First-principles calculations of electronic structures and optical properties of group-IIIA elements doped wurtzite CdS

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ABSTRACT

The electronic structures and optical properties of pure and group-IIIA elements doped wurtzite CdS are investigated using first-principles density-functional approach. The results indicate that when a group-IIIA element is introduced into CdS, the Fermi level moves upward into the conduction band from the band gap of undoped CdS, and the contributions of the s states of cations to the total density of states of CdS near the Fermi level are very large. The calculated optical properties show that absorption peaks located in the visible spectrum appear in group-IIIA doped CdS, but the intensities of the peaks are very weak, especially for the polarization vectors perpendicular to the c axis. Our calculations provide reasonable explanations to the experimental observations of the greatly decrease of resistivity of CdS while retaining high transparency with the doping of group-IIIA element.

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1. Introduction

II–VI wide-gap semiconductors represent a large family of compounds (such as ZnO, ZnS, ZnSe, CdS, CdTe, CdSe etc.), which have been applied to various fields [1–3]. Among them, CdS has attracted considerable attention due to its wide applications in optoelectronic devices such as solar cells, infrared windows, optical detectors, and light emitting diodes [4–9]. Pristine CdS generally shows n-type conduction because of native defects of sulfur vacancies [10,11]. Owing to high optical transmittance (70–80% in the visible range) [12,13] and wide direct band-gap (2.42 eV at room temperature) [14], CdS is also a promising photovoltaic material utilized as n-type window layers in heterojunction thin film solar cells based on p-type CdTe or Cu(In, Ga)Se$_2$ absorber layer [15–17]. However, the resistivity of the pure CdS is very high (being in the order of 10^7–$10^8 \, \Omega$ cm) [13,18,19], which severely limits its applications, especially in the field of solar cells. Lowering resistivity and increasing visible light transmittance of CdS films are recognized as the two basic requirements for the window materials of solar cells. Recently, it was reported experimentally that the resistivity of CdS film could be dramatically decreased when a group-IIIA element was introduced [19–21]. For example,

Khallaf et al. [21] observed that the resistivity of Ga-doped CdS thin film could be as low as $1.2 \times 10^{-2} \, \Omega$ cm and its transmittance at the visible light range could exceed 80%. To further improve the optical and electrical properties of CdS, it is important to understand the underlying mechanism of doping effect in CdS. Since the electronic band structure is the key element to determine the physical properties of a material. It is nontrivial to calculate the band structure and then obtain the optoelectronic properties of CdS based compounds. In the present paper, we perform first-principles band structures and optical properties calculations to investigate the doping effects of B, Al, Ga, and In impurities on the electronic band structure and optical properties of CdS, using local density approximation (LDA) within the density functional theory (DFT). Our results show that the optoelectronic properties of CdS can be significantly improved with proper doping of group-IIIA elements, which would be of benefit to the optoelectronic and photovoltaic devices applications.

2. Calculation methods

CdS can be in the form of either zinc blende or wurtzite structures, the latter is considered to be the stable phase [22,23]. Hence we focus on wurtzite CdS in the present paper. The unit cell of wurtzite CdS is a hexagonal prism, which belongs to the space group $P6_3mc$ (No. 186). Our calculations were performed by employing a first-principles calculation software package CASTEP

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[24] based on the DFT. The LDA method was adopted to describe the exchange–correlation interaction in terms of the Perdew–Zunger [25] parameterization to the Ceperley–Alder [26] form. The interactions between valence electrons and ionic core were described by Vanderbilt ultrasoft pseudopotential [27]. The cut-off energy in plane wave expansion was set to be 350 eV, and $4 \times 4 \times 4$ k-points mesh generated according to the Monkhorst–Pack [28] scheme in the first Brillouin zone was employed in the present work. The undoped and group-IIIA doped CdS calculations were performed both with 32-atom $2 \times 2 \times 2$ supercell of wurtzite CdS. For each of the group-IIIA doped cases, one of the 16 atoms of Cd was replaced by one impurity (B, Al, Ga, or In) atom (corresponding to a 6.25% level of doping). In all cases, geometry optimizations were carried out and convergences were assumed when the forces on atoms less than 10 meV/Å.

3. Results and discussions

The calculated lattice parameters of the optimized structure of undoped CdS are $a = 4.096$ Å and $c = 6.663$ Å, in good agreement with the experimental and other theoretical results [23,29,30]. For the B, Al, Ga, and In doped cases, the parameters a are 4.042, 4.078, 4.085, and 4.100 Å, and c are 6.537, 6.658, 6.645, and 6.695 Å. The lattice parameters of B, Al, and Ga doped CdS are slightly less than that of the undoped one, being consistent with the experimental results [12]. Since the effective ionic radii of B^{3+} (0.25 Å), Al^{3+} (0.53 Å), and Ga^{3+} (0.61 Å) are smaller than that of Cd^{2+} (0.92 Å) [31], the shrinkage of the lattice parameters of B, Al, and Ga doped CdS is reasonable. Although the ionic radius of In^{3+} (0.76 Å) [31] is also smaller than that of Cd^{2+}, the lattice parameters (a and c) of In-doped CdS increase. Experimentally, the lattice constant increases with increasing indium concentration were detected in indium doped CdS films and nanowires [32,33].

Fig. 1(a) and (b) shows the calculated electronic band structure and density of states (DOS) of pure CdS, respectively. The top of the valence band is chosen to be the zero energy scale. The Fermi level locates at 0.46 eV. From this figure, one can see that the maximum of the valence band and the minimum of the conduction band are both located at the Γ point in the Brillouin zone. This confirms direct-gap semiconductor feature of the undoped CdS, which is identical with the reported results [11,34]. The Calculated band gap of the pure CdS is 1.10 eV, being smaller than the experimental value of 2.42 eV [14] due to the well-known shortcoming of LDA, which usually underestimates the gaps [30]. The band dispersion of the bottom of the conduction band is much higher than that of the top of the valence band, suggesting smaller effective mass of electrons than that of the holes in CdS. To identify the contributions from various orbitals of the anion and cation, we decompose the total density of states into s, p, and d orbital. As shown in Fig. 1(b), the conduction band mainly consists of Cd $5s$, $5p$ states. The sulfur $3p$ and Cd $5s$, $5p$ orbitals hybridize to form the valence band, and the calculated valence-band width is 4.7 eV, being comparable to the result (4.5 eV) obtained from angle resolved photoelectron spectroscopy (ARPES) [35]. The two peaks below -5 eV in Fig. 1(b) correspond to two flat energy bands (not shown). The band located around -7.5 eV comes from the Cd $4d$ state and the width of the d band is 1.2 eV, which is in good agreement with the ARPES result of 1.2 eV [35]. The other band with a narrow width of 0.6 eV, mainly formed by the sulfur $3s$ state, is located around -12.2 eV, which is basically the same as the x-ray-emission spectroscopy results of -12.5 eV [36].

The electronic band structures and the partial densities of states of B, Al, Ga, and In doped wurtzite CdS were also calculated. Fig. 2 presents the representative results of B-doped and Ga-doped CdS, in which the energies are given with respect to the Fermi level. The valence band of Ga-doped (B-doped) CdS is mainly composed of Cd $5s$, $5p$ electronic states strongly hybridized with sulfur $3p$ and the outer s, p orbitals of Ga atom (B atom), in which the outer s state of dopant atom mainly locates at the bottom. The conduction band of Ga-doped (B-doped) CdS is mainly formed from Cd $5s$, $5p$ states mixed with sulfur $3p$ and the outer s, p states of Ga atom (B atom). The d state of dopant atom (Ga $3d$) lies near -16.5 eV with a very small width of about 0.2 eV for Ga-doped CdS, indicating highly localized characteristic of the electronic state (the right panels in Fig. 2). Comparing to the undoped CdS,
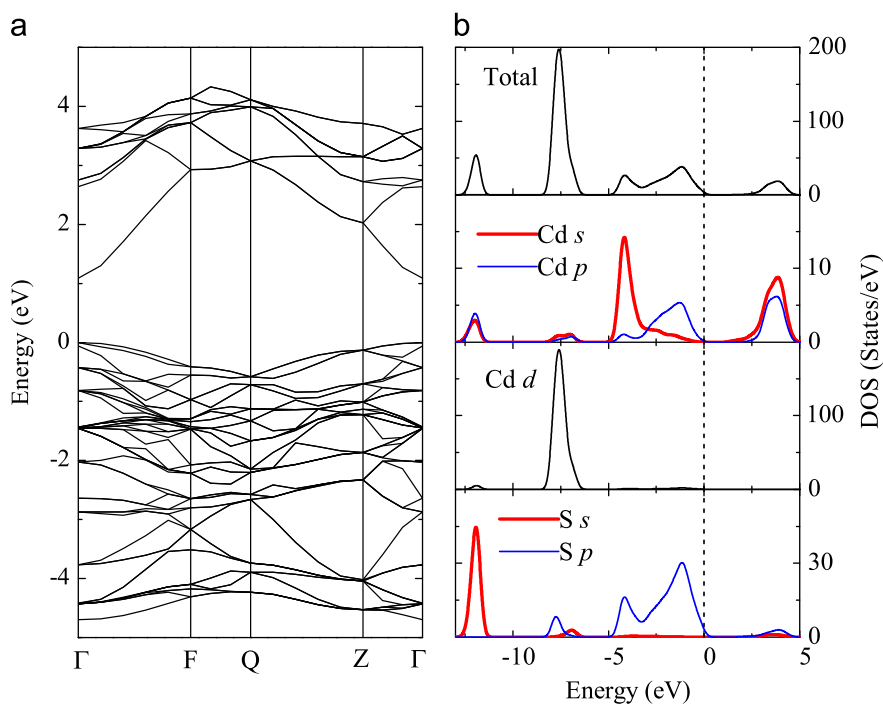

Fig. 1. (Color online) (a) Electronic band structure, and (b) partial density of states for undoped wurtzite CdS. The top of the valence band is set to zero on the energy axis.