INFLUENCE OF ELECTRON-ELECTRON COLOUMB REPULSION ON PHOTOTHRESHOLD OF THE GROUP III-VI LAYERED SEMICONDUCTORS

F.M. HASHIMZADE, N.B. MUSTAFAEV

Institute of Physics Azerbaijan National Academy of Sciences
H. Javid av, 33, Baku, 370143

The photothreshold correction related to electronic relaxation has been calculated for the group III-VI layered semiconductors. The band structure and anisotropy of dielectric permeability of the semiconductors have been taken into account. Results of the calculation are compared with experimental data. The best agreement is obtained for GaSe.

1.Introduction

The group III-VI layered semiconductors are useful for various electronic devices. The semiconductors consist of a pile of packets with atoms bound by covalent and ionic-covalent bonds inside the packet, whereas between the packets there are only weak Van der Waals forces. As a consequence, the semiconductors are easily cleaved parallel to the layers, and the resultant surfaces are very smooth. The surfaces are inert against adsorption, and they have a low density of surface states. These features of the layered semiconductors facilitate greatly the fabrication of homojunctions, heterojunctions, metal-semiconductor Schottky barriers and metal-insulator-semiconductor structures (see e.g. Ref.1). They can be used as photodiodes, high-speed switches, spectral and/or electric memory devices, light modulators and solar energy converters.

The molecular-beam epitaxial growth of InSe and GaSe crystals reported in Refs.2 and 3 makes it also possible to build InSe/GaSe quantum-well structures and superlattices. For such structures, theoretical studies of energy spectrum were made in Refs.4 and 5. It follows from the considerations that a determination of the band parameters has paramount importance for the group III-VI layered crystals.

2. Photothreshold Problem

By definition, a photothreshold $\ddot{O}$ is the energy required for an electron transition from the top of valence band to the vacuum level. For diamond-like crystals, it has been stated that experimental values of Ö are by 3 to 4 eV smaller than the energy value at the top of valence band calculated using the tight-binding method (see Ref.6). Similar disagreement between experimental and calculated values of work of exit occurs also in metals. In paper [7], a shift of the photoemission threshold of metals was interpreted in terms of the electron-electron Coloumb repulsion. In principle, the same interpretation had been suggested earlier by authors of paper [8] in order to explain the Coloumb shift of photothreshold in diamond-like semiconductors. According to Ref.8, the photothresholds are considerably lowered due to the relaxation of valence electrons around positive hole. A certain amount of negative polarization charge is attracted from the hole during the relaxation. It repels the photoelectron and increases its kinetic energy by the same amount that the remaining electron system of total Coloumb energy loses in the final state as compared with the initial state. If the hole relaxation self-energies are subtracted from the distances between valence-band maxima and vacuum level, then the large discrepancies between one-electron

LCAO predictions and experimental observations of photothreshold are essentially removed. However, some difference (less than 1 *eV*) remains by reason of surface charge and other effects discussed in Ref.9.

In the present paper, the energy correction related to electron-electron correlation has been calculated for the group III-VI layered semiconductors. The approach developed in Ref.8 has been used. We have modified the calculation procedure in order to take into account the anisotropy of dielectric permeability in the layered semiconductors. The valence-band wavefunctions needed for our calculation have been taken from Ref.10. According to Ref.10, the valence-band top in the group III-VI layered semiconductors is formed only by valence-electron states of cation. For these semiconductors, the top energy values were obtained by using conventional one-electron tight-binding theory [11, 12] and empirical pseudopotential method [13]. In Refs.12 and 13, the absolute position of energy bands was not given. Nevertheless, one can determine energies of valence-band maxima starting from the given position of *s*-level of the anion. In order to evaluate photothreshold, the energy correction calculated by us has to be subtracted from the values of valence-band top energy given in Refs.11-13. The photothreshold values calculated in this manner have been compared with their experimental values given in Refs.14-17.

3. Basic Formulae

The correlation part of self-energy due to electron relaxation is defined as [8]

$$S_v^{rel}(\vec{k}) = \frac{1}{2}\int\frac{d\vec{q}}{(2\pi)^3}[V_0(\vec{q}) - V(\vec{q})] \, , \qquad (1)$$

where

$$V_0(\vec{q}) = \frac{4\pi}{q^2}e^2 \mid r_v(\vec{q})\mid^2 \qquad , \qquad (2)$$

$$r_v(\vec{q}) = \int d\vec{r}\exp(i\vec{q}\vec{r})\psi_{v\vec{k}}^*(\vec{r})\psi_{v\vec{k}}(\vec{r}) \, , \qquad (3)$$

Here ψ_{vk} is the Bloch wavefunction of a valence electron, $V_0(\vec{q})$ is the Fourier transformation of the electrostatic interaction potential, and $V(\vec{q})$ is the Fourier transformation of the screened Coulomb potential.

Within the bond-orbital approximation, the Bloch factor for electrons (at the top of valence band) has the following form [10]:

$$\boldsymbol{f}_v(\vec{r}) = \left(1 + b_c^2\right)^{-1/2}\left[b_c \boldsymbol{f}_s^c(\vec{r}) \mp \boldsymbol{f}_{p_z}^c(\vec{r})\right] \qquad (4)$$

Here

$$\boldsymbol{f}_s^c(\vec{r}) = \frac{1}{\sqrt{3\boldsymbol{p}}}\, \boldsymbol{b}_c^{5/2}\, r\, exp(-\boldsymbol{b}_c r) \qquad (5)$$

and

$$\boldsymbol{f}_{p_z}^c(\vec{r}) = \sqrt{\frac{2\boldsymbol{b}_c^7}{15\boldsymbol{p}}}\, zr\, exp(-\boldsymbol{b}_c r) \qquad (6)$$

are the Slater wavefunctions of a cation atom (these functions are often used for LCAO calculations), b_c is a parameter

which characterizes the hybridization of electronic s- and p_z-states of the cation.

The signs $\mp$ refer to two different cations taking part in the cation-cation covalent bond. As for $\boldsymbol{b}_c$, in Ref.8 this parameter is given for cubic crystals in the units of $2\boldsymbol{p}/a$ (a is the lattice constant). For our calculations, it is more convenient to give $\boldsymbol{b}_c$ in units of the reciprocal length of cation-anion bond l. In layered GaSe, InSe and GaS crystals, the values of l are close to those of GaAs, InAs and ZnS, respectively.

The Coulomb potential screening has been taken into account by analogy with Ref.8, but a distinction has been made between the components of static dielectric permeability parallel $\mathring{a}_0^{||}$ and perpendicular $\mathring{a}_0^{\perp}$ to the crystal axis C, i.e. we have used the following expression:

$$\boldsymbol{e}^j(\vec{q}) = 1 + \left[\left(\boldsymbol{e}_o^j - 1\right) - 1 + \frac{q^2}{q_{TF}^2} + \frac{4}{3}\cdot\frac{1}{(\boldsymbol{p}_{aB})^2}\cdot\frac{q^4}{q_{TF}^6}\right]^{-1}, \quad (7)$$

where the superscript $j = ||, \perp$ corresponds to the directions parallel and perpendicular to C, a_B is the Bohr radius, and q_{TF} is the Thomas-Fermi wavevector of valence electrons.

4. Comparison with Experiment

Values of the parameters needed for numerical calculation are given in table 1.

Table 1.

Parameters of the group III-VI layered semiconductors.

	GaSe	GaS	InSe
b_c [10]	1.02	1.02	1.10
L (nm) [12,13]	0.246	0.234	0.263
$\boldsymbol{b}_c l$	4.35	5.17	4.38
$\varepsilon_0^{\perp}$	7.44 [18]	7 [19]	6.2 [19]
$\varepsilon_0^{||}$	5.76 [18]	5.9 [19]	4.9 [19]
q_{TF}(nm^{-1})	19.438	19.833	18.765

In Table 2, we give values of the relaxation self-energy correction $\sum_v^{rel}$ calculated on the basis of formulae (1) to (7). The difference between the value $\sum_v^{rel}$ calculated by us and the valence-band top energy $|E_v|$ taken from [11] is given in the

same table. A comparison of the difference $|E_v| - \sum_v^{rel}$ with the experimental values of photothreshold $\boldsymbol{F}_{exp}$, given in table 2, shows the best agreement for GaSe.

Table 2.

The relaxation self-energy correction $\sum_v^{rel}$, the valence-band top energy $|E_v|$ and experimental values of photothreshold $\boldsymbol{F}_{exp}$. All values are given in units of eV.`

	GaSe	GaS	InSe
$\sum_v^{rel}$	2.4	3	2.3
$|E_v|$ [11] - $\sum_v^{rel}$	5.5	4.9	5.4
$\boldsymbol{F}_{exp.}$ [14]	5.4±0.1	6.5±0.15	
$\boldsymbol{F}_{exp.}$ [15]	5.3 – 5.4	5.5 -5.8	5.8
$\boldsymbol{F}_{exp.}$ [16]			5.8
$\boldsymbol{F}_{exp.}$ [17]			5.0

We could not obtain a good agreement for GaS and InSe. Nevertheless, the agreement is not generally worse than for of the diamond-like semiconductors (see table 2 in [8]), and it is within an accuracy of the used calculation method. Some difference remains by reason of surface charge and other effects discussed in [9].

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