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THE İNFLUENCE OF BORON ATOMS ON THE ABSORPTİON AND LUMİNESCENCE SPECTRA OF THİN GaSe, InSe FILMS AND GaSe/InSe HETEROSTRUCTURES

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ABSTRACT

The absorption and luminescence spectra of thin GaSe, InSe films doped with boron atoms and heterostructures based on them were experimentally studied. The studied samples were obtained by a modified chemical vapor deposition method (SILAR). The absorption and luminescence spectra were recorded using a Nd:YAG laser with built-in 2nd and 3rd harmonic generators. It was shown that boron impurities affect the exciton absorption band and the width of the photoluminescence spectral lines.

I. INTRODUCTION

Gallium selenide (GaSe) and indium selenide (InSe) crystals belong to layered semiconductor compounds of the A^3B^6 type, in which there is a strong ionic-covalent bond along the layers, while weak Van der Waals bonding occurs between the layers. Weak bonding between the layers leads to the formation of tetralayers with thicknesses of ~ 63 nm for GaSe, and the relative arrangement of monolayers in tetralayers forms β-, ε-, γ- and δ- modifications of the crystalline structure [1]. The displacement of tetralayers relative to each other leads in turn to the formation of stacking faults. Experiments show that such defects are distributed randomly in the direction perpendicular to the crystal axis and cause the formation of potential barriers with an average height of $\Delta E \approx 20$ meV for charge carriers in the direction of the [2]. axis. The InSe compound has similar packing defects in the crystal structure. Low hardness and tendency to micro-deltatation of layered GaSe and InSe crystals make them practically unsuitable for mechanical treatment of the working surfaces of samples at an angle to the axis and lead to an increase in optical losses in the crystal. The formed point and linear defects in the crystal structure, due to uncontrollable factors in the process of growing single crystals, do not allow wide application of layered crystals with the required characteristics. To solve this problem, they resort to improving the technology of growing single crystals and doping the crystal with isovalent elements with respect to Ga, In and Se, as well as various rare earth elements [3-6]. In this work, boron was chosen as the doping element. An isolated boron atom has an unstable configuration of valence electrons s^2p^1. However, during the formation of a condensed state, this configuration is transformed into an energetically more stable configuration s^1p^2 due to the single-electron transition $s^2p^1 \rightarrow s^1p^2$. For the latter, in turn, transitions according to the scheme $s^1p^2 + s^1p^2 \rightarrow s^1p^3 + s^1p^1$ are possible [7]. Therefore, the boron impurity in multicomponent compounds behaves in a variety of ways. For example, boron atoms implanted in n-type GaAs create deep impurity centers in the forbidden zone of the crystal at a depth of 0.55 and 0.70 eV. In this study, we examined CdSe thin films created on glass substrates using the chemical deposition method and analyzed them using spectroscopic ellipsometry. We used a dispersion model to calculate the optical constants and determine the thickness, dielectric permittivity (real and imaginary part), refraction, and extension coefficients of the thin layers. We found that the width of the forbidden zone in the 350 nm and 400 nm thick cadmium selenide thin films corresponds to Eg = 1.9 eV and Eg = 2.2 eV. The widening of the forbidden zone is attributed to the phase formation process within the thin layers. [8]. After thermal annealing, these centers disappear, turning into a compensating acceptor center. When boron atoms condense in interaction with selenium atoms, an isotypic structure (BSe2) is formed with an optimal distance of 198 nm between B–Se atoms [9]. In the crystal structure of gallium selenide, the distance between Ga–Se and In–Se atoms is 247 nm. Of course, when replacing gallium and indium with impurity boron atoms in the crystal structure of GaSe and InSe, a stronger bond with selenium atoms arises than the Ga-Se and In-Se bond. Therefore, it can be expected that doping GaSe and InSe with boron atoms can eliminate the above-mentioned disadvantages and improve the sought-after practical characteristics of these crystals.

Of particular interest is the study of the effect of boron atoms on epitaxial GaSe/InSe heterostructures, since semiconductor structures with a variable band gap are widely used in the manufacture of optoelectronic devices [10].

In this paper, the absorption and luminescence spectra of thin GaSe, InSe films and GaSe/InSe heterostructures doped with boron atoms under the action of laser radiation are experimentally studied.

II. EXPERIMENTAL METHODOLOGY

The studied samples were obtained by a modified chemical deposition method (Successive Ionic Layer Adsorption and Reaction- SILAR). Thin films of GaSe and InSe on a glass substrate were grown by hydrochemical deposition from a solution containing sodium selenosulfate (Na_2SeSO_3) and gallium trichloride ($GaCl_3$) and indium ($InCl_3$). The initial raw materials used were especially pure Na_2SeSO_3 and $GaCl_3$ according to the following reactions:

$$Na_2SO_3 + Se \rightarrow Na_2SeSO_3$$

$$In + 3HCl \leftrightarrow GaCl_2 + \frac{3}{2}H_2$$

$$Ga + 3HCl \leftrightarrow GaCl_2 + \frac{3}{2}H_2$$

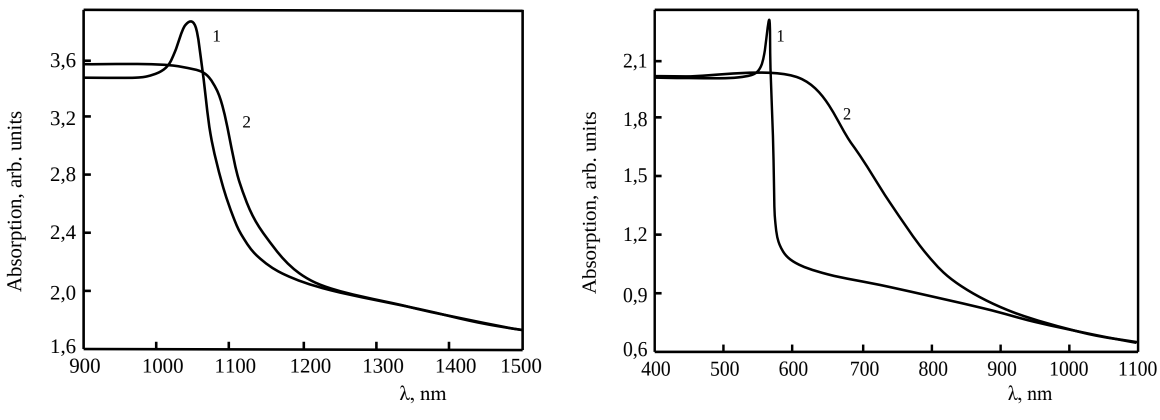
Then, aqueous solutions of sodium selenosulfate and gallium chloride were prepared in the ratio necessary for the formation of and InSe, with a composition corresponding to the stoichiometric composition. Thin films of the compound and InSe were grown in the following sequence: four containers with liquids were used. The first contained a solution of gallium or indium chloride, the second distilled water, the third a solution of sodium selenosulfate and the fourth, also distilled water. The substrates were kept in these containers successively for 20 seconds, 10 seconds, 15 seconds and 10 seconds, respectively. This process was repeated 30 times in a row.

A pulsed Nd:YAG laser with built-in 2nd and 3rd harmonic generators designed to generate radiation with wavelengths of 1064, 532 and 335 nm was used as a radiation source. The laser pulse duration was 10 ns with a maximum power of ~12 MVt/cm2. The radiation intensity was varied using calibrated neutral light filters. Using a lens, the laser beam was focused onto the sample surface with a spot diameter of ~2.0 mm. The absorption and photoluminescence spectra were studied using an automated M833 double dispersion monochromator with computer control and a photodetector recording radiation in the wavelength range of 350-2000 nm. The experimental technique is similar to that presented in. Thus, as the bond lengths of the same chemical elements decrease, the frequency of vibrations increases. Therefore, in studies carried out at high pressures, an increase in the vibration frequency is observed as the crystal lattice is destroyed [11].

III. EXPERIMENTAL RESULTS AND THEIR DISCUSSION

Figure 1a (curve 1) shows the absorption spectrum of thin GaSe films without boron doping. As can be seen from the figure, the sharp peak corresponds to the energy Eexp~2.077 eV. In our opinion, this peak is associated with free excitons, since it is known that the fundamental edge of the GaSe absorption band is due to free exciton transitions with an exciton binding energy of ~20 meV [12]. The width of the GaSe band gap, determined from the dependence $\alpha^2 \sim f(h\nu)$, turned out to be equal to $E_g = 2{,}097$ eV.

The absorption spectrum of thin GaSe films doped with boron atoms (0.1 V) differs significantly from the absorption spectrum of pure samples (Fig. 1, a, curve 2). In the absorption spectrum of doped samples, a decrease in exciton absorption and a shift of the absorption band edge to the long-wave region of the spectrum (~5 nm) are observed. The band gap of boron-doped GaSe samples was found to be ~2.073 eV.



a *b*

Fig. 1. *Absorption spectra of GaSe (a) and InSe (b): 1 – pure; 2 – doped with boron atoms.*

Similar patterns are observed for InSe thin films. Unlike GaSe, the absorption spectra of InSe thin films are in the near infrared region of the spectrum. In samples undoped with boron atoms, exciton absorption corresponds to the energy Eexp~1.14 eV, and the band gap is 1.16 eV. The shift of the absorption band edge to the long-wavelength region of the spectrum in doped samples is ~9 nm. Fig. 2 shows the absorption spectra of the GaSe/InSe heterostructure of pure (black line) and boron-doped (red line) components. As can be seen from the figure, three absorption bands are observed in the absorption spectrum of pure GaSe/InSe at 597 nm, 465 nm and 485 nm.

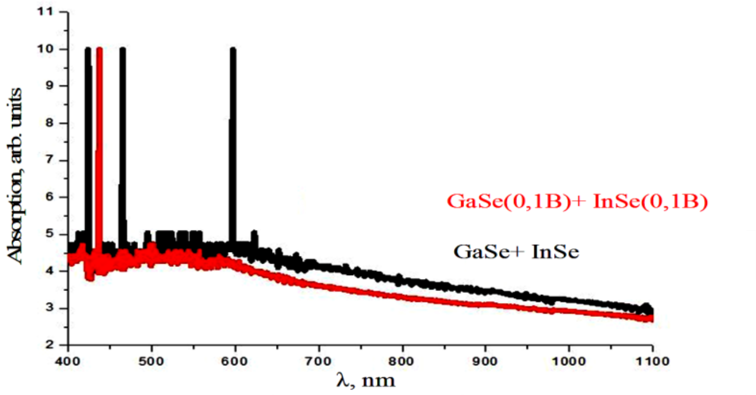


Fig. 2. *Absorption spectra of the GaSe/InSe heterostructure, pure (black line) and doped (red line) with boron atoms.*

In our opinion, the absorption band in thin GaSe films with a maximum at λ=597 nm is related to exciton absorption at the edge of intrinsic absorption. Two other high-energy bands, at 465 nm and 485 nm, are apparently due to interband transitions in the region of the continuous spectrum of InSe. Referring to the data in, we can say that the features in the absorption spectrum of InSe that we observed are related to hyperbolic excitons and impurities located in the region of the continuous spectrum. The chemical deposition process was carried out at room temperature (27 ºC) for 48 hours without rotation.During the process, a white precipitate formed at the bottom of the glass. After three to four hours, this precipitate andthe clear solution in the beaker first turned dark yellow and then red, consistent with CdSe. After this procedure, thesaucer was removed from the glass, washed with distilled water and dried [14] However, the absorption line at λ=475 nm observed in the GaSe(0.1B)-InSe(0.1B) heterostructures is apparently related to boron impurities. As experiments show, in GaSe/InSe structures doped with boron atoms, only one absorption band with a maximum at λ=475 nm is observed (Fig. 2b). The fact that the band of this line is absent in the absorption spectrum of pure GaSe/InSe structures apparently indicates that this line is associated with boron atoms.

Fig. 3a (curve 1) shows the photoluminescence spectrum of a thin GaSe film without boron doping upon excitation by the second harmonic of a Nd:YAG laser (λ=532 nm). As can be seen from the figure, the maximum emission corresponds to a wavelength of ~597 nm. The half-width of the emission line, which is only ~5-8 A^0, is noteworthy. Comparison of the emission line with the absorption spectra allows us to state that the observed recombination emission is also caused by exciton transitions at the edge of intrinsic absorption. Based on the experimental data obtained, it can be assumed that a number of changes in the photoelectric parameters of photodiodes when irradiated with high-energy particles are apparently associated with a specific feature of the crystal structure of layered materials, i.e. interaction of radiation defects arising in crystalline layers and interlayer spaces. [15] It should be noted that the high emission intensity and its narrowness, several angstroms in size, allow us to state that thin GaSe films can be used as an active element for creating a semiconductor quantum generator on their basis.

Unlike undoped samples, in doped thin GaSe films, as in the case of absorption spectra, the emission spectra shift toward longer waves, and the line half-width increases by a factor of ~10 and is ~80 Å^0 (Fig. 3, a, curve 2). In our opinion, the increase in the half-width is due to boron impurities, which create shallow donor levels near the conduction band.

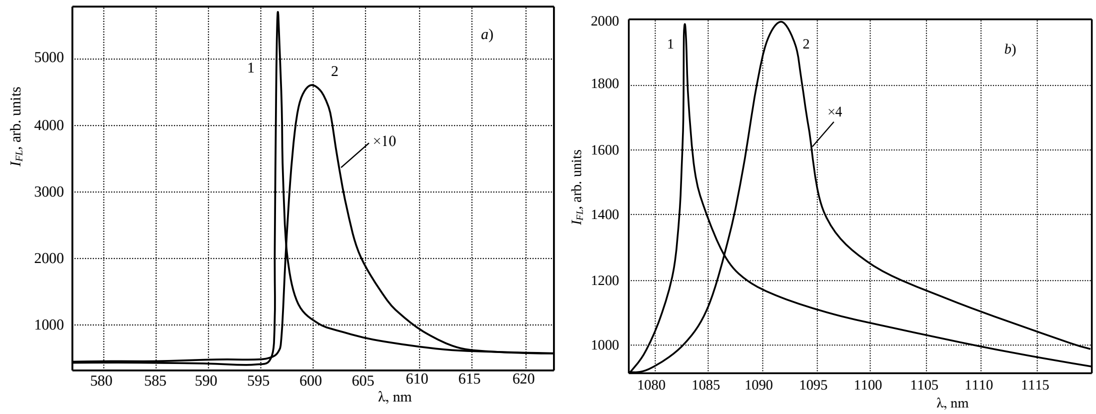


Fig. 3. *Luminescence spectra of pure thin films of GaSe (a) and InSe (b): 1 – pure; 2 – doped with boron atoms.*

Similar features are observed in the luminescence spectra of InSe thin films (Fig. 3, b). The maximum emission corresponds, to the near IR region of the spectrum and is equal to 1083 nm. The half-width of the emission line is ~10 Å^0. When doped with boron atoms, as in the case of GaSe, the half-width of the line increases and is equal to ~50 Å^0.

IV. CONCLUSION

Thin GaSe, InSe films and GaSe/InSe heterostructures with and without boron doping were fabricated by chemical vapor deposition. The absorption and photoluminescence spectra of the materials were studied using a pulsed Nd:YAG laser. It was found that the presence of boron impurities not only affects the absorption band edge of GaSe and InSe thin films, but also leads to the disappearance of the exciton absorption of the GaSe/InSe heterostructure associated with hyperbolic excitons in the continuous spectrum region. Common to all luminescence spectra of GaSe, InSe thin films is that boron impurities lead to a broadening of the emission band.

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