Sn doped CdTe as candidate for intermediate-band solar cells: A first principles DFT+GW study

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Abstract. In this work, we investigate the electronic properties and defect formation energies of Sn doped CdTe combining first principles density-functional theory and many body GW calculations. Due to the Sn dopant, an isolated impurity band is formed in the middle of the forbidden band gap of CdTe allowing the absorption of sub-bandgap photons via an intermediate-band. Our results suggest CdTe:Sn as a promising candidate for the development of third-generation intermediate-band solar cells with theoretical efficiencies up to 63.2%.

1. Introduction

In traditional semiconductor photovoltaic cells, electrons are directly excited from the valence band (VB) to the conduction band (CB). Inserting a partially filled intermediate-band (IB) into the forbidden band gap enables two additional transitions to the unoccupied bands allowing the absorption of sub-bandgap photons. Just as plants break the water molecule in the chlorophyll function, two photons are used to produce an electron-hole pair of high free energy using a semi-filled isolated intermediate-band (IB) as an intermediate step [1, 2, 3]. This process not only increases the photocurrent without degrading the open-circuit voltage, but also reduces energy losses due to thermal relaxation of optically excited carriers [4]. This kind of solar cell presents efficiencies higher than those established by the Shockley-Queisser thermodynamic limit of 31% for single-junction solar cells [5]. The theoretical limiting efficiency of intermediate-band solar cells (IBSCs) is 63.2%, comparable to the efficiency for optimized triple-junction solar cells [6, 7].

The quest for finding optimal IBSCs been focused on alloys that naturally exhibit an IB [8, 9, 10] and arrays of quantum dots (QDs) that form an IB [11, 12, 13]. Walukiewicz et. al. [14, 15] were the first to produce an IB material based on highly mismatched alloys (HMAs). Wang and co-workers [4] demonstrated an overall 50% increase in power conversion efficiency in an IB solar cell based on ZnTe:O, where the intermediate-band position is tunable with alloy [4]. Ahsan et. al. [16] experimentally confirmed a two-photon excitation in an intermediate-band solar cell based on GaNAs alloy. Recently, a Sn-doped thin film of $CuGaS_2$ chalcopyrite were synthesized based on theoretical band structure calculations [17].

In the present work, we investigate the defect formation energies, charge transition levels, and theoretical band-structures of Sn doped CdTe using the highly accurate DFT+GW approach [18, 19, 20]. Our calculations show that an isolated intermediate-band in the middle of the

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forbidden gap is formed in Sn doped CdTe, which could be a promising candidate for high-efficiency photovoltaic cells.

2. Methods

2.1. Computational methods

First-principles total energy and band structure calculations were performed using the generalized gradient approximation density functional of Perdew, Burke, and Ernzerhof (PBE) [21] as implemented in the plane-wave based Quantum-ESPRESSO package [22]. Electron-ion interactions were described by GBRV ultrasoft pseudopotentials [23]. The valence wave functions were expanded in a plane-wave basis with cutoff energy of 390 eV. To avoid finite-size effects as much as possible, the defect calculations are performed within a 512-atom cubic supercell where all the atoms are fully relaxed until the forces on every atom were less than 0.025 eV/Å. The Brillouin zone was sampled with the Γ point only.

Many body GW calculations were carried out within the Vienna Ab Initio Simulation Package (VASP) [24, 25]. We use the one-shot G_0W_0@HSE approach, because some improvements can be achieved via the use of a better starting point [26]. The number of bands where chosen to be 1600 for bulk CdTe. Due to the slow convergence of the quasiparticle energies, an extrapolation to an infinite number of states is required. A scheme based on the $1/N$ convergence behavior of the quasiparticle energy, where N is the size of the basis set, was carried out for this purpose. Spin-orbit coupling was included as a correction.

2.2. Formation energies

The formation energy of a defect X in charge state q is defined as [27]

$$\Delta H_f[X^q] = E(q, \mathbf{R}_q) - E[bulk] - \sum_i n_i\mu_i + q(E_{\mathrm{VBM}} + E_F) + E_{corr}, \tag{1}$$

where $E(q, \mathbf{R}_{q'})$ is the total energy of a system in charge state q and atomic positions $\mathbf{R}_{q'}$, and E[$bulk$] is the total energy for the perfect crystal using an equivalent supercell [28, 27]. The integer n_i indicates the number of atoms of type i that have been added or removed from the supercell, and μ_i are the corresponding chemical potentials of these species. E_F is Fermi energy referenced to the valence band maximum E_{VBM} in the perfect supercell, corrected by aligning the core potential of atoms far from the defect with that in the nondefective bulk supercell, and E_{corr} is a correction term that accounts for the electrostatic interactions between supercells. The scheme proposed by Lany and Zunger [29] was applied to calculate charge corrections.

The chemical potential μ_i for ith atom species can be written as

$$\mu_i = \mu_i^{bulk} + \Delta\mu_i, \tag{2}$$

where μ_i^{bulk} is the chemical potential of species i in solids, and $\Delta\mu_i$ is a relative chemical potential referenced to μ_i^{bulk}. In the case of CdTe, if the system is under thermal equilibrium and there is no Te or Cd precipitation, we have

$$\Delta\mu_{\mathrm{Cd}} + \Delta\mu_{\mathrm{Te}} = \Delta H_f[\mathrm{CdTe}], \tag{3}$$

$$\Delta H_f[\mathrm{CdTe}] < \Delta\mu_{\mathrm{Te}} < 0, \tag{4}$$

$$\Delta H_f[\mathrm{CdTe}] < \Delta\mu_{\mathrm{Cd}} < 0, \tag{5}$$

where ΔH_f[CdTe] is the formation energy of CdTe. ΔH_f[CdTe] is calculated to be -0.90 eV, in good agreement with the experimental value of -0.96 eV.

Most of CdTe crystals are grown by techniques which suppresses the loss of Cd during growth, resulting in a Te-rich material with high concentration of Cd vacancies (V_{Cd}) and Te anti-sites (Te_{Cd}). Experimental measurements show that residual oxygen has a concentration typically orders of magnitudes higher than other residual impurities and comparable to intrinsic defects [30]. In order to put reasonable limits on the chemical potentials of Sn defects, we consider restrictions that prevent the formation of phases with the host atoms and the precipitation of the bulk phases of Tin. The relative chemical potential $\Delta\mu_{Sn}$ is restricted by

$$\Delta\mu_{Sn} + 2\Delta\mu_O \leq \Delta H_f[SnO_2] \tag{6}$$

The formation energy of SnO_2 is calculated to be -6.01 eV with PBE functional, in excellent agreement with the experimental value of -5.99 eV. In order to obtain the relative chemical potential $\Delta\mu_O$, we consider CdTe to be in thermodynamic equilibrium with $CdTeO_3$ in the Te-rich limit [31, 32]. We find $\Delta\mu_O = -1.88$ eV. From eq. (6) we get $\Delta\mu_{Sn} \leq -2.25$ eV.

2.3. DFT + GW formalism

One shortcoming of the density functional theory is its failure to produce accurate excited states. Among other things, it gives rise to the well-known underestimation of the quasiparticle gap [33, 34] which render difficult the accurate description of midgap charged defect states [29, 19]. PBE severely underestimates the ionization potentials (IPs) for most semiconductors, while the commonly used hydrid functional of Heyd, Scuseria, and Ernzerhof (HSE) [35] good produces band gaps of small-gap materials, but tends to underestimate both IPs and electron affinities (EAs) [36], and fails in producing accurate binding energies of d-states in II-VI semiconductors [37].

The thermodynamic transition level $\epsilon(q/q+1)$ from charge state q to charge state $q+1$ is the IP of the system in the state q, i.e,

$$\epsilon(q/q+1) = E(q, \mathbf{R}_q) - E(q+1, \mathbf{R}_{q+1}) - E_{VBM} \tag{7}$$

By adding and subtracting $E(q+1, \mathbf{R}_q)$, equation (1) can be rewritten as

$$\epsilon(q/q+1) = [E(q+1, \mathbf{R}_q) - E(q+1, \mathbf{R}_{q+1})] + [E(q, \mathbf{R}_q) - E(q+1, \mathbf{R}_q)] - E_{VBM} \tag{8}$$

The first term corresponds to the relaxation energy $E(q+1, \mathbf{R}_q) - E(q+1, \mathbf{R}_{q+1})$ and can be calculated at the DFT level (the problem of the discontinuity in the chemical potential does not arise as the electron number remains constant). The second term, $E(q, \mathbf{R}_q) - E(q+1, \mathbf{R}_q)$, which defines the vertical excitation, is not well described within density functional theory, but a correction can be calculated using the ab initio GW method.

Our calculations are made within the DFT+GW formalism developed in Refs. [18, 19]. However, due to the high computational cost of performing GW calculations on charged supercells large enough to avoid spurious interactions between neighboring cells, we approximated the valence-band and conduction-band offsets by those of the bulk CdTe.

3. Results and discussion

3.1. Formation energies of Cd vacancy and Sn impurities in CdTe

The dominant intrinsic defect is believed to be Cd vacancy. It behaves as a dominant doubly charged acceptor and is responsible for the p-type conductivity and low resistivity of undoped CdTe [38, 39]. Hence, we also include (V_{Cd}) in the present study.

Sn substituted on both the Cd and Te sublattices, and the possibility of occupying an interstitial site were considered. Figure 1 shows the defect formation energies of Sn impurities and Cd vacancy as a function of E_F under Te-rich growth conditions. Our results show that Sn atoms should reside on Cd sites, in agreement with previous theoretical studies [40, 41].

For samples of undoped CdTe, the Fermi energy is pinned near the middle of the band gap and (V_{Cd}) will be in the double negatively charge state. In order to preserve the crystal electroneutrality, (Sn_{Cd}) should tend to bind with (V_{Cd}) forming (Sn_{Cd}−V_{Cd}) complexes.

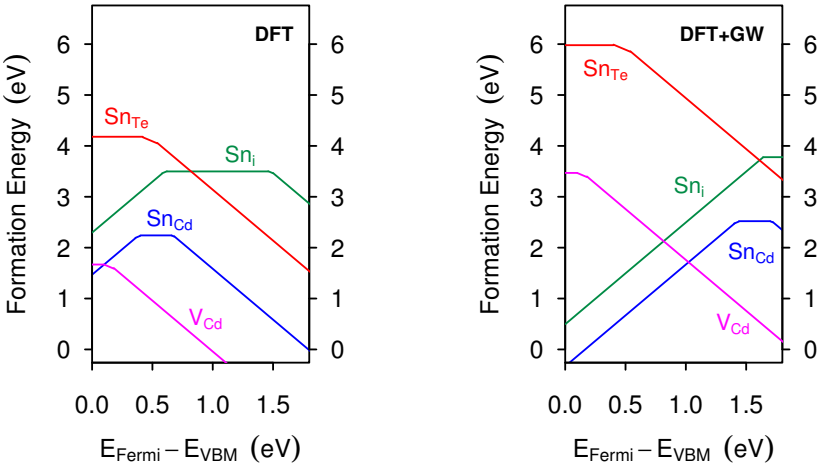

Figure 1. Formation energies of Cadmium vacancy and Sn impurities in various charge states under Te-rich conditions as a function of the Fermi level inside the band gap in CdTe. The slope of an energy line indicates the charge state of the defect. (Left) Formation energies calculated at DFT-PBE level. (Right) Formation energies calculated within the DFT+GW formalism.

3.2. Formation of an isolated intermediate-band in CdTe:Sn

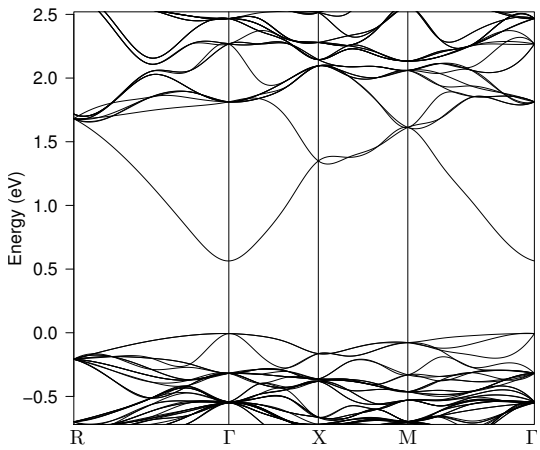

Figure 2. Kohn-Sham band structure of CdTe calculated using a 216 atom supercell. The VBM is set to be zero.

Figure 2 shows the theoretical band structure of perfect CdTe calculated using a 216-atom supercell. As shown in Figure 3, in both CdTe:$(Sn_{Cd})^{+2}$ and CdTe:(Sn_{Cd}−V_{Cd}) an isolated

intermediate-band is formed in the middle of the forbidden band gap. The impurity band, derived mainly from Sn 5*s* states, is unoccupied. The IB scheme requires that the IB must be partially filled in order to allow three direct bandgap transitions (VBM→IB, IB→CBM, VBM→CBM). However, the filling of the IB vary with light intensity, cell voltage, density of IB-states, concentration of native defects, and its position in the forbidden band gap. Strandberg and Reenaas [42] have shown that partial filling can be achieved by optical pumping or photofilling when the cell is exposed to concentrated light. A photofilled IBSC can give efficiencies comparable to those of a prefilled IBSC.

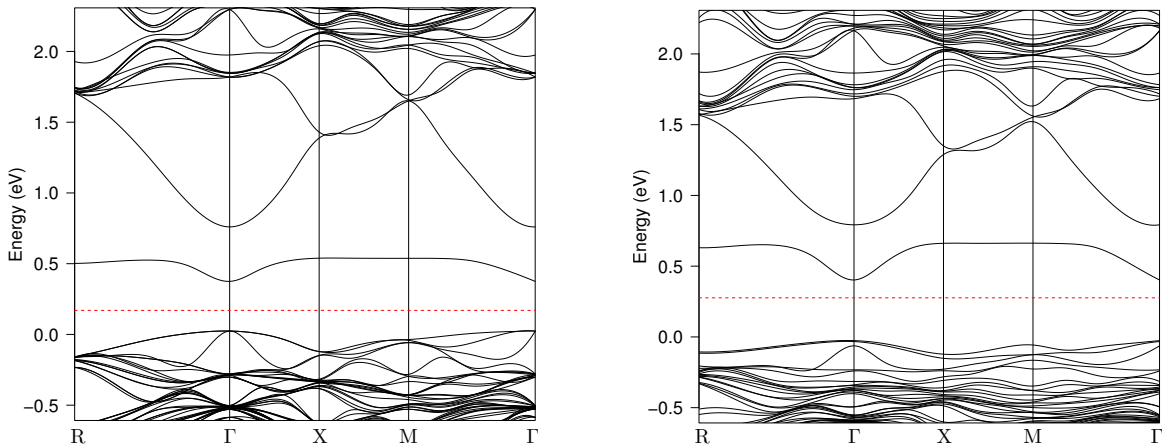

Figure 3. (Left) Konh-Sham band-structure of CdTe:$(Sn_{Cd})^{+2}$. (Right) Band-structure of CdTe:$(Sn_{Cd}-V_{Cd})$ in the neutral charge state. The dotted red line indicates the position of the average electrochemical potential. The VBM is set to be zero.

According to Shockley-Read-Hall theory [43, 44], impurity states closer to the midgap are harmful as non-radiative recombination centers. The transition of a delocalized CB electron to a localized impurity state causes the impurity level to cross the CB (taking into account lattice vibrations). The energy of the electron is therefore transformed into potential energy of the impurity in a single step [2, 45]. Fortunately, the non-radiative recombination can be prevented through charge redistribution [46] or if the density of impurities are highly enough to exceed the Mott transition [47].

4. Conclusions

In summary, we have studied the defect formation energies, charge transition levels, and band-structures of Sn doped CdTe combining density-functional theory and many body GW calculations. An isolated impurity band derived mainly from Sn 5s states is formed in the middle forbidden band gap of bulk CdTe, allowing three direct bandgap transitions (VBM→IB, IB→CBM, VBM→CBM). Our results suggest that CdTe:Sn could be a promising candidate for the development of third-generation high-efficiency intermediate-band solar cells.

Acknowledgments

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