https://doi.org/10.15407/ujpe65.3.231

I.P. STUDENYAK,[1] M. KRANJČEC,[2] V.YU. IZAI,[1] V.I. STUDENYAK,[1] M.M. POP,[1] L.M. SUSLIKOV [1]

[1] Uzhhorod National University
(46, Pidhirna Str., Uzhhorod, Ukraine; e-mail: studenyak@dr.com)
[2] University North
(33, J. Krzanica Str., Varazdin, Croatia)

ELLIPSOMETRIC AND SPECTROMETRIC STUDIES OF $(Ga_{0.2}In_{0.8})_2Se_3$ THIN FILM

Thermal evaporation technique is used to deposite $(Ga_{0.2}In_{0.8})_2Se_3$ thin films. The refractive index and extinction coefficient dispersions are obtained from the spectral ellipsometry measurements. The dispersion of the refractive index is described in the framework of the Wemple–Di Domenico model. The optical transmission spectra of a $(Ga_{0.2}In_{0.8})_2Se_3$ thin film are studied in the temperature range 77–300 K. The temperature behavior of the Urbach absorption edge, as well as the temperature dependences of the energy pseudogap and Urbach energy, are investigated. The influence of different types of disordering on the optical absorption edge of a $(Ga_{0.2}In_{0.8})_2Se_3$ thin film is discussed. Optical parameters of a $(Ga_{0.2}In_{0.8})_2Se_3$ thin film and a single crystal are compared.

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

1. Introduction

Semiconductor $(Ga_xIn_{1-x})_2Se_3$ solid solutions in the compositional range $0.02 < x < 0.55$ crystallize in the defect wurtzite structure with hexagonal symmetry ($P6_1$ or $P6_5$ space group) and belong to the γ_1-phase of the Ga_2Se_3-In_2Se_3 system [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 processes in the above-mentioned semiconductors.

We note that γ_1-$(Ga_xIn_{1-x})_2Se_3$ possesses the low electric conductivity ($\backsim 10^{-10}$ S/cm), but the photoconductivity in the γ_1-phase is almost by three orders of magnitude higher than in other phases [1]. The infrared reflection spectra and Raman scattering spectra studied in Refs. [3, 4] confirm a similarity of the crystalline structure of γ_1-phase and $\gamma-In_2Se_3$. The optical absorption edge in γ_1-$(Ga_xIn_{1-x})_2Se_3$ crystals at low absorption levels is shown to be formed by indirect interband optical transitions [5], the temperature and hydrostatic pressure effects on the absorption edge being studied in Refs. [6–8]. The interrelation between photoluminescence and optical absorption spectra were investigated in Refs. [9–11]. Refractometric, birefringent and gyrotropic properties of γ_1-$(Ga_xIn_{1-x})_2Se_3$ crystals were studied in Refs. [12–18] in detail. In addition, γ_1-$(Ga_xIn_{1-x})_2Se_3$ crystals are characterized by a high optical activity along the optical axis and are promising materials for acousto-optical modulators of laser irradiation [18, 19].

In the present paper, we report on the ellipsometric studies of the optical constants, temperature studies of the optical absorption edge, investigations of the temperature dependences of the energy pseudogap and Urbach energy, as well as the disordering processes in a $(Ga_{0.2}In_{0.8})_2Se_3$ thin film.

2. Experimental

$(Ga_{0.2}In_{0.8})_2Se_3$ crystals were obtained by the Bridgman technique. $(Ga_{0.2}In_{0.8})_2Se_3$ thin films were sputtered onto a quartz glass substrate by the thermal evaporation, their thickness being 2.0–2.5 μm. The structure of the deposited films was analyzed by X-ray diffraction; the diffraction spectra show the films

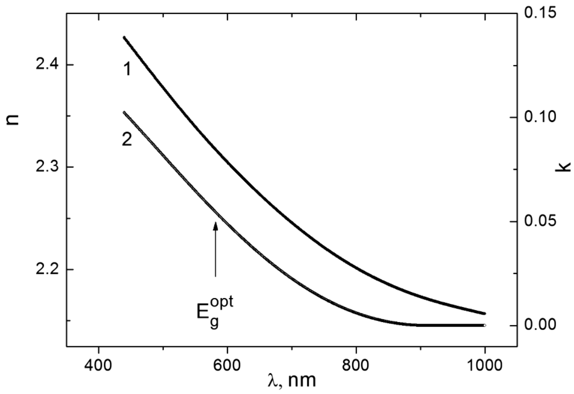

Fig. 1. Spectral dependences of the refractive index n (*1*) and extinction coefficient k (*2*) for a $(Ga_{0.2}In_{0.8})_2Se_3$ thin film at room temperature

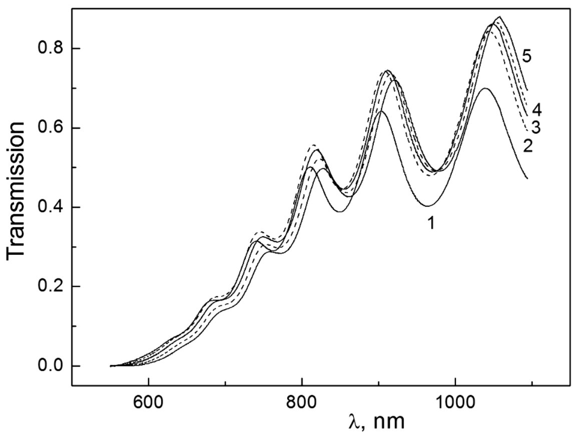

Fig. 2. Optical transmission spectra of a $(Ga_{0.2}In_{0.8})_2Se_3$ thin film at various temperatures: 77 (*1*), 150 (*2*), 200 (*3*), 250 (*4*), and 300 K (*5*)

to be amorphous. The composition of the thin films was determined by EDX on a Hitachi S4300 SEM.

A spectroscopic ellipsometer Horiba Smart SE was used for the measurements of the optical constants of a $(Ga_{0.2}In_{0.8})_2Se_3$ thin film. Measurements were carried out in the spectral region from 440 nm to 1000 nm at an incident angle of 70^o. Optical transmission spectra of a $(Ga_{0.2}In_{0.8})_2Se_3$ film were measured in the temperature interval 77–300 K by using a LOMO KSVU-23 grating monochromator. The spectral dependences of the absorption coefficient were derived from the interference transmission spectra [20].

3. Results and Discussionl

Refractive indices n and extinction coefficients k for a $(Ga_{0.2}In_{0.8})_2Se_3$ thin film were obtained from the spectral ellipsometry measurements which were carried out in the spectral interval 440–1000 nm (Fig. 1). In the transparency region, the refractive index dispersion is observed. Moreover, the refractive index increases more, when approaching the absorption edge. Among the number of models which describe the refractive index dispersion, we use the well-known Wemple–Di Domenico (WDD) model [21], where the refractive index dispersion is studied in the transparency region below the gap, using the single-oscillator approximation [21]:

$$n^2(E) - 1 = \frac{E_d E_0}{E_0^2 - E^2}. \tag{1}$$

Here, E_0 is the single-oscillator energy, and E_d is the dispersion energy. The dispersion energy E_d characherizes the average strength of interband optical transitions and is related to changes in the structural ordering of the material (ionicity, anion valency, and coordination number) [21]. From Eq. (1), the E_0 and E_d values were determined for a $(Ga_{0.2}In_{0.8})_2Se_3$ thin film (E_0 = 4.26 eV and E_d = 14.21 eV). According to the relation $E_0 \approx 2E_g^{\rm opt}$ [22], the optical band gap was estimated as $E_g^{\rm opt} = 2.13$ eV. It should be noted that E_g and the energy pseudogap E_g^α obtained from the analysis of absorption edge spectra do not differ by more than 12%. The static refractive index n_0 was calculated by the equation

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

and equals 2.08 for a $(Ga_{0.2}In_{0.8})_2Se_3$ thin film. By using the parameters of the WDD model, one can calculate the such important parameter as the ionicity [23]:

$$f_i = \left[\frac{E_0}{E_d}\right]^{1/2}, \tag{3}$$

which equals 0.55 for a $(Ga_{0.2}In_{0.8})_2Se_3$ thin film.

Interferential transmission spectra of a $(Ga_{0.2}In_{0.8})_2Se_3$ thin film at various temperatures within the interval 77–300 K are shown in Fig. 2. As the temperature increases, a red shift of the transmission spectra is observed. Optical absorption edge spectra in the range of their exponential behavior in a $(Ga_{0.2}In_{0.8})_2Se_3$ thin film are presented in Fig. 3. It should be noted that, similarly to a

$(Ga_{0.2}In_{0.8})_2Se_3$ single crystal, they are described by the Urbach rule [24]

$$\alpha(h\nu,T)=\alpha_0\exp\left[\frac{\sigma(h\nu-E_o)}{kT}\right]=\alpha_0\exp\left[\frac{h\nu-E_0}{E_U(t)}\right], \quad (4)$$

where E_U is the Urbach energy, σ is the absorption edge steepness parameter, α_0 and E_0 are the convergence point coordinates of the Urbach bundle. The parameters α_0 and E_0 for a $(Ga_{0.2}In_{0.8})_2Se_3$ thin film, as well as for a $(Ga_{0.2}In_{0.8})_2Se_3$ single crystal [10], are given in Table.

The temperature variation of the Urbach absorption edge in a thin film similarly to a single crystal is explained by the electron-phonon interaction (EPI). The insert to Fig. 3 shows the temperature dependence of the absorption edge steepness parameter σ. From the dependence of $\sigma(T)$, the EPI parameters are calculated using the Mahr formula [25]

$$\sigma(T)=\sigma_0\left(\frac{2kT}{\hbar\omega_p}\right)\tanh\left(\frac{\hbar\omega_p}{2kT}\right), \quad (5)$$

where $\hbar\omega_p$ is the effective phonon energy in a single-oscillator model, describing the electron-phonon interaction (EPI), and σ_0 is a parameter related to the EPI constant g as $\sigma_0=(2/3)g^{-1}$ (parameters $\hbar\omega_p$ and σ_0 are given in Table). For a $(Ga_{0.2}In_{0.8})_2Se_3$ thin film, $\sigma_0<1$ that is the evidence of the strong EPI [26]. It should be noted that, in the thin film, compared to a single crystal [10], the EPI is enhanced (this corresponds to a decrease of the σ_0 parameter), and the energy $\hbar\omega_p$ of the effective phonon, taking part in the absorption edge formation, practically remains unchanged (Table).

For the spectral characterization of the Urbach absorption edge, we used the value of the energy pseudogap E_g^α (E_g^α is the energy position of an exponential absorption edge at a fixed absorption coefficient $\alpha=10^4$ cm^{-1}) which is listed in Table for a thin film (for a single crystal, $\alpha=10^3$ cm^{-1} [10]). The temperature dependences of the energy pseudogap E_g^α and the Urbach energy E_U for a $(Ga_{0.2}In_{0.8})_2Se_3$ thin film are presented in Fig. 4 and can be described in the Einstein model by the relations [27, 28]

$$E_g^\alpha(T)=E_g^\alpha(0)-S_g^\alpha k\Theta_E\left[\frac{1}{\exp(\frac{\Theta_E}{T})-1}\right], \quad (6)$$

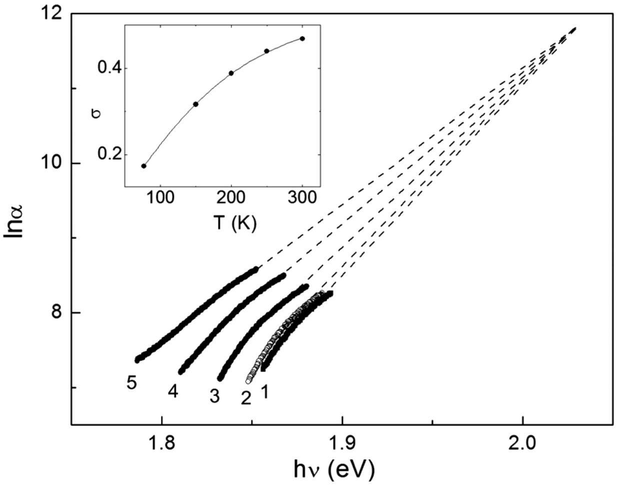

Fig. 3. Spectral dependences of the absorption coefficient for a $(Ga_{0.2}In_{0.8})_2Se_3$ thin film at various temperatures: 77 (*1*), 150 (*2*), 200 (*3*), 250 (*4*), and 300 K (*5*). The insert shows the temperature dependence of the steepness parameter σ

$$E_U(T)=(E_U)_0+(E_U)_1\left[\frac{1}{\exp(\frac{\Theta_E}{T})-1}\right], \quad (7)$$

where E_g^α (0) and S_g^α are the energy pseudogap at 0 K and a dimensionless constant, respectively; Θ_E is the Einstein temperature corresponding to the average frequency of phonon excitations of a system of non-coupled oscillators, and $(E_U)_0$ and $(E_U)_1$ are constants. The obtained E_g^α (0), S_g^α, Θ_E, $(E_U)_0$, and $(E_U)_1$ parameters for a thin film and a single crystal [10] are given in Table. The temperature dependences

Parameters of the Urbach absorption edge and EPI for a $(Ga_{0.2}In_{0.8})_2Se_3$ single crystal (for the $E||c$ polarization) [10] and a $(Ga_{0.2}In_{0.8})_2Se_3$ thin film

Material	Single crystal	Thin film
α_0 (cm^{-1})	2.5×10^{10}	1.33×10^5
E_0 (eV)	2.688	2.029
E_g^α (eV)	2.003	1.887
E_U (meV)	38	55
σ_0	0.835	0.581
$\hbar\omega_p$ (meV)	43	44
Θ_E (K)	499	415
$(E_U)_0$ (meV)	26	38
$(E_U)_1$ (meV)	54	76
$E_g^\alpha(0)$ (eV)	2.198	1.930
S_g^α	19.9	4.4

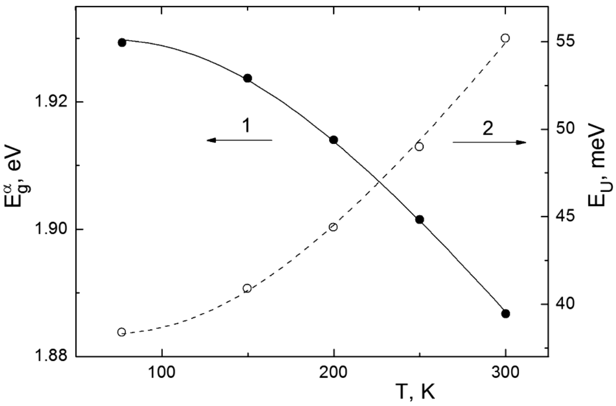

Fig. 4. Temperature dependences of the energy pseudogap E_g^α (*1*) and the Urbach energy E_U (*2*) of a $(Ga_{0.2}In_{0.8})_2Se_3$ thin film

of the energy pseudogap E_g^α and the Urbach energy E_U for a thin film calculated from Eqs. (6) and (7) are shown in Fig. 4 as solid and dashed lines, respectively.

It is well-known that the Urbach energy E_U is characterized by the degree of disordering for the different solids. For a thin film, the lengthy Urbach tails which result in the high value of the Urbach energy E_U are observed. In Ref. [29], the influences of the temperature and structural disordering on the shape of the Urbach absorption edge are studied. Thus, according to Ref. [29], the Urbach energy E_U is described by the equation

$$E_U=(E_U)_T+(E_U)_X+(E_U)_C=(E_U)_T+(E_U)_{X+C}, \quad (8)$$

where $(E_U)_T$, $(E_U)_X$, and $(E_U)_C$ are the contributions of the temperature and structural and compositional disorderings to E_U, respectively. It should be noted that the first term on the right-hand side of Eq. (7) represents the sum of structural and compositional disorderings, and the second one represents the temperature disordering. For the estimation of the contribution of the different types of disordering to the Urbach energy E_U, we used the procedure described in Ref. [30]. It is worth to note that the absolute value of the contribution of the sum of structural and compositional disorderings to the Urbach energy of a thin film increases more than by 45% in comparison with a single crystal [10].

Finally, in a $(Ga_{0.2}In_{0.8})_2Se_3$ thin film, we have observed: (1) a red shift of the optical absorption edge of a thin film compared to a single crystal [10]; (2) the thin film is more disordered than the single crystal [10], since the Urbach energy increases from 38 meV to 55 meV; (3) EPI enhances; (4) the absolute value of the sum of the contributions of structural and compositional disorderings to the Urbach energy increases from 26 meV to 38 meV.

4. Conclusions

$(Ga_{0.2}In_{0.8})_2Se_3$ films were deposited onto a quartz substrate by the thermal evaporation technique. The ellipsometric studies were performed in the spectral region from 440 nm to 1000 nm. The optical constants (refractive indices and extinction coefficients) for a thin film were obtained from the spectral ellipsometry measurements. In the transparency region, the dispersion of refractive indices is observed, and the refractive indices increase, by approaching the absorption edge. The dispersion of the refractive index of a $(Ga_{0.2}In_{0.8})_2Se_3$ thin film is described in the framework of the Wemple–Di Domenico model. The spectral dependences of the absorption coefficient were derived from the spectrometric studies of interference transmission spectra. The temperature variation of the transmission spectra, as well as the temperature behavior of the absorption edge spectra in the range of its exponential behavior are studied. A typical Urbach bundle is observed, and the temperature dependences of the energy pseudogap and the Urbach energy are analyzed. The influence of different types of disordering on the Urbach tail is studied, and the comparison of the Urbach absorption edge parameters for a thin film and a single crystal is performed.

1. S. Popović, B. Čelustka, Ž. Ružić-Toroš, D. Broz. X-ray diffraction study and semiconducting properties of the system Ga_2Se_3-In_2Se_3. *Phys. Stat. Sol. (a)* **41**, 255 (1977).
2. J. Ye, T. Yoshida, Y. Nakamura, O. Nittono. Realization of giant optical rotatory power for red and infrared light using III_2VI_3 compound semiconductor $(Ga_xIn_{1-x})_2Se_3$. *Jap. J. Appl. Phys.* **35**, 4395 (1996).
3. P. Dubček, B. Etlinger, K. Furić, M. Kranjčec. Raman spectra of $(Ga_xIn_{1-x})_2Se_3$. *Phys. Stat. Sol. (a)* **122**, K87 (1990).
4. P.P. Dubček, B. Etlinger, B. Pivac, M. Kranjčec. Infrared investigation of phonon modes in $(Ga_xIn_{1-x})_2Se_3$ solid solution in the $0.1 \leq x \leq 0.4$ concentration range. *Solid State Commun.* **81**, 735 (1992).
5. M. Kranjčec, B. Čelustka, B. Etlinger, D. Desnica. The indirect allowed optical transition in $(Ga_{0.3}In_{0.7})_2Se_3$. *Phys. Stat. Sol. (a)* **109**, 329 (1988).
6. D.I. Desnica, M. Kranjčec, B. Čelustka. Optical absorption edge and Urbach's rule in mixed single crystals of

$(Ga_xIn_{1-x})_2Se_3$ in the indium rich region. *J. Phys. Chem. Solids* **52**, 915 (1991).
7. M. Kranjčec, D.I. Desnica, B. Čelustka, Gy.Sh. Kovacs. The effect of pressure on the optical absorption edge in $(Ga_{0.3}In_{0.7})_2Se_3$. *Phys. Stat. Sol. (a)* **139**, 513 (1993).
8. M. Kranjčec, D.I. Desnica, B. Čelustka, Gy.Sh. Kovacs, I.P. Studenyak. Fundamental optical absorption edge and compositional disorder in γ_1-$(Ga_xIn_{1-x})_2Se_3$ single crystals. *Phys. Stat. Sol. (a)* **144**, 223 (1994).
9. M. Kranjčec, I.P. Studenyak, Yu.M. Azhniuk, S.I. Perechynskiy. Investigations of photoluminescence and optical absorption edge in semiconductors crystals of γ_1-$(Ga_xIn_{1-x})_2Se_3$ solid solutions. *Ukr. Fiz. Zh.* **50**, 1260 (2005).
10. M. Kranjčec, I.P. Studenyak, Yu.M. Azhniuk. Photoluminescence and optical absorption edge in γ_1-$(Ga_xIn_{1-x})_2Se_3$ mixed crystals. *Phys. Stat. Sol. (b)* **238**, 439 (2005).
11. M. Kranjčec, I.P. Studenyak. Temperature changes in the photoluminescence and the intrinsic absorption edge of the $(Ga_{0.1}In_{0.9})_2Se_3$ crystal. *Optics and Spectroscopy* **100**, 80 (200).
12. J. Ye, T. Yoshida, Y. Nakamura, O. Nittono. Optical activity in the vacancy ordered III_2VI_3 compound semiconductor $(Ga_{0.3}In_{0.7})_2Se_3$. *Appl. Phys. Lett.* **67**, 3066 (1995).
13. M. Kranjčec, I.D. Desnica, B. Čelustka, A.N. Borec, Gy.Sh. Kovacs, Z.P. Hadmashy, L.M. Suslikov, I.P. Studenyak. On some crystal-optic properties of γ_1-$(Ga_xIn_{1-x})_2Se_3$ single crystals. *Phys. Stat. Sol. (a)* **153**, 539 (1996).
14. I.P. Studenyak, M. Kranjčec, L.M. Suslikov, D.Sh. Kovach. Piezobirefringence in γ_1-$(Ga_xIn_{1-x})_2Se_3$ single crystals. *Optics and Spectroscopy* **95**, 427 (2003).
15. I.P. Studenyak, M. Kranjčec, L.M. Suslikov, D.Sh. Kovach. Influence of temperature on birefringence of γ_1-$(Ga_xIn_{1-x})_2Se_3$ single crystals. *Ukr. Fiz. Zh.* **48**, 910 (2003). (in Ukrainian).
16. M. Kranjčec, I.P. Studenyak, L.M. Suslikov, Gy.Sh. Kovacs, E. Cerovec. Birefringence in γ_1-$(Ga_xIn_{1-x})_2Se_3$ single crystals. *Opt. Mat.* **25**, 307 (2004).
17. I.P. Studenyak, M. Kranjčec, O.M. Borets. Compositional variation of optical and refractometric parameters of γ_1-$(Ga_xIn_{1-x})_2Se_3$ mixed crystals. *J. Optoelectron. Adv. Mater.* **5**, 865 (2003).
18. I.P. Studenyak, M. Kranjčec, L.M. Suslikov. Optical activity of γ_1-$(Ga_xIn_{1-x})_2Se_3$ crystals. *Optics and Spectroscopy* **95**, 599 (2003).
19. M. Kranjčec, I.D. Desnica, I.P. Studenyak, B. Čelustka, A.N. Borec, I.M. Yurkin, Gy.Sh. Kovacs. Acousto-optic modulator with a $(Ga_{0.4}In_{0.6})_2Se_3$ monocrystal as the active element. *Applied Optics* **36**, 490 (1997).
20. R. Swanepoel. Determination of the thickness and optical constants of amorphous silicon. *J. Phys. E: Sci. Instrum.* **16**, 1214 (1983).
21. S.H. Wemple, M.Di Domenico. Behaviour of the dielectric constant in covalent and ionic materials. *Phys. Rev. B* **3**, 1338 (1971).
22. K. Tanaka. Optical properties and photoinduced changes in amorphous As-S films. *Thin Solid Films* **66**, 271 (1980).
23. M.S. Tubbs. A spectroscopic interpretation of crystalline ionicity. *Phys. Stat. Sol. (b)* **41**, k61 (1970).
24. F. Urbach. The long-wavelength edge of photographic sensitivity and of the electronic absorption of solids. *Phys. Rev.* **92**, 1324 (1953).
25. H. Sumi, A. Sumi. The Urbach-Martienssen rule revisited. *J. Phys. Soc. Japan* **56**, 2211 (1987).
26. M.V. Kurik. Urbach rule (Review). *Phys. Stat. Sol. (a)* **8**, 9 (1971).
27. M. Beaudoin, A.J.G. DeVries, S.R. Johnson, H. Laman, T. Tiedje. Optical absorption edge of semi-insulating GaAs and InP at high temperatures. *Appl. Phys. Lett.* **70**, 3540 (1997).
28. Z. Yang, K.P. Homewood, M.S. Finney, M.A. Harry, K.J. Reeson. Optical absorption study of ion beam synthesized polycrystalline semiconducting $FeSi_2$. *J. Appl. Phys.* **78**, 1958 (1995).
29. G.D. Cody, T. Tiedje, B. Abeles, B. Brooks, Y. Goldstein. Disorder and the optical-absorption edge of hydrogenated amorphous silicon. *Phys. Rev. Lett.* **47**, 1480 (1981).
30. M. Kranjčec, I.P. Studenyak, M.V. Kurik. On the Urbach rule in non-crystalline solids. *J. Non-Cryst. Solids* **355**, 54 (2009).

Received 28.08.18

І.П. Студеняк, М. Краньчец, В.Ю. Ізай,
В.І. Студеняк, М.М. Поп, Л.М. Сусліков

ЕЛІПСОМЕТРИЧНІ ТА СПЕКТРОМЕТРИЧНІ ДОСЛІДЖЕННЯ ТОНКОЇ ПЛІВКИ $(Ga_{0,2}In_{0,8})_2Se_3$

Р е з ю м е

Тонкі плівки $(Ga_{0,2}In_{0,8})_2Se_3$ були отримані методом термічного напилення. За допомогою методики спектральної еліпсометрії отримано дисперсійні залежності показника заломлення та коефіцієнта екстинкції. Дисперсію показника заломлення описано в рамках моделі Уемпла–Ді Доменіко. Спектри оптичного пропускання тонкої плівки $(Ga_{0,2}In_{0,8})_2Se_3$ досліджено в інтервалі температур 77–300 К. Вивчено температурну поведінку урбахівського краю поглинання, а також температурні залежності ширини псевдозабороненої зони та урбахівської енергії. Обговорюється вплив різних типів розупорядкування на край оптичного поглинання тонкої плівки $(Ga_{0,2}In_{0,8})_2Se_3$. Проведено порівняння оптичних параметрів тонкої плівки та монокристала $(Ga_{0,2}In_{0,8})_2Se_3$.