EXCITON SPECTRA AND ENERGY BAND STRUCTURE OF CuAlSe$_2$ CRYSTALS

N.N. Syrbu[1], V.V. Ursaki[2], A.V. Dorogan[1], A. Masnik[1].

Universitatea Tehnică a Moldovei

[1]*Technical University of Moldova, 168 Stefan cel Mare Avenue, 2004 Chisinau, Republic of Moldova*
[2]*Institute of Applied Physics, Academy of Sciences of Moldova, 5 Academy Street, 2028 Chisinau, Republic of Moldova*

Abstract: *The main exciton parameters and the refined values of the energy intervals V_1 (Γ_7) - C_1(Γ_6), V_2 (Γ_6) - C_1(Γ_6) and V_3 (Γ_7) - C_1(Γ_6) in CuAlSe$_2$ crystals are discussed. The effective masses of electrons (m^*_{c1}), and holes (m^*_{V1}, m^*_{V2}, m^*_{V3}) are estimated. The contours of reflectivity spectra at high photon energies (E>Eg) are calculated on the basis of Kramers-Kronig relations.*
Keywords: chalcopyrites; optical reflectivity; exciton polaritons; dielectric function; band structur.

1. Introduction

CuAlSe$_2$ compound belongs to I-III-VI$_2$ group semiconductors and crystallizes into a chalcopyrite structure with the space group $I_{2d}^4 - D_{2d}^{12}$. The materials from this group present interest for applications in optoelectronic devices, particularly for the development of solar cells [1-3]. Photoluminescence properties of CuAlSe$_2$ crystals doped with Er^{3+} ions and photoelectrical properties of surface barrier structures based on CuAlSe$_2$ crystals have been previously investigated. These compounds possess a strong anisotropy of optical properties both in the visible and infrared spectral range.

2. Experimental data and discussions

According to theoretical calculations of energy band structure, the band-gap minimum in CuAlSe$_2$ crystals is formed by direct electronic transitions in the center of the Brillouin zone . The lower conduction band is of Γ_6 symmetry, while the upper V_1, V_2, V_3 valence bands are of Γ_7, Γ_6 and Γ_7 symmetry, respectively. The interaction of electrons from the conduction band Γ_6 (C_1) and holes from the valence band Γ_7 (V_1) is determined by the product of irreducible representations $\Gamma_1 \times \Gamma_6 \times \Gamma_7 = \Gamma_3 + \Gamma_4 + \Gamma_5$. A Γ_4 exciton allowed in the E∥c polarization, a Γ_5 exciton allowed in the E⊥c polarization, and a Γ_3 exciton forbidden in both polarizations are formed in the long-wavelength region as a result of this interaction. The interaction of a hole from the Γ_6 band with an electron from the Γ_6 band leads to the formation of three exciton series with Γ_1, Γ_2 and Γ_5 symmetries. The Γ_5 excitons are allowed, while Γ_1 and Γ_2 excitons are forbidden in E⊥c polarization according to the selection rules.

The $n = 1$ (ω_t = 2.8212 eV, ω_L = 2.8237 eV) and $n = 2$ (2.8390 eV) lines as well as a weak line at 2.8442 eV of the Γ_4 exciton hydrogen-like series are observed in the reflectivity spectra of CuAlSe$_2$ crystals measured at 10 K in the E∥c, k⊥c polarization. The reflectivity spectra in the region of the $n = 1$ line are of a usual excitonic shape with a maximum and a minimum. These peculiarities are due to presence of the transversal and longitudinal excitons. A longitudinal-transversal exciton splitting of 2.5 meV is estimated for the Γ_4 excitons from these data. A Rydberg constant of 24 meV is determined for the Γ_4 exciton series from the position of $n = 1$ and $n = 2$ lines. The energy of the continuum (E_g, $n = \infty$) is equal to 2.845 eV. These energy values of the ground ($n = 1$) exciton states are in a satisfactory accordance with previously reported values measured at 77 K for A-, B- and C-excitons, fig.1.
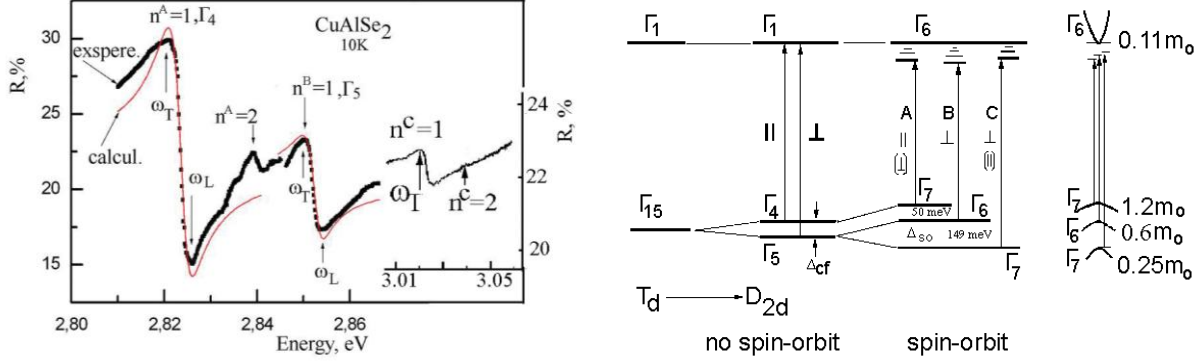
Fig. 1. The energy values of the exciton states and Band structure at the Γ point illustrating the transition from zincblende (T_d) to chalcopyrite $CuAlSe_2$ crystals.

3. Calculation of optical functions from the reflection spectra using the Kramers-Kronig correlation

The measurement of the coefficient of reflection, i.e. the amplitude of the Fresnel coefficient of reflection, in the wide energy interval in the case of a normal incidence allows one to determine the phase of the reflected radiation beam. The coefficient of reflection can be presented as:

$$r = \frac{n - ik - 1}{n - ik + 1} = \sqrt{R}e^{-i\varphi} \qquad (5)$$

where R is the coefficient of reflection at a normal incidence angle, n is the refraction index, k is the extinction index, and φ is the phase angle. The Kramers-Kroning relation describes the relation between the phase and the amplitude of the complex Fresnel coefficient of reflection at a normal incidence angle:

$$\varphi(\omega_0) = \frac{\omega_0}{\pi} \int_0^\infty \frac{\ln R(\omega)}{\omega_0^2 - \omega^2} d\omega. \qquad (6)$$

To calculate the exact value of φ, it is necessary to have the spectrum of the index of reflection in an infinite frequency interval, while the real experimental spectrum is measured in a limited frequency interval $a \le \omega \le b$.

In the present work, the reflectivity spectra of $CuAlSe_2$ crystals are measured in the energy interval from 2.5 eV to 6 eV with a polarized light. A structure of maxima (a_1-a_{10}, e_1-e_9) associated with interband transitions in different points of the Brillouin zone is observed in the reflectivity spectrum measured at energies $E > E_g$ at 77K in $E \parallel c$ and $E \perp c$ polarization (Fig. 2). As previously proposed [4], the φ values in the high energy region ($b \le \omega \le \infty$), where the spectra have not been measured, were calculated by means of an extrapolation of the spectral dependence of the coefficient of reflection by using the function $R(\omega) = c\omega^{-p}$, where C, p are some constants [4]. The $R(\omega) = R(a)$ approximation was used in the region of $0 \le \omega \le a$ without taking into account the contribution of lattice vibrations to the coefficient of reflection in this spectral interval.

The optical functions have been determined by using the calculated φ values and the experimental values of R:

$$n = \frac{1 - R}{1 - 2\sqrt{R}\cos\varphi + R} \qquad k = \frac{2\sqrt{R}\sin\varphi}{1 - 2\sqrt{R}\cos\varphi + R} \qquad \varepsilon_1 = n^2 - k^2 \text{ and } \varepsilon_2 = 2nk. \qquad (7)$$

Figure 2 presents the spectra of the coefficient of reflection R and the real part of the dielectric permeability $\varepsilon_1(\omega)$ obtained from the calculations of the reflectivity spectra using the Kramers-Kronig relations for $CuAlSe_2$ crystals for $E \parallel c$ and $E \perp c$ polarization. As expected, the maxima of the coefficient of reflection correspond to the short-wavelength decrease of the ε_1 function. The anisotropy of spectral dependencies of ε_1, ε_2, n and k is observed in $CuAlSe_2$ crystals in $E \parallel c$ and $E \perp c$ polarizations. Materials with chalcopyrite structure possess a bigger birefringence as compared to crystals with wurtzite structure.
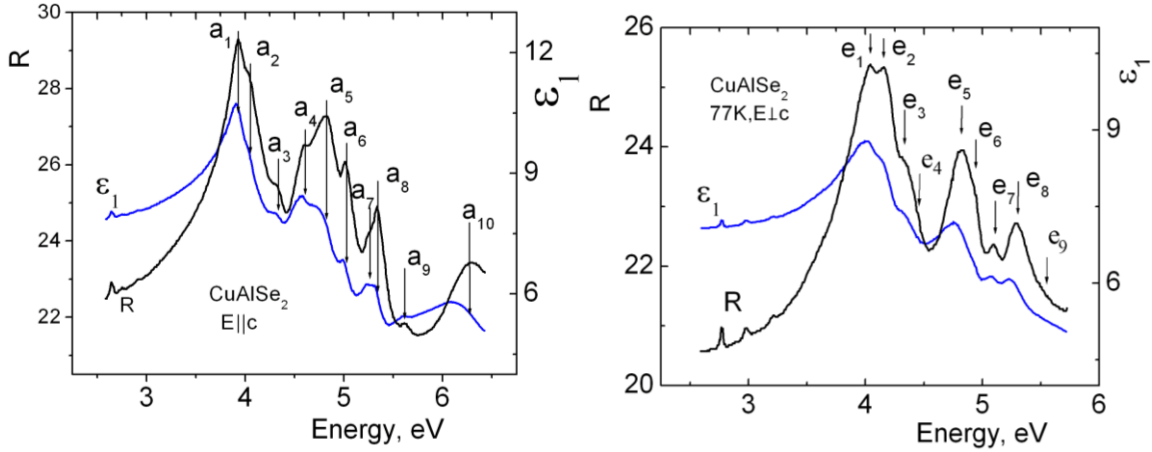
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Fig. 2. The spectra of the coefficient of reflection R and the real part of the dielectric permeability $\varepsilon_1(\omega)$ obtained from the calculations of the reflectivity spectra using the Kramers-Kronig relations for CuAlSe$_2$ crystals for E‖c polarization (a) and E⊥c polarization (b).

The difference between the optical isotropy wavelength λ_o and the fundamental absorption edge in semiconductors with chalcopyrite structure is bigger as compared to wurtzite semiconductors. The spectral dependence of the absorption coefficient determined as $\alpha(\lambda) = \dfrac{4\pi}{\lambda} k(\lambda)$ is of a major importance for the development of solar cells and optoelectronic photodetectors. The bigger is the value of the absorption coefficient fundamental absorption region, the bigger is the amount of energy converted into electricity.
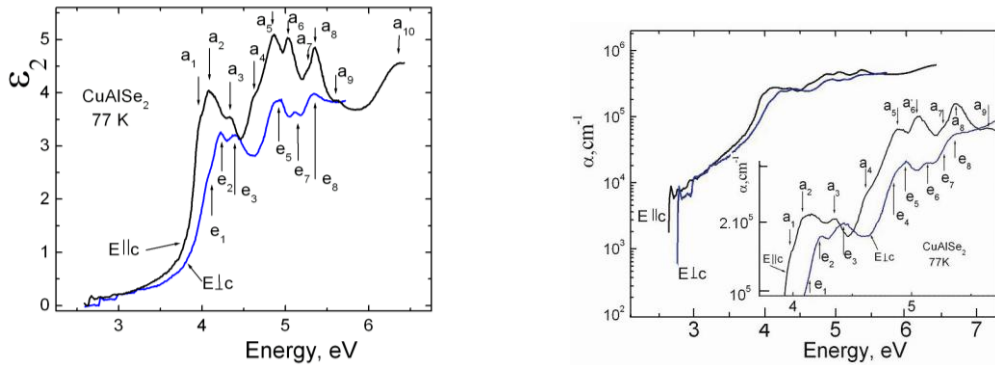

Fig. 3. The imaginary part of the dielectric permeability $\varepsilon_2(\omega)$ for E‖c and E⊥c polarizations for CuAlSe$_2$ crystals and Spectral dependence of the absorption coefficient of CuAlSe$_2$ crystals at E‖c and E⊥c polarization at 77 K.

Figure 3 presents the imaginary part of the dielectric permeability $\varepsilon_2(\omega)$ for E‖c and E⊥c polarizations and absorption spectra in the region of $E > E_g$ obtained from the calculation of transmission and reflection spectra of CuAlSe$_2$ crystals. One can see that the value of the absorption coefficient is rather high in both the polarizations of the light wave.

The energy band structure in the neighborhood of Z, X, P points was calculated without taking into account the spin-orbital and the crystal field interaction. The valence bands are degenerated in these points. Actually, the valence bands are split which results in a big number of polarized electronic transitions revealed in the reflectivity spectra. Intense a_1-a_{10} and e_1-e_9 maxima are observed in the reflectivity spectra of CuAlSe$_2$ crystals measured in E‖c and E⊥c polarizations in the region of $E > E_g$ (Fig. 2,3). Some features were observed in the region of 2.5, 3.5 and 4.5 eV in the ellipsometry measurements performed at room temperature in CuAlSe$_2$ crystals. These features are better resolved with decreasing the temperature. By analogy with A$_1$, E$_1$ transitions observed in CuInS$_2$, CuGaS$_2$ and CuGaSe$_2$ crystals previously observed in E‖c and E⊥c polarizations, respectively, we attribute the maxima observed in the spectral dependence of the R/ε at 3.921/3.905 eV (a$_2$) in E‖c polarization and 4.045/4.045 eV (e2) in E⊥c polarization to $\Gamma_7(V_1)$-$\Gamma_6(C_1)$

electronic transitions .The maxima a_2 (4.045/4.045 eV) and e_2 (4.157/4.157 eV) are observed in the short-wavelength region of the a_1, e_1 maxima in E||c and E⊥c polarizations, respectively. The difference of energies of a_2, e_2 and a_1, e_1 maxima is nearly equal to the splitting of the valence bands in the center of the Brillouin zone (123-150 meV) due to the crystal field and spin-orbital interaction. Therefore, the a_2, e_2 maxima are also assigned to the electronic transitions in the center of the Brillouin zone from the $\Gamma_7(V_3)$ valence band to the $\Gamma_7(C_2)$ conduction band.Two peaks a_3(4.299/4.299 eV) and e_3(4.314/4.314 eV) are observed in spectra of CuAlSe$_2$ in E||c and E⊥c polarizations, respectively. An analogous maximum A_3 was observed at 3.55 eV in unpolarized spectra of CuGaSe$_2$ crystals [4]. This maximum was assigned to $N_1(V_3)$-$N_1(C_1)$ transitions. Similar transitions were observed at 3.50 eV ($E_1(\Delta X)$ XΓ) in ellipsometry spectra of CuGaSe$_2$ crystals measured at 300 K in E||c polarization [5]. These ellipsometry data were treated in terms of $\Gamma_5(V)$- $\Gamma_1(C)$ transitions. The energy intervals between the upper valence band and the lower conductance band in CuGaSe$_2$ crystals in the neighborhood of P and Z points equal to 2.04 E_0, where E_0 is the minimum energy interval at the Γ point, while this interval is of 2.43E_0 at the N point.

The energy intervals in the neighborhood of P and Z points are significantly narrower than the respective intervals at the N point. On the basis of these data, one can assign the maxima A_3, E_3 and A_4, E_4 in the reflectivity spectra of CuGaSe$_2$ crystals to the transitions at the P and Z points. On the basis of these data, one can suggest that the peaks a_3(4.299/4.299 eV) and e_3(4.314/4.314 eV) observed in spectra of CuAlSe$_2$ crystals in E||c and E⊥c polarizations are due to Z(V_1)-Z (C_1) or P(V_1)-P(C_1) transitions, while the peaks a_4(4.596/4.585 eV) and e_4(4.464/4.464 eV) are due to Z(V_2)-Z (C_1) or P(V_2)-P(C_1) transitions.The peaks a_5(4.797/4.788 eV) and e_5(4.821/4.821 eV) observed in spectra of CuAlSe$_2$ crystals can be attributed to X(V_1)-X(C_2) transitions.The maxima a_6(5.017/5.008 eV) and e_6(4.932/4.932 eV) observed in CuAlSe$_2$ crystals in E‖c and E⊥c polarizations, respectively, are probably due to transitions between the V_2-C_1 bands at the X point. The splitting of the valence bands at the X point equals to 0.22 eV in this case. However, it could be that these peaks are due to transitions at the $T_3(V_1)$- $T_1(C_1)$ point as suggested for CuGaSe$_2$ crystals in ref[4,5]. An A_6 maximum was observed at 5.16 eV in ref. 17, while an ($E1$(B)) maximum was revealed at 4.89 eV (E⊥c) in ellipsometry spectra measured at 300 K which was attributed to transitions at the T point. Since according to theoretical and experimental data [4,5] the interband interval at the N point is bigger that those at the X, P and Z points, one can consider that the peaks a_7(5.261/5.261 eV) and e_7(5.104/5.104 eV) observed in E||c and E⊥c polarizations, respectively, are due to transitions from the V_1 band to the C_1 band at the N point. The peaks a_8(5.331/5.331 eV) and e_8(5.290/5.290 eV) observed in E||c and E⊥c polarizations, respectively, are probably due also to transitions at the N(V_2)-N(C_1) point. The maxima a_9(5.602/5.602 eV) and e_9(5.491/5.491 eV) are observed in the reflectivity spectra in the more short-wavelength spectral region. These features can be assigned to N(V_3)-N(C_1) transitions.

Conclusions

The calculations of the contours of reflectivity spectra in a wide energy interval performed in this work for CuAlSe$_2$ crystals on the basis of Kramers-Kronig relations give additional information for the interpretation of electronic transitions.

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