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First-principle calculations of band energy structure of $CdSe_{0.5}S_{0.5}$ solid state solution thin films

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The electronic band structure of the solid-state $CdSe_{0.5}S_{0.5}$ thin film solution in the framework of the density functional theory calculations is investigated. The structure of the sample is constructed on the original binary compound CdS, which crystallizes in the wurtzite phase. Transformations of the electronic energy spectra for the solid-state $CdSe_{0.5}S_{0.5}$ solution, which occur in the process of transition from bulk crystals to thin films, are analyzed. The refractive index and high-frequency dielectric constant are calculated. All of the calculated parameters correlate well with the known experimental data.

Keywords: density functional theory, band structure, thin films, solid-state solution.

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Introduction

Taking into account the recent tendencies in modern electronics, one can witness that polycrystalline layers of semiconductors become more and more interesting for applications if compared with bulk semiconductors. Unlike single crystals or epitaxial structures, the synthesis of polycrystalline (both bulk and layered) semiconductors is characterized by a simpler and more efficient production process, which requires neither highly precise growth equipment nor high-cost single-crystal substrates. These factors make semiconductor materials and devices based on the layers or thin films less expensive.

In particular, polycrystalline layers are of great interest for the developers of inexpensive solar cells for terrestrial applications. The authors of the works [1−3] rightfully affirm that wide use of polycrystalline semiconductors in electronics has been limited for a long time by the availability of numerous extended defects such as grain boundaries or dislocations. At present, however, the current progress in development of these materials has led to the situation when polycrystallinity of the materials represents more hope for the future than a problem.

As an example, the grain boundaries in such semiconductors manifest specific electrical and recombination characteristics, which can be employed in a number of devices. Being a serious violation of the quality of the crystal lattice, these boundaries play a role of an effective internal getter that promotes removal of residual impurities and point defects from the bulk of the material. This property of inter-grain boundaries can be used when improving exploitation characteristics of appropriate semiconductor-based electronic devices and, in particular, their thermal and radiation stability [4].

Thin films of cadmium chalcogenides (CdX, with X = S, Se and Te, and solid-state solutions based on them) represent a large $A^{II}B^{VI}$ group of crystalline materials that reveal a canonical semiconducting behavior. These materials embrace large and important research field because of their wide application potential in various fields of optoelectronic devices. CdS and CdSe form cubic and hexagonal phases, depending mainly on the choice of method for its synthesis and on the specific growth parameters [5–8].

The principal aim of the present paper is to present the important results concerned with the energy properties of the solid-state $CdSe_{0.5}S_{0.5}$ thin film solution. Concentration behavior of their physical properties will be study in future works.

In this context, a number of issues will be touched upon and the appropriate problems will be solved. They include the following: complex theoretical studies of transformations of the electronic energy spectra for the solid-state $CdSe_{0.5}S_{0.5}$ solution, which occur in the process of transition from bulk crystals [9] to thin films. These studies involve the calculations of band-energy diagrams with a density functional theory.

Although the above subject represents a hot topic of the present-day studies [9, 10], as far as we know, there has been no attempt in the literature to calculate the electron band energy structure of solid-state $CdSe_{0.5}S_{0.5}$ thin film solution.

I. Methods of calculation

The theoretical calculations were performed within the framework of the density functional theory (DFT). The solid-state $CdSe_{0.5}S_{0.5}$ solution was constructed on the ‘parent’ compound of CdS [11] with wurtzite crystal structure. The Vanderbilt’s ultrasoft pseudopotentials [12–14] were used for the ion potentials. To describe the exchange-correlation energy of the electronic subsystem, a functional in the approximation of generalized gradient (GGA) and the Purdue–Burke–Ernzerhof (PBEsol) parameterization [13–15] was used. As a correlation potential, the Ceperlay–Alder and Gell–Mann–Brueckner equations were applied to the high electron-density boundaries.

The charge-density distribution was calculated by the method of special points involving the techniques of charge damping. The relaxation of ion positions on the basis of calculated atomic forces was achieved for each crystal structure, and then the integral stress of the cell was determined.

The value $E_{\text{cut-off}}$= 260 eV for the energy of cutting-off the plane waves was used in our calculations. The convergence of the total energy was about 5×10^{6} eV/atom. The integration over the Brillouin zone (BZ) was performed on the 2×1×1 grid of k points using the Monkhorsta–Pack scheme [16].

The atomic coordinates and the unit cell parameters were optimized using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) method [17]. Optimization was continued until the forces acting on the atoms became less than 0.01 eV/Å, the maximum displacement less than 10^{-6} Å, and the mechanical stresses in the cell less than 0.02 GPa. The energy band diagram was constructed using the points of the BZ in the inverse space, which were as follows: G(0, 0, 0), F(0, 0.5, 0), Q(0, 0.5, 0.5), Z(0, 0, 0.5).

The models of thin films were formed from a three-dimensional crystal along the [1 0 0], [0 1 0] and [0 0 1] axis (see Fig. 1). The distance between the formula units was increased by approximately 50 nm, thus forming a vacuum gap to avoid interaction between the layers. If using orienting substrates (sapphire, monocrystals CdTe, Si, NaCl, et al.), these structures (solid-state $CdSe_{0.5}S_{0.5}$ thin film solution) with preferring orientation [1 0 0], [0 1 0] or [0 0 1] can be obtained experimentally [1].

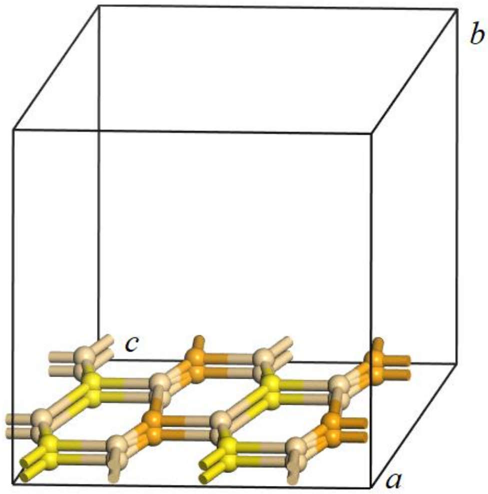
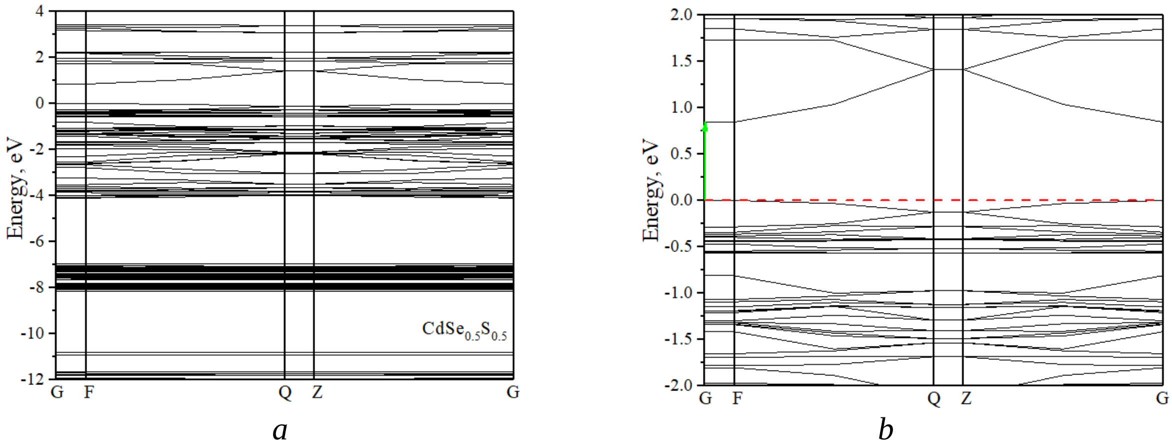


Fig. 1. Models of solid-state $CdSe_{0.5}S_{0.5}$ thin film solution with orientation along [0 1 0] axis used for calculation.

II. Results and Discussion

The calculated band structure of the solid-state



a *b*

Fig. 2. Electron band energy structure of the solid-state $CdSe_{0.5}S_{0.5}$ thin film solution with orientation along [0 1 0] axis (a). Rescale of electron band energy structure (b) near the band gap (red dash line – correspond to position of Fermi energy level (E_F), green arrow – correspond to E_g^d.

$CdSe_{0.5}S_{0.5}$ thin film solution with orientation along [0 1 0] axis is presented in Fig. 2. Here, the Fermi level E_F corresponds to the energy $E = 0$. The bandgap of $CdSe_{0.5}S_{0.5}$ thin films is found to be of the direct type, which is denoted as $E_g^{(d)}$ (Fig. 2). In this material, the indirect optical transitions involving phonons can also occur at the photon energies $h\nu > E_g^{(d)}$. This is similar to the cases realized in the corresponding binary compounds CdSe and CdS [11, 18].

The difference of anisotropies for the valence- and conduction-band dispersions E(k) is evident. The top of the valence band is flatter and the conduction band shows higher dispersion. This is caused by the fact that holes have less mobility, if compared with electrons. The maximal dispersion E(k) is observed for the bands along the directions G–Z and F–Q in the BZ.

Our analysis of energy-band spectrum for the $CdSe_{0.5}S_{0.5}$ thin films testifies that the bandgap E_g is localized in the center of the BZ, i.e. at the G point. The bandgap is estimated as E_g= 0.846 eV (E_g= 1.90(2) eV [19] for $CdSe_{0.65}S_{0.35}$ thin film; E_g= 2.15(2) eV [19] for $CdSe_{0.36}S_{0.64}$ thin film). Using value bowing parameter b=0.079 eV [19] was obtained experimental value of bandgap for the solid-state $CdSe_{0.5}S_{0.5}$ thin film solution. Obtained value is E_g= 2.03 eV. Although this value is notably smaller than, e.g., the experimental bandgap known for the pure CdSe (1.68 eV [18]) or CdS (2.39 eV [11]) thin films, it is well known that the calculations based on the density-functional theory of semiconductors and the local-density or generalized-gradient approximations usually underestimate notably the bandgap [11, 17, 18]. Using the experimental data of the bandgap (for $CdSe_{0.65}S_{0.35}$ thin films [19]), we have obtained the value of 'scissor' factor being equal to ΔE= 1.184 eV (the 'scissor' factor may be used for comparison of theoretical and experimental optical spectra in the range of electron excitations [20]). Obtained value of operator 'scissor' matches a higher value for the bulk sample than for thin film.

Now we proceed to the refractive index, which represents a fundamental optical parameter related to the band structure of optoelectronic materials. A number of empirical relationships linking the refractive index n with the bandgap E_g are known from the literature (Moss, Ravindra, Herve and Vandamme, and Tripathy) [21]. According to these models, a refractive index of a semiconductor (with a bandgap being usually inside the range 0 < E_g < 5 eV) can be calculated as

$$n_M^4 E_g = C,\ n_R = a - bE_g,\ n_{H-V}^2 = 1 + [A/(E_g + B)]^2,\ n_T = n_0[1 + \alpha e^{-\beta E_g}], \tag{1}$$

where the normal conditions are assumed, the bandgap units are eV, and the n's subscripts abbreviate the authors mentioned above. In Eqs. (1), we have C = 95 eV, a = 4.084 eV, b = 0.62 eV^{-1}, A = 13.6 eV, B = 3.47 eV, n_0 = 1.73, α = 1.9017 and β = 0.539 eV^{-1} [21]. In spite of a wide variety of empirical relationships, sometimes there arise some problems with interpreting quantitatively the refractive index in terms of Eqs. (1) and preferring one formula over the other (see Refs. [21]). The calculated values of n using the various models of interest are listed in Table 1 (the calculated bandgap E_g of $CdSe_{0.5}S_{0.5}$ includes the 'scissor' factor).

Table 1.

Energy and optical parameters of the solid-state $CdSe_{0.5}S_{0.5}$ thin film solution with orientation along [0 1 0] axis.

Parameters		Value
E_g, eV		0.846
ΔE, eV		1.184
n	Moss	2.62
	Ravindra	2.83
	Herve and Vandamme	2.67
	Tripathy	2.83
ε_∞	Moss	6.86
	Ravindra	8.01
	Herve and Vandamme	7.13
	Tripathy	8.01

Using different models given by Eqs. (1), we have calculated the n values for the $CdSe_{0.5}S_{0.5}$ thin film (see Table 1), which corresponds to the photon energies $h\nu$ exactly equal to the bandgaps. The refractive index of 2.69 (λ= 500 nm) for $CdSe_{0.65}S_{0.35}$ and 2.69 (λ= 500 nm) for $CdSe_{0.36}S_{0.64}$ was obtained in [19]. Comparing the obtained results (see Table 1) with the literature, we can assume that the Herve and Vandamme relation most accurately allows establishing the value of the refractive index.

Based on the values of n calculated from the different relations, we also calculate the high-frequency dielectric constant ($\varepsilon_\infty = n^2$, see Table 1).

The analysis of partial contributions of individual levels to the function of the total density of states (Fig. 3) and the partial contributions of individual bands to the electronic density allows us to find genesis of the valence and conduction bands for the solid-state $CdSe_{0.5}S_{0.5}$ thin film solution. The lowest bands from –14 to –10 eV are formed by the s states of Se/S. The following bands dispersed at the energy marker from –9 to –6 eV are formed because of the contributions of the d states of Cd. The peak of the valence complex is practically formed by the p states of Se/S, with 'contamination' of the p states of Cd. But the conduction band bottom is mainly formed by the s and p states of Cd and Se/S. Taking into account the selection rule, the results of calculations of the electron energy spectrum, and the electron density of states, we can assume that the smallest bandgap is formed by direct s–p transitions.

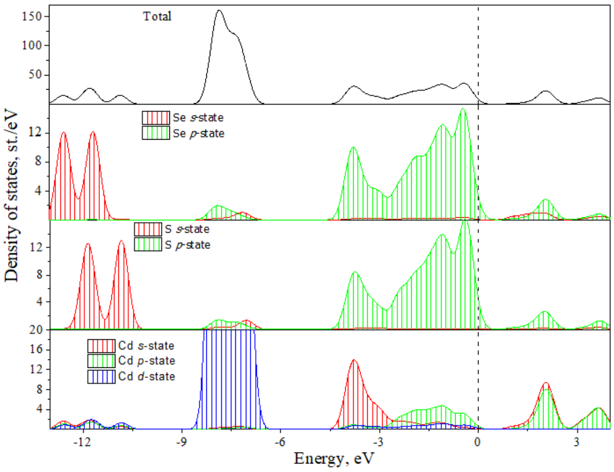


Fig. 3. Electron density of states of the solid-state CdSe$_{0.5}$S$_{0.5}$ thin film solution with orientation along [0 1 0] axis.

Conclusion

The main results of the work reported in the present work can be summarized as follows:

1. First-principle theoretical studies of the electronic energy spectrum for the solid-state CdSe$_{0.5}$S$_{0.5}$ thin film solution with different orientations have been carried out using the reliable techniques of density functional theory and known approximations. It has been established that the smallest bandgap is localized at the center of the BZ (i.e., at the point G). Therefore, our substances should reveal direct optical transitions.

2. It has been found that the dispersion of energy levels for the cadmium chalcogenide samples under study decreases during transition from a single-crystal bulk sample to a thin film.

3. Based on the obtained theoretical data of bandgap, the refractive index and high-frequency dielectric constant were calculated. It is established that the Herve and Vandamme relation most accurately allows determining the value of the refractive index and high-frequency dielectric constant.

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Першопринципні розрахунки зонної енергетичної структури тонких плівок твердого розчину заміщення $CdSe_{0.5}S_{0.5}$

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Досліджено електронну зонну структуру тонкої плівки твердого розчину заміщення $CdSe_{0.5}S_{0.5}$ в рамках теорії функціоналу густини. Структура зразка тонкої плівки була побудована на основі вихідної бінарної сполуки CdS, яка кристалізується в структурі вюрциту. Проаналізовано динаміку зміни електронного енергетичного спектру твердого розчину заміщення $CdSe_{0.5}S_{0.5}$ в процесі переходу від монокристалу до тонкої плівки. Розраховано показник заломлення та високочастотну діелектричну проникність. Усі розраховані параметри добре корелюють з відомими експериментальними даними.

Ключові слова: теорія функціоналу густини, зонна структура, тонкі плівки, твердий розчин заміщення.