Chemical trends of defect formation and doping limit in II-VI semiconductors: The case of CdTe

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Using first-principles band structure methods we studied the general chemical trends of defect formation in II-VI semiconductors. We systematically calculated the formation energies and transition energy levels of intrinsic and extrinsic defects and defect complexes in the prototype CdTe and investigated the limiting factors for *p*-type and *n*-type doping in this material. Possible approaches to significantly increase the doping limits are discussed. Our general understanding of the chemical trends of defect formation energies and transition energy levels in CdTe is expected to be applicable also to other II-VI semiconductors.

I. INTRODUCTION

Many semiconductors such as CdTe, ZnSe, and related II-VI compounds and alloys will not be very useful if they cannot be doped.[1] Many optoelectronic device applications also require that materials can be doped both *n* type and *p* type. For example, the success in the fabrication of blue emitting ZnSe laser diodes[2] is mainly due to the ability to obtain a sufficient *p*-type doping in this material. It has been known for a long time that CdTe is the only II-VI compound that can be doped relatively easily either *p* or *n* type.[3,4] However, the dopability of CdTe is relatively low, especially for *p*-type doping.[5-8] In most cases, the achieved hole carrier density is less than 10^{15} cm^{-3}. This has become a major issue in device fabrication using CdTe. The mechanism of the low dopability in CdTe is not well understood.

Generally speaking, there are three main factors that could limit the dopability. (i) The desired dopant may have a low solubility. (ii) The desired dopant has good solubility, but the defect transition energy level may be too deep, thus, the defect is not ionized at normal operating temperature. (iii) The desired dopant has good solubility and is ionizable, but as the Fermi energy shifts due to the increased carrier density, oppositely charged native defects or defect complexes of the dopant (e.g., *DX* centers[9,10] or *AX* centers[11,12]) could form, thus, limiting further change of the Fermi energy. To identify which one of these factors dominates for the *p*- or *n*-type doping, and the general chemical trends of defect formation in CdTe, we have systematically calculated the formation energies and transition energy levels of intrinsic and extrinsic defects and defect complexes in CdTe using the first-principles band structure method. Our calculations show that *n*-type doping in CdTe is limited by the spontaneous formation of the intrinsic V_{Cd}^{2-} when the Fermi energy is near the conduction band minimum (CBM). In some cases of extrinsic doping [e.g., in CdTe:*X* with *X*=(Al, Ga, and In)], it could also be limited by the spontaneous formation of the *DX* centers. For *p*-type doping in CdTe, it is either limited by the formation of Cd$_i$ or limited by not having a dopant with both high solubility *and* shallow acceptor levels. Some of the dopants have shallow acceptor levels, but their formation energies are too high (e.g., CdTe:N or CdTe:P). Other dopants have relatively low formation energy, but their acceptor level is too deep (e.g., CdTe:Cu). In some cases, it could also be limited by the formation of compensating interstitial de-

fects (e.g., Na$_i$ in CdTe:Na). The *AX* center, however, is not a limiting factor for *p*-type doping. We have also studied the effect of codoping/cluster doping[13-15] on the dopability in this material. We find that (a) under equilibrium growth conditions codoping/cluster doping in general do not reduce the formation energy of the defect complexes below that of a single point defect. (b) Codoping/cluster doping do not lower the defect ionization energy except when the defect complex is made of a single donor and a single acceptor such as (V$_{Cd}$+Cl$_{Te}$). Our general understanding of the doping limits in CdTe is expected to be applicable to other II-VI semiconductors. It, thus, provides a solid basis for overcoming the doping limit in these materials.

The rest of the paper is organized as follows. Section II describes our calculation method. Section III discusses the importance of setting up the correct chemical potential range in the defect study. Sections IV and V present our calculated formation energies and single particle energy levels, respectively, of tetrahedrally coordinated point defects. Section VI shows the chemical trends of the calculated defect transition energy levels. In Secs. VII and VIII we discuss the origin of the doping limits in CdTe and the effects of codoping/cluster doping. Finally, Sec. IX gives a brief summary of the paper.

II. METHODS OF CALCULATION

The band structure and total energy calculations in this study are performed using the all electron, general potential, linearized augmented plane wave (LAPW) method[16] within the local density approximation (LDA).[17] We use the Ceperley-Alder exchange-correlation potential[18] as parametrized by Perdew and Zunger.[19] The Cd 4*d* electrons are treated in the same footing as the other valence states. The Brillouin zone integration for the charge density and total energy calculations are performed using the ten special *k* points for the zinc blende structure and equivalent *k* points for the superstructures.[20] The single electron energy levels, however, are determined at the Γ point and are aligned using core electron energy levels. To reduce the well known LDA band gap error,[21] we perform the calculations nonrelativistically. With a energy cutoff of 8.5 Ry for the LAPW basis functions, the calculated lattice constant and bulk modulus for zinc blende CdTe are 6.541 Å and 516 kbar, respectively, in reasonably good agreement with experimental values[22] of 6.482 Å and 445 kbar. The calculated band gap at the theo-

retical lattice constant is 1.48 eV (1.59 eV at the experimental lattice constant), also in good agreement with the experimental value[22] of 1.61 eV.

The defect system is modeled by putting a defect or defect complex at the center of a periodic supercell. Most of the calculations are performed with a 32 atom supercell. In some cases, however, a 64 atom supercell is used to check the convergence. For charged defect, a uniform background charge is added to keep the global charge neutrality of the periodic supercell. All the internal structural parameters of the supercell are optimized by minimizing the total energy and quantum mechanical forces. To determine the defect formation energy and defect transition energy levels, we calculate the total energy $E(\alpha,q)$ for a supercell containing the relaxed defect α in charge state q. We also calculate the total energy E(CdTe) for the same supercell in the absence of the defect, as well as the total energies of the elemental solids or gases at their stable phases. From these quantities we deduce the defect formation energy $\Delta H_f(\alpha,q)$ as a function of the electron Fermi energy[23] E_F as well as on the atomic chemical potentials[24,25] μ_i:

$$\Delta H_f(\alpha,q)=\Delta E(\alpha,q)+n_{\mathrm{Cd}}\mu_{\mathrm{Cd}}+n_{\mathrm{Te}}\mu_{\mathrm{Te}}+n_A\mu_A+qE_F, \tag{1}$$

where $\Delta E(\alpha,q)=E(\alpha,q)-E(\mathrm{CdTe})+n_{\mathrm{Cd}}E(\mathrm{Cd})+n_{\mathrm{Te}}E(\mathrm{Te})+n_AE(A)+qE_{\mathrm{VBM}}$. E_F is referenced to the valence band maximum (VBM) of CdTe. μ_i is the chemical potential of constituent i referenced to elemental solid/gas with energy $E(i)$. The n's are the number of Cd, Te, and extrinsic defect A, and q is the number of electrons, transferred from the supercell to the reservoirs in forming the defect cell. The defect transition energy level $\epsilon_\alpha(q/q')$ is the Fermi energy E_F in Eq. (1) at which the formation energy $\Delta H_f(\alpha,q)$ of defect α and charge q is equal to that of another charge q' of the same defect, i.e.,

$$\epsilon_\alpha(q/q')=[\Delta E(\alpha,q)-\Delta E(\alpha,q')]/(q'-q). \tag{2}$$

Due to the finite cell size, basis set, and k-point sampling used in the present calculation we estimate that the error in the calculated formation energy is about 0.2 eV and the error in the calculated transition energy is about 0.1 eV. The error could be larger if the defect is very localized and has a high charge state.[26] Due to the neglect of the relativistic effects, the error could also be slightly larger if the atomic number of the donor impurity (e.g., F or Cl) differs significantly from that of Cd or Te.

III. CHEMICAL POTENTIAL DEPENDENCE OF THE FORMATION ENERGY

Equation (1) indicates that the defect formation energy, and consequently, the solubility of the dopants, depend sensitively on the atomic chemical potential, as well as on the electron Fermi energy. This is because in forming the defect, particles are exchanged between the host and chemical reservoirs. For example, to form the substitutional defect $\mathrm{Na_{Cd}}$ (Na on Cd site) one has to take a Na atom from the Na chemical reservoir, put it into the host, and remove a Cd atom from the host, and put it into the Cd chemical reservoir.

Therefore, the formation energy of $\mathrm{Na_{Cd}}$ decreases if the chemical potential of Cd decreases or if the chemical potential of Na increases. Furthermore, to form positively charged defect ($q>0$, e.g., Cd interstitial Cd_i^{2+}) one has to put the electrons removed from the defect to an electron reservoir with its characteristic energy E_F. Thus, the positively charged defect will have a higher formation energy in n-type CdTe where the Fermi energy is close to the CBM. Similarly, negatively charged defects ($q<0$, e.g., Cd vacancy V_{Cd}^{2-}) have a higher energy in p-type material where the Fermi energy is close to the VBM. Therefore, in principle, by adjusting the chemical potential of the dopant or the Fermi energy, one can control the dopant solubility.

Under equilibrium growth conditions, however, there are some thermodynamic limits on the achievable values of the chemical potentials μ_i: First, to avoid precipitation of Cd, Te, and the elemental dopant A ($A=$Na,Cu,In,Cl, etc.), μ_i are bound by

$$\mu_{\mathrm{Cd}}\leqslant0, \quad \mu_{\mathrm{Te}}\leqslant0, \quad \mu_A\leqslant0. \tag{3}$$

Second, μ_i are limited to those values that maintain a stable CdTe compound, so

$$\mu_{\mathrm{Cd}}+\mu_{\mathrm{Te}}=\Delta H_f(\mathrm{CdTe}), \tag{4}$$

where $\Delta H_f(\mathrm{CdTe})$ is the formation energy of solid CdTe. The calculated $\Delta H_f(\mathrm{CdTe})=-0.79$ eV is in good agreement with the experimental value ranged from -0.73 to -0.96 eV.[27–29] Finally, to avoid the formation of secondary phases between the dopants A and the host elements, μ_i is limited by

$$n\mu_A+m\mu_{\mathrm{Cd}}\leqslant\Delta H_f(A_n\mathrm{Cd}_m)$$

or

$$n\mu_A+m\mu_{\mathrm{Te}}\leqslant\Delta H_f(A_n\mathrm{Te}_m). \tag{5}$$

Figure 1 plots the calculated chemical potential region accessible under equilibrium growth condition for CdTe:Na in the two dimensional ($\mu_{\mathrm{Cd}},\mu_{\mathrm{Na}}$) plane, as defined by Eqs. (3)–(5). It shows that because Na forms very stable compound $\mathrm{Na_2Te}$ with Te (with a calculated formation energy of -2.84 eV), the highest possible μ_{Na} at the Cd-rich condition [$\mu_{\mathrm{Cd}}=0,\mu_{\mathrm{Te}}=\Delta H_f(\mathrm{CdTe})=-0.79$ eV] is -1.02 eV. Under the Te-rich condition ($\mu_{\mathrm{Cd}}=-0.79$ eV, $\mu_{\mathrm{Te}}=0$), μ_{Na} is further reduced to less than -1.42 eV. Above these chemical potential limits, secondary $\mathrm{Na_2Te}$ compound will form, thus stopping the doping process. This low available Na chemical potential is one of the limiting factors for Na doping in CdTe.

Similar plots can also be obtained for other impurities or defect complexes. For example, in the case of codoping [e.g., $(2\mathrm{Cu_{Cd}}+\mathrm{Cl_{Te}})$] or cluster doping [e.g., $(4\mathrm{Cu_{Cd}}+\mathrm{Cl_{Te}})$] of CdTe with both Cu and Cl, the chemical potentials of Cu, Cl, Cd, and Te are limited by the formation of CuCl, $\mathrm{CdCl_2}$, and $\mathrm{Cu_2Te}$. Because the calculated formation energy of $\mathrm{CdCl_2}$ is -4.0 eV, the highest possible Cl chemical potential is -1.6 eV at the Cd-poor condition. This indicates that the formation energy of $\mathrm{Cl_{Te}}$ will be relatively high. It is, thus, crucial
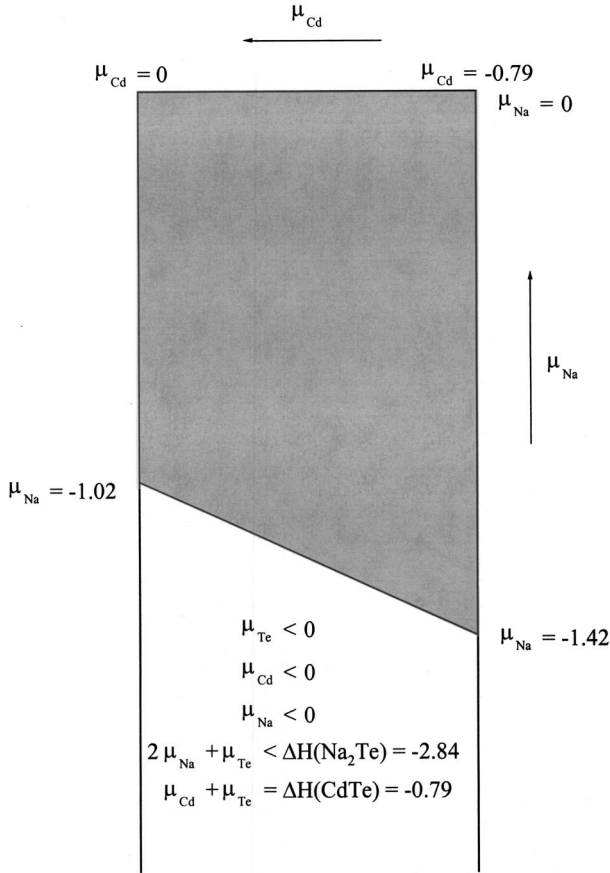
FIG. 1. Calculated available equilibrium chemical potential region for CdTe:Na in the two-dimensional (μ_{Cd}, μ_{Na}) plane. The shaded area is forbidden under equilibrium growth condition.

to consider all these chemical potential limits in searching for the lowest possible formation energy of defect complexes.

To overcome the solubility problem, one may alternatively search for a kinetic pathway to suppress the formation of the precipitates or the secondary phases. This could be done either by increasing the dopant chemical potential through nonequilibrium process such as epitaxial growth[30] or by using metastable compounds such as NaTe, CuTe, or plasma source[31,32] in which Na and Cu have higher chemical potentials.

IV. FORMATION ENERGY OF THE NEUTRAL POINT DEFECT

For point defects, we first consider tetrahedrally coordinated defect centers in which each shell of atoms around the defects relaxes symmetrically by the same amount. Possible nonsymmetric relaxations for some of the defects (e.g., the formation of the DX and the AX centers) will be discussed later in this paper. Table I lists the calculated formation energies $\Delta E(\alpha, q)$ of tetrahedrally coordinated point defects at neutral charge state ($q=0$) and $\mu_i=0$, from which one can deduce the defect formation energy at different chemical potentials through Eq. (1).

For intrinsic defects, the accessible chemical potential re-

TABLE I. Calculated formation energies $\Delta E(\alpha, q)$ [Eq. (1)] of tetrahedrally coordinated point defects at neutral charge state ($q=0$) and $\mu_i=0$.

Defect	Formation energy (eV)	Defect	Formation energy (eV)
V_{Cd}	2.67	Cd_{Te}	3.92
V_{Te}	3.24	Te_{Cd}	3.70
Te_i^a	3.52	Cd_i^a	2.26
Te_i^c	3.41	Cd_i^c	2.04
Na_{Cd}	0.45	Al_{Cd}	1.17
Cu_{Cd}	1.31	Ga_{Cd}	1.23
Ag_{Cd}	1.32	In_{Cd}	1.23
Au_{Cd}	1.30	F_{Te}	−0.08
N_{Te}	2.62	Cl_{Te}	0.48
P_{Te}	1.83	Br_{Te}	0.62
As_{Te}	1.68	I_{Te}	0.99
Sb_{Te}	1.72	Cu_i^a	2.14
Bi_{Te}	1.96	Cu_i^c	2.24
Na_i^a	0.60	Na_i^c	0.45

gion is given by Eqs. (3) and (4). For example, for neutral V_{Cd}^0, the lowest formation energy occurs at the Cd-poor condition with $\Delta H_f(V_{Cd}^0)=2.67-0.79=1.88$ eV. There are two interstitial sites in the zinc blende structure, one site is surrounded by anions (a) and the other is surrounded by cations (c). For charge neutral Cd interstitial, we find that Cd_i^c has a lower formation energy than Cd_i^a. The lowest possible formation energy for the neutral Cd_i occurs at the Cd-rich condition with $\Delta H_f(Cd_i^0)=2.04$ eV. The charge neutral Te_i^c surrounded by the cations is also more stable with the lowest formation energy of 3.41 eV at the Te-rich limit.

For impurities (extrinsic defects), Eq. (5) should also be considered. For example, for Na_{Cd}^0, the lowest formation energy occurs at the Cd-poor condition with $\Delta H_f(Na_{Cd}^0)=0.45-0.79+1.42=1.08$ eV. This is because at the Cd poor condition ($\mu_{Cd}=-0.79$ eV), the highest possible μ_{Na} is -1.42 eV (see Fig. 1). Similar analyses show that for charge neutral In_{Cd}, Cl_{Te}, and Na_i, the minimum formation energies are 1.00, 1.69, and 1.47 eV, respectively, after taking into account that the calculated formation energies of In_2Te_3 and $CdCl_2$ are -1.68 and -4.01 eV, respectively. For the isovalent O_{Te} defect, the calculated $\Delta E(O_{Te}, q=0)=-0.41$ eV. The lowest formation energy occurs when $\mu_{Cd}+\mu_O=\mu_{CdO}=-2.46$ eV, so it is independent of μ_{Cd} with $\Delta H_f(O_{Te}^0)=-0.41-0.79+2.46=1.26$ eV. One interesting observation is that the formation energy of Cu_2Te is close to zero. Therefore, the lowest formation energy of Cu_{Cd}^0 at the Cd-poor conditions is $\Delta H_f(Cu_{Cd}^0)=1.31-0.79=0.52$ eV. Thus, the solubility of Cu ($\Delta H_f=0.52$ eV) is much larger than that of Na ($\Delta H_f=1.08$ eV). Our analysis indicates that impurities that do *not* form strong bonds with the host elements have higher solubilities than impurities that form strong bonds with the host elements, contrary to naive thoughts. This is because if the impurity does not form strong bond with the host atom, it will also be less likely to form secondary phases.
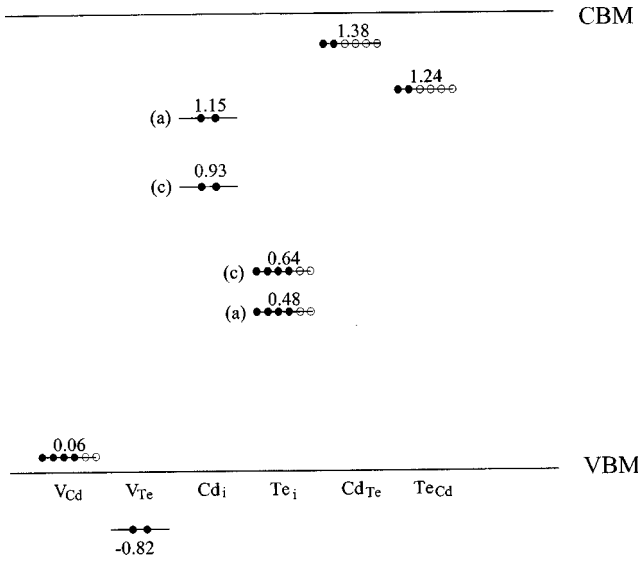
FIG. 2. Calculated single particle electron energy states for the tetrahedrally coordinated neutral intrinsic defects. The solid and open dots indicate the occupation of each state.

V. SINGLE PARTICLE ENERGY STATE OF THE DEFECT

For simple extrinsic impurities, one in principle can predict whether a dopant is a donor with a single particle energy state close to the CBM or an acceptor with a single particle energy state close to the VBM by simply counting the number of the valence electrons of the dopants and the host elements. For example, one can expect that group-I elements substituting on the Cd site X_{Cd}^{I} (X^{I}=Na, Cu, Ag, and Au) or group V elements substituting on the Te site Y_{Te}^{V} (Y^{V}=N, P, As, Sb, and Bi) give acceptors, whereas group-III elements substituting on the Cd site X_{Cd}^{III} (X^{III}=Al, Ga, or In) or group-VII elements substituting on the Te site Y_{Te}^{VII} (Y^{VII}=F,Cl,Br,I) or group-I interstitials (Cu$_i$ and Na$_i$) give donors.

For intrinsic defects, the situation is more complicated. Figure 2 shows the single particle energy states of tetrahedrally coordinated charge neutral defects (for simplicity, spin-orbit splitting is not included). Generally speaking, when a high valence atom is replaced by a low valence atom (e.g., Cd$_{Te}$) or by a vacancy (V_{Cd} and V_{Te}), defect states are created from the host valence (v) band states that move upward in energy. The defect states consist of a low-lying singlet a_1^v state and a high-lying threefold-degenerate t_2^v states. Depending on the potential, both t_2^v and a_1^v can be above the VBM. These states are occupied by the nominal valence electrons of the defect plus the valence electrons associated with the neighboring atoms (six electrons if the defect is surrounded by four Te atoms or two electrons if it is surrounded by four Cd atoms). For example, for charge neutral V_{Cd}, the defect center has a total of $0+6=6$ electrons. Two of them will occupy the a_1^v state and the remaining four electrons will occupy the t_2^v states just above the VBM, so V_{Cd} is an acceptor. For charge neutral V_{Te}, there are only $0+2=2$ electrons associated with this defect center, and they will occupy only the a_1^v state, which is found to be below the VBM. The t_2^v states for V_{Te} are above the CBM, therefore,

V_{Te} can only be a donor. For the antisite defect Cd$_{Te}$, there are $2+2=4$ electrons associated with the defect center. Two of them occupy the a_1^v state and the other two occupy the t_2^v states. Due to the large electronegativity difference between Cd and Te, however, the partially occupied t_2^v states move up considerably, and are close to the CBM. Thus, Cd$_{Te}$ is a *donor*. On the other hand, if a low valence atom is replaced by a high valence atom (e.g., Te$_{Cd}$) or if a dopant goes to an interstitial site (e.g., Cd$_i$ and Te$_i$), the defect states a_1^v and t_2^v will remain inside the valence band. Instead, the defect states a_1^c and t_2^c are created from the host conduction (c) band states that move downward in energy. Depends on the potential, both the a_1^c and t_2^c states can be in the gap. For Te$_{Cd}$, there are $6+6=12$ electrons associated with this defect center. Eight of them will occupy the bonding a_1^v and t_2^v states. Two of them will occupy the a_1^c state and the remaining two will occupy the t_2^c state. Since the partially occupied t_2^c state is close to the CBM, Te$_{Cd}$ is also a donor. For the interstitial defect, Cd$_i$ has two electrons that will fully occupy the a_1^c state and is thus expected to be a donor. The Te$_i$ defect center has six electrons. Two will occupy the a_1^c state and the remaining four will occupy the t_2^c states. Since the partially occupied t_2^c states are closer to the VBM, Te$_i$ is expected to be a deep acceptor.

It is important to know the characters of the single electron energy state. For example, both the Cd$_{Te}$ and Te$_{Cd}$ defect states have the t_2 symmetry. However, Cd$_{Te}$ has the t_2^v character whereas Te$_{Cd}$ has the t_2^c character. As a result, Te$_{Cd}$ will behave differently from Cd$_{Te}$. Indeed, we find that a neutral Te$_{Cd}$ is unstable against the C_{3v} distortion[33] where the Te atom on the Cd site is displaced along the $\langle 111 \rangle$ direction (similar to the *DX* center), whereas Cd$_{Te}$ is stable at the T_d substitutional site. Charge neutral Te$_i$ with the t_2^c character is also found to be unstable against the C_{3v} distortion,[33] whereas V_{Cd} with the t_2^v character is stable against the C_{3v} distortion. Another important issue often encountered in the LDA calculations is to estimate the effects of the LDA band gap corrections on the calculated energy states. Although both V_{Te} and Cd$_i$ have a_1 defect states, V_{Te} has the a_1^v character while Cd$_i$ has instead the a_1^c character. Thus, one would expect that the energy level of Cd$_i$ will follow closely with the CBM while the energy level of V_{Te} will not.

Figure 2 shows that the state of Cd$_i^a$ is higher in energy than that for Cd$_i^c$. Table I shows that Cd$_i^a$ also has higher formation energy than Cd$_i^c$ when the defect state is fully occupied. However, for doubly charged Cd$_i^{2+}$ (i.e., the defect state is empty), because the energy gain by removing the two electrons from the defect state is more in Cd$_i^a$ than that in Cd$_i^c$, the order of the stability could be reversed. Indeed, we find that for $q=2+$, Cd$_i^a$ has a lower formation energy than Cd$_i^c$. Similarly, Te$_i^c$ has a lower formation energy than Te$_i^a$ when the charge state is neutral (Table I). However, Fig. 2 shows that it costs more energy to put two electrons on Te$_i^c$ than on Te$_i^a$. Our total energy calculation indeed shows that for $q=-2$, Te$_i^a$ has lower formation energy than Te$_i^c$. This demonstrates an interesting point that the stable position of a
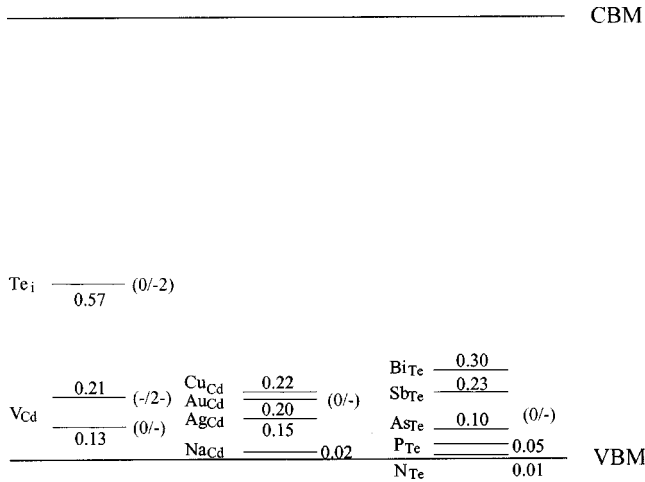
FIG. 3. Calculated acceptor transition energy levels for the tetrahedrally coordinated point defects.

defects could depend sensitively on its charge state.[34] Another interesting case is V_{Te}. For neutral V_{Te}^0 the occupied a_1^v state is resonant inside the valence band. For V_{Te}^{2+}, however, the neighboring Cd atoms expand significantly due to a Coulomb repulsion, increasing the V_{Te}-Cd distance by almost 50% from 2.327 to 3.391 Å. Such large atomic displacements push the empty a_1^v defect state up well inside the band gap, thus lowering the total energy.

VI. DEFECT TRANSITION ENERGY LEVELS

Figure 3 presents our calculated acceptor transition energy levels and Fig. 4 gives the donor transition energy levels for tetrahedrally coordinated point defects. These results are obtained by using Eq. (2). From these figures and the data in Table I and Figs. 3 and 4, one can derive using Eq. (1) the formation energies of charged defects as a function of the Fermi energy and chemical potentials.

For example, Fig. 3 shows that at $E_F = 0.13$ eV above the VBM, $\Delta H_f(V_{Cd}^-)$ equals to $\Delta H_f(V_{Cd}^0) = 2.67$ eV at the Cd-
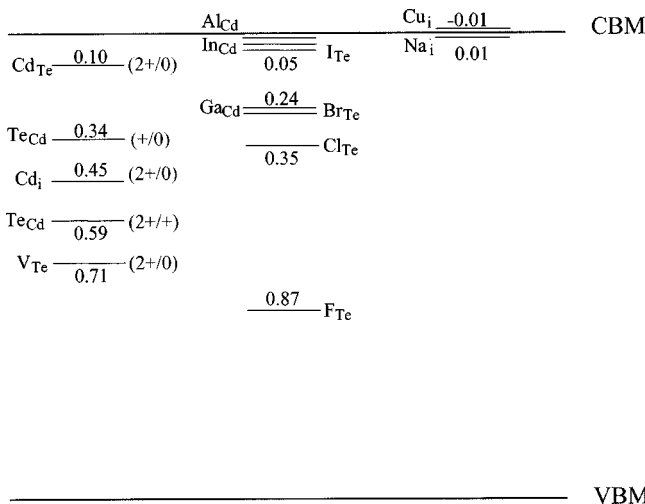
FIG. 4. Calculated donor transition energy levels for the tetrahedrally coordinated point defects.

rich condition (Table I). Thus, for E_f at the VBM ($E_F = 0$), the formation energy of $\Delta H_f(V_{Cd}^-)$ will be $2.67 + 0.13 = 2.80$ eV [Eq. (1)]. Similarly, for E_F at the CBM and at the Cd-rich condition, the formation energy of Cd_{Te}^{2+} is $(3.92 - 0.79 + 2 \times 0.10) = 3.33$ eV.

A. Acceptor levels

Figure 3 shows that the intrinsic defects, V_{Cd} has relatively shallow transition energy levels $(0/-)$ and $(-/2-)$ at 0.13 and 0.21 eV above the VBM, respectively, while Te_i has a deep acceptor level $(0/2-)$ at 0.57 eV above the VBM.[35] For Te_i, the $q = -1$ charged state is unstable with respect to dissociating into the $q = -2$ and $q = 0$ states, i.e., Te_i is a negative-U system. A defect often has a negative U if the atomic position of the defect depends sensitively on its charge state. Clearly, V_{Cd} is the most prominent intrinsic acceptor for CdTe. However, the transition energy levels are still too high to reach high hole density at room temperature.

For A_{Cd} extrinsic impurity doping, where $A = $ Cu, Ag, and Au, the calculated $(0/-)$ transition energy levels are at 0.22, 0.15, and 0.20 eV above the VBM, respectively. These $(0/-)$ transition energy levels are relatively deep because the coupling between the delocalized d orbitals of the group-IB atoms and the Te p orbital is large.[36] Among the three noble metal atoms, Ag has the lowest d orbital energy and the largest atomic size, so the p-d repulsion is the weakest for Ag substitution on the Cd site. Consequently, Ag_{Cd} has the shallowest $(0/-)$ transition energy level. If we replace the group-IB atom by a group-IA atom such as Na that does not have active valence d orbitals, the $(0/-)$ acceptor level should be even shallower. Indeed, we find that the $(0/-)$ level of Na_{Cd} is only at 0.02 eV above the VBM. Thus, Ag_{Cd} and Na_{Cd} could be important acceptors for CdTe.

For B_{Te} extrinsic impurity doping, where $B = $N,P,As,Sb, Bi, the calculated $(0/-)$ transition energy levels are at 0.01, 0.05, 0.10, 0.23, and 0.30 eV, respectively. The transition energy level decreases monotonically when the atomic number of B decreases. This is because in this case the defect state has an anion p character and is localized on the B atom. When the atomic number of B decreases, its p atomic orbital energy also decreases (becoming more electronegative), thus, lowering the energy of the defect state. The shallow $(0/-)$ transition energy levels for N_{Te}, P_{Te}, and As_{Te} indicate that they could be important p-type dopants for CdTe. However, the defect formation energy of N_{Te} is large (Table I) due to the large size mismatch between N and Te.

B. Donor levels

Figure 4 shows that most of the intrinsic donor levels are deep inside the band gap. Only Cd_{Te} has a relatively shallow $(2+/0)$ transition energy level at 0.10 eV below the CBM. However, the formation energy of the antisite defect Cd_{Te} is very large (Table I). We find that Cd_{Te}, Cd_i, and V_{Te} are all negative-U systems because the atomic positions of these defects depend sensitively on their charge states. For example, for Cd_{Te}, the Cd_{Te}-Cd bond length changes significantly from 2.814 Å for $q = 0$ to 3.053 Å for $q = +2$.

For extrinsic A_{Cd} impurity doping, where $A =$ Al, Ga, and In, the calculated $(+/0)$ transition energy levels are at 0.02, 0.24, and 0.04 eV below the CBM, respectively. The Ga_{Cd} transition energy level is deeper than Al_{Cd} and In_{Cd} because the defect state has mostly the cation s character and the Ga $4s$ orbital is lower in energy than the Al $3s$ and In $5s$ orbitals. Because Al_{Cd} and In_{Cd} both have very shallow $(+/0)$ transition energy levels, they could be important n-type dopant for CdTe.

For B_{Te} impurity doping, where $B =$ F, Cl, Br, and I, the calculated $(+/0)$ transition energy levels varies significantly. They changes from very deep inside the band gap for F_{Te} (at $E_{CBM} - 0.87$ eV) to very shallow for I_{Te} (at $E_{CBM} - 0.05$ eV). In fact, F_{Te} has a singly occupied state in the middle of the band gap, thus, it can behave either as a single donor *or* a single acceptor. The reason that the transition energy levels move up in energy towards the CBM (i.e., getting shallower) as the atomic number of the B atom increases is mainly because the donor state has a large anion s character. As the atomic number increases from F to I, the valence s orbital energy of the B atom also increases, thus the donor level gets shallower. In addition, the increased atomic size from F to I also contributes to this chemical trend. Our calculation suggests that iodine could be a good n-type dopant for CdTe.

For interstitial defects Cu_i and Na_i, the calculated $(+/0)$ transition energy levels are very shallow. This indicates that they could be strong candidates as efficient n-type dopant for CdTe. It is interesting to notice that Na_{Cd} also could be a good p-type dopant since it creates shallow acceptor levels.

VII. THE DOPING LIMITS

Our analyses above identified a number of shallow acceptors and donors that could be candidates for efficient p- and n-type doping in CdTe. However, to be good dopants, they should avoid either self compensation or compensation by intrinsic defects. They should also have reasonably small formation energy, so that significant amount of dopant can be introduced into the host. In the following we discuss to what extent these dopants can lead to desired carrier concentrations.

A. Compensation by intrinsic defects

Figure 5 shows the calculated defect formation energy of low-energy intrinsic defects as a function of the Fermi energy. In this plot the slope of the energy line gives the charge state of the defect at that E_F. The transition energy level is the Fermi energy at which the slope change values. We find that at the Cd-rich limit [Fig. 5(a)], undoped CdTe tends to be charge neutral with the Fermi energy close to the center of the band gap. This is because if E_F is below the mid gap (i.e., for p-type samples) the donor defect Cd_i^{2+} will become the dominant intrinsic defect that compensates the intentional acceptors. However, if E_F is above the mid gap (i.e., for n-type sample), then the compensating acceptor defect V_{Cd}^{2-} will become the dominant intrinsic defect. Thus, the Fermi energy will more or less be pinned in the middle of the band
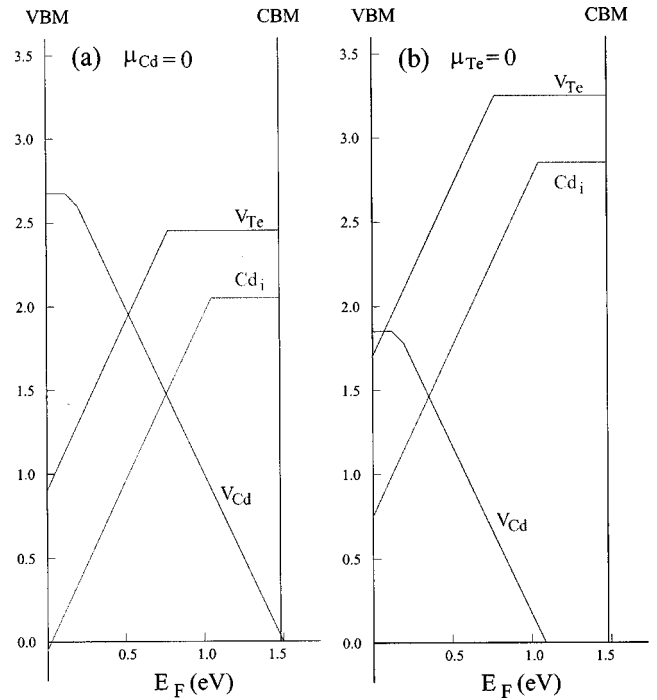

FIG. 5. Calculated formation energies of the low-energy intrinsic defects as a function of the electron Fermi energy at (a) the Cd-rich limit and (b) the Te-rich limit. The slope of the energy line gives the charge state of the defect. The transition energy level corresponds to the Fermi energy at which the slope changes.

gap. On the other hand, at the Te-rich limit, undoped CdTe tends to be slightly p type, because E_F is pinned at a level closer to the VBM. Therefore, we expect that under equilibrium growth conditions, undoped CdTe should be either semiinsulating or p type. Furthermore, the negatively charged V_{Cd}^{2-} can form spontaneously even at the Cd-rich condition when E_F is close to the CBM (see Fig. 5). This sets up an intrinsic limit on the possible n-type doping in CdTe. However, no such intrinsic limit exists for p-type doping because under the Te-rich condition no positively charged compensating intrinsic defects can spontaneously form.

Figure 5 shows that the dominant intrinsic defect that compensates acceptors is Cd_i and the dominant intrinsic defect that compensates donors is V_{Cd}. Therefore, to avoid the formation of the intrinsic compensating defect, for p-type doping the growth should be carried out at the Te-rich condition where the formation energy of Cd_i is relatively large [Fig. 5(b)]. Under the Te-rich condition, however, A_{Cd}^I has the lowest formation energy whereas B_{Te}^V has the highest formation energy. It is therefore beneficial to use group-I elements as p-type dopants. This explains why it is often difficult to dope II-VI materials p-type using group V elements because B^V often has very low solubility in the host at the Te-rich limit. To increase the solubility of group V elements in CdTe, one has to change the growth condition to the Cd-rich condition. But under the Cd-rich condition the compensating defect Cd_i can form more easily, thus reducing the efficiency of p-type doping. However, dopants such as N or P create very shallow acceptor levels in CdTe. Thus, if one can enhance the incorporation of N and P in CdTe through non-
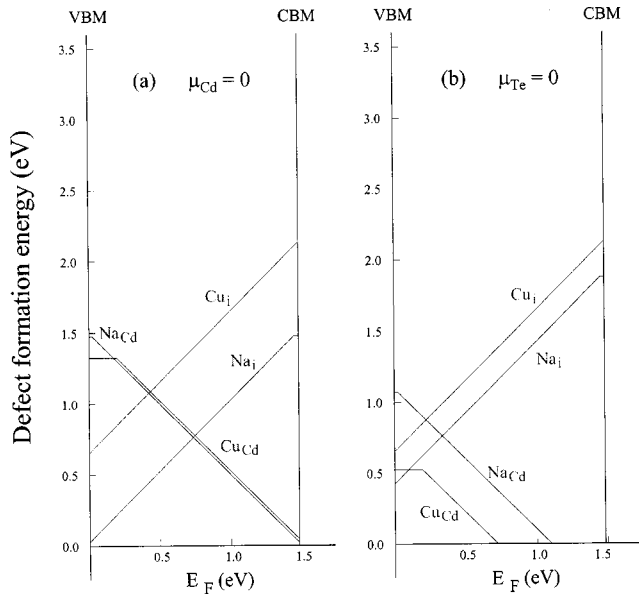
FIG. 6. Calculated formation energies for Na_{Cd}, Na_i, Cu_{Cd}, and Cu_i as a function of the electron Fermi energy at (a) the Cd-rich limit and (b) the Te-rich limit.
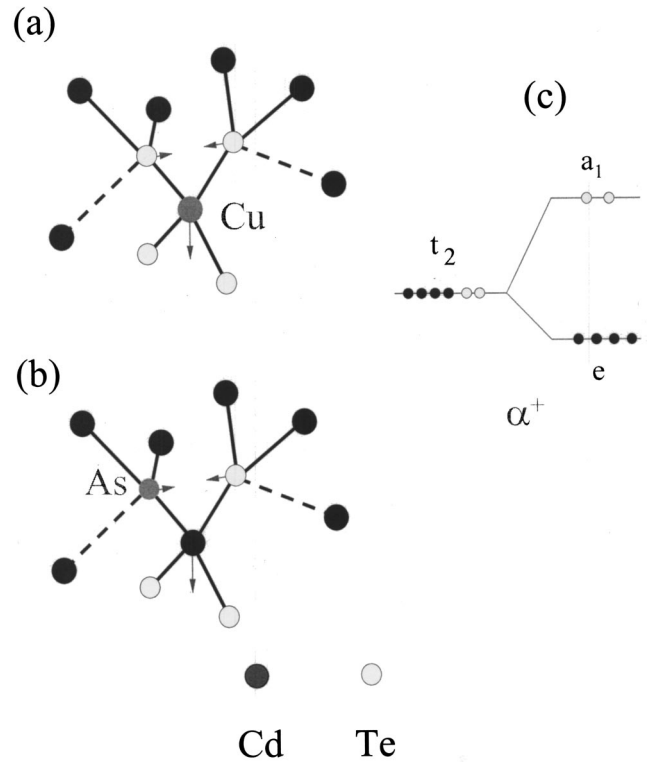

FIG. 7. A schematic plot of the double bond breaking (DBB) model of the AX center for (a) cation substitutional defect and (b) anion substitutional defect. Panel (c) shows schematically how the AX center can be stabilized by the lowering of the electronic energy.

equilibrium process (e.g., MBE growth, ion implantation, photoassisted doping, radical-assisted doping, electron beam annealing, etc.),[7,30,37–39] it may be possible to significantly enhance the hole carrier density in CdTe. On the other hand, to avoid the formation of compensating acceptor V_{Cd} for n-type doping, the growth should be carried out under the Cd-rich condition where the formation energy of V_{Cd} is relatively large [Fig. 5(a)]. However, under the Cd-rich condition A_{Cd}^{III} has the highest formation energy whereas B_{Te}^{VII} has the lowest formation energy, therefore, it is usually favorable to use group-VII elements as n-type dopants if they produce shallow donor levels.

B. Impurity self-compensation

For impurity doping, the doping process can also be stopped by the formation of self-compensating defect or defect complexes. As an example, Fig. 6 compares the formation energies of Na_{Cd} with Na_i, and that of Cu_{Cd} with Cu_i, as a function of the Fermi energy at the Cd- and Te-rich conditions, respectively. From Fig. 6, it is clear that although Na creates shallow levels in CdTe, it cannot be a good dopant. This is because if Na_{Cd} is used as a p-type dopant, when the Fermi energy is lowered, positively charged Na_i interstitial will be more stable. Therefore, more and more Na will move to the interstitial site, compensating the p-type dopant Na_{Cd}. The opposite is also true if we use Na_i as the n-type dopant. This occurs under both the Cd- and Te-rich conditions. This self-compensation effectively changes the shallow Na_{Cd} $(-/0)$ transition and the shallow Na_i $(0/+)$ transition to a deep negative U $[Na_{Cd}(-)/Na_i(+)]$ transition. However, unlike conventional defects, this transition energy depends on the host chemical potential and usually has a nonzero activation energy. The situation is somewhat different for Cu. Under the Cd-rich condition self-compensation also takes place. However, under the Te-rich condition, Cu_{Cd} always

has a lower formation energy than Cu_i, i.e., no self-compensation exists. Therefore, Cu could be a good p-type dopant in CdTe. However, the deep $(0/-)$ transition energy level of Cu_{Cd} at 0.20 eV limits the hole carrier density in CdTe. Furthermore, Cu is a fast diffuser in CdTe because it has a very small diffusion barrier[40] in CdTe. This could be another factor that limits the device applications using Cu-doped CdTe.

C. The AX centers

As originally proposed by Park and Chadi,[11,12] p-type doping in II-VI semiconductors can also be limited by the formation of the AX centers that compensate acceptors. The AX center forms through a double bond breaking (DBB) mechanism,[11] as shown in Fig. 7, where two next neighbor anions move towards each other, breaking two neighboring bonds and forming an anion-anion bond. The AX center can be a possible stable defect if the t_2^v defect states has holes (preferentially two holes, such as in Cu_{Cd}^+, N_{Te}^+, etc.), because the DBB-like lattice distortion breaks the local T_d symmetry into C_{2v}, moving the a_1 state up and the e states down. If the a_1 state is unoccupied and the e states are fully occupied [Fig. 7(c)], such an atomic displacement can lower the electronic energy, in addition to the formation of the strong anion-anion bond. However, breaking two neighboring cation-anion bonds also costs energy. If the AX center becomes stable, it can convert a negatively charged shallow acceptor (e.g., N_{Te}^-) into a positively charged deep donor

[e.g., $AX^+(N_{Te})$], thus limiting the doping process. To see whether the AX center could be a limiting factor for p-type doping in CdTe we have calculated the AX formation energy defined as the energy difference[41,42]

$$\Delta E(AX) = E(AX,q) - E(\alpha,q). \qquad (6)$$

Here $E(AX,q)$ is the total energy of an AX center with charge state q (in most cases $q = +1$) and $E(\alpha,q)$ is the total energy of the corresponding tetrahedrally coordinated defect α at the same charge state. A negative $\Delta E(AX)$ will indicate that the AX center is stable. We find that for Cu_{Cd}^+, the AX center is unstable. It will move back to the original T_d geometry without any energy barrier. For N_{Te}^+, P_{Te}^+, As_{Te}^+, and Sb_{Te}^+, we find that $\Delta E(AX)$ are 1.00, 0.71, 0.66, 0.64 eV, respectively, indicating that the AX centers are only metastable. These results suggest that the energy increase caused by breaking the two cation-anion bonds in forming the AX center is larger than the energy gain by forming a new anion-anion bond [Fig. 7(c)]. The bond-breaking energies increase as the atomic number of the dopant decreases from Sb to As to P to N. The calculated dopant-Te bond lengths are 2.99, 2.75, 2.64, and 2.17 Å, respectively for Sb, As, P, and N. This can be compared with the calculated Te-Te bond length of 4.625 Å in pure CdTe. Our results indicate that the formation of the AX center is not a limiting factor for p-type doping in CdTe.

D. The DX center

Another important defect complex originally proposed by Chadi and Chang[9] is the DX center that compensates donors. DX center often exists in III-V semiconductors[9,43] and has also been reported to present in II-VI compounds.[10,44–46] The DX center forms through a single bond breaking (SBB) model,[9] as shown in Figs. 8 and 9. Here, the substitutional cation defect or Cd next to a substitutional anion defect displaces along the $\langle 111 \rangle$ direction, breaking one bond and changing the local symmetry from T_d to C_{3v}. Accompanied by the displacement, the t_2^c state in the conduction band split into an a_1 and an doubly degenerate e state. The $a_1(t_2^c)$ couples with the $a_1(a_1^c)$ state, pushing one of them down [Fig. 8(c)]. If the a_1 state is occupied (preferentially by two electrons, such as in In_{Cd}^-), such an atomic displacement can lead to electronic energy gain. However, breaking the bond in the $\langle 111 \rangle$ direction also costs energy. If the DX center becomes stable, it can convert a positively charged shallow donor (e.g., In_{Cd}^+) into a negatively charged deep acceptor [e.g., $DX^-(In_{Cd})$], thus limiting the doping process. We have calculated the DX formation energy defined as the the energy difference[41,42]

$$\Delta E(DX) = E(DX,q) - E(\alpha,q). \qquad (7)$$

Here $E(DX,q)$ is the total energy of the DX center at the charge state q (in most cases $q = -1$) and $E(\alpha,q)$ is the total energy of the corresponding tetrahedrally coordinated defect α at the same charge state. A negative $\Delta E(DX)$ will indicate that the DX center is more stable. We find that for Al_{Cd}^-, Ga_{Cd}^-, and In_{Cd}^-, $\Delta E(DX)$ are -0.50, -0.41, and -0.49 eV,
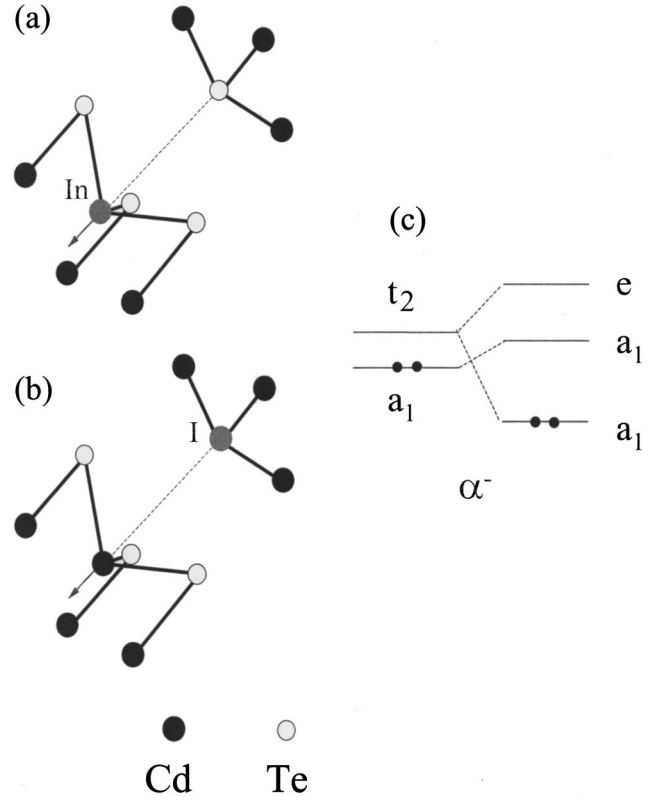

FIG. 8. A schematic plot of the single bond breaking (SBB) model of the DX center for (a) cation substitutional defect and (b) anion substitutional defect. Panel (c) shows schematically how the DX center can be stabilized by the lowering of the electronic energy.

respectively, so they are all stable. This indicates that the DX centers are much more common in this II-VI compound. This is consistent with the fact that as ionicity increases the energy cost in forming the DX centers decreases.[47] Thus, although Al or In substitution on the Cd site creates a shallow donor level when they are tetrahedrally coordinated, they are not good n-type dopants for CdTe because the effective negative-U (α^+/DX^-) transition energy levels are much deeper. For Cl_{Te}^-, Br_{Te}^-, and I_{Te}^-, the calculated $\Delta E(DX)$ are 0.55, 0.28, and -0.17 eV, respectively. Thus, the formation of DX center is not a limiting factor for anion substitutional donor except for I_{Te}.

VIII. EFFECTS OF CODOPING/CLUSTER DOPING

There have been discussions that by using codoping/cluster doping[13–15] one may be able to (a) enhance the dopant solubility by lowering the formation energy of the defect complex through interactions (mostly the Coulomb interaction) between the constituents of the defect complex and (b) lower the defect transition energy levels through the coupling between the donor-acceptor states. We have tested these suggestions by calculating the defect formation energies and defect transition energy levels of the defect complexes $V_{Cd} + Cl_{Te}$, $V_{Cd} + Cu_i$, $2Cu_{Cd} + Cl_{Te}$, $In_{Cd} + 2Sb_{Te}$, and $4Cu_{Cd} + Cl_{Te}$. The calculated charge neutral defect formation energies ΔE are 1.13, 2.72, 1.67, 2.34, and 5.15 eV, respectively,
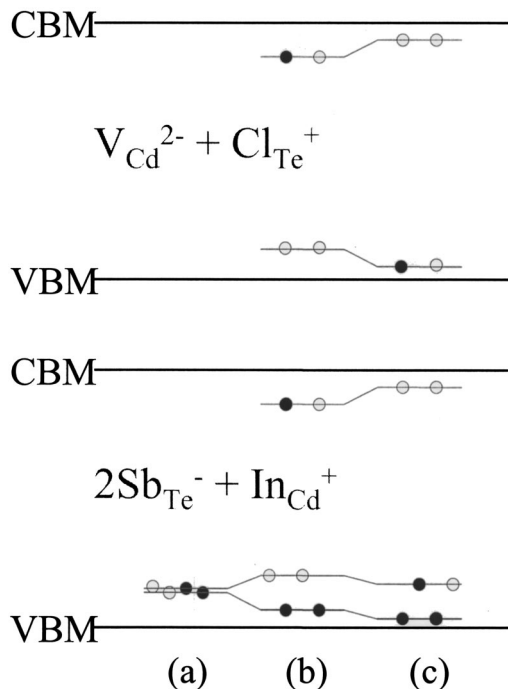
FIG. 9. Schematically plots show the effects of codoping on the transition energy levels. The upper panel shows defect complex has only a single donor and a single acceptor, and the lower panel shows defect complex contains more point defects. Column (a) shows the acceptor levels before the acceptor-acceptor interaction, column (b) shows the effect of acceptor-acceptor interaction but before the donor-acceptor interaction, and column (c) shows the final energy levels after the donor-acceptor interaction.

for these five defect complexes at $\mu_j = 0$. Under equilibrium growth conditions and taking into account of the the accessible chemical potentials, the lowest possible defect formation energies for these charge neutral defect complexes are 1.95, 1.93, 1.70, 1.20, and 3.60 eV, respectively. The calculated $(0/-)$ transition energy levels are at 0.10, 0.17, 0.22, 0.24, and 0.32 eV, respectively. These results show that (a) in general, codoping/cluster-doping does not lower the formation energies of the defect complexes below that of the corresponding single point defects (for V_{Cd}^0, Cu_{Cd}^0, and Sb_{Te}^0, the lowest possible formation energies are 1.88, 0.52, and 1.10 eV, respectively), because the Coulomb interaction between the donors and acceptors is not sufficient enough to compensate the energy cost of creating the extra individual point defects. This is especially true in the case of cluster doping (e.g., $4Cu_{Cd} + Cl_{Te}$) where interaction between the close-packed Cu_{Cd} acceptors also increases the formation energy of the cluster. However, in some cases, the formation energy of the defect complexes (e.g., $V_{Cd} + Cl_{Te}$) are not too much higher than the corresponding point defect (e.g., V_{Cd}), but due to the introduction of new chemical species, one may

have larger freedom to adjust the chemical potentials during growth. Therefore, codoping could be useful in increasing dopant incorporation under nonequilibrium growth conditions, e.g., increasing the Cl chemical potential but limiting the formation of $CdCl_2$ precipitates in CdTe. (b) The calculated defect transition energy level increases by 0.1 eV for $4Cu_{Cd} + Cl_{Te}$ but are essentially unchanged for $2Cu_{Cd} + Cl_{Te}$ and $In_{Cd} + 2Sb_{Te}$ defect complexes with respect to that of Cu_{Cd} and Sb_{Te}. This is because despite the nearest neighbor donor-acceptor coupling lowers the acceptor levels, the acceptor-acceptor interaction raises the acceptor levels. Furthermore, the donor-acceptor level repulsion is weak because the two states have different atomic characters and symmetries. We find that for defect complexes with a single donor and a single acceptor such as $V_{Cd} + Cl_{Te}$, the donor-acceptor coupling lowers the transition energy level by 0.03 eV. Thus, incorporation of a small amount of chlorine in CdTe could be beneficial to the p-type doping in CdTe. This conclusion is consistent with experimental observations of $CdCl_2$ treated samples.[48]

IX. SUMMARY

In summary, using first-principles band structure methods, we have systematically calculated the formation energies and transition energy levels of intrinsic and extrinsic defects in CdTe. We show that p-type doping in CdTe is mostly limited by not having a dopant with both high solubility *and* shallow acceptor level. For example, CdTe:N or CdTe:P have shallow acceptor levels, but their defect formation energies are too high. CdTe:Cu has a relatively low formation energy, but its acceptor level is too deep. In other cases, doping is also limited by the formation of compensating interstitial defects (e.g., Na_i in CdTe:Na). The AX centers are unstable in CdTe, therefore, they are not limiting factors in p-type doping in CdTe. On the other hand, n-type doping in CdTe is limited by the spontaneous formation of intrinsic V_{Cd}^{2-} when the Fermi energy approaches the CBM. In some cases of extrinsic doping [e.g., in CdTe:X, $X = $(Al, Ga, and In)], it is also limited by the formation of the DX centers. Our analysis suggests that overall, Ag and P are likely to be the best p-type dopants and iodine should be the best n-type dopant. Our general understanding of the doping limits in CdTe is expected to be applicable to other II-VI semiconductors, and our results can be used as a guideline to overcome the doping limit in these systems.

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[41] Our definition of *AX* center formation energy is different from the original definition of Park and Chadi (Refs. 11 and 12) who defines $\Delta E(AX) = E(AX^+) - [E(\alpha^-) + E(2h)]$, where $E(2h)$ is the energy of the two holes captured by the defect α^-. because we compare total energy of two defects with the same charge state, we do not need to know accurately the energy levels of the holes and electrons, which are often difficult to determine in small supercell calculations. The two definitions are identical if the defect α has zero U. Similarly, our definition of *DX* center formation energy is different from the original definition of Chadi and Chang (Refs. 9 and 10) who define $\Delta E(DX) = E(DX^-) - [E(\alpha^+) + E(2e)]$, where $E(2e)$ is the energy of the two electrons captured by the defect α^+. Again, the two definitions are identical if the defect α has zero U.

[42] We find that $\Delta E(DX)$ and $\Delta E(AX)$ are very sensitive to the change of the band gap, thus, the *LDA* band gap correction. When the band gap increases (e.g., under pressure), $\Delta E(DX)$ decreases (becoming more stable), whereas $\Delta E(AX)$ increases (becoming less stable). These trends can be traced back to the differences between the atomic characters of these deep level states and that of the corresponding tetrahedrally coordinated shallow defect states.

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