

**First-principles study of back-contact effects on CdTe thin-film solar cells**

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Forming a chemically stable low-resistance back contact for CdTe thin-film solar cells is critically important to the cell performance. This paper reports theoretical study of the effects of the back-contact material,  $\text{Sb}_2\text{Te}_3$ , on the performance of the CdTe solar cells. First-principles calculations show that Sb impurities in  $p$ -type CdTe are donors and can diffuse with low diffusion barrier. These properties are clearly detrimental to the solar-cell performance. The Sb segregation into the grain boundaries may be required to explain the good efficiencies for the CdTe solar cells with  $\text{Sb}_2\text{Te}_3$  back contacts.

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**I. INTRODUCTION**

CdTe is an important thin-film solar-cell material. It has a direct band gap of 1.5 eV, near the optimum for conversion efficiency in a single-junction solar cell under terrestrial irradiation. Its high light absorption coefficient allows efficient solar energy absorption within a thin film, reducing material cost of the solar cells. These basic material properties of CdTe are excellent for thin-film photovoltaic applications but many other factors also contribute to the overall solar-cell performance. The back-contact materials affect both efficiency and lifetime of the CdTe solar cells because the contact resistance reduces the carrier collection and the impurity diffusion from the back contact to the CdTe layer causes cell degradation.<sup>1</sup> Therefore, forming a chemically stable low-resistance back contact is extremely important to the CdTe solar-cell performance.

The CdTe-based solar cells are heterojunction cells with polycrystalline  $n$ -type CdS and  $p$ -type CdTe thin films. Due to the high work function of the  $p$ -type CdTe (5.7 eV), it is difficult to find a good metal with higher work function to form an ohmic contact with CdTe. The currently highest efficiency (16.5%) CdTe solar cells have Cu-containing compounds (such as  $\text{Cu}_2\text{Te}$ ) as the back contact<sup>2,3</sup> because Cu reduces contact resistance. However, Cu can diffuse into CdTe and CdS films, and thus play additional roles, such as accumulating in the grain boundaries (GBs) and the junction region,<sup>4,5</sup> which may create conductive channels that shunt the solar cell. It has long been suspected that the degradation of the CdTe solar cells is related to the Cu diffusion.<sup>4</sup> The instability of the Cu contact prompted the research on the alternative back-contact materials. Recent studies show that using a  $\text{Sb}_2\text{Te}_3$  back contact without Cu results in an ohmic contact and enhanced solar-cell stability but slightly lower initial cell efficiency (15.8%) compared to those with Cu back contacts (16.5%).<sup>6,7</sup> However, there are also reports that show the existence of contact barrier<sup>8</sup> and significant Sb diffusion into the CdTe layer (especially in the presence of oxygen) (Ref. 9) when the  $\text{Sb}_2\text{Te}_3$  contact is used.

The Sb impurity had been studied as an acceptor in CdTe by first-principles calculations,<sup>10</sup> and it was thought that the Sb diffusion into CdTe should enhance  $p$ -type conductivity.<sup>1</sup> In this paper, we report detailed studies of Sb impurity properties, including energetics and diffusion, in CdTe. We show

that Sb is a donor in  $p$ -type CdTe and can diffuse into the CdTe layer. It appears that the assumption that most of the Sb impurities should segregate into the GBs needs to be invoked to explain the good solar-cell performance with  $\text{Sb}_2\text{Te}_3$  back contacts.

**II. METHODS**

We performed density-functional calculations to study the Sb-related defects in CdTe. The hybrid functionals were used to calculate defect formation energies<sup>11</sup> while the defect diffusion barriers were calculated using local-density approximation. The exchange-correlation energy functional used in our hybrid-functional calculations is similar to PBE0 functional<sup>12</sup> [which has 25% Hartree-Fock (HF) exchange] except that the fraction of the HF exchange energy in the total exchange energy is adjusted to 16.5%, which results in the calculated CdTe band gap of 1.55 eV, close to the experimental value of 1.61 eV.<sup>13</sup> The hybrid-functional calculations which include a fraction of nonlocal HF exchange energy partially correct the electron self-interaction error in the local exchange energy approximations and offer improved band gaps in semiconductors.<sup>14</sup> The electron-ion interactions are described using projector augmented wave potentials.<sup>15</sup> The valence wave functions were expanded in a plane-wave basis with a cutoff energy of 274 eV. All the calculations were performed using 64-atom cubic cells. A  $2 \times 2 \times 2$  grid was used for the  $k$ -point sampling of Brillouin zone. All the atoms were relaxed to minimize the Feynman-Hellmann forces to below 0.02 eV/Å. The CdTe lattice constant calculated using the hybrid functional is 6.59 Å, in good agreement with the experimental values of 6.477 Å.<sup>16</sup>

The defect formation energy is given by

$$\Delta H_f = \Delta E - \sum_i n_i (\mu_i + \mu_i^{ref}) + q(\epsilon_{\text{VBM}} + \epsilon_f), \quad (1)$$

where  $\Delta E$  is the energy difference between the defect-containing and defect-free supercells, and  $n_i$  is the difference in the number of atoms for the  $i$ th atomic species between the defect-containing and defect-free supercells.  $\mu_i$  is a relative chemical potential for the  $i$ th atomic species, referenced to  $\mu_i^{ref}$ . For Cd and Te,  $\mu_{\text{Cd}}^{ref}$  and  $\mu_{\text{Te}}^{ref}$  are the chemical potentials in bulk Cd and bulk Te, respectively.  $q$  in Eq. (1) is the defect charge state.  $\epsilon_f$  is the Fermi energy referenced to the

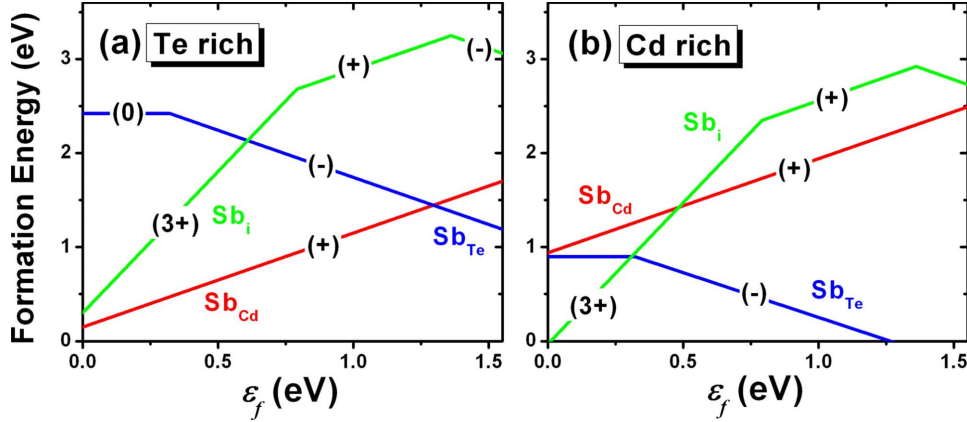


FIG. 1. (Color online) Calculated formation energies for substitutional  $\text{Sb}_{\text{Cd}}$  and  $\text{Sb}_{\text{Te}}$  and interstitial  $\text{Sb}_i$  in CdTe as a function of electron Fermi energy at both Te-rich and Te-poor limits. Sb-rich limit is considered in these calculations (see text in Sec. II). Less Sb-rich conditions will result in higher formation energies than those shown in this figure. The slope of an energy line indicates the charge state of the defect, as shown in the figure. The transition levels are given by the Fermi energy at which the slope changes.

valence-band maximum (VBM),  $\varepsilon_{\text{VBM}}$ , which is taken as bulk VBM corrected by aligning the core potential of atoms (averaged within a sphere centered at the atom) far away from the defect in the defect-containing supercell with that in the defect-free supercell. The defect transition energy level,  $\varepsilon(q/q')$ , is the Fermi level,  $\varepsilon_f$  in Eq. (1), at which the formation energies of the defect at the charge states  $q$  and  $q'$  are equal to each other.

If the system is under thermal equilibrium and there is no Te or Cd precipitation, we have  $\mu_{\text{Cd}} + \mu_{\text{Te}} = \Delta H_f(\text{CdTe})$  and  $\Delta H_f(\text{CdTe}) < \mu_{\text{Te}} < 0$ , where  $\Delta H_f(\text{CdTe})$  is the enthalpy of formation for bulk CdTe. The calculated  $\Delta H_f(\text{CdTe})$  is  $-1.12$  eV, in reasonable agreement with the experimental value of  $-0.96$  eV.<sup>16</sup> For Sb impurities in CdTe, we set  $\mu_{\text{Sb}}^{\text{ref}}$  to the chemical potential of bulk Sb and impose the conditions of  $\mu_{\text{Sb}} < 0$  and  $2\mu_{\text{Sb}} + 3\mu_{\text{Te}} < \Delta H_f(\text{Sb}_2\text{Te}_3)$ , where  $\Delta H_f(\text{Sb}_2\text{Te}_3)$  is the enthalpy of formation for bulk  $\text{Sb}_2\text{Te}_3$ .  $\Delta H_f(\text{Sb}_2\text{Te}_3)$  is calculated to be  $-0.65$  eV, in good agreement with the experimental value of  $-0.585$  eV.<sup>9</sup> When calculating the formation energies of Sb impurity defects, we use the maximum value of  $\mu_{\text{Sb}}$ , i.e., the smaller of  $[\Delta H_f(\text{Sb}_2\text{Te}_3) - 3\mu_{\text{Te}}]/2$  and 0. Thus, at the Te-rich limit ( $\mu_{\text{Te}} = 0$ ),  $\mu_{\text{Sb}} = \Delta H_f(\text{Sb}_2\text{Te}_3)/2$ , and at the Te-poor limit [ $\mu_{\text{Te}} = \Delta H_f(\text{Sb}_2\text{Te}_3)$ ],  $\mu_{\text{Sb}} = 0$ .

### III. RESULTS

Sb is an acceptor in CdTe when it substitutes a Te atom ( $\text{Sb}_{\text{Te}}$ ). The calculated  $(0/-)$  transition level of  $\text{Sb}_{\text{Te}}$  is  $E_v + 0.32$  eV. Sb can also occupy the Cd site as  $\text{Sb}_{\text{Cd}}$ . The  $T_d$  symmetry of the defect determines that the defect states should consist of a low-lying singlet  $a_1$  state and a high-lying threefold degenerate  $t_2$  state. Our calculations show that the  $a_1$  state lies below the VBM and the  $t_2$  state lies above the conduction-band maximum (CBM). Thus,  $\text{Sb}_{\text{Cd}}$  prefers the  $+1$  charge state because the two additional electrons at  $\text{Sb}_{\text{Cd}}^+$  relative to a native Cd atom fills exactly the  $a_1$  level whereas the  $t_2$  level ( $\sim 0.8$  eV above the CBM) cannot be charged. Displacing the  $\text{Sb}_{\text{Cd}}$  atom along the  $[111]$  lattice direction

will reduce the defect symmetry from  $T_d$  to  $C_{3v}$  and split the  $t_2$  level to a lower-lying  $a_1$  level and a higher-lying  $e$  level. If the split-off  $a_1$  level can descend below the CBM, it may trap one or two electrons to stabilize  $\text{Sb}_{\text{Cd}}^0$  or  $\text{Sb}_{\text{Cd}}^-$ . However, such Jahn-Teller distortion is not stable according to our calculations. Thus,  $\text{Sb}_{\text{Cd}}$  is a donor ( $\text{Sb}_{\text{Cd}}^+$ ) for all the attainable Fermi levels within the band gap.

Sb can also occupy the interstitial site, surrounded by four Cd ( $\text{Sb}_{i,\text{Cd}}$ ) or four Te atoms ( $\text{Sb}_{i,\text{Te}}$ ) forming a tetrahedron. The defect states that host the Sb valence electrons consist of a low-lying  $a_1$  state and a high-lying  $t_2$  state as determined by the  $T_d$  defect symmetry. We find that the  $a_1$  state lies below the VBM and the  $t_2$  state lies above the CBM for both  $\text{Sb}_{i,\text{Cd}}^{3+}$  and  $\text{Sb}_{i,\text{Te}}^{3+}$  with the former being more stable than the latter by 0.07 eV. As a result, only the  $a_1$  state can host two of the five valence electrons of Sb, stabilizing  $\text{Sb}_i^{3+}$ . More electrons can be bound at  $\text{Sb}_i$  if  $\text{Sb}_i$  is displaced from the center of the tetrahedral interstitial site. The stable  $\text{Sb}_i^+$  and  $\text{Sb}_i^-$  structures are found in the calculations. These two structures can be viewed as Cd-Sb and Te-Sb split interstitials, respectively.

Figure 1 shows the formation energies of  $\text{Sb}_{\text{Cd}}$ ,  $\text{Sb}_{\text{Te}}$ , and  $\text{Sb}_i$ . Both Te-rich and Cd-rich limits are considered. Note that the experimental conditions for CdTe growth are typically Te rich. Furthermore, the CdTe surface etching, which produces a Te-rich surface, is usually performed before the deposition of the back-contact materials.<sup>1,3</sup> Figure 1 shows that, in  $p$ -type CdTe under the typical Te-rich conditions, the Sb impurity is stable as a donor on the Cd site ( $\text{Sb}_{\text{Cd}}^+$ ).  $\text{Sb}_{\text{Te}}^-$  is stable only when the Fermi level is high. Sb interstitial ( $\text{Sb}_i$ ) has generally higher energy than substitutional Sb in CdTe at the Te-rich limit.

We have also calculated the diffusion barrier of  $\text{Sb}_{\text{Cd}}^+$ , which is only 0.55 eV. In comparison, the calculated diffusion barriers for Cd vacancy ( $V_{\text{Cd}}^{2-}$ ), substitutional Cu ( $\text{Cu}_{\text{Cd}}^-$ ), and  $\text{Sb}_i^{3+}$  are 1.08, 1.23, and 1.03 eV, respectively. Cu is considered here because it is the commonly used back-contact material for CdTe solar cells. The diffusion of  $\text{Sb}_{\text{Cd}}^+$  and  $\text{Cu}_{\text{Cd}}^-$  are assumed to be assisted by Cd vacancies, which are abundant in  $p$ -type CdTe. Thus, the diffusion paths of

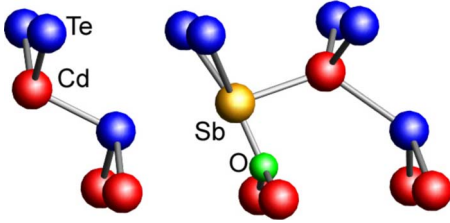


FIG. 2. (Color online) Structure of the  $(\text{Sb}_{\text{Cd}}\text{-O}_{\text{Te}})^{-}$  complex.

$\text{Sb}_{\text{Cd}}^{+}$ ,  $\text{V}_{\text{Cd}}^{2-}$  and  $\text{Cu}_{\text{Cd}}^{-}$  are similar, involving the swing of a Sb, Cd, or Cu atom from one Cd vacancy to another one nearby. The Sb, Cd, and Cu ions in these defects have the oxidation states of +3, +2, and +1, respectively. It appears that higher oxidation state of the diffusing ion has lower diffusion barrier. This may be explained by the fact that the interstitial site at the midpoint of the swing path is closest to the four negatively charged Te ions on the [001] plane, which have Coulomb attraction to the positively charged diffusing ions. Our calculations show that the midpoint of the swing path for the Sb ion even corresponds to a dip in the potential landscape for a diffusing Sb ion. This is in contrast to the Cd and Cu ions, for which the midpoint of the swing paths correspond to the peaks of the barriers. The above calculated defect diffusion barriers show that the diffusions of  $\text{Sb}_{\text{Cd}}^{+}$  and  $\text{Sb}_i^{3+}$  are easier than that of  $\text{Cu}_{\text{Cd}}^{-}$  in bulk CdTe, and that the Cd-vacancy-assisted diffusion of  $\text{Sb}_{\text{Cd}}^{+}$  is limited by the  $\text{V}_{\text{Cd}}^{2-}$  diffusion since the diffusion barrier of  $\text{V}_{\text{Cd}}^{2-}$  is higher than that of  $\text{Sb}_{\text{Cd}}^{+}$ .

Oxygen is usually present during the CdTe thin-film growth and the postgrowth annealing.<sup>3</sup> Thus, we have also considered the Sb-O impurity complex. We find that  $\text{Sb}_{\text{Cd}}^{+}$  can bind the substitutional O ( $\text{O}_{\text{Te}}$ ) with a binding energy of 0.5 eV. At  $-1$  charge state, the  $(\text{Sb}_{\text{Cd}}\text{-O}_{\text{Te}})^{-1}$  complex undergoes a structural transformation that results in the formation of a Sb-Cd bond and the breaking of a Sb-Te and a Cd-O bond as shown in Fig. 2. The lone pair localized at the threefold coordinated Te atom in Fig. 2 induces a filled deep level at  $\sim 0.6$  eV above the VBM. At neutral charge state,  $(\text{Sb}_{\text{Cd}}\text{-O}_{\text{Te}})^0$  has a half-filled dangling bond on the threefold-coordinated Te atom. The calculated  $(+/-)$  and  $(+/-0)$  transition levels are  $E_v + 1.16$  eV and  $E_v + 1.41$  eV, respectively. The  $\text{Sb}_{\text{Cd}}\text{-O}_{\text{Te}}$  complex is a negative- $U$  center [due to the large structural relaxation of  $(\text{Sb}_{\text{Cd}}\text{-O}_{\text{Te}})^{-}$ ]. The structural transformations for  $(\text{Sb}_{\text{Cd}}\text{-O}_{\text{Te}})^{-}$  is essentially a DX transformation discussed previously in III-V and II-VI semiconductors.<sup>17,18</sup> These results suggest that the  $\text{Sb}_{\text{Cd}}\text{-O}_{\text{Te}}$  complex is a deep electron trap in CdTe. However, the electron trapping is not expected to be efficient because the required structural transformation should involve an energy barrier.

#### IV. DISCUSSION

$\text{Sb}_{\text{Cd}}^{+}$  is a lower-energy defect in  $p$ -type CdTe as shown in Fig. 1. Our calculations also show that the diffusion barrier of  $\text{Sb}_{\text{Cd}}^{+}$  is small, allowing Sb to diffuse into the CdTe thin film at the typical  $\text{Sb}_2\text{Te}_3$  back-contact deposition temperature of  $\sim 300$  °C. These results are consistent with the ex-

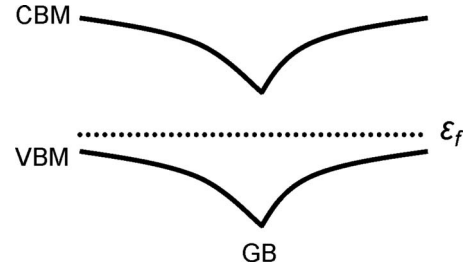


FIG. 3. Schematic of band bending at a grain boundary in  $p$ -type polycrystalline CdTe caused by donor impurity accumulation in the grain boundary.

perimental observation of the Sb concentration of  $\sim 10^{18}$   $\text{cm}^{-3}$  in as-grown CdTe thin films with  $\text{Sb}_2\text{Te}_3$  back contacts.<sup>9</sup> Our calculations show that Sb tends to bind with O, also consistent with the experimental finding that air annealing significantly promotes the influx of Sb associated with O to a depth of about 1  $\mu\text{m}$ .<sup>9</sup>

The results shown in Fig. 1(a) were calculated using the maximum  $\mu_{\text{Sb}}$  value at the Te-rich limit. Under these conditions, the formation energy of  $\text{Sb}_{\text{Cd}}^{+}$  is fairly low, even lower than that of  $\text{V}_{\text{Cd}}$  (Refs. 19 and 20) in the low Fermi level region. Thus, the  $\text{Sb}_{\text{Cd}}^{+}$  donors should be able to effectively compensate the  $\text{V}_{\text{Cd}}$  acceptors in  $p$ -type CdTe, which is clearly detrimental to the solar-cell performance. However, the good cell efficiency of 15.8% had been reported for the CdTe solar cells with  $\text{Sb}_2\text{Te}_3$  back contact.<sup>6,7</sup> We are also not aware of any experimental results that indicate the acceptor compensation by Sb donors in CdTe although secondary-ion-mass spectroscopy results clearly show large amount of Sb impurities in  $p$ -type polycrystalline CdTe layer.<sup>9</sup> It should be noted that most of the experimental characterizations of CdTe solar cells were performed on polycrystalline CdTe-based cells. In single-crystal CdTe, there are evidences of Bi-related donor defect centers which compensate acceptors and lead to semi-insulating CdTe.<sup>21-23</sup> Combining all these experimental and theoretical results, it appears that perhaps the majority of the Sb impurities in the polycrystalline CdTe thin films segregate into the GBs, which are known to be the impurity gettering centers. It is also likely that Sb segregates into the GBs together with O (possibly forming secondary phase such as  $\text{Sb}_2\text{O}_3$ ) as a result of the strong Sb-O bonding.

The accumulation of large amount of the positively charged donors in the GBs causes Coulomb repulsion to the incoming holes from the grain bulk, creating band bending at GBs, as illustrated in Fig. 3.<sup>24,25</sup> The resulted internal electrical field separates photogenerated electrons and holes and thus reduces their recombination. The Fermi level is higher in the GBs, possibly leading to semiconductor-type inversion if the donor concentration in the GBs is sufficiently large. The electron photocurrent is expected to increase in the GBs. As discussed in Sec. III, the electron trapping at  $\text{Sb}_{\text{Cd}}\text{-O}_{\text{Te}}$  is barrier limited and thus should not be efficient. However, the band bending at GBs also creates barriers for hole transport across the GBs.<sup>24,25</sup> Based on the above discussion, it appears that the donors in the grain bulk have both positive and negative effects on the solar-cell performance.<sup>24,25</sup> Although the net effect remains unclear, it has been suggested that the



band bending at GBs is the main reason for the better performance of polycrystalline CdTe than its single-crystal counterpart in the thin-film solar cells.<sup>24,25</sup> The overall effect of donor accumulation at GBs on the carrier separation and transport still needs further experimental studies. But it should be clear that removing  $\text{Sb}_{\text{Cd}}$  donors from the grain bulk of  $p$ -type CdTe thin film is certainly beneficial to the solar-cell performance. This is why we believe that Sb segregation into GBs should take place to explain the high efficiency (15.8%) of the CdTe solar cells with  $\text{Sb}_2\text{Te}_3$  back contacts.

Despite the possible gettering effect of the GBs, some Sb donor impurities may remain in the grain bulk and have the negative effects of reducing the hole concentration in the grain bulk and increasing the back-contact resistance. These problems may explain the lower initial efficiency of the CdTe solar cells with  $\text{Sb}_2\text{Te}_3$  back contacts compared to those with Cu contacts.

It is known that the CdTe solar cells with Cu back contacts have the problem of Cu diffusion deep into the CdTe/CdS/TCO (transparent conducting oxide) junction areas.<sup>4,5</sup> Our calculations show a even lower diffusion barrier for  $\text{Sb}_{\text{Cd}}^+$  than for  $\text{Cu}_{\text{Cd}}^-$ . However, the internal electrical field in the  $p$ - $n$  junction of the solar cell should repel the positively charged donors (such as  $\text{Sb}_{\text{Cd}}^+$ ) but attract the negatively

charged acceptors (such as  $\text{Cu}_{\text{Cd}}^-$ ). Thus,  $\text{Sb}_{\text{Cd}}^+$  may not diffuse into the CdTe/CdS junction area.

## V. SUMMARY

We report the theoretical study of the effects of  $\text{Sb}_2\text{Te}_3$  back contacts on the performance of the CdTe solar cells. We show by first-principles calculations that Sb can diffuse into the  $p$ -type CdTe thin film to form low-energy  $\text{Sb}_{\text{Cd}}^+$  donor defects.  $\text{Sb}_{\text{Cd}}^+$  can further bind with  $\text{O}_{\text{Te}}$  to form a  $\text{Sb}_{\text{Cd}}\text{-O}_{\text{Te}}$  complex. The Sb donor impurities in CdTe bulk should have the negative effects of reducing hole concentration and increasing back-contact resistance. However, such scenario is inconsistent with the high efficiency observed for the CdTe solar cells with  $\text{Sb}_2\text{Te}_3$  back contacts. Thus, we postulate that the majority of the Sb donor impurities may segregate into the GBs. The accumulation of donors at the GBs inside  $p$ -type CdTe should cause the band bending at the DBs, which has the benefit of separating photogenerated electrons and holes.

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