

EXCITONIC ABSORPTION OF THE LIGHT IN HETEROJUNCTIONS $\text{Bi}_2\text{O}_3\text{-InSe}$

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Abstract

The interface layer of the $\text{Bi}_2\text{O}_3/\text{InSe}:\text{Cd}$ (0.10 at. %) heterojunction was investigated using optical and electroreflection spectra. The fundamental absorption edge of $\text{InSe}:\text{Cd}$ interface layer, at 78 K, is formed by the excitonic absorption band $n=1$, with maximum at 1.328 eV. Its direct optical band gap corresponds to electron transitions at the M point of the Brillouin zone, and is equal to 2.557 eV at 78 K.

Introduction

InSe monocrystals belong to the class of layered semiconductors with mixed electric conductivity (ionic-electronic) [1, 2]. They are semiconductors with indirect optical band amounting to 1.29 eV at $T = 293$ K. InSe is an effective material for optoelectronics, especially for light conversion devices [3, 4], nonlinear optical devices [5], and energy accumulators with solid electrolyte [6].

Weak bounds between layered packages allow obtaining of the films with width necessary for optical research in a wide interval of wave lengths by cleaving [7].

Optical properties of the InSe crystals were intensely researched through optical absorption at the edge of the intrinsic band. Their conductivity was also studied. It was determined that the width of the interdicted band is 1.533 eV at a temperature of 1.6 K [8] and that the bind energy of the excitons is 15 meV [8, 9]. The edge of the fundamental absorption band is formed by direct excitons that are clearly manifested in the absorption spectra [10], photoconductivity spectra [11] and mostly in the photoluminescence spectra at low temperatures [12].

Structural defects, as well as the exterior factors (pressure, temperature), directly influence the exciton processes, leading to the localization of excitons at the intensification of the process of interaction with phonons at the shielding of the exciton bounds.

Experimental

n-InSe monocrystals were obtained using the method of Bridgman-Stockbarger from the elementary compound In and Se with a purity of 99.999% taken in stoichiometric quantities. The synthesis of the primary compound was made in ampoules of quartz, the interior surface of which was carbonized. By cleaving of monocrystalline blocks films with thickness from 0.3 μm to 1.5 mm necessary for optical measurers were obtained.

Using thermal evaporation in vacuum of $5 \cdot 10^{-5}$ Torr, a layer with a thickness of 90-120 nm and a surface of $\sim 10 \text{ mm}^2$ was applied on one of the freshly cleaved surfaces of the crystals. Oxidation of the metallic layer was exercised in the normal atmosphere by slow increasing of the temperature from room temperature to ~ 510 K with a rate of $\sim 1.5^\circ\text{s}^{-1}$. Duration

of the oxidation process was controlled by measurement of the transmission coefficient of the He-Ne laser radiation ($\lambda = 1.15 \mu\text{m}$) in the structure InSe- Bi oxide. Structure of the Bi oxide layer was studied using diffraction of X-rays with the XRD Shimadzu diffractometer, using the CuK_α radiation. The presence of two diffraction lines for angles $2\theta = 27^\circ$ and 37° indicates that state of the bismuth oxide consists mostly of the phase α - Bi_2O_3 .

Resistance on the surface of the Bi_2O_3 layer in the studied structures was of 360-450 Ω . Thickness of the InSe and Bi_2O_3 films (0001) grown on the surface of the InSe films was determined from the measurements of the number N of interference minims of the He-Ne laser ($\lambda = 1.50 \text{ nm}$) at the rotation of the film around the axis oriented perpendicular to the direction of the light beam. Rotation angle φ was measured with by means of a GS-5 Goniometer.

The samples used for measurements at temperatures from 78 to 300 K were mounted inside a cryostat with nitrogen vapors. Temperature was controlled with a Cu-constantan thermocouple. Optical transmission and electroreflection spectra were analyzed by means of a monochromatic with refraction grating (600 mm^{-1}) of the MDR-2 (LOMO) type with energetic resolution not higher than 0.7 meV. The light beam was measured with a photomultiplier with a photocathode of Ag-O-CS at a temperature of -50°C.

Thin layers of indium oxide (ITO) or In_2O_3 are used as optical transparent electrodes on InSe films [13, 14]. The In oxide layer was obtained by reactive evaporation in $\text{Ar}+\text{O}_2$ (75:25) atmosphere in a continuous regime using a cathode of In as a target. The temperature of the InSe substrate was 250°C. Optical transmission of the indium dioxide layer was 87%. Resistance of the In_2O_3 films of the lateral surfaces of the InSe film was $8 \cdot 10^{-2} \Omega \cdot \text{cm}$. For vacuum evaporation, an electrode in form of ring with the internal diameter of 3 mm was applied in order to obtain the homogeneous electric field on the surface of the Bi_2O_3 layer.

Results and discussion

The absorption coefficient α of the InSe monocrystalline films and of the Bi_2O_3 -InSe structures was calculated from the measurements of transmission t and reflection R of the light from relation (1)

$$t = \frac{(1 - R)^2 \cdot e^{-\alpha d}}{e^{\alpha d} - R^2 \cdot e^{-\alpha d}}, \quad (1)$$

where d is the thickness of the sample.

Figure 1a presents the absorption spectra of the InSe monocrystalline films before application of the Bi_2O_3 layer at the temperatures 78 and 293 K (curves 1 and 2, respectively) and of the structure Bi_2O_3 -InSe at the same temperatures (curves 3 and 4, respectively).

As one can see from the same diagrams, in the region of the edge of the intrinsic band, the absorption coefficient in the InSe films, as well as in the Bi_2O_3 -InSe structures, at a temperature of 293 K in a narrow energy interval ($\sim 30 \text{ meV}$) grows rapidly up to $1180 \div 1200 \text{ cm}^{-1}$, afterwards it grows with the energy. At a temperature of 78 K in the region of the edge of the intrinsic absorption band, a narrow absorption band with a maximum at 1.328 eV for InSe films, as well as for Bi_2O_3 -InSe structures, becomes evident. The absorption coefficient in the maximum of the edge band is 2380 cm^{-1} for InSe films and 1820 cm^{-1} for Bi_2O_3 -InSe structures. At the same time, a much more rapid growth of the absorption coefficient ($\Delta\alpha/\Delta h\nu$) is observed in the InSe films as compared to the Bi_2O_3 -InSe structures at the temperature 78 K as well as at the room temperature.

As can be seen in Fig. 1b, in the interval of energies $2.50 \div 2.55 \text{ eV}$ in the absorption spectrum at temperatures 78 and 293 K, a repeated absorption threshold is observed. Inside a

narrow temperature interval (0.5 eV) the absorption coefficient at a temperature of 293 K increases threefold: from 520 cm^{-1} to 1540 cm^{-1} . More evident is the growth of the absorption coefficient at a temperature of 78 K. At this temperature, the absorption coefficient increases from 2800 cm^{-1} at an energy of 2.30 eV to 17000 cm^{-1} at $h\nu = 2.7 \text{ eV}$. Considering the growth of the absorption coefficient in the maximum of this band, as well as the rate of growth with the energy of the absorption coefficient, this threshold can be associated to the direct band-band optical transitions.

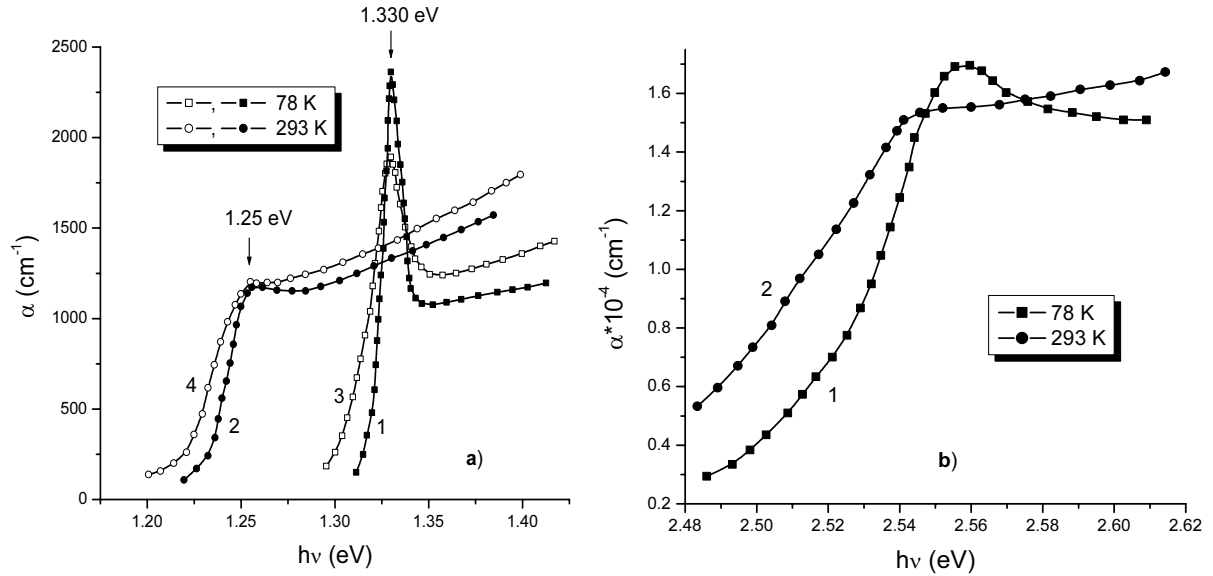


Fig. 1. a) Absorption spectra of the monocrystalline InSe films (1, 2) and of the Bi_2O_3 -InSe (3, 4) at a temperature of 78 K (1, 3) and 293 K (2, 4); b) Absorption spectrum of the Bi_2O_3 -InSe inside the intrinsic absorption band at temperatures 78 K (1) and 293 K (2).

Relatively small difference between refraction indexes of the Bi_2O_3 and InSe layers is limiting the possibilities of the optical research methods of the layer from the contact surface. In order to amplify the signal reflected from the contact surface, the electroreflection method (ER) ($\omega = 1.2 \text{ kHz}$, $U_{\sim} = 5 \text{ V}$) was applied. The ER spectrum (Fig. 2) contains two bands – one in the region of absorption of indirect excitons in InSe (a) and the second in the interval of the absorption through direct optical transition threshold (b).

The alternative electric field applied to the heterojunctions is localized in the region of contact layer Bi_2O_3 -InSe and leads to the modification of the absorption coefficient $\Delta\alpha$ as well of the refraction index Δn . Since the variation in the refraction index $\Delta n/n$ in the electric field is much smaller than the variation in the absorption coefficient $\Delta\alpha$, the electroreflection signal ($\Delta R/R$) is given by the expression [14]

$$\frac{\Delta R}{R} = 2d \cdot \Delta\alpha, \quad (2)$$

where d is the thickness of the layer to which the electric field is applied and $\Delta\alpha$ is the modular absorption coefficient of the electric field in the layer InSe from the interface of the heterojunction InSe- Bi_2O_3 . Phonon energy for which the $\Delta R/R = f(h\nu)$ function passes through 0 is considered to be the width of the interdicted band E_g .

Figure 2 presents the modulated reflection spectrum in the alternative electric field (frequency 1.2 kHz) at $T = 78 \text{ K}$. The Bi_2O_3 -InSe junction was illuminated through the optical transparent layer Bi_2O_3 . Oscillation of the function $\Delta R/R = f(h\nu)$ in the region of the absorption band of the direct excitons, as well as at localized energies of the absorption threshold from deep inside intrinsic band, is observed.

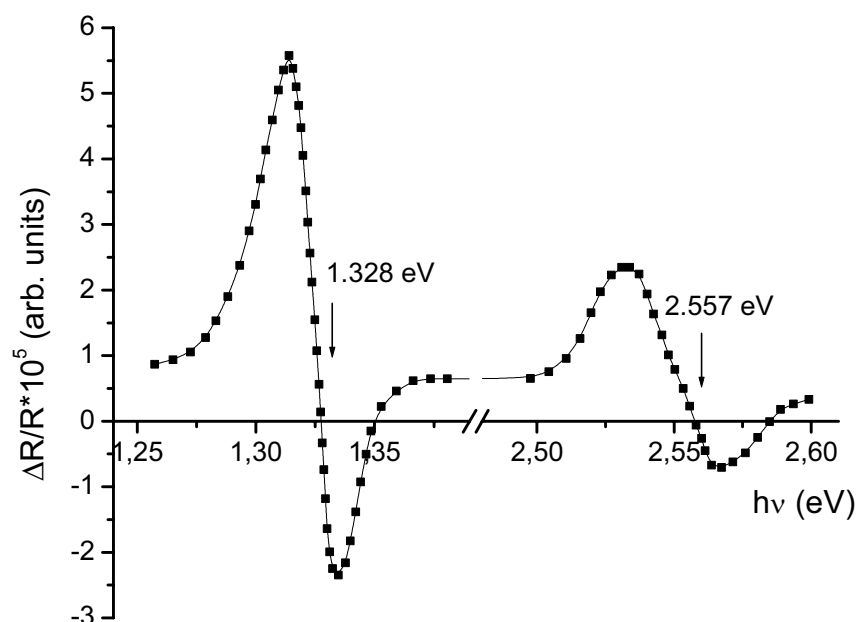


Fig. 2. Electroreflection of the light from the surface of Bi_2O_3 -InSe contact at 78 K (applied voltage to the structure is ~ 5 V and the frequency is 1.2 kHz).

As shown in graphs 1 and 2 (Fig. 1a), the presence of the Bi_2O_3 layer on the surface of the InSe monocrystalline film leads to a decrease in the absorption coefficient of the absorption band of the direct excitons. The decrease in the absorption coefficient without influence on the exciton energy band can be conditioned by the presence of some structural defects that are shielding the electron-hole bounds.

The increase in absorption coefficient at $T = 293$ K, as well as at 78 K, in the region of the fundamental absorption band can be determined by the dissipation of the light in the oxide layer from the surface of the Bi_2O_3 -InSe structure. Normally, the oxide layers obtained through thermal oxidation of the metal layer from the surface (0010) of the InSe layered crystals are monostructured [15, 16], which leads to a decrease in the optical transmission of the Bi_2O_3 -InSe structures.

At the same time, the Bi_2O_3 layers lead to an increase in the absorption coefficient in the region of exciton absorption ($T = 78$ K). This tendency of the dependency of the spectra of the absorption coefficient is also present in the region of the intrinsic absorption band edge (Fig. 1, curves 3 and 4) at a temperature of 293 K.

In the region of the absorption band edge, the absorption coefficient α for InSe films, as well as for Bi_2O_3 -InSe structures, (Fig. 3) decreases exceptionally with energy. The slope of this characteristic decreases not only at the increase in temperature from 78 to 293 K but also at the transition from the InSe films to the Bi_2O_3 structures. It is experimentally proven [17, 18] and theoretically confirmed [19] that the absorption coefficient is described by an exponential function of the energy of the phonons $h\nu$ of type [17, 18]

$$\alpha(h\nu) = \alpha_0 \exp\left[\frac{\sigma(T)}{kT}(h\nu - E_0)\right], \quad (3)$$

where α_0 , E_0 are the characteristics of the studied material, k is the Boltzman constant, T is the absolute temperature, $\sigma(T)$ is the parameter dependent on temperature not only in the case of interaction of excitons with phonons but also in the case of dissipation of those from the structural and stoichiometric defects [20, 21].

The parameter $\sigma(T)$, which determines the absorption band edge, is written through an empirical formula of T and the phonon energy $\hbar \omega_f$ [10]

$$\sigma(T) = \sigma_0 \left(\frac{2kT}{\hbar \omega_f} \right) \tanh \left(\frac{\hbar \omega_f}{2kT} \right), \quad (4)$$

where the parameter σ_0 is a characteristic of time of the interaction of the excitons with phonons and crystalline defects of the material.

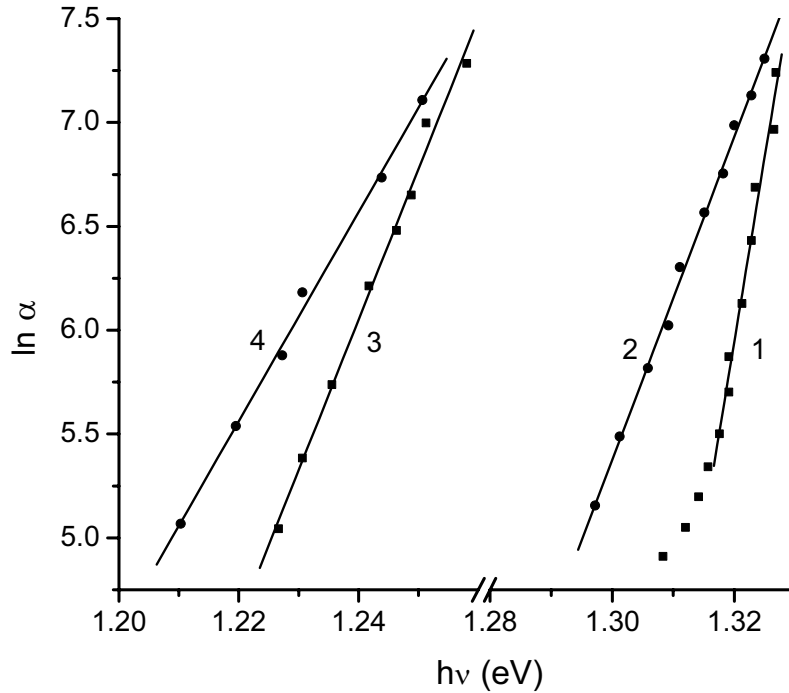


Fig. 3. Function $\ln \alpha = f(h\nu)$ for InSe (1, 3) layers and Bi_2O_3 -InSe (2, 4) structures at temperatures 78 K (1, 2) and 293 K (3, 4).

The decrease in the σ parameter in the Bi_2O_3 -InSe structures as compared to the InSe films can be explained by the creation of the structural defects in them (thermal diffusion of Se from the film and of bismuth atoms inside the InSe film) as a result of thermic oxidation of bismuth on the InSe film surface.

The thermal stability of the structural defects in the Bi_2O_3 -InSe structures is also confirmed by the linear dependence of the function $\ln(\alpha)=f(h\nu)$ at 293 K (2).

The presence of the Bi_2O_3 layer on the surface of the InSe film, as well as the alleged diffusion of the selenium and bismuth atoms, does not influence the energetic spectrum in the layer InSe from the region of contact. Spectra of electroreflection $\Delta R/R=f(h\nu)$ from Fig. 2 have the form characteristic of band-band electronic transitions [22]. The energy $h\nu$ for which $\Delta R/R = 0$ corresponds to the minimum energy between the valence band and the conduction band. At a temperature of 78 K (see Fig. 2) the energy is 1.328 eV and exactly coincides with the energy of the free excitons in state $n = 1$.

Point ($\Delta R/R = 0$) inside the intrinsic absorption band of the InSe film from the Bi_2O_3 - InSe junction corresponds to 2.557 eV.

Conclusions

- Inside InSe crystals, indirect optical transitions with formation of free excitons with energy 1.330 eV ($T = 78$ K) and direct optical transitions with the direct band gap being 2.560 eV ($T = 78$ K) and 2.542 eV ($T = 293$ K) take place.
- Thermal treatment at temperatures 500-510 K in the normal atmosphere of the Bi-InSe structure leads to the formation of the bismuth oxide, and in the region of contact a layer of InSe doped with Bi is formed.
- In the process of thermal treatment of the InSe structure with a thin Bi layer, the diffusion of Bi in InSe takes place, by which new energy states in the band gap of the InSe crystals and also of bound centers of the excitons are created. Bound energy of the excitons formed in the Bi_2O_3 – InSe contact layer is 19 meV.
- InSe layer from the interface of the structure was studied using the ER method. Spectrum $\Delta R/R$ from the 1.3 eV region is interpreted as exciton electroreflection.

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