Excitonic polaritons of zinc diarsenide single crystals

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ARTICLE INFO

ABSTRACT

Excitonic polaritons of $ZnAs_2$ single crystals had been investigated. Parameters of singlet excitons with Γ_2^- (z) symmetry and orthoexcitons $2\Gamma_1^-$ (y)+Γ_2^- (x) had been determined. Spectral dependencies of ordinary and extraordinary dispersion of refractive index had been calculated using interferential reflection and transmittance spectra. It was shown, that A excitonic series were due to hole (V_1) and electron (C_1) bands. The values of effective masses of electrons (m_c^*=0.10 m_0) and holes (m_{v1}^*=0.89 m_0) had been estimated. It was revealed that the hole mass m_{v1}^* changes from 1.03 m_0 to 0.55 m_0 at temperature increasing from 10 K up to 230 K and that the electron mass m_c^* does not depend on temperature. The integral absorption A (eV cm^{-1}) of the states n=1, 2 and 3 of Γ_2^- (z) excitons depends on the $A_n \approx n^{-3}$ equality, which it is characteristic for S-type excitonic functions. Temperature dependences of the integral absorption of ground states for Γ_2^- (z) and Γ_2^- (x) excitons differ. The ground states of B and C excitons formed by $V_3 - C_1$ and $V_4 - C_1$ bands and its parameters had been determined.

1. Introduction

The zinc diarsenide ($ZnAs_2$) belongs to the compounds of $A^{II}B^V$ group and crystallizes in a lattice with C_{2h}^5 spatial group. The investigation of such materials as $ZnAs_2$ is of an interest since the crystals possess a strong anisotropy of optical properties, narrow band-gap (1.5 eV at 10 K [1–3]) and can be technologically bonded to GaAs based structures. Active elements and different device structures had been developed based on $ZnAs_2$ using the anisotropy of optical properties [4–11]. The monoclinic crystal $ZnAs_2$ is a direct band-gap semiconductor with a low symmetry where hydrogen-like excitonic states are excited due to electrical-dipole and dipole-forbidden transitions [12–14].

The reflectivity excitonic spectra of $ZnAs_2$ crystals grown by gas phase and melt techniques were investigated at 10 K and E∥c and E⊥c polarizations are presented in the current work. The theoretical calculations of reflection spectra shapes of excitonic ground states had been carried out and the exciton parameters had been determined. The absorption interference spectra of thin monocrystals were measured for the first time at the allowed polarization (E∥c) and energy range within free exciton neighborhood (E > $E_{n=1}$). The ground and excited states of excitons were assigned. The main parameters of excitonic polaritons were determined.

2. Experimental method

$ZnAs_2$ single crystals grown from gas phase in closed quartz ampoules represented thin layers with parallel surfaces. The **C** axis of the crystals was oriented along the longer facet. The single crystals grown from melt had the next geometrical parameters: diameter 1 cm and length 3–4 cm, being easily cleaved along the cleavage plane. The reflection and transmittance spectra had been measured using the double spectrometer SDL-1 (dispersion: 7 Å/mm; luminosity: 1:2). Samples were mounted on the cold-finger of a cryogenic system "LTS-22 C 330 Work Horse-Type Optical". Fig. 1 shows the installation scheme used for measurements.

The registration of transmittance interference spectra has been adjusted for allowing the electronic system to detect the average intensity value between maximum and minimum ones. This value was estimated as the zero value of interference spectra intensity. The electronic system was registering the positive intensity values (J > 0), while the negative ones were being transformed into positive signal. Negative fringes on interference spectra are drawn by dash line in Fig. 2A (1, 2, 3, …), though the negative part of spectra was registered as positive signal (fringes 1, 2, 3 etc.). The value of the refractive index corresponds to the intermediate wavelength, positioned between λ_1 and λ_2, according to the calculus equation of the refractive index calculated from interference spectra. The method mentioned above allows us to
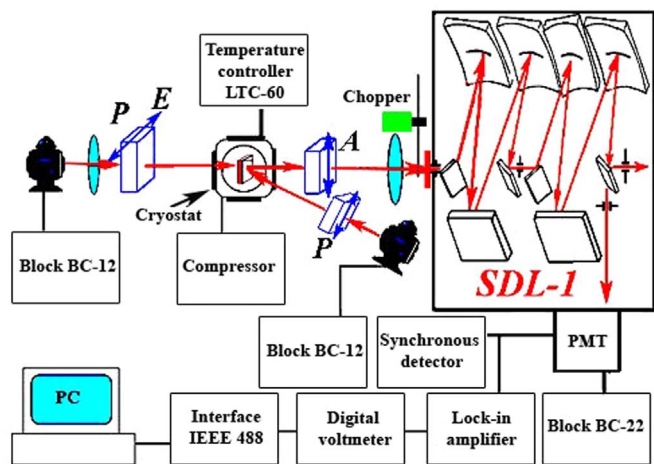
Fig. 1. The installation scheme for measuring optical spectra of reflection, absorption and interference of transmittance.
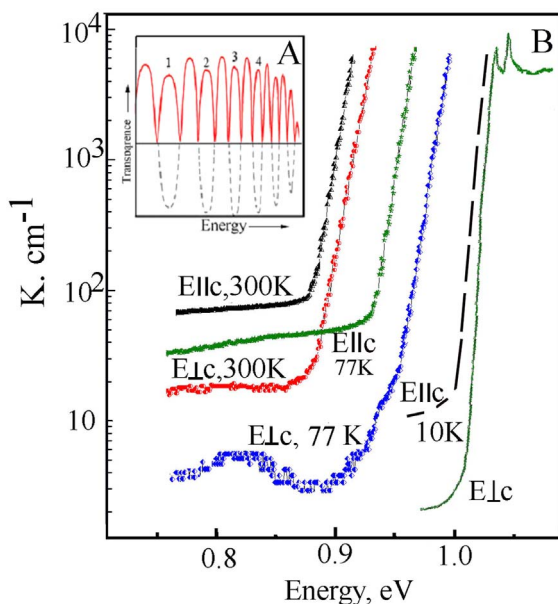

Fig. 2. Interference transmittance spectra (A). Absorption spectra of ZnAs$_2$ crystals in the minimum region of band gap (B).

accurately determine the spectral position of the central part of intensity maxima and minima of interference spectra, while the spectral distribution of the refractive index is calculated more correctly. Spectral dependences of refractive index n had been calculated from interference spectra using the expression:

$$n = \frac{M}{2d\left(1/\lambda_1 - 1/\lambda_2\right)},\qquad(1)$$

where d is the sample's thickness, λ_1 and λ_2 are the wavelengths of two transmittance maxima (or minima). M equals one for two near located peaks.

3. Experimental results and discussions

3.1. Optical spectra in the absorption edge region

The ZnAs$_2$ single crystals crystallize in a lattice with spatial group C$_{2h}^5$=P21/c with eight formula units in a unit cell having the lattice parameters a=8.85 Å, b=7.21 Å, c=7.56 Å and β=102.3°. Investigations of the anisotropy of optical properties for the fundamental absorption region had been carried out for the first time by authors of Refs. [1,2].

In the papers it was shown that the absorption edge was being formed by direct polarized electronic transitions. The absorption at E||c polarization is higher than one at E⊥c in the transparency region [2]. The sharp increase of the absorption coefficient measured at 300 K starts beginning with the energy value 0.90 eV for the E||c polarization and 0.89 eV energy value for the E⊥c polarization (Fig. 2). Absorption edges were shifted toward higher energies with temperature decrease. The temperature shift coefficient β=ΔE/ΔT equals 3.11×10^{-4} eV/° and 4.61×10^{-4} eV/° for the E||c and E⊥c polarizations, respectively, in a temperature range of 77–300 K. The coefficient mentioned above equals 3.51×10^{-4} eV/° in a temperature range of 10–77 K and E||c polarization and 2.061×10^{-4} eV/° for the E⊥c it polarization. Such a difference of temperature shift coefficients of the semiconductor's edge was also observed in other crystals of A^{II}B^{V} group [2–4]. This phenomenon is conditioned by the fact that the direct electronic transitions, which are responsible for the edge absorption, occur, according to the selection rules, form different valence bands into conduction band, within the center of Brillouin zone.

Fig. 3A shows the reflection (R) and transmittance (T) spectra of crystals with 0.45 μm thicknesses and the absorption spectra (K) of 408 μm crystals grown from gas phase. An interference value close to 1.3 eV is observed in the transmittance spectra of thin samples (0.45 μm). The fringe pattern changes near the absorption edge and is almost fully correlated with the absorption coefficient of thicker crystals. A well pronounced maximum is revealed at 10 K in the region of interference pattern change for crystals of a 408 μm thickness (Fig. 3A). A weak maximum is revealed in the reflection spectra at E⊥c polarization. The position of this maximum shifts to lower energy values with temperature increase. The difference of maximum and minimum values of reflection is within 4–5% at room temperature, in the resonance region.

The amplitude values of reflection spectra (R) at 10 K and E||c polarization changes between 20% and 50% (Fig. 3B). The maximum of the reflection spectra shifts towards lower energies with temperature increase and the amplitude decreases almost down to null values at 300 K. Fig. 3B shows also the reflection spectra in case of non polarized light (curve α). Weak features (B and C) are observed in the high-energy part of the spectra.

Contours of measured and calculated reflection spectra at E||c polarization of ZnAs$_2$ crystals received from gas phase are presented in Fig. 4. Lines n=1 at 1.0402 eV, n=2 at 1.0497 eV and n=3 at 1.0515 eV had been observed in the reflection spectra measured at 10 K and E||c polarization. The shape of the reflection spectra for n=1 changes from 20% up to 50%. Rydberg constant for free excitons calculated using the energy positions of lines n=1 and n=2 equals 12.6 meV, and the one calculated using the positions n=2 and n=3 equals 12.9 meV. If accepting the exciton binding energy equal to 12.9 meV, one can determine the band gap value equal to Eg=1.0531 eV. The exciton binding energy value 12.6 meV obtained from calculation using the n=1 and n=2 lines is close to 12.0 meV value, which was also calculated in Refs. [10,13] using the positions of n=1 and n=2 lines. The values of Rydberg constant calculated using the positions of n=1, n=2 lines and n=2, n=3 lines are close to each other, with a faint experimental error.

The calculations of reflection spectra shapes had been carried out in the frame of the Thomas-Hopfield model [16] taking into account the spatial dispersion, the presence of a "dead" layer (DL) with additional boundary conditions of Pekar [17]. The dielectric permittivity function near the excitonic resonance can be written as follows [15,18]:

$$\varepsilon\left(\omega,\vec{k}\right) = \varepsilon_b + \frac{2\varepsilon_b\omega_{LT}\omega_0}{\omega_0^2 - \omega^2 + \frac{\hbar^2 k^2}{2M}\omega_0 - i\gamma\omega}\qquad(2)$$

where ε$_b$ is the background dielectric constant conditioned by the contributions of all interaction mechanisms, except the examined oscillator; ω$_0$ is the transversal frequency of exciton; M=m$^*_C$+m$^*_V$ is the translational mass of exciton: k is the wave-vector; ω$_{LT}$=ω$_L$−ω$_0$ is