PHOTOLUMINESCENCE OF Bi_2O_3-InSe HETEROJUNCTIONS

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Introduction

Optical and photoelectrical properties from the immediate proximity of the band gap in the strongly anisotropic crystals constitute a major technical interest.

The stratified structure specific of $A^{III}B^{VI}$ group crystals determine the anisotropy of their physical properties [1-3].

Among intensely researched crystals from this group, there are the GaSe and InSe compounds [4-7]. The optical band of InSe crystals has a width of 1. 238 at T = 293 K [8]; this material is attributed to the group of promising semiconductors for photodetectors and elements of solar energetic [9-11]. At the same time, the low concentration of surface states points out the opportunity of using this material in the form of a thin layer, both GaS and GaSe, as an element of supernetworks and structures with quantum points being photoconducting and photoluminescent in the near IR spectra [12].

Studies concerning stability of characteristics of the InSe crystals and the photovoltaic structures based on them, under the effect of ionizing radiation and particles with high energy (protons, neutrons) have proven that, as a result, photosensibility increases [13, 14].

Photoelectric and photoluminescent proprieties depend on the diagram of the states localized in the gap band of the materials and on their recombination properties.

Numerous data on the spectra of recombination levels induced by the structural defects and the atoms of impurities in the InSe crystal, purposefully doped or nondoped, can be obtained from the analysis of the optical spectra and photoluminescence [15-19].

The thermal treatment of monocrystals leads to Se atoms emission and to occupancy of intrinsic vacancies by impurity atoms. The vacancies from the InSe monocrystals surface layer are actively occupied by oxygen atoms, and the InSe-In_2O_3 semiconductor junction formation, photosensible in large spectra of wavelengths [20-22].

The aim of this work consists in the characterization of the process of recombination of nonequilibrium charge carriers, through radioactive states created at the interface of InSe-Bi_2O_3 heterojunctions.

Experimental

Monocrystals of n-InSe were obtained from elementary components In and Se with the purity of 99.999%, taken in stoichiometric quantities, using the Bridgman-Stockbarger method. The synthesis of the primary compound was done in quartz phials whose interior surfaces were carbonized. The concentration of the majority charge carriers at T = 293 K is n = $3.5*10^{14}$ cm^{-3}. The mobility of the electrons at T = 293 K is $\mu_n \approx 2{,}1\cdot10^2$ cm^2/Vs. Through splitting from monocrystalline blocks, films with a thickness from 0.3 μm to 1.5 mm were obtained, which were necessary for optical measurements.

On one of the freshly cleaved surfaces of the InSe plates with the thickness of 0.1÷0.3 mm, by thermal evaporation in vacuum $5 \cdot 10^{-5}$ Torr, a layer of Bi with the thickness of 90 – 120 nm and area ~10 mm^2 was applied. The oxidation of the metallic layer was exercised in standard atmosphere by slow heating from room temperature to ~ 510 K with a rate of ~ 1.5°s^{-1}. The duration of the oxidation process was controlled by measurements of the transmission coefficient of the He – Ne (λ = 1.15 μm) laser radiation through InSe structure – Bi oxide. The structure of the Bi oxide layer was examined by X-rays diffraction with the XRD 6000 Shimadzu diffractometer, using the CuK$_\alpha$ radiation. The presence of 2 diffraction lines at the angles of 2θ = 27° and 37° indicates that the bismuth oxide layer is preponderantly in phase α - Bi_2O_3.

Results and discussion

The PL Spectra from the perpendicular surface of the C of the monocrystalline films from InSe at T = 78 K are presented in Fig. 1. The structure of the spectrum consists of two bands: the first A is relatively narrow, localized in the immediate vicinity of the intrinsic absorption band edge with an absolute maximum at 1.318 eV; the second B has a wide symmetric contour, whose maximum is situated in the interval of energies from 1.09 eV to 1.12 eV. The maximum of the band B slowly moves towards small energies with ~ 30 meV with the decrease in the density of the excitant beam ~ 270 times.

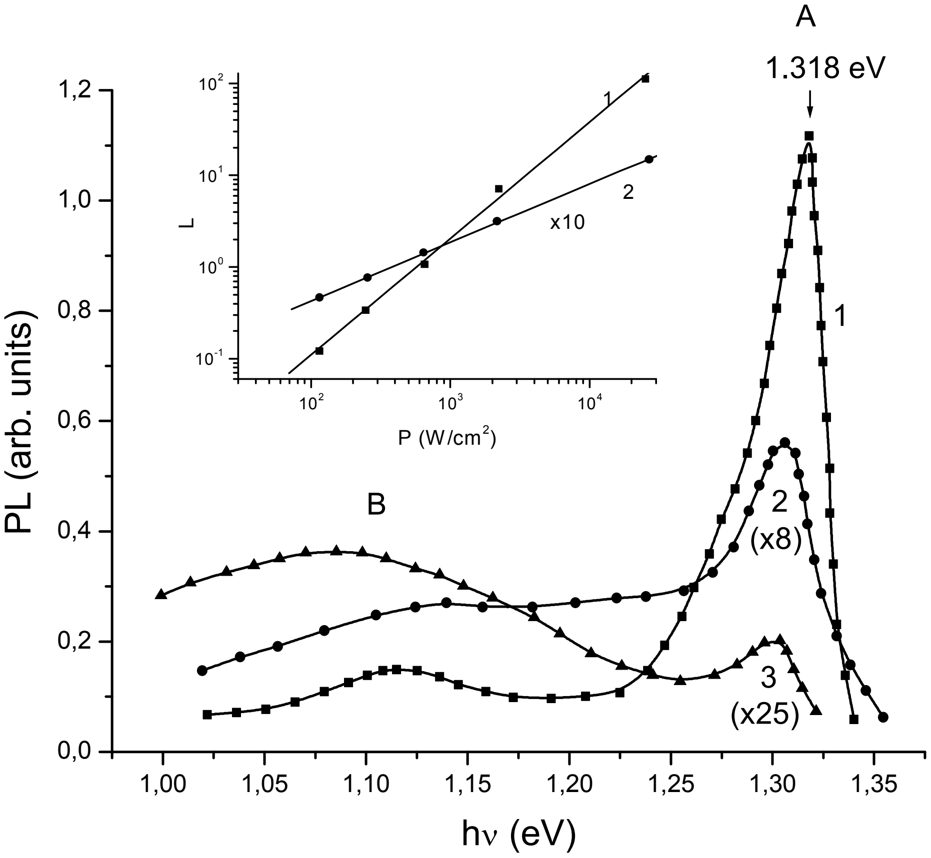

Fig. 1. The PL spectra of the InSe crystals at a temperature of 78 K. The density of the beam that excites: 3.2·10^4 W/cm^2 (*1*); 2.5·10^3 W/cm^2 (*2*); 1.2·10^2 W/cm^2 (*3*). In the inset: The dependence of the intensity PL(L) in the 1st band and the 2nd band from the intensity of excitation (*P*): *n* = 1.35 (*1*); *n* = 0.7 (*2*).

A structure with 2 bands is kept also in the PL spectrum from the interface of the Bi_2O_3 – InSe junctions (Fig. 2). The PL band from the border is clearly evidenced at high excitation intensities. If in the PL spectrum of the InSe films, on which the Bi_2O_3 layer is still being prepared, the border band A has a contour very close to symmetry, this PL band from the interface layer of the structure Bi_2O_3 – InSe has a strong, asymmetric contour towards small energies from the maximum. It prevails in the B band of the PL spectrum, with a maximum at 1.120 eV.

The presence of the structural defects in the InSe layer from the interface of the junctions leads to the attenuation of the luminescence of the exciton band ($\hbar\omega_{ex}$ = 1.310 eV); at the same time, it enhances the intensity of the bands from the red region of the spectrum. As it was demonstrated in work [19], the structural defects in InSe decrease the intensity of the linked exciton band and, at the same time, enhance considerably the PL in the localized bands at energies $\hbar\omega < \hbar\omega_{ex}$.

The layer from the contact surface was investigated using the method of electroreflection. This method is applied with success for the research of the material layer from the interface of the heterojunctions made of materials with the refractive indexes close to [23]. PL edge band (A) with a maximum of 1.318 eV is strongly influenced by the intensity of excitement (L). Band B PL intensity with a maximum located in the region 1.09÷1.12 eV decreases more monotonously. We also mention that the intensity of band A rapidly decreases with temperature and at a temperature of ~120 K this band is completely attenuated. The energetic interval between the free excitons of the absorption spectra and band A in Fig. 2 is 11 meV.

As it can be seen from the assembly in Fig. 2, the relation between the intensity of A and B PL (L) bands and the excitation intensity P can be written as a power function

$$L = P^n, \tag{1}$$

where the power factor n gets the values 1.35 and 0.7 for band A and B, respectively.

The thermal attenuation in a narrow temperature range (78÷150 K) and the superalignment dependence of the photoluminescence intensity on the excitation intensity are two criteria by which this line may be taken as excitonic [24, 25].

Hence, we can consider that the PL band (A) is formed as a result of radioactive annihilation of the localized excitons. The bond energy between the excitons and the localization centers is 11 meV.

With the use of type (1) power function, the L (P) feature of the band B can be described (supplement to Fig. 2), only that the power factor for this band is of proper value (n ≈ 0.7). The proper size of the power factor in the relation (1) is characteristic for the PL bands of an impure nature [2].

PL spectra at T = 78 K from the interface of Bi_2O_3 – InSe junctions (Fig. 2) have the same structure of two dominant bands, one edge (A) with a maximum of 1.310 eV and the other with a symmetrical broad outline (B) with a maximum in the region of 1.120 eV.

The keeping of the symmetrical outline at the radiation of an excitation intensity of ~100 times and the linear dependence of the photoluminescence intensity L to the excitation intensity, as it is shown in [26], are characteristic of the impure bands, the process of light excitation and emission of which takes place in a luminescent centre.

The PL band of edge A (Fig. 2) with a maximum of 1.310 eV is distinguished clearly at higher excitation densities ($P \approx 2.1 \cdot 10^4$ Wt/cm^2). When the excitation density decreases by less than an order, only a vague trace of this line remains. The branch to high energies of this band extends to ~1.34 eV. We associate this band with the luminescence annihilation of the excitons localized near the structural defects formed at the interface of the Bi_2O_3 – InSe junction and in the InSe layer because of the reciprocal diffusion of Bi and Se.

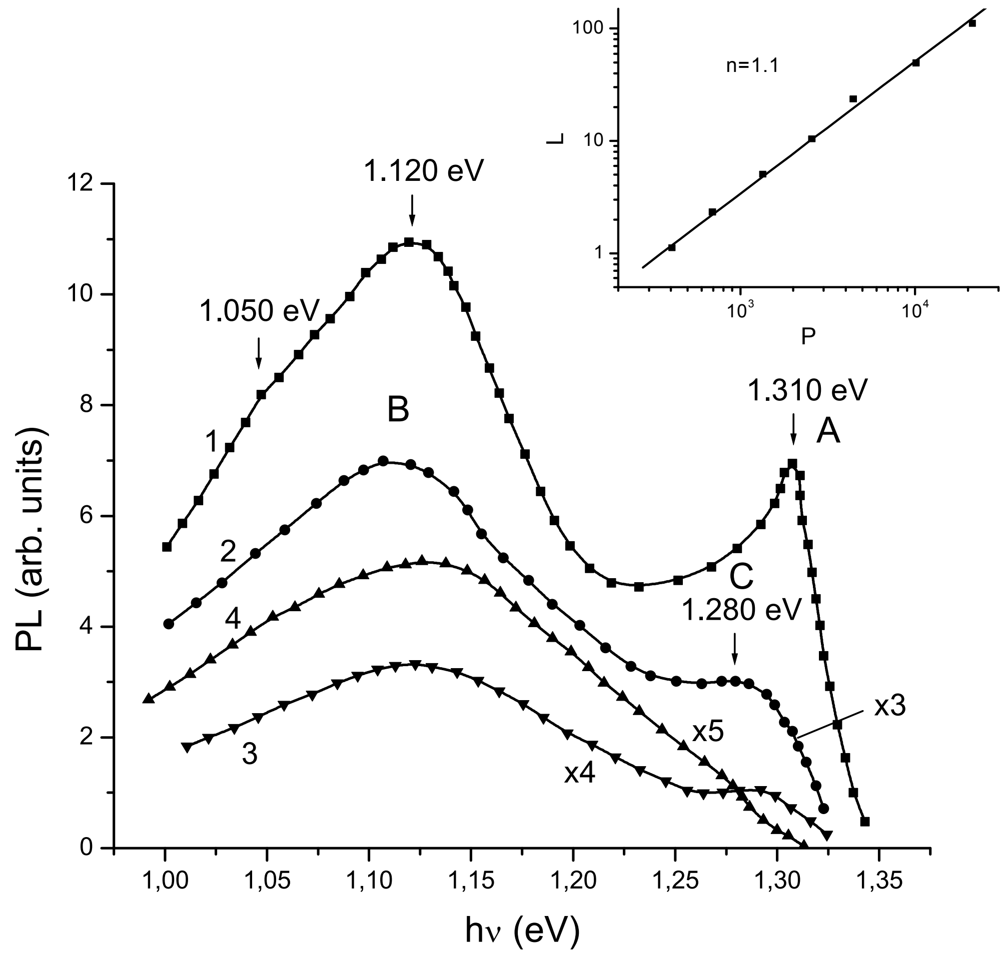

Fig. 2. The spectrum characteristics of PL of the Bi_2O_3-InSe structures at a temperature of 78 K under excitation with laser radiation He-Ne (λ = 632.8 *nm*, $h\nu$ = 1.96 *eV*) with the density: $2.1 \cdot 10^4$ W/cm^2 (*1*); $6.0 \cdot 10^3$ W/cm^2 (*2*); $1.4 \cdot 10^3$ W/cm^2 (*3*); $5.0 \cdot 10^2$ W/cm^2 (*4*). Inset: The dependence of the intensity PL(L) on the density of excitation (*P*) of the band $h\nu$ = 1.120 eV.

In the immediate vicinity of the band A (Fig. 2, curve *1*) an additional band (C) is attached. This band is much more clearly distinguished at lower excitation densities. The maximum of band C is localized at ~ 1.280 eV.

It is shown in work [19] that the structural defects lead to the formation of an additional PL band localized at energies close to the exciton band.

The Se atoms diffused from the nodes of the crystal lattice form donor energy levels, while Bi may form impure acceptor levels as well. The 1.280-eV band in [4] is interpreted as a recombination donor–valence band.

Conclusions

The PL spectrum of the monocrystalline layers of InSe at T = 78 K contains the emission line of the linked excitons ($\hbar\omega_{ex}$ = 1.318 eV) with the bind energy of 14 meV and the intensity band being low by nature - impurity (intrinsic defects) with the energy 1.1 eV.

– In the process of the thermal treatment of the monocrystalline films of InSe with a thin layer of Bi, diffusion processes take place resulting in the formation of new energy states in the band gap of the InSe crystals and meanwhile of the new centers of bonding of excitons. The bonding energy of the excitons that are formed in the thin contact layer of Bi_2O_3 – InSe is 19 meV.

- The intensity of the PL band of the InSe layer from the interface of the Bi_2O_3-InSe heterojunctions grows at the same time with the intensity of the exciton beam, following an exponent function, whose power is 1.35 for the border band and 0.7 for the band with the maximum at 1.120 eV.

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