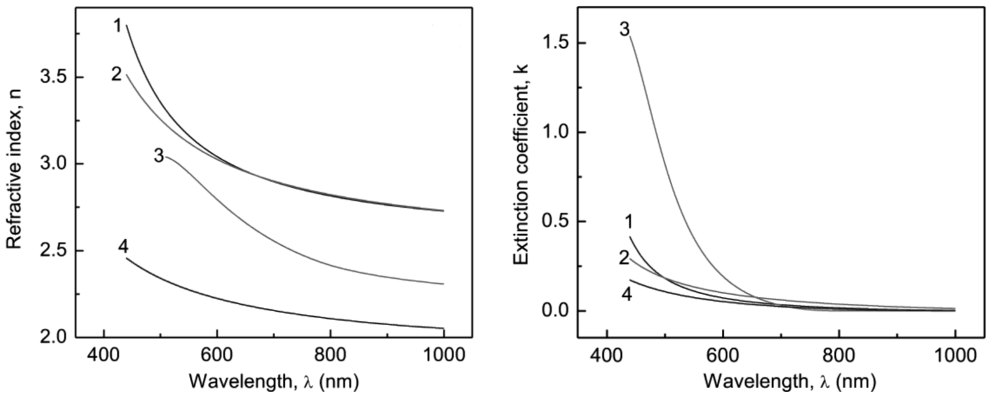
$$\alpha = \frac{1}{d}\ln\left[\frac{(1-R_1)(1-R_2)(1-R_3)}{T}\right], \tag{4}$$

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. For the characterization of the absorption edge spectral position in $(Ga_xIn_{1-x})_2Se_3$ films, such parameter as the energy pseudogap $E_g^\alpha$ ($E_g^\alpha$ is the energy position of the exponential absorption edge) at the fixed absorption coefficient value $\alpha$=$10^4$ cm$^{-1}$ was determined. The Urbach energy $E_U$ was calculated as the energy width of the exponential absorption edge

$$\left(E_U = \frac{\Delta(h\nu)}{\Delta(\ln\alpha)}\right).$$

## 3. Experimental Results and Discussion

Dispersion dependences of the refractive indices and extinction coefficients for the X-ray-irradiated $(Ga_xIn_{1-x})_2Se_3$ films with $0.1 \le x \le 0.4$ at the maximal exposure time (210 min) are presented in Fig. 1. In the transparency region, a slight dispersion of the refractive index for the X-ray-irradiated $(Ga_xIn_{1-x})_2Se_3$ films is observed, increasing with approaching the optical absorption edge. With an increase in the irradiation time, the nonlinear variation of the refractive index in the X-ray-irradiated $(Ga_xIn_{1-x})_2Se_3$ films is revealed (Fig. 2). However, the dependences of refractive indices on the irradiation time differ significantly for $(Ga_xIn_{1-x})_2Se_3$ films with different contents of Ga atoms. Thus, for $(Ga_{0.1}In_{0.9})_2Se_3$ films with an increase in the irradiation time up to 210 min, the nonlinear increase in the refractive index by 0.088 at $\lambda = 1$ $\mu$m is revealed (Fig. 2).




*a* *b*

***Fig. 1.*** Spectral dependences of the refractive index $n$ (*a*) and the extinction coefficient $k$ (*b*) for the irradiation time of 210 min for $(Ga_xIn_{1-x})_2Se_3$ films: $x = 0.1$ (*1*), $x = 0.2$ (*2*), $x = 0.3$ (*3*), and $x = 0.4$ (*4*)

With an increase in the content of Ga atoms to $x = 0.2$ in the $(Ga_{0.2}In_{0.8})_2Se_3$ film, the refractive index almost does not change (the value of refractive indices for non-irradiated and irradiated films differ by less than 0.2%) with the increase in the irradiation time up to 210 min. A completely different situation is observed for $x = 0.3$ in $(Ga_{0.3}In_{0.7})_2Se_3$ films: during first 30 min of the X-ray irradiation, the refractive index sharply decreases from 2.461 to 2.260. Further, with increasing the irradiation time up to 210 min, the refractive index increases to the value of 2.308. For $(Ga_{0.4}In_{0.6})_2Se_3$ films, there is a situation similar to $(Ga_{0.3}In_{0.7})_2Se_3$ films, but changes in the refractive index are less: during first 30 min of the X-ray irradiation, the refractive index decreases. Further, with increasing the irradiation time up to 210 min, this index increases to the value of 2.052, which is less than for the non-irradiated film. It should be noted that the dependences of the refractive indices of $(Ga_xIn_{1-x})_2Se_3$ films on the exposure time can be used to create and calibrate optical sensors ($x = 0.1$) and relay switches ($x = 0.3$). At the same time, a $(Ga_{0.2}In_{0.8})_2Se_3$ film can be used as a radiation-resistant coating.

The various models for the theoretical description of a refractive index dispersion are widely used – from purely empirical to semiempirical, in which the adjustable parameters are endowed with a certain physical meaning [24]. Among them, the most commonly used models are the following: Cauchy, Drude, Sellmeier, Lorentz, Wemple–DiDomenico, *etc.* [24]. It should be noted that the Cauchy dispersion law is

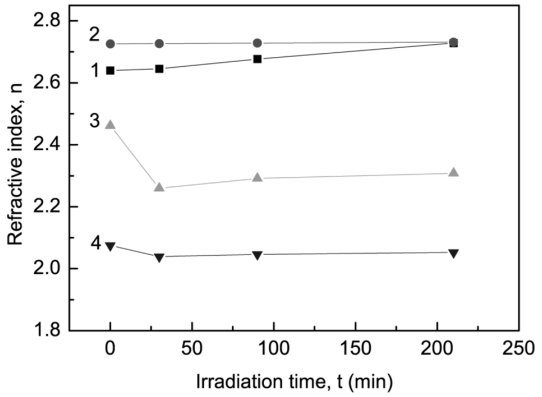



***Fig. 2.*** The dependences of the refractive index at $\lambda = 1$ $\mu$m on the irradiation time for X-ray-irradiated $(Ga_xIn_{1-x})_2Se_3$ films: (*1*) $x = 0.1$, (*2*) $x = 0.2$, (*3*) $x = 0.3$, and (*4*) $x = 0.4$

purely empirical [24]:

$$n(\lambda) = n_0 + \frac{b}{\lambda^2} + \frac{c}{\lambda^4} + ..., \qquad (5)$$

where $b$, $c$, ... are some adjustable parameters. The number of the terms can reach 10–15. The results of calculations within the Cauchy model using two parameters are shown in Table 1.

We also applied the Sellmeier dispersion relation which is semiempirical for describing the refractive index dispersion of non-irradiated and X-ray-irradiated $(Ga_{0.1}In_{0.9})_2Se_3$ thin films [24]:

$$n^2(\lambda) = 1 + \frac{B_1\,\lambda^2}{\lambda^2 - C_1} + \frac{B_2\,\lambda^2}{\lambda^2 - C_2} + \frac{B_3\,\lambda^2}{\lambda^2 - C_3} + ..., \quad (6)$$

where $B_1$, $C_1$, $B_2$, $C_2$, ... are some adjustable parameters. More terms can be added for different oscillator positions. The Sellmeier model calculations using two polynomials are presented in Table 2.

Among the models, which describe the refractive index dispersion based on the relationship between the refractive index and the energy gap, one should, first of all, mention the well-known Wemple–DiDomenico (WD) model for which the refractive index dispersion can be described by the relation [25]

$$n^2(E) - 1 = \frac{E_d^{\mathrm{WD}}\, E_0^{\mathrm{WD}}}{(E_0^{\mathrm{WD}})^2 - E^2}, \tag{7}$$

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

*Table 1.* **Parameters of the Cauchy model for the irradiation time of 210 min for $(Ga_xIn_{1-x})_2Se_3$ films**

| Films | $n_0$ (eV) | $b$ (eV) | $c$ (eV) |
|---|---|---|---|
| $(Ga_{0.1}In_{0.9})_2Se_3$ | 2.652 | 0.053 | 0.031 |
| $(Ga_{0.2}In_{0.8})_2Se_3$ | 2.582 | 0.168 | 0.002 |
| $(Ga_{0.3}In_{0.7})_2Se_3$ | 2.206 | 0.031 | 0.004 |
| $(Ga_{0.4}In_{0.6})_2Se_3$ | 1.945 | 0.110 | –0.004 |

*Table 2.* **Parameters of the Sellmeier model for the irradiation time of 210 min for $(Ga_xIn_{1-x})_2Se_3$ films**

| Films | $A_1$ | $b_1$ | $A_2$ | $b_2$ |
|---|---|---|---|---|
| $(Ga_{0.1}In_{0.9})_2Se_3$ | 0.013 | 0.209 | 5.729 | 0.109 |
| $(Ga_{0.2}In_{0.8})_2Se_3$ | 0.451 | 0.106 | 5.351 | 0.106 |
| $(Ga_{0.3}In_{0.7})_2Se_3$ | 0.968 | 0.175 | 2.568 | 0.103 |
| $(Ga_{0.4}In_{0.6})_2Se_3$ | 0.638 | 0.103 | 2.248 | 0.103 |

*Table 3.* **Parameters of the Wemple–DiDomenico model, optical band gap, static refractive index, and ionicity for the irradiation time of 210 min for $(Ga_xIn_{1-x})_2Se_3$ films**

| Films | $E_0^{\mathrm{WD}}$ (eV) | $E_d^{\mathrm{WD}}$ (eV) | $E_g^{\mathrm{opt}}$ (eV) | $n_0^{\mathrm{WD}}$ | $f_i^{\mathrm{WD}}$ |
|---|---|---|---|---|---|
| $(Ga_{0.1}In_{0.9})_2Se_3$ | 3.81 | 21.46 | 1.91 | 2.600 | 0.42 |
| $(Ga_{0.2}In_{0.8})_2Se_3$ | 3.79 | 21.94 | 1.89 | 2.610 | 0.42 |
| $(Ga_{0.3}In_{0.7})_2Se_3$ | 2.90 | 10.07 | 1.45 | 2.110 | 0.54 |
| $(Ga_{0.4}In_{0.6})_2Se_3$ | 3.97 | 11.55 | 1.98 | 1.978 | 0.59 |

characterizes the average strength of interband optical transitions and is related to the changes in the structural ordering of the material (ionicity, anion valency, and coordination number of the material). The above-mentioned parameters of the WD model for X-ray-irradiated $(Ga_xIn_{1-x})_2Se_3$ films are listed in Table 1. According to the relation $E_0^{\mathrm{WD}} \approx E_g^{\mathrm{opt}}$ [26], the optical band gap value $E_g^{\mathrm{opt}}$ is estimated and presented in Table 3. The values of such parameters of the WD model as the static refractive index

$$n_0 = \left[1 + \frac{E_d}{E_0}\right]^{\frac{1}{2}}, \tag{8}$$

and the ionicity [27]

$$f_i = \left[\frac{E_0}{E_d}\right]^{\frac{1}{2}}, \tag{9}$$

are also presented in Table 3.

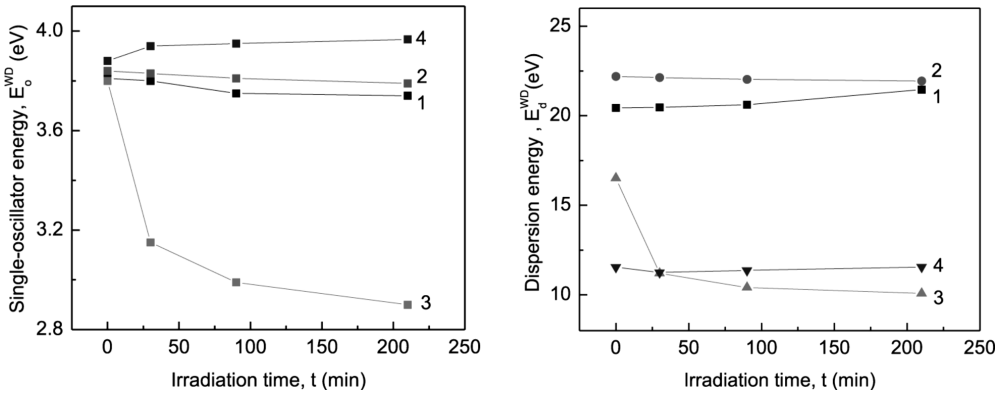
In addition, the dispersion dependences of the refractive indices for $(Ga_xIn_{1-x})_2Se_3$ films can be described by the known optical-refractometric (OR) relation [28]:

$$\frac{1}{3}\frac{n^2(h\nu)+2}{n^2(h\nu)-1} = \left(\frac{\eta_s}{2}\right)^s \left(1 + \frac{E_g^{\alpha}}{E_{pv}}\right)^s - \left(\frac{h\nu}{E_s}\right)^s, \tag{10}$$

where $s = 2$ for the medium part of the transparency range, and $s = 3$ for its high-energy part; $E_g^{\alpha}$ is the energy pseudogap; $\eta_s$ and $E_s$ are fitting parameters. The energy of the valence electron plasma vibrations $E_{pv}$ is determined as [28]

$$E_{pv} = 28.82\sqrt{\frac{n_v\,\rho}{\mu}}, \tag{11}$$

where $n_v$ is the number of valence electrons per formula unit, $\rho$ is the density, $\mu$ is the molar mass. Note that the choice of the OR relation is determined by its advantages with respect to other empirical formulae proposed by Sellmeier, Moss, Ravindra, Wemple, and DiDomenico [25,29,30] and based on relating such important parameters as the refractive index $n$, energy pseudogap $E_g^{\alpha}$, and energy of plasma vibrations of valence electrons $E_{pv}$. This enables the dispersion of the refractive index to be successfully described. The values of the parameters that provide the best fit between the calculated and experimental $n_\lambda$ dependences of the refractive indices for $(Ga_xIn_{1-x})_2Se_3$ films are shown in Table 4.




*a* *b*

***Fig. 3.*** The dependences of the single-oscillator energy $E_0^{\mathrm{WD}}$ (*a*) and the dispersion energy $E_d^{\mathrm{WD}}$ (*b*) on the irradiation time for X-ray-irradiated $(Ga_xIn_{1-x})_2Se_3$ films: $x = 0.1$ (*1*), $x = 0.2$ (*2*), $x = 0.3$ (*3*), and $x = 0.4$ (*4*)

It is shown that, with an increase in the X-ray irradiation time, the single-oscillator energy $E_0^{\mathrm{WD}}$ and dispersion energy $E_d^{\mathrm{WD}}$ undergo various changes (Figure 3). Figure 3 shows that the single-oscillator energy $E_0^{\mathrm{WD}}$ for $(Ga_xIn_{1-x})_2Se_3$ films with $x = 0.1$, 0.2 and 0.3 decreases, whereas, for the film with $x = 0.4$, it increases. For films with $x = 0.3$ and 0.4, the greatest changes occur in the first 30 minutes of the irradiation. In total, the parameter $E_0^{\mathrm{WD}}$ for $(Ga_xIn_{1-x})_2Se_3$ films with $x = 0.1$, 0.2 and 0.3 decreases by 0.07 eV, 0.05 eV, and 0.90 eV, respectively, whereas, for the film with $x = 0.4$, it increases by 0.09 eV. It should be noted that the dispersion energy $E_d^{\mathrm{WD}}$ for $(Ga_xIn_{1-x})_2Se_3$ films with $x = 0.1$ and 0.4 slowly increases by 1.02 eV and 0.01 eV, respectively. For $(Ga_xIn_{1-x})_2Se_3$ films with $x = 0.2$ and 0.3, there occurs a decrease in the parameter $E_d^{\mathrm{WD}}$ by 0.25 eV and 5.81 eV, respectively. However, for the film with $x = 0.3$, the largest changes by 5.31 eV occur in the first 30 min of the irradiation.

Figure 4 presents the optical transmission spectra at various irradiation times at room temperature for X-ray-irradiated $(Ga_xIn_{1-x})_2Se_3$ films. It is shown that the optical transmission spectra are similar, and the shift of the short-wave part of the spectra is due to and correlates with changes in the position and shape of the absorption edge, which is reflected, as will be shown later, on the exposure time dependences of the energy pseudogap and Urbach energy. Interference maxima are observed in the long-wave region of transmission spectra with the highest transmittance

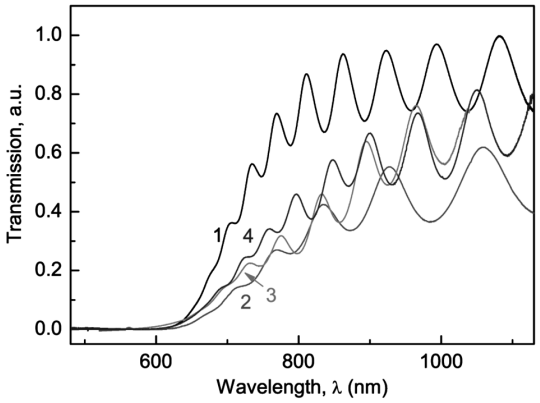



***Fig. 4.*** Optical transmission spectra for the irradiation time of 210 min for $(Ga_xIn_{1-x})_2Se_3$ films: $x = 0.1$ (*1*), $x = 0.2$ (*2*), $x = 0.3$ (*3*), and $x = 0.4$ (*4*)

*Table 4.* **Parameters of the OR relation for the irradiation time of 210 min for $(Ga_xIn_{1-x})_2Se_3$ films**

| Films | $E_g^{\alpha}$ (eV) | $E_{pv}$ (eV) | $E_2$ (eV) | $E_3$ (eV) | $\eta_2$ | $\eta_3$ |
|---|---|---|---|---|---|---|
| $(Ga_{0.1}In_{0.9})_2Se_3$ | 1.88 | 15.08 | 8.88 | 6.72 | 1.269 | 1.394 |
| $(Ga_{0.2}In_{0.8})_2Se_3$ | 1.66 | 15.45 | 10.41 | 7.60 | 1.314 | 1.455 |
| $(Ga_{0.3}In_{0.7})_2Se_3$ | 1.77 | 15.67 | 8.90 | 6.54 | 1.305 | 1.430 |
| $(Ga_{0.4}In_{0.6})_2Se_3$ | 1.91 | 15.96 | 8.30 | 6.53 | 1.436 | 1.515 |

found for the film with $x = 0.1$ and the smallest one for the film with $x = 0.2$.

Spectral dependences of the absorption coefficient in the range of their exponential behavior at various

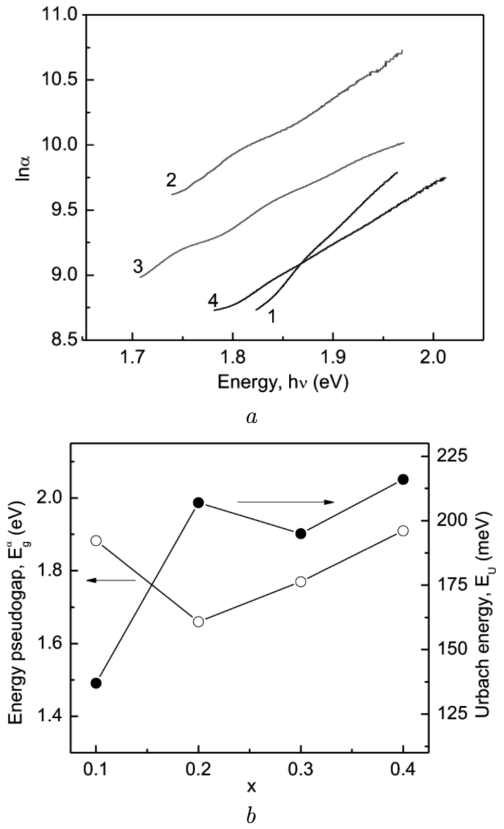



***Fig. 5.*** Spectral dependences of ln $\alpha$ for the irradiation time of 210 min for $(Ga_xIn_{1-x})_2Se_3$ films: $x = 0.1$ (*1*), $x = 0.2$ (*2*), $x = 0.3$ (*3*), and $x = 0.4$ (*4*) (*a*); Compositional dependences of the energy pseudogap $E_g^{\alpha}$ and the Urbach energy $E_U$ for the irradiation time of 210 min for $(Ga_xIn_{1-x})_2Se_3$ films (*b*)

irradiation times for X-ray-irradiated $(Ga_xIn_{1-x})_2Se_3$ films are shown in Fig, 5. In Ref. [5], it is shown that the optical absorption edge for $(Ga_xIn_{1-x})_2Se_3$ crystals in the region of its exponential behavior is described by the Urbach rule

$$\alpha(h\nu, T) = \alpha_0 \exp\left[\frac{h\nu - E_0}{E_U(T)}\right], \tag{12}$$

where $E_U(T)$ is the Urbach energy, $\alpha_0$ 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. It should be noted that, similarly to $(Ga_xIn_{1-x})_2Se_3$ crystals, the optical absorption edge in $(Ga_xIn_{1-x})_2Se_3$ films is also described by the Urbach relation [31–33]. It is worth to mention that the temperature variation of the Urbach absorption edge in the thin films under study similarly to that of the single crystals is explained by the electron-phonon interaction (EPI). Such parameters of EPI as $\hbar\omega_p$ (effective phonon energy in the single-oscillator model describing the EPI and $\sigma_0$ (parameter related to the EPI constant $g$ as $\sigma_0 = \frac{2}{3}g^{-1}$) can be calculated from the temperature dependence of the absorption edge steepness parameter $\sigma$ using the Mahr formula [34]

$$\sigma(T) = \sigma_0 \left(\frac{2kT}{\hbar\omega_p}\right) \tanh\left(\frac{\hbar\omega_p}{2kT}\right). \tag{13}$$

For $(Ga_xIn_{1-x})_2Se_3$ thin films, $\sigma_0 < 1$, and thre is the evidence for the strong EPI [34]. It should be noted that, in the thin films, compared to the single crystal, the EPI is enhanced (this corresponds to a decrease of the $\sigma_0$ parameter). Among the numerous theoretical treatments of the Urbach rule, the most often cited are (i) the Sumi–Toyozava model of self-trapped excitons and (ii) Dow–Redfield (DR) microelectric-field theory (internal Franz–Keldysh effect) [35, 36]. According to this theory, the broadening of the excitonic maxima with an increase in the temperature and the resulting exponential absorption edge are related to the interaction of excitons with microelectric fields generated by LO phonons in ionic crystals [36]. Using the procedure suggested in Ref. [37], where the influence of the external electric field $F_e$, causing the internal Franz–Keldysh effect, is replaced by the root-mean-square value of the phonon-induced internal electric field $F_p$, we have revealed the qualitative agreement between the DR theory and the absorption processes in $(Ga_{0.1}In_{0.9})_2Se_3$ thin films [31].

In the X-ray-irradiated $(Ga_xIn_{1-x})_2Se_3$ films, we also observed the Urbach shape of the optical absorption edge (Figure 5). It should be noted that the behavior of the optical absorption edge of $(Ga_xIn_{1-x})_2Se_3$ films under the X-ray irradiation repeats the behavior of the short-wavelength part of transmission spectra at the irradiation. At the maximum irradiation time (210 min) with increasing the content of Ga atoms, the exponential absorption edge is firstly (at $x = 0.2$) sharply shifted to the low-energy region and then, at $x = 0.3$ and $x = 0.4$, starts, on the contrary, to shift to the high-energy region. In this case, the absorption edge is smeared as a result of the compositional disordering. This affects the compositional dependences of the energy pseudogap and Urbach energy (Figure 5).

Let us analyze the dependences of the energy pseudogap and Urbach energy on the X-ray irradiation time in $(Ga_xIn_{1-x})_2Se_3$ films with $x = 0.1 - 0.4$, which is presented in Fig. 6. It can be seen that, for different values of $x$, the parameters of the absorption edge behave themselves differently. For $(Ga_{0.1}In_{0.9})_2Se_3$ and $(Ga_{0.2}In_{0.8})_2Se_3$ films with an increase in the irradiation time up to 210 min, the nonlinear decrease of $E_g^\alpha$ values by 0.057 eV and 0.15 eV, respectively, is observed. For $(Ga_xIn_{1-x})_2Se_3$ films with $x = 0.3$ and 0.4, the similar behavior is observed: during the first 30 min, the energy pseudogap $E_g^\alpha$ values increase by 0.011 eV for $x = 0.3$ and by 0.041 eV for $x = 0.4$. Then they decrease. For the film with $x = 0.3$, this decrease is 0.031 eV, whereas, for the film with $x = 0.4$, $E_g^\alpha$ value is also slightly decreased, but everything remains higher by 0.019 eV compared to the non-irradiated film. It should be noted that the dependence of the energy pseudogap of the $(Ga_xIn_{1-x})_2Se_3$ films with $x = 0.1$ and 0.2 on the exposure time can be used to create optical X-ray irradiation sensors.

The Urbach energy $E_U$ in $(Ga_xIn_{1-x})_2Se_3$ films increases with the irradiation time by 21 meV for $x = 0.1$, 61 meV for $x = 0.2$, and 6 meV for $x = 0.3$, and, apparently, the largest changes by 42% are observed for the film with $x = 0.2$. For $(Ga_{0.4}In_{0.6})_2Se_3$ films, the $E_U$ value during first 30 min of the X-ray irradiation decreases by 19 meV. Then, as the irradiation time increases, it increases by 13 meV. But it is anywhere by 6 meV smaller than that for an non-irradiated film.

It is well known that the Urbach energy $E_U$ is characterised by the disordering level of the investigated system and is described by the equation [38]

$$E_U = (E_U)_T + (E_U)_X + (E_U)_C, \qquad (14)$$

where $(E_U)_T$, $(E_U)_X$, and $(E_U)_C$ are the contributions of the temperature, structural, and compositional disorderings to $E_U$, respectively. The temperature disordering is caused by the thermal vibrations of the atoms and structural elements. The structural disordering is determined by the high concentration of disordered vacancies, pores, and other structural imperfections. Compositional disordering arises due to the cation substitution of In atoms by Ga. The presence of the above types of disordering results in the density-of-states tails affecting the absorption in the interval of optical absorption edges. According to Eq. (14), the observed increase in the Urbach energy $E_U$ (Figure 6) as a result of the irradiation occurs due to the increase in the contribution of the structural disordering caused by the X-ray irradiation. It should be noted that the most significant growth of the Urbach energy $E_U$ by 42% observed in X-ray-irradiated $(Ga_{0.2}In_{0.8})_2Se_3$ films is the evidence of the formation of defect states in the band gap and an increase in the structural disordering due to the X-ray irradiation.

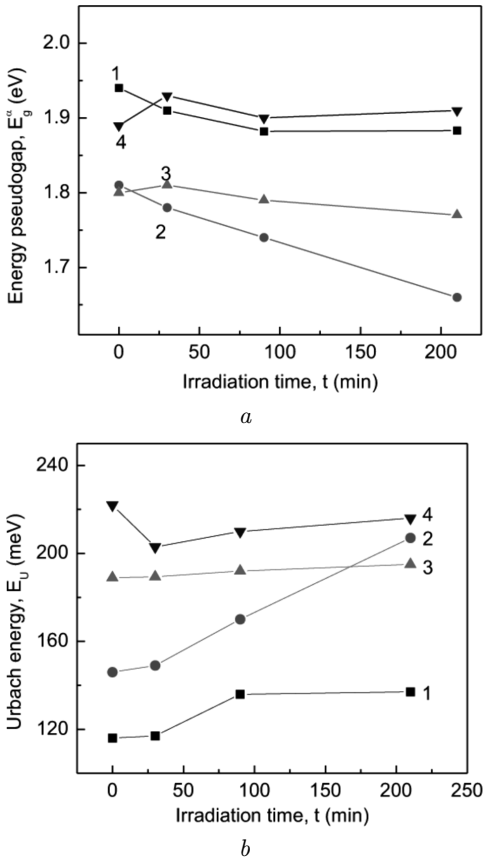



***Fig. 6.*** Dependences of the energy pseudogap $E_g^\alpha$ (*a*) and Urbach energy $E_U$ (*b*) on the irradiation time for X-ray-irradiated $(Ga_xIn_{1-x})_2Se_3$ films: $x = 0.1$ (*1*), $x = 0.2$ (*2*), $x = 0.3$ (*3*), and $x = 0.4$ (*4*)

## 4. Conclusions

Amorphous $(Ga_xIn_{1-x})_2Se_3$ films with $0.1 \le x \le 0.4$ deposited by the thermal evaporation technique are irradiated using the wideband radiation of a Cu-anode X-ray tube at different exposition times. The spectral dependences of the refractive index and ex-

tinction coefficient are measured by the spectral ellipsometry technique in the interval from 440 nm to 1000 nm, while the absorption coefficient is derived from the spectrometric studies of interference transmission spectra.

In the transparency region, the dispersion of refractive indices for the non-irradiated and X-ray-irradiated $(Ga_xIn_{1-x})_2Se_3$ films is observed and described by the well-known Cauchy, Sellmeier, Wemple–DiDomenico models and the optical-refractometric dispersion relation. According to the results of the fitting, the parameters for the above-mentioned dispersion models are obtained. They satisfactorily describe the dispersion of refractive indices for X-ray-irradiated $(Ga_xIn_{1-x})_2Se_3$ films with $0.1 \leq x \leq 0.4$. In the case of the Wemple–DiDomenico dispersion model, the dependences of such parameters as the single-oscillator energy $E_0^{\rm WD}$ and dispersion energy $E_d^{\rm WD}$ on the irradiation time have been analyzed in detail. The obtained time dependences of the refractive indices for irradiated films indicated the possibility of applications of $(Ga_xIn_{1-x})_2Se_3$ films as optical sensors, relay switches, and radiation-resistant coatings.

It is shown that the optical absorption edges for the non-irradited and X-ray-irradiated $(Ga_xIn_{1-x})_2Se_3$ films have an exponential form. The appearance of Urbach "tails" of the absorption is associated with the electron-phonon interaction which is strong in $(Ga_xIn_{1-x})_2Se_3$ films under study. The compositional dependences of such important parameters as the energy pseudogap and Urbach energy for X-ray-irradiated $(Ga_xIn_{1-x})_2Se_3$ films have been analyzed. Nonlinear behavior of the energy pseudogap $E_g^{\alpha}$ with a minimum at the $x = 0.2$ concentration and a nonlinear increase in the Urbach energy $E_{\rm U}$ are established. They are caused by an increase in the contribution of the structural disordering to $E_{\rm U}$ as a result of the influence of the X-ray irradiation. On the basis of the time dependences of the energy pseudogap $E_g^{\alpha}$, the conclusion is made about the possibility of applications of $(Ga_xIn_{1-x})_2Se_3$ films as X-ray irradiation optical sensors, which would work on a shift of the absorption edge during irradiation. The films of the composition $(Ga_{20}In_{80})_2Se_3$ have the highest sensitivity to X-rays among the studied films $(Ga_xIn_{1-x})_2Se_3$.

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МАТЕРІАЛИ ДЛЯ ОПТИЧНИХ СЕНСОРІВ РЕНТГЕНІВСЬКОГО ОПРОМІНЮВАННЯ НА ОСНОВІ ПЛІВОК $(Ga_xIn_{1-x})_2Se_3$

Плівки $(Ga_xIn_{1-x})_2Se_3$ з $0{,}1 \le x \le 0{,}4$ осаджено методом термічного напилення. Досліджувані плівки

$(Ga_xIn_{1-x})_2Se_3$ було опромінено широкосмуговим випромінюванням рентгенівської трубки з мідним анодом при різному часі експозиції. Методом спектральної еліпсометрії досліджено спектральні залежності показника заломлення та коефіцієнта екстинкції. Досліджено спектри оптичного пропускання плівок $(Ga_xIn_{1-x})_2Se_3$ після впливу рентгенівського випромінювання, залежно від часу опромінення. Визначено параметри урбахівського краю поглинання для свіжоприготованих та опромінених плівок $(Ga_xIn_{1-x})_2Se_3$. Спектральні залежності показника заломлення плівок $(Ga_xIn_{1-x})_2Se_3$ проаналізовано в рамках моделей Коші, Селмайєра та Уемпла–ДіДомініко. Проаналізовано детальну зміну параметрів моделі Уемпла–ДіДомініко для неопромінених та опромінених плівок $(Ga_xIn_{1-x})_2Se_3$. Обговорено перспективи використання плівок $(Ga_xIn_{1-x})_2Se_3$ як матеріалів для оптичних сенсорів рентгенівського випромінювання.

*Ключові слова*: плівка, спектральна еліпсометрія, спектри пропускання, рентгенівське опромінення, енергетична псевдощілина, показник заломлення.