Hybrid Functional Calculations for Antimony Doping in CdTe

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***Abstract*—CdTe-based solar cells are leading thin-film photovoltaic technology, with efficiencies over 22%, but still much lower than the theoretical maximum of 29%. Further improvements will rely on increasing the open-circuit voltage Voc, which, in turn, depends on carrier density and lifetime. Using hybrid density functional calculations, we investigate Sb doping of CdTe, focusing on its limitation as shallow acceptor and the formation of compensating AX center. Paying special attention to supercell size and effects of spin-orbit coupling, we predict an ionization energy of 116 meV in the dilute limit, much closer to recent experimental value of 103 meV from temperature-dependent Hall measurements in bulk single crystals, and in contrast to much larger values from previous calculations. We also find that the Sb-related AX centers are not major compensation centers in Sb-doped CdTe.**

***Index Terms*—CdTe, group-V acceptor, defects, *p*-type**

I. Introduction

Among thin-film photovoltaic technologies, cadmium telluride (CdTe) is the leading technology that is commercially available. Several factors, such as low cost, rapid industrial production, long lifetime, high absorption coefficient, and a direct band gap of 1.5 eV, have driven the research on CdTe, placing CdTe-based PV modules in direct competition to crystalline silicon (c-Si) modules [1]. A record efficiency of CdTe cells of 22.1% has been recently reported by First Solar [2]. However this efficiency is still far below the theoretical limit of $\sim$29%, mainly attributed to the low open-circuit voltage Voc which can be improved by increasing the hole concentration. From device modeling, increasing the hole concentration in the CdTe absorber from current typical values of 10^{14} to 10^{16} cm^{-3} would lead to efficiencies reaching 25% [3].

One common way to obtain high hole concentrations in semiconductors is adding impurities that act as shallow acceptors; among the most promising p-type dopants in CdTe, Sb stands out for the similar atomic radii as Te (1.45 vs 1.40 Å) and similar atomic electronic structures – they sit next to each other on the periodic table, with Sb on the left of Te) [4], [5]. Thus, introducing Sb on the Te sites is expected to minimize the strain energy associated with the acceptor impurity and to lead to a shallow acceptor level such that at room temperature (or operating device temperatures) a large fraction of the impurities are ionized, efficiently leaving holes in the valence. However, early theoretical studies indicated a rather high ionization energy of 230 meV for Sb substituting on the Te site [6]; more recent hybrid density functional calculations give 150 meV [8]; but also indicates likely formation of AX compensation center, resulting in low doping efficiency and, thus, low hole concentrations [7], [8]. A recent analysis of temperature-dependent Hall measurements on CdTe single crystals doped with Sb indicates a much lower ionization energy of 103 meV [5], enabling hole concentration of $\sim 10^{16}$ cm^{-3}. This result indicates some compensation, but not as severe as that predicted by recent calculations [8]. To understand this apparent contradiction between theory and experiment, we revisit the properties of the Sb impurity in CdTe using hybrid density functional theory, paying special attention to the effects of spin-orbit coupling and the finite size of the supercell for dealing with shallow acceptors.

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II. Method of calculations

Our calculations are based on density functional theory (DFT) and the projected augmented wave (PAW) method [9], as implemented in the Vienna ab initio simulation package (VASP) [10]. Since DFT within the standard approximations LDA and GGA severely underestimate band gaps, we use the Heyd-Scuseria-Ernzerhof (HSE) hybrid functional to correct the band gap [11]. To accurately describe not only the band gap but the ionization potential (position of the valence band with respect to vacuum level), we use a Hartree-Fock exchange mixing parameter of 33% and include the spin orbit coupling (SOC). An energy cut off of 254 eV is used for the plane-wave basis set. The calculated band gap of 1.502 eV and equilibrium lattice parameter of 6.545 Å are in good agreement with the experimental data [12], [13]. The SOC lifts the valence-band maximum (VBM) by 0.307 eV, with a spitting $\Delta_{\rm SOC}$ of 0.940 eV. The calculated ionization potential of 5.4 eV is closer to the experimental value than standard DFT [14].

For the calculations of the Sb impurity, supercells of 64 atoms, 216 atoms and 512 atoms are used. The formation energy of a defect X ($\rm Sb_{Te}$ in this case) in charge state q in CdTe is given by:

$$E^f(X^q) = E_{tot}(X^q) - E_{tot}(\text{bulk}) + \sum_i n_i\mu_i + q(\varepsilon_F + E_{VBM}), \quad (1)$$

where $E_{tot}(X^q)$ is the total energy of the supercell containing the defect in charge state q, $E_{tot}(\text{bulk})$ is the total energy of the supercell representing the perfect bulk material, μ_i is a chemical potential of atom i referenced to the total energy of the reservoir for the atom i. n_i is a number of atoms i that

are removed ($n_i > 0$) or added ($n_i < 0$) to the supercell to form the defect. The Fermi level ε_f is referenced to VBM. The Fermi level position at which the formation energy of a defect in a charge state q equals to the formation of the same defect in a charge state q' defines the transition level (q/q') which is given by:

$$(q/q') = \frac{E^f(X^q; \varepsilon_F = 0) - E^f(X^{q'}; \varepsilon_F = 0)}{q' - q}, \qquad (2)$$

where $E^f(X^q; \varepsilon_F = 0)$ is the formation energy of X^q taken from Fermi level at 0 eV. The transition level $(0/-)$ for the acceptor Sb_{Te} is the acceptor level or the acceptor ionization energy (E_a).

III. Results and Discussion

Sb has one less electron than Te, so when it substitutes on the Te site in CdTe, it acts as an acceptor. Our calculations show that for the substitutional Sb_{Te}, we have a low-lying a_1 state buried in the valence band (well below the VBM) and three-fold degenerate t_2 state near the VBM. In the neutral charge state Sb^0_{Te}, there is one hole t_2 state, which would in principle leads to a Jahn-Teller distortion. We find, however, that this effect is quite small, which we attribute to the delocalization of the hole wavefunction. In the negative charge state Sb^-_{Te}, the t_2 state is completely filled. Due to the delocalization of the acceptor state and the interaction of the negatively charged impurity with its periodic image due to the 3D periodic boundary conditions, we expect a slow convergence of the acceptor transition level, $(0/-)$, with the supercell size, leading to an artificially large ionization energy in the finite supercell calculations.

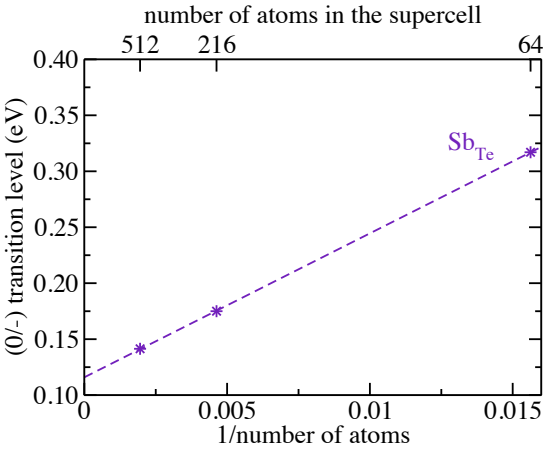

Fig. 1. Calculated $(0/-)$ acceptor transition level of Sb_{Te} in CdTe using 64-, 216-, and 512-atoms supercells as function of the inverse of the number of atoms in the supercell.

To remove the artificial interaction, we extrapolate the calculated $(0/-)$ transition level to the dilute limit. The extrapolation of the transition level as a function of 1/L (where L is the linear dimension of the supercell) or 1/number of atoms→0 is expected to give the transition level in the dilute limit regime, where the charged impurity does not interact with its periodic image. The results for Sb_{Te} using 64-, 216-, and 512-atoms supercells are shown in Fig. 1. As expected, larger supercell cell sizes lead to lower acceptor ionization energies. The extrapolation to the dilute limit gives an ionization energy of 116 meV, close to the experimental value of 103 meV obtained from temperature-dependent Hall measurements in high-quality Sb-doped CdTe bulk single crystals.

We also investigated the formation of Sb-related AX center in CdTe. By removing an electron from the charge neutral Sb^0_{Te}, leaving two hole in the t_2 state, the Sb atom undergoes a large displacement along the [110] direction, and forms a bond with a neighboring Te atom, breaking their original bonds with one of the Cd atoms. This large local lattice relaxation, that can be attributed to a Jahn-Teller distortion, splits the t_2 state into a lower energy twofold degenerate e state (occupied by four electrons) below the VBM, and an empty a_1 state (two holes) at a much higher energy, resonant in the conduction band. The resulting defect is, therefore, stable in the positive charge state, resulting in self-compensation, i.e., an acceptor center that upon ionization becomes a donor center often called an AX center [17]. The charge state associated with the AX center is quite localized around the defect and completely contained in the supercell, even for the 64-atoms supercell.

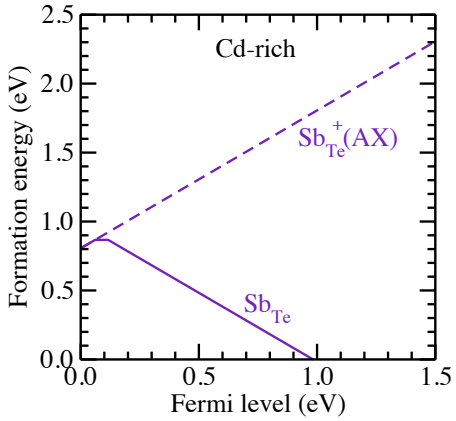

Fig. 2. Formation energies of Sb in CdTe, including the neutral (b^0_{Te}, negatively charged Sb^-_{Te}, and the donor AX center $Sb^+_{Te}(AX)$.

The calculated formation energy of Sb^0_{Te}, Sb^-_{Te}, and $Sb^+_{Te}(AX)$ are shown in Fig. 2. The results show that the AX center (dashed line) is only stable when the Fermi level is very close to the VBM, i.e., within 70 meV. This finding suggests that the AX centers are unlikely to limit hole concentration in CdTe, contrary to previous DFT and hybrid DFT calculations [7], [8]. We attribute the difference between our results and the results of previous calculations to the SOC, that raises the VBM and, consequently, places the $(+/0)$ transition level at lower energies relative to the VBM.

For comparison with experiments, we plot the calculated hole concentration as a function of temperature in Fig. 3. Taking the calculated ionization energy E_a=116 meV, and

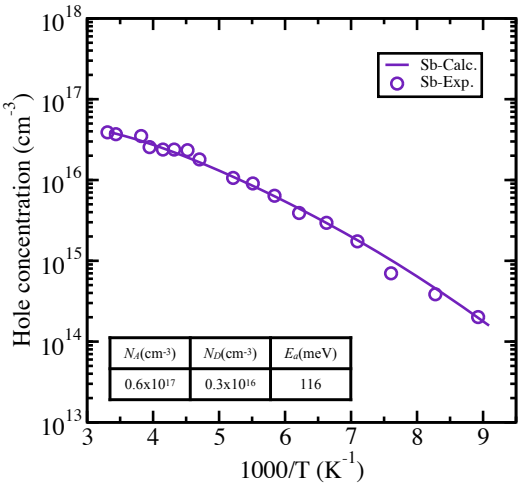

Fig. 3. Calculated hole concentration for a total Sb concentration of 6x10^{16} cm^{-3} and assuming 5% compensating donors (unknown origin), compared to temperature-dependent Hall data from [5].

assuming a total Sb concentration (N_A) of 6x10^{16} and a 5% donor concentration (N_D) as compensation centers give good agreement with temperature-dependent Hall transport measurements. We note that increasing Sb concentration by 5% would overestimate the hole concentration at high temperatures, and increasing the concentration of compensating donors by 5% would severe the agreement at low temperatures, decreasing the hole concentration. We also note that increasing the ionization energy E_a by 50 meV would significantly lower the hole concentration in the whole temperature range, and could not explain the experiment data.

Regarding the origin of the compensating centers, we first argue that the formation of AX center seems not to be a problem in the case of Sb-doped CdTe. From previous calculations that include effects of SOC [18], we would conclude that Cd interstitial (Cd$_i$) and Te vacancies (V_{Te}) are the most likely defects that could act as compensation centers. However, considering the rather low migration barrier of Cd$_i$ of 0.52 eV [19], we expect these defects to be highly mobile and, therefore, not stable. We then speculate that (V_{Te}) would be the most likely compensating defects in p-type CdTe.

IV. Summary

Understanding the behavior of the Sb doping is important for designing CdTe solar cells with higher doping efficiencies. In this work, we employ hybrid density functional calculations with the inclusion of spin-orbit coupling to investigate formation energies and ionization energies of the Sb acceptor in CdTe, and explore the stability of the related AX center. The calculated ionization energy of 116 meV in the dilute limit is in good agreement with the experiment data. Furthermore, our calculations indicate that the formation of AX centers is not a problem for Sb-doped CdTe, and that other native point defects are likely acting as compensation centers. By using the calculated ionization energies, and assuming a dopant concentration and a relatively low donor compensation, we can accurately predict the hole concentration seen in recent experiments.

Acknowledgments

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