STUDY OF PHOTOLUMINESCENCE AND OPTICAL ABSORPTION EDGE IN SEMICONDUCTING CRYSTALS OF γ_1-$(Ga_x\ In_{1-x})_2Se_3$ SOLID SOLUTIONS

M. KRANJČEC, I.P. STUDENYAK[1], YU.M. AZHNIUK[2], S.I. PERECHYNSKYI[1]

University of Zagreb, Geotechnical Department
(7, Hallerova Aleja, Varaždin 42000, Croatia; e-mail: m_kranjcec@yahoo.com),

[1]**Uzhhorod National University**
(46, Pidhirna Str., Uzhgorod 88000, Ukraine; e-mail: studenyak@dr.com),

[2]**Institute of Electron Physics, Nat. Acad. Sci. of Ukraine**
(21, Universytetska Str., Uzhgorod 88000, Ukraine; e-mail: azhn@ukrpost.net)

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Experimental studies of photoluminescence and optical absorption edge in γ_1-$(Ga_xIn_{1-x})_2Se_3$ crystals with $x = 0.1 \div 0.4$ have been carried out. The exciton- and impurity-related bands in the photoluminescence spectra, as well as the exponential shape of the absorption edge, have been revealed at the temperature $T = 77$ K. The compositional dependences of the spectral position of the photoluminescence band, its halfwidth, the optical pseudogap, and the absorption edge energy width have been investigated. The influence of various types of disordering in a crystal lattice on the processes of optical absorption and photoluminescence in γ_1-$(Ga_xIn_{1-x})_2Se_3$ solid solutions has been studied.

1. Introduction

Semiconducting solid solutions $(Ga_xIn_{1-x})_2Se_3$, within the interval of concentrations $0.02 < x < 0.55$, crystallize in the defect wurtzite structure and possess the hexagonal symmetry (either of $P6_1$ or $P6_5$ spatial group) [1]. A characteristic attribute of this structure is high concentration of vacancies which are capable to form spirals along the optical axis c of the crystal [2]. The alternation of cations with vacancies provides a disordered distribution of the latter, which provokes stochastic fluctuations of the electric potential in the crystal lattice, which, in its turn, affects the development of physical processes in the materials under consideration.

The optical properties of γ_1-$(Ga_xIn_{1-x})_2Se_3$ crystals have been studied in detail and described in a number of works[3—15]. For example, the researches of the Raman scattering of light and the light reflection in the infrared spectral range confirmed the similarity between the crystalline structures of γ_1-$(Ga_xIn_{1-x})_2Se_3$ and γ-In_2Se_3 compounds [3, 4]. Earlier [5], it was shown that the edge of optical absorption in γ_1-$(Ga_xIn_{1-x})_2Se_3$ crystals, provided low levels of absorption, is formed by indirect interband optical transitions, with a number of works [6–8] being devoted to the influence of temperature and hydrostatic pressure on it. Researches of refractometric, birefringent, and gyrotropic properties of γ_1-$(Ga_xIn_{1-x})_2Se_3$ crystals testified to that they are characterized by high optical activity along their optical axis and are perspective materials for fabricating the acoustooptical modulators of laser emission [9–15].

This work aims at establishing the influence of a variation in the composition of γ_1-$(Ga_xIn_{1-x})_2Se_3$ crystals on the photoluminescence and absorption edge spectra, as well as at studying, on their basis, the processes of disordering in the crystal lattice of the solid solutions in question.

2. Experimental Part

γ_1-$(Ga_xIn_{1-x})_2Se_3$ crystals with $x = 0.1 \div 0.4$ were grown up making use of the Bridgman method [8]. The non-polarized photoluminescence spectra were investigated on a DFS-24 double-grating spectrometer. Photoluminescence was excited by means of an Ar-laser with the emission wavelength $\lambda = 488.0$ nm.

The researches of the optical absorption edge spectra were carried out for two polarizations of incident irradiation, $\mathbf{E} \parallel \mathbf{c}$ and $\mathbf{E} \perp \mathbf{c}$, using the installation and technique described in work [16]. The light beam propagated in the direction perpendicular to the optical axis, so that the optical activity along it can be neglected. The thickness of specimens ranged from several mm's down to 30 μm, which allowed us to cover a wide interval of variations in the absorption factor (from

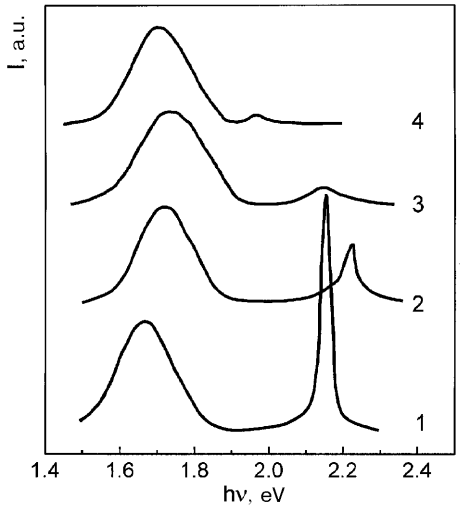

Fig. 1. Photoluminescence spectra of γ_1-$(Ga_xIn_{1-x})_2Se_3$ crystals at the temperature $T = 77$ K for various values of x: 0.1 (*1*), 0.2 (*2*), 0.3 (*3*), and 0.4 (*4*)

10 to 1500 cm^{-1}). The relative error of the determination of the absorption factor did not exceed 10%. For low-temperature researches, a cryostat of the UTREKS type with an accuracy of temperature stabilization and measurement of ±0.5 K was applied.

3. Results of Experimental Researches and Their Discussion

3.1. Photoluminescence spectra of γ_1-$(Ga_xIn_{1-x})_2Se_3$ crystals

Fig. 1 presents the spectra of low-temperature photoluminescence of γ_1-$(Ga_xIn_{1-x})_2Se_3$ crystals measured from the as-cleaved surfaces oriented perpendicularly to the optical axis. Two bands — a high-energy, narrow band E_1 at 2.153 eV and a low-energy broad band E_2 at 1.668 eV — were revealed in the photoluminescence spectrum of a $(Ga_{0.1}In_{0.9})_2Se_3$ crystal at $T = 77$ K, with the intensity of band E_1 being twice the intensity of band E_2. Taking into account the spectral position and the halfwidth of band E_2, it can be attributed to the impurity-related type; it may correspond to the recombination of a free current carrier and that coupled to a local center (transitions of the type "band—local center"). The high-energy narrow band E_1 may be excitonic and may correspond to the annihilation of a free exciton in the ground state ($n = 1$).

Compositional researches of the γ_1-$(Ga_xIn_{1-x})_2Se_3$ solid solution crystals with $x = 0.1 \div 0.4$, executed at $T = 77$ K, showed that as the content of Ga atoms

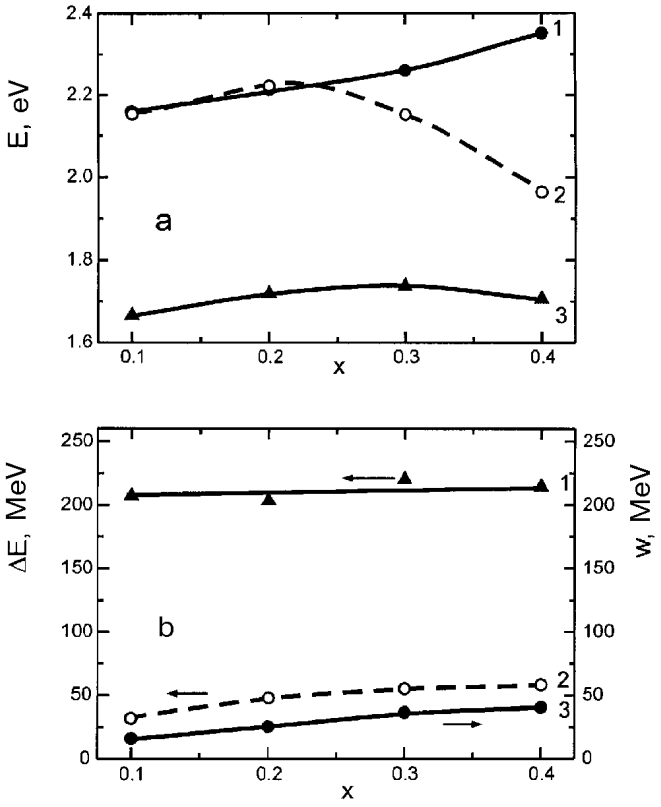

Fig. 2. Dependences of (panel *a*) the optical pseudogap width (for polarization $\mathbf{E} \parallel \mathbf{c}$) (*1*), the spectral positions of excitonic (*2*) and impurity-related (*3*) photoluminescence bands, and (panel *b*) the energy width of the exponential absorption edge (*3*), the halfwidths of the excitonic (*2*) and impurity-related (*1*) photoluminescence bands on the composition parameter x for γ_1-$(Ga_xIn_{1-x})_2Se_3$ crystals at $T = 77$ K

increases, the band of excitonic photoluminescence shifts nonlinearly (with upward bowing) towards the long-wave range (except for the solid solution with $x = 0.2$) and broadens; and its intensity decreases abruptly (Figs. 1 and 2). On the contrary, the impurity-related band tends, with the increase of x, to shifting towards the short-wave range (except for the solid solution with $x = 0.4$) and broadens; and its intensity remains almost constant.

3.2. Optical absorption edge spectra of γ_1-$(Ga_x\ In_{1-x})_2Se_3$ crystals

The fulfilled investigations show that the absorption edge in γ_1-$(Ga_xIn_{1-x})_2Se_3$ crystals, at $T = 77$ K and provided polarization $\mathbf{E} \parallel c$, has an exponential shape in the range of direct interband optical transitions (Fig. 3).

It should be noted that, for polarization $\mathbf{E} \perp c$, the absorption edge is not exponential. A similar anisotropy of the absorption edge shape was observed in such materials as Se, GeSe, and Ge [17–19].

When Ga atoms were substituted for In ones, the researched crystals of solid solutions manifested the shift of the absorption edge towards the high-energy range (Fig. 3). In this case, the energy width w of the exponential absorption edge (the value reciprocal to the slope of the absorption edge) increases. The modifications of the energy position and the energy width of the absorption edge stimulated by the cation substitution In→Ga are defined by the influence of compositional disordering, which was observed in solid solution crystals [20].

Owing to the fact that the direct interband optical transitions in solid solution crystals under investigation are disguised by the absorptional long-wave exponential "tails", it is impossible to determine the true width of the direct energy gap. In this case, frequently used is the width of the optical pseudogap E_g^* which corresponds to the energy position of the absorption edge at a fixed absorption level $\alpha = 10^3$ cm^{-1}. The applicability of E_g^* instead of the direct energy gap width in the case where the form of the absorption edge is exponential, was shown to be true in works [21,22]. The concentration dependence $E_g^*(x)$ snown in Fig. 2 is nonlinear with upward bowing. It is known that the concentration-induced variations in the optical pseudogap width can be described with the help of the relationship [23]

$$E_g^*(x) = E_g^*(0) + [E_g^*(1) - E_g^*(0)]x - cx(1-x), \qquad (1)$$

where $E_g^*(x=0) \equiv E_g^*(0)$ and $E_g^*(x=1) \equiv E_g^*(1)$ are the values of the optical pseudogap width in crystals with relevant end compositions in a series of solid solutions, and c is the so-called bowing parameter, which is a measure of the deviation of the function $E_g^*(x)$ from linearity. The best fitting of the experimental dependence $E_g^*(x)$ by relationship (1) was obtained with the following parameters: $E_g^*(0) = 2.136$ eV, $E_g^*(1) = 3.208$ eV, and $c = 0.9$ eV (the positive value of c indicates that the dependence $E_g^*(x)$ is bowed downward). According to work [23], the dependence $E_g^*(x)$ can be bowed owing to such factors: 1) bulk distortion of energy bands, stimulated by a variation in the lattice parameters of solid solution crystals, 2) variations in electronegativity, and 3) structural modifications which occur when cation bonds change their lengths.

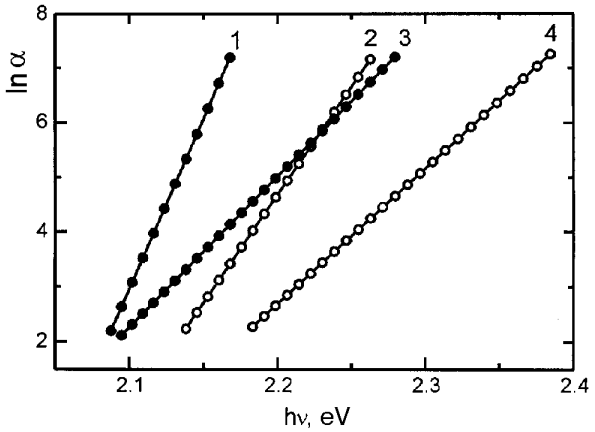

Fig. 3. Spectral dependences of the logarithm of the absorption factor of γ_1-$(Ga_xIn_{1-x})_2Se_3$ crystals at $T = 77$ K for various values of x: 0.1 (*1*), 0.2 (*2*), 0.3 (*3*), and 0.4 (*4*)

3.3. Disordering processes in γ_1-$(Ga_xIn_{1-x})_2Se_3$ crystals

According to the data of works [24, 25], the width of the optical pseudogap E_g^* and the energy width of the absorption edge w reflect the influence of different kinds of disordering on the long-wave absorption edge:

$$E_g^* = E_{g,0}^* - k_g(W_T^2 + W_S^2 + W_C^2), \qquad (2)$$

$$w = k_0(W_T^2 + W_S^2 + W_C^2), \qquad (3)$$

where k_0 and k_g are constants; $E_{g,0}^*$ is the width of the optical pseudogap of a perfect crystal without disordering; W_T^2, W_S^2, and W_C^2 are the mean-square deviations from the electric potential in an ideally ordered lattice induced by temperature (due to thermal vibrations of the lattice) and the structural and compositional disorderings, respectively. The structural disordering in the researched crystals is intrinsic by its nature and is governed by a high concentration of disordered vacancies in the cation sublattice, while the compositional disordering arises owing to the cation substitution of In atoms by Ga ones. Disordering of any of the indicated types results in the emergence of the tails in the density of states of the energy bands, which affects the absorption processes in the range of the intrinsic absorption edge.

If one takes into account that the contributions of different kinds of disordering to w are equivalent, independent, and additive, formula (3) looks like

$$w = w_X + w_T + w_C, \qquad (4)$$

where w_X, w_T, and w_C are the structural, temperature-related, and compositional contributions, respectively, to

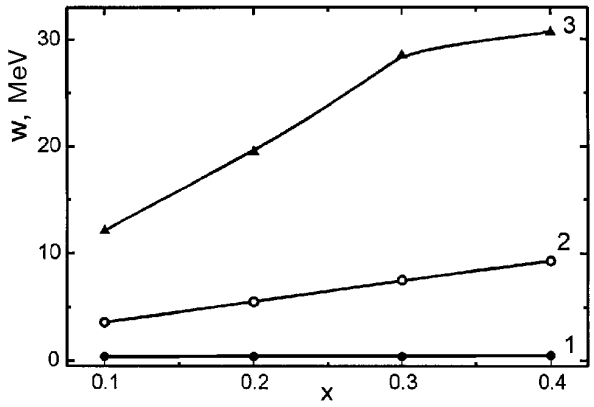

Fig. 4. Concentration dependences of the contributions of the temperature-related w_T (*1*) and the structural w_X (*2*) and compositional w_C (*3*) disorderings to the energy width of the absorption edge at $T = 77$ K for γ_1-$(Ga_xIn_{1-x})_2Se_3$ crystals

disordering. We notice that, in the crystals with extreme compositions of solid solutions, only the structural, w_X, and temperature, w_T, kinds of disordering are valid. Using the results of researches of the temperature dependence of the absorption edge of γ_1-$(Ga_xIn_{1-x})_2Se_3$ crystals [8] and a technique described in work [26], we estimated the contribution of each kind of disordering to the energy width w of the exponential absorption edge at $T = 77$ K. The concentration dependences of w_X, w_T, and w_C thus obtained for the crystals of γ_1-$(Ga_xIn_{1-x})_2Se_3$ solid solutions are presented in Fig. 4. As the concentration of Ga atoms grows, the contributions w_X and w_C increase, whereas the contribution w_T remains constant. We note that the contribution of the compositional disordering is crucial, being more than thrice as much as that of the structural disordering. According to work [25], the concentration behavior of the compositional disordering contribution w_C can be described by the relation $w_C = Ax(1 - x)$, where A is a fitting parameter. For γ_1-$(Ga_xIn_{1-x})_2Se_3$ crystals, $A = 130$ meV, whereas for hydrogenated a-SiC and a-SiC solid solutions, $A = 337$ and 192 meV, respectively [25].

The comparative analysis of the concentration dependences of the halfwidth ΔE_1 of the excitonic photoluminescence band and the energy width w of the exponential absorption edge shows (Fig. 2) that they are similar, and there is some correlation between them. This testifies to that the compositional disordering affects the processes of both absorption and emission of light in semiconducting crystals of γ_1-$(Ga_xIn_{1-x})_2Se_3$ solid solutions.

4. Conclusions

The compositional researches of photoluminescence and optical absorption edge in γ_1-$(Ga_xIn_{1-x})_2Se_3$ crystals with $x = 0.1 \div 0.4$ have been carried out. The excitonic and impurity-related bands have been revealed in the relevant photoluminescence spectra at low temperatures; the character of their concentration transformation has been investigated. The exponential form of the optical absorption edge at $T = 77$ K for polarization $\mathbf{E} \parallel \mathbf{c}$ has been found, and its key parameters have been determined. It has been established that the concentration variations of the excitonic photoluminescence band halfwidth correlate well with analogous changes of the energy width of the exponential absorption edge, being caused by the processes of compositional disordering in the crystal lattice of γ_1-$(Ga_xIn_{1-x})_2Se_3$ solid solutions. The contributions of temperature-related and the structural and compositional disorderings to the energy width of the absorption edge have been estimated, and their concentration dependences have been obtained. It has been shown that the compositional behavior of the energy width of the absorption edge is mainly determined by the concentration behavior of the compositional disordering contribution.

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ДОСЛІДЖЕННЯ ФОТОЛЮМІНЕСЦЕНЦІЇ ТА КРАЮ ОПТИЧНОГО ПОГЛИНАННЯ В НАПІВПРОВІДНИКОВИХ КРИСТАЛАХ ТВЕРДИХ РОЗЧИНІВ γ_1-$(Ga_x\ In_{1-x})_2Se_3$

М. Краньчец, І.П. Студеняк, Ю.М. Ажнюк, С.І. Перечинський

Р е з ю м е

Проведено дослідження фотолюмінесценції та краю оптичного поглинання кристалів γ_1-$(Ga_xIn_{1-x})_2Se_3$ з x=0,1÷0,4. Виявлено смуги екситонної та домішкової фотолюмінесценції, а також експоненціальну форму краю поглинання при T=77 K. Досліджено концентраційні залежності спектрального положення та півширини смуг фотолюмінесценції, а також ширини оптичної псевдощілини та енергетичної ширини краю поглинання. Вивчено вплив різних типів розупорядкування кристалічної гратки на процеси оптичного поглинання та фотолюмінесценції у твердих розчинах γ_1-$(Ga_xIn_{1-x})_2Se_3$.