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Carrier compensation in semi-insulating CdTe: First-principles calculations

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Carrier compensation in semi-insulating CdTe has been attributed to the compensation of surplus shallow acceptors by deep donors, usually assumed to be Te antisites. However, our first-principles calculations show that intrinsic defects may not have a significant effect on the carrier compensation due either to lack of deep levels near midgap or to low defect concentration. We demonstrate that an extrinsic defect, O_{Te}-H complex, may play an important role in the carrier compensation in CdTe because of its amphoteric character and reasonably high concentration.

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I. INTRODUCTION

Semi-insulating CdTe and its alloy CdZnTe (CZT) used in room-temperature x- and γ-ray semiconductor detectors have found a wide range of applications in medical imaging, industrial process monitoring, and nuclear safeguard and national security.[1,2] Performance of the CdTe and CZT based detectors relies on the collection efficiency of free carriers generated by gamma ray energy deposition. High resistivity ($>10^9\ \Omega$ cm) is thus required to reduce the free-carrier noise in the device.[1,3] The dominant intrinsic defect in CdTe is believed to be Cd vacancy (which is an acceptor) because of the normally Te-rich growth environment related to the high Cd vapor pressure.[1,3,4] To compensate the excess holes, shallow donor impurities are often introduced into CdTe. However, an exact compensation of shallow donors and acceptors is practically impossible. It was then suggested that the semi-insulating behavior in CdTe is due to defects that induce deep donor levels close to the middle of the band gap,[5,6] as long as the deep donor concentration exceeds the difference of ionized shallow acceptor and shallow donor concentrations. The identity of this deep donor remains an open question but is usually assumed to be a Te antisite (Td_{Cd}).[6–8] The Cd interstitial (Cd_i) has also been suggested as a possibility.[9]

Clearly, the understanding of the carrier compensation mechanism in CdTe is an important step towards further improvement of the detector performance. Many experimental techniques have been used to study the gap levels in CdTe and their possible role in the carrier compensation.[1] Dozens of gap levels have been observed and their ionization energies have been measured.[1,3,10–13] However, the anticipated deep donor level, as required in the deep-donor mediated carrier compensation model,[6] has not been convincingly detected. A midgap level at $E_c - 0.75$ eV has been found in n-type CdTe by deep level transient spectroscopy (DLTS),[13] and was tentatively assigned to Td_{Cd}.[6] But thermoelectric effect spectroscopy (TEES) measurement on semi-insulating CdTe did not find any donor levels near the midgap.[12] Also, the origins of the observed gap levels are very difficult to identify due to a large number of different types of intrinsic defects, intentionally doped and residual impurities, and their complexes.[1,10,11]

There are several theoretical studies of the defects in CdTe based on first-principles calculations. It has been shown that the Cd vacancy is the dominant intrinsic acceptor,[14] consistent with experiments. But the result that the Cd interstitial is the dominant intrinsic donor at both Te-rich and Cd-rich limits[14] is inconsistent with observed Te precipitates under Te-rich growth conditions.[15] More recent calculations show acceptor levels rather than donor levels near the midgap.[12] There are also some earlier calculations on defects in CdTe.[16] However, the defect structures reported in these calculations appear to be not the fully relaxed ground-state structures.[17]

In this paper, we first examine the intrinsic defects in CdTe, based on first-principles calculations, for their possible role in the carrier compensation. We find that the Te_{Cd} induces a gap level that is too shallow to pin the Fermi level close to the midgap. The Cd_i and Te vacancy (V_{Te}) indeed induce midgap levels, but their equilibrium concentrations are low especially under Te-rich conditions. Therefore, these intrinsic defects may not be responsible for the high resistivity in CdTe. We show, instead, that an extrinsic defect, O_{Te}-H complex, is an excellent candidate for the carrier-compensating defect.

Oxygen is usually abundant ($\sim 10^{16}$ cm^{-3}) in CdTe grown by various Bridgman techniques[7,18] because of the strong Cd-O bond. [The heat of formation for CdO (−2.68 eV) is much lower than that of CdTe (−0.96 eV).[19]] Hydrogen also forms strong bonds with oxygen and can be incorporated into CdTe together with oxygen, similar to the hydrogen incorporation with nitrogen into nitrogen doped CdTe (Ref. 20) and GaAs.[21,22] It is well known that hydrogen is amphoteric in many semiconductors, and typically takes a charge state counteracting the prevailing conductivity. Our calculations indeed show that the O_{Te}-H complex induces a $(+/-)$ transition level near the midgap. Hence this level can compensate both electron and hole carriers.

II. METHOD

We performed calculations based on density functional theory within the local density approximation, as implemented in VASP.[23] The electron-ion interactions are described by projector augmented wave pseudopotentials.[24] The valence wavefunctions are expanded in a plane-wave basis with cutoff energy of 400 eV. All the calculations were preformed using 64-atom cubic cells. A $2\times2\times2$ 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 calculated CdTe lattice constant is 6.420 Å, in good agreement with the experimental values of 6.477 Å.[19]

The defect formation energy is given by

$$\Delta H_f = \Delta E - \sum_i n_i(\mu_i + \mu_i^{\text{ref}}) + q(\varepsilon_{\text{VBM}} + \varepsilon_f), \qquad (1)$$

where ΔE 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 ith atomic species between the defect-containing and defect-free supercells. μ_i is a relative chemical potential for the ith atomic species, referenced to μ_i^{ref}. For Cd and Te, $\mu_{\text{Cd}}^{\text{ref}}$ and $\mu_{\text{Te}}^{\text{ref}}$ are the chemical potentials in bulk Cd and bulk Te, respectively. q in Eq. (1) is the defect charge state. ε_f is the Fermi energy referenced to the valance band maximum (VBM), ε_{VBM}, which is taken as bulk VBM corrected by aligning the core potential of atoms far away from the defect in the defect-containing supercell with that in the defect-free supercell.[25] 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 heat of formation for CdTe. $\Delta H_f(\text{CdTe})$ is calculated to be -0.72 eV, in reasonable agreement with the experimental value of -0.96 eV.[19] More details of the formation energy calculations can be found in Ref. 25. The defect transition energy level, $\varepsilon(q/q')$, is the Fermi level, ε_f in Eq. (1), at which the formation energies of the defect at the charge states q and q' are equal to each other.

For hydrogenated substitutional oxygen (O_{Te}), we define the hydrogenation energy as

$$\Delta E_{\text{H}} = \Delta E - n_{\text{H}}(\mu_{\text{H}}^{\text{mol}} + \mu_{\text{H}}) + q(\varepsilon_{\text{VBM}} + \varepsilon_f), \qquad (2)$$

where ΔE is the energy difference between the supercells that contain the hydrogenated and unhydrogenated O_{Te}, respectively, n_{H} is the number of H atoms in the hydrogenated O_{Te}, μ_{H} is the hydrogen chemical potential referenced to $\mu_{\text{H}}^{\text{mol}}$, which is equal to half of the energy of an isolated H_2 molecule, and q is the charge state of the hydrogenated O_{Te}.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the calculated formation energies of basic intrinsic defects in CdTe at both Te- and Cd-rich limits using Eq. (1). At both limits, V_{Cd} is the dominant intrinsic acceptor in agreement with experiments[1,3] and previous calculations.[14] However, there are several important findings in the present calculations. (1) Our calculated formation energy for neutral Te_{Cd} is substantially lower than previously reported.[26] Consequently, the Te_{Cd} is a negative-U center with its (+2/0) donor level only 0.35 eV above the VBM. (2) We find that the Te interstitial, Te_i, prefers to squeeze in with another regular Te on one Te lattice site to form a split interstitial, $(\text{Te-Te})_{\text{spl}}$. At neutral charge state, the $(\text{Te-Te})_{\text{spl}}$ is 1.50 eV more stable than the normal Te_i structure (a Te atom at the interstitial site surrounded by four Cd atoms[14]). While the Te_i was shown to be a deep acceptor,[14] the $(\text{Te-Te})_{\text{spl}}$ is a deep donor with its (+/0) and (+2/+) donor levels calculated at 0.22 and 0.02 eV above the VBM, respectively. (3) V_{Te} has T_d symmetry at (+2) charge state. However, our calculations show that, at neutral and (−2) charge states, V_{Te} undergoes Jahn-Teller distortions to take C_{2v} and D_{2d} symmetries, respectively, which were not found previously.[14,16] As a result, V_{Te} is a negative-U center for both electron and hole with its (+2/0) donor level and (0/−2) acceptor level located near the midgap (see Fig. 1).

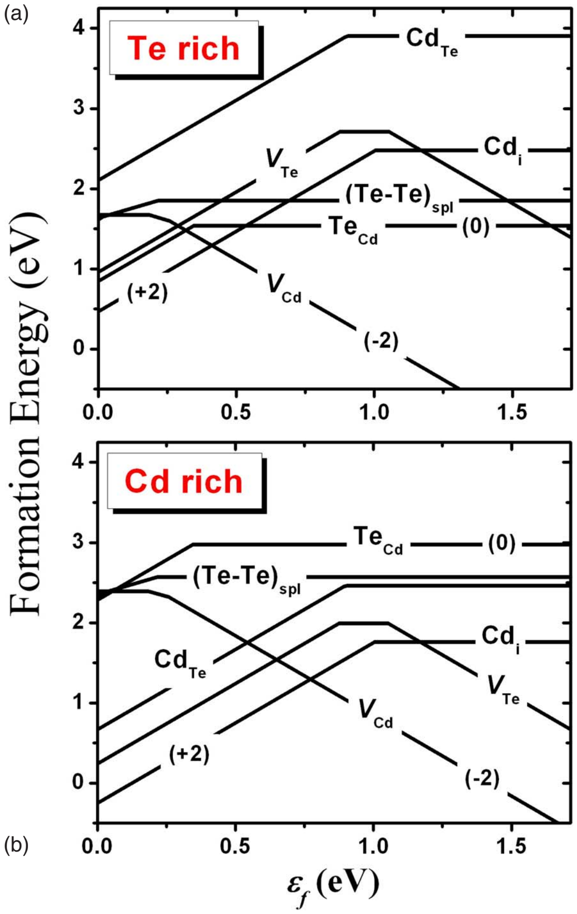

FIG. 1. (Color online) Calculated formation energies for various intrinsic defects in CdTe as a function of electron Fermi energy at (a) Te-rich and (b) Cd-rich limits. The slope of an energy line indicates the charge state of the defect, as selectively shown. The transition levels are given by the Fermi energy at which the slope changes.

Based on the results shown in Fig. 1, we find that, in semi-insulating CdTe (in which the Fermi level lies near the midgap), Te_{Cd} and $(\text{Te-Te})_{\text{spl}}$ should have appreciable concentrations under Te-rich conditions, consistent with the experimentally observed Te precipitates under Te-rich growth conditions.[15] However, the donor levels of both Te_{Cd} and $(\text{Te-Te})_{\text{spl}}$ are too low to pin the Fermi level close to the midgap, which casts doubt on the prevailing assumption that Te_{Cd} compensates the shallow acceptors.[2,7,8] The V_{Te} induces both deep donor and acceptor levels near the midgap, but the V_{Te} concentration may be too low (due to its relatively high formation energy) for V_{Te} to have a significant effect on the carrier compensation.

Cd_i is also a negative-U center, with its (+2/0) donor level at $E_c-0.71$ eV, near midgap (see Fig. 1). However, its formation energy is relatively high (2.48 eV for neutral Cd_i) at the Te-rich limit. Moreover, the calculated small diffusion barriers for Cd_i, i.e., 0.36 and 0.61 eV at (+2) and neutral charge states, respectively, suggest that, in the typical p-type semi-insulating CdTe which favors (+2) charge state for Cd_i, Cd_i can equilibrate with its reservoir at a very low temperature during the slow sample cooling process, resulting in negligible Cd_i concentration. Thus Cd_i should contribute little to the carrier compensation. However, $[\mathrm{Cd}_i]$ can increase if the CdTe sample undergoes postgrowth annealing under saturated Cd pressure. It was reported that such annealing at 800 °C turned CdTe samples from p-type to n-type and a deep donor level at $E_c-0.75$ eV was observed,[13] in good agreement with our calculated Cd_i-induced level at $E_c-0.71$ eV.[27]

The postgrowth annealing of CdTe samples under Cd vapor pressure reduces $[V_{\mathrm{Cd}}]$, but, on the other hand, it may also create an abundance of Cd_i, which not only creates electron carrier traps but may also cause unexpected degradation of CdTe radiation detector. The CdTe detector is operated under electric field for carrier collection. Since the Cd_i^{+2}'s are fast diffusers as shown above, they can easily diffuse to the negative electrode and strongly screen the electric field there. The resulted nonuniform carrier trapping and nonuniform electric field distribution negatively affect the device performance.

Our exploration of intrinsic defects does not yield a convincing candidate that can explain the carrier compensation in the semi-insulating CdTe. We then turn to extrinsic defects. In the intentionally undoped CdTe grown by Brigman techniques, residual oxygen has a concentration typically orders of magnitudes higher than other residual impurities and comparable to intrinsic defects.[7,18] When H binds O_{Te}, we find that it prefers the bond-center (BC) site for (+) and neutral charge states and the antibonding (AB) site for (−) charge state, respectively (see insets of Fig. 2 for structures). Figure 2 shows that O_{Te}-H is stable as donor or acceptor depending on the Fermi level. The neutral O_{Te}-H is unstable. The hydrogenation energies in Fig. 2 were calculated using Eq. (2) with $\mu_{\mathrm{H}}=0$. Table I shows the hydrogenation energies of the O_{Te}-H complex at (+), neutral, or (−) charge state with H at BC or AB site. The H vibrational frequencies calculated within harmonic approximation are also included in Table I to assist the experimental identification of these complexes.

The O_{Te}-H (+/−) transition level is calculated to be $E_c-0.73$ eV, near the midgap (see Fig. 2). Since the O_{Te}-H complex has low energy, it is expected to have appreciable concentration. As an amphoteric defect, the O_{Te}-H complex compensates either p-type or n-type carriers, whichever is in excess. Based on these results, we propose that *the O_{Te}-H complex may play an important role in the semi-insulating behavior of CdTe*.

The puzzling TEES results,[12] which do not show any deep donor levels near the midgap in both undoped and Al-doped CdTe samples, can be understood by considering the O_{Te}-H complex as the deep donor. In a typical TEES experiment, the deep level needs to be first populated by photoexcited carriers. Then the thermally emitted carriers from the deep level are recorded. But the O_{Te}-$\mathrm{H}^+(BC)$ does not induce a optical level inside the band gap. [The (+/−) level shown in Fig. 2 is a thermodynamic transition level, not an optical level.] The lowest unoccupied defect level is the empty Cd orbital on the threefold coordinated Cd, which resonates inside the conduction band (calculated to be at $E_c+0.56$ eV). Thus, the photons with typically near band-gap energy in the TEES experiment would fail to excite electrons into the empty Cd orbital. For O_{Te}-$\mathrm{H}^-(AB)$, which indeed induces an filled optical level inside the bandgap (calculated to be at $E_v+0.29$ eV) with mainly Cd lone-pair character, once occupied by the excited holes, the complex undergo barrierless structural transformation to O_{Te}-$\mathrm{H}^+(AB)$, and simultaneously, the emptied Cd orbital moves up into the conduction band at a calculated level of $E_c+0.67$ eV. Thus, the trapped holes on the Cd orbital cannot be emitted back to the valence band. Consequently, the TEES cannot observe the O_{Te}-H complex. Similarly, the O_{Te}-H may also escape the detection of the DLTS. The defect levels with large level oscillation upon charging (due to large structural relaxation) can be difficult

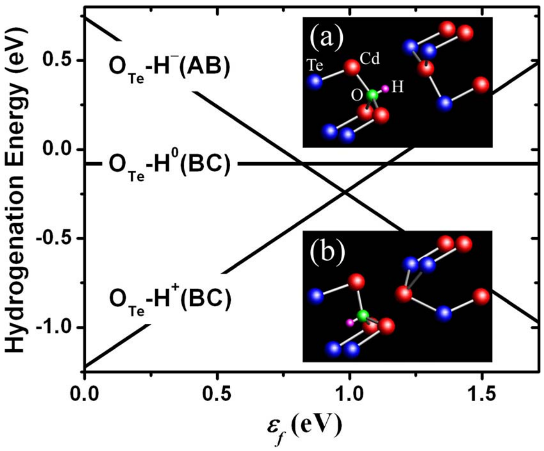

FIG. 2. (Color online) Calculated lowest hydrogenation energies for O_{Te}-H complexes at (+), neutral, and (−) charge states as a function of electron Fermi energy. The transition levels are given by the Fermi energy at which two energy lines cross. Insets show the structures of (a) O_{Te}-H^+ (BC) and (b) O_{Te}-H^- (AB) complexes.

TABLE I. Hydrogenation energies at VBM and vibrational frequencies of O_{Te}-H complexes with different H sites and charge states. Wag modes are twofold degenerate as indicated in the parentheses following the wag frequencies.

		ν (cm^{-1})	
	ΔE_{H} (eV/H)	Stretch	Wag
$\mathrm{H}^+(BC)$	−1.22	3559	692(2)
$\mathrm{H}^+(AB)$	−1.19	3466	756(2)
$\mathrm{H}^0(BC)$	−0.08		
$\mathrm{H}^0(AB)$	0.13		
$\mathrm{H}^-(BC)$	0.84	2849	781(2)
$\mathrm{H}^-(AB)$	0.74	3365	723(2)

to detect, as has seen demonstrated previously for other systems, e.g., BO_2 complex in boron doped silicon.[28]

From the above discussion, we can see that O_{Te}-$H^+(BC)$ does not trap electron carriers easily even though the $(+/0)$ transition level is below the CBM. The trapping at the $(+/0)$ level requires the phonon assistance because the lowest unoccupied defect level, i.e., the empty Cd orbital, is above the CBM. Such trapping is thus barrier-limited, resulting in low carrier capture cross section, which is good for the device performance. The O_{Te}-$H^-(AB)$, on the other hand, should be a very effective hole trap, which is undesired.

O_{Te} can trap a second H to form a neutral complex. We have investigated five O_{Te}-2H structure models, i.e., α-H_2^*, β-H_2^*, γ-H_2^*, canted O-2H, and H_2^{**}. The naming convention follows that used for N-2H dihydrides in GaAs:N.[22,29] The γ-H_2^* is found to be most stable. However, the hydrogenation energy of γ-H_2^* is still 0.06 eV/H higher than that of O_{Te}-$H^+(BC)$ at midgap. Thus, for typical p-type semi-insulating CdTe, the electrically active O_{Te}-H complexes should be more abundant than the electrically inactive O_{Te}-2H complexes. We have also studied V_{Cd} and V_{Te} that can bind H in CdTe but find that H binds more strongly with O_{Te} than V_{Cd} and V_{Te}.

In the literature for CdTe radiation detectors, hydrogen has received little attention because it has never been appreciably measured by glow-discharge mass spectroscopy. However, we note that hydrogen is ubiquitous and thus the hydrogen background can easily overwhelm the signal from the CdTe sample. Thus, other techniques that are sensitive to the chemical environment of hydrogen, such as infrared (IR) measurements, may be the better tools for studying hydrogen in CdTe. There have been some IR studies of CdTe in the far- and mid-infrared regions (<2200 cm^{-1}),[30,31] which does not cover the O-H stretching modes typically >3000 cm^{-1}. However, the observed local vibrational modes (LVMs) ~ 700 cm^{-1}[30] may be related to our calculated O-H wagging modes (see Table I). A recent IR study of CdTe found two O-related LVMs at 1097 and 1108 cm^{-1}. These two modes may be related to the O-H wagging modes under certain symmetry-breaking compressive environment, which increases the wagging frequencies and also lifts the degeneracy of the two wagging modes.[32]

IV. CONCLUSIONS

We show that, contrary to the previous models, no intrinsic defects can explain the carrier compensation in the semi-insulating CdTe. Instead, we demonstrate that the O_{Te}-H complex may play an important role in the carrier compensation because it induces a $(+/-)$ transition level near the midgap, which can compensate either excess electron or excess hole carriers. Our findings are also important for CdTe-based solar cell applications since large quantities of both O and H are introduced during the CdTe growth.[33]

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Ref. 14. However, our calculated Jahn-Teller energy is 1.21 eV, significantly different from the result from Ref. 14 (0.33 eV). We repeated the calculations using the LAPW method with a 32-atom supercell as employed in Ref. 14 and found that the Jahn-Teller energy is 1.11 eV, in good agreement with our result obtained using pseudopotential method.

[27] The observed midgap level of $E_c - 0.75$ eV (Ref. 13) was assumed to be $\mathrm{Td_{Cd}}$-induced and played a critical role in the deep-donor-mediated carrier compensation model (Refs. 6 and 8). However, this level is not observed in the high-resistivity CdTe samples grown under typical Te-rich conditions without postgrowth annealing under saturated Cd pressure (Ref. 12).

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