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Carrier density and compensation in semiconductors with multiple dopants and multiple transition energy levels: Case of Cu impurities in CdTe

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Doping is one of the most important issues in semiconductor physics. In many cases, when people describe carrier concentration as a function of dopant density and Fermi energy, they usually assume only one type of dopant with single transition energy level in the system. However, in reality, the situation is often more complicated, that is, in a semiconductor device, it usually contains multidopants and each can have multitransition energy levels. In this paper, using detailed balance theory and first-principles calculated defect formation energies and transition energy levels, we derive formulas to calculate carrier density for semiconductor with multidopants and multitransition energy levels. As an example, we studied CdTe doped with Cu, in which V_{Cd}, Cu_{Cd}, and Cu_i are the dominant defects/impurities. We show that in this system, when Cu concentration increases, the doping properties of the system can change from a poor p-type, to a poorer p-type, to a better p-type, and then to poor p-type again, in good agreement with experimental observations.

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I. INTRODUCTION

One of the most important issues in semiconductor physics is to control the charge carriers through doping. This is because the application of semiconductors as novel electrical and optical devices depends critically on their doping properties.[1–6] For example, CdTe solar cell has a relatively low efficiency (16.5%) (Ref. 7) comparing with its theoretical limit ~29%.[8,9] One of the main reasons is due to the low doping level or hole concentration of CdTe.[10,11] Therefore, to improve its solar conversion efficiency, it is necessary to understand and control its doping properties. Charge carriers can usually be introduced into the system either through intrinsic defects or external impurity doping. Traditionally, dopant is distinguished as donor if the dopant transition energy level is close to the conduction band minimum (CBM), so it is easier to donate an electron to the CBM than to accept an electron from the valence band maximum (VBM), or acceptor if the dopant transition energy level is close to the valence band maximum, so it is easier to accept an electron from the VBM than to donate an electron to the CBM. Based on the number of electrons dopant donates (accepts), it can also be classified as single donor (acceptor) if it can donate (accept) one electron, or double donor (acceptor) if it can donate (accept) two electrons, and so on. Dopant can be further classified as shallow or deep dopant depending on the position of defect level. Although the distinction is not unique, a dopant transition energy level is usually considered shallow if the transition energy level (ionization energy) is less than 0.05 eV from the band edges and deep if more than 0.05 eV.[12] These classifications of dopants are well defined when a single dopant is concerned, as shown in most of the text books;[1,2,12] however, when a system contains multidopants and each dopant has multitransition energy levels, then the situations are more complicated. For example, Sb substitution on the Te site, Sb_{Te}, is a nominal acceptor,[13] but it can behave as a donor when it coexists with a relatively shallower acceptor, Cd vacancy (V_{Cd}), because in this case, electrons at the higher Sb_{Te} level can donate to the lower V_{Cd} level. Moreover, a dopant can usually donate (accept) one or two or even more electrons, thus the dopant can have several charge states and the population of the dopants in each of the charge states depends on the transition energy level, temperature, the coexistence of other defects, and ultimately the resulting Fermi energy of the electrons. A comprehensive understanding of how to treat these complicated situation has not been presented in the common text books,[1,2,12] which usually describe, for simplicity, only single donor or acceptor.

In this paper, we will first derive some general formulas to show how to calculate charge carrier concentrations as a function of temperature and dopant concentrations when a system contains multidopants with multitransition energy levels. In our approach, all the dopants are treated equally, i.e., we do not preclassify the dopants. The charge states of the dopants are obtained self-consistently. To be more concrete, we will use the doping of Cu in CdTe as an example to describe how the formulas are derived and how dopants interact with each other. The concept can be easily extended to other semiconductor systems. We choose CdTe:Cu as an example because CdTe is one of the most important thin-film solar cell materials and it generally contains Cd vacancies as the most important intrinsic defect, which is a double acceptor, and Cu as an important impurity for improving the efficiency. Cu substitution on Cd site, Cu_{Cd}, is usually a single acceptor and Cu interstitial, Cu_i, is usually a single donor. Experimentally, the observed effect of Cu on p-type doping in CdTe is very interesting.[14–17] After the CdTe polycrystalline, thin film is deposited using a method such as close space sublimation (CSS), and a $CdCl_2$ process is performed, the film is coated with ZnTe:Cu, followed by annealing at a certain temperature for back contact. The concentration of Cu in the sample is controlled by the annealing temperature. It is noticed that very low level of Cu inclusion may further reduce the already low conductivity (due to low p-doping level) of the intrinsic CdTe thin film. Increasing the level of Cu involvement to a certain level, a reversal from deterioration to improvement of conductivity occurs, which leads to an optimized CdTe

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thin film confirmed by the high efficiency of the solar cell. Further incorporation of Cu into CdTe, however, will turn it from p-type to insulating, or even n-type. Such a complicated and puzzling effect on the property and quality of the CdTe thin film—turning from a poor p-type to a poorer p-type, then to a better and optimized p-type, and then to insulating, when Cu incorporation in CdTe increases—has not been fully understood or explained.

In the following discussion, we will assume that the dominant dopant in CdTe is V_{Cd}, Cu_{Cd}, and Cu_i. We will calculate the hole concentration in CdTe as a function of Cu incorporation using the detailed balance theory with input parameters obtained from first-principles calculations. We find that the above discussed puzzling effect can be explained qualitatively by the interaction between the Cd vacancy states and the Cu impurity states, as well as the self-compensation of the Cu impurity states. The model proposed here is suitable for other complicated systems.

II. THEORETICAL DESCRIPTION

The concentrations of holes (positive charge) and electrons (negative charge) in the system are given by

$$\begin{aligned} p_0 &= N_v e^{(E_v - E_f)/k_B T} = N_v e^{-E_f/k_B T} \\ n_0 &= N_c e^{-(E_c - E_f)/k_B T} = N_c e^{(E_f - Eg)/k_B T}, \end{aligned} \tag{1}$$

where E_f is Fermi energy, E_v and E_c are VBM and CBM energies, and N_v and N_c are the effective density of states of the valence bands and conduction bands, respectively. It is usually convenient to set $E_v = 0$ and $E_c = E_g$, where E_g is the band gap. For CdTe at room temperature, we use $E_g = 1.5$ eV. The equations above are based on nondegenerate statistics. They are excellent approximations as far as the Fermi energy is several $k_B T$ away from band edges, which is true for a wide range of semiconductor applications. For a few cases, as the Fermi energy is close to band edges, degenerate statistics, i.e., Fermi-Dirac formula, has to be employed instead. The generalization of the equations is straightforward.[1,18] Assuming parabolic band, the effective density of states, N_v and N_c, are given by

$$\begin{aligned} N_v &= \frac{2(2\pi m_p^* k_B T)^{3/2}}{h^3} \\ N_c &= \frac{2(2\pi m_n^* k_B T)^{3/2}}{h^3}. \end{aligned} \tag{2}$$

The effective mass, including the spin degeneracy and spin-orbit coupling in the valence band are given by

$$\begin{aligned} m_p^* &= \left[(m_p)_l^{3/2} + (m_p)_h^{3/2}\right]^{2/3} \\ m_n^* &= m_n. \end{aligned} \tag{3}$$

For CdTe, $m_p^* = 0.84 m_0$ and $m_n^* = 0.095 m_0$ (Ref. 19), with m_0 is the mass of free electron. Without any dopant, the charge neutrality condition requires

$$p_0 = n_0, \tag{4}$$

which gives the intrinsic value $E_f = 0.792$ eV and $p_0 = n_0 = 9.7 \times 10^5$ cm^{-3} at $T = 300$ K for CdTe. After doping, the dopants in the system are partially ionized at a finite temperature. Suppose the concentrations of negative and positive charge induced by dopant ionizations are N_A^- and N_D^+, the charge neutrality condition requires

$$p_0 + N_D^+ = n_0 + N_A^- \ . \tag{5}$$

Solving this equation self-consistently, we can get the Fermi energy and hole/electron concentration at equilibrium as a function of temperature and dopant concentrations.

For a system with a dopant α that has multiple charge states, the number of the dopant α in charge state q is given by

$$n_\alpha(q) \propto g_q e^{-\Delta H_f(\alpha,\, q)/k_B T}, \tag{6}$$

so we first need to know the formation energy of dopant α at charge state q and its degeneracy factor g_q, which is the number of possible electron configurations. For a single defect level that can hold one spin-up and one spin-down electron, such as those derived from CBM, the number of possible electron configurations is given by $\binom{2}{n} = 1, 2$, and 1, when this defect level has no electron, one electron, or two electrons ($n = 0$, 1, 2). For a doubly degenerate level that can hold up to two spin-up and two spin-down electrons, such as those derived from VBM of zinc-blende semiconductors with light hole and heavy hole states, the number of possible configurations is $\binom{4}{n} = 1,4,6,4,1$, when this defect level has $n = 0,1,2,3$, or 4 electrons. Similar degeneracy factor g_q can be derived for other situations. In general, $g_q = \sum_i \exp(-E_i/k_B T)$ with the summation over all the possible configurations, where E_i is the energy of the ith configuration relative to the lowest energy $E_1 = 0$. For simplicity, we assume the energies are all the same, i.e., $E_i = 0$ for all configurations, which is true for most cases. However, for some cases, such as neutral V_{Cd}, the assumption does not hold exactly. But even in this case, our test calculations show that the reduction of g_q does not affect our results below.

Let us first consider that the system contains only Cd vacancies. The formation energy of Cd vacancy in various charged state is given by[4,20]

$$\begin{aligned} \Delta H_f(V_{cd},0) &= \Delta E(V_{Cd},0) + \mu_{Cd} \\ \Delta H_f(V_{Cd},-) &= \Delta H_f(V_{Cd},0) + \epsilon_{V_{Cd}}(0/-) - E_f \\ \Delta H_f(V_{Cd},2-) &= \Delta H_f(V_{Cd},0) + \epsilon_{V_{Cd}}(0/-) \\ &\quad + \epsilon_{V_{Cd}}(-/2-) - 2E_f, \end{aligned} \tag{7}$$

where $\Delta E(V_{Cd},0)$ is the formation energy of neutral V_{Cd} referenced to bulk Cd, i.e., at chemical potential $\mu_{Cd} = 0$, and $\epsilon_{V_{Cd}}(q/q')$ is the transition energy level of V_{Cd} from charge state q to q'. All the formation energy and transition energy levels of the involved dopant states are listed in Table I. They are calculated using first-principles supercell approaches as described in Ref. 20.

If there are totally $N_{V_{Cd}}$ vacancies in the system, we have

$$N_{V_{Cd}} = n_{V_{Cd}}(0) + n_{V_{Cd}}(-) + n_{V_{Cd}}(2-), \tag{8}$$

where $n_{V_{Cd}}(q)$ is the number of V_{Cd} in charge state q. The probability that V_{Cd} is in charge state q is obtained from Eq. (6). At neutral charge state, the defect level, which is four-fold degenerate (including spin), has two electrons and two holes, so under our assumption $g_0 = 6$; after ionization, $g_- = 4$ because for $q = -1$, there is one hole and three electrons on the defect level, and $g_{2-} = 1$ because all the states are now occupied.

With Eqs. (6)–(8), we have

$$
\begin{aligned}
n_{V_{Cd}}(0) &= N_{V_{Cd}} \frac{6}{6 + 4e^{-(\epsilon_{V_{Cd}}(0/-)-E_f)/k_BT} + e^{-(\epsilon_{V_{Cd}}(0/-)+\epsilon_{V_{Cd}}(-/2-)-2E_f)/k_BT}} \\
n_{V_{Cd}}(-) &= N_{V_{Cd}} \frac{4e^{-(\epsilon_{V_{Cd}}(0/-)-E_f)/k_BT}}{6 + 4e^{-(\epsilon_{V_{Cd}}(0/-)-E_f)/k_BT} + e^{-(\epsilon_{V_{Cd}}(0/-)+\epsilon_{V_{Cd}}(-/2-)-2E_f)/k_BT}} \\
n_{V_{Cd}}(2-) &= N_{V_{Cd}} \frac{e^{-(\epsilon_{V_{Cd}}(0/-)+\epsilon_{V_{Cd}}(-/2-)-2E_f)/k_BT}}{6 + 4e^{-(\epsilon_{V_{Cd}}(0/-)-E_f)/k_BT} + e^{-(\epsilon_{V_{Cd}}(0/-)+\epsilon_{V_{Cd}}(-/2-)-2E_f)/k_BT}}.
\end{aligned}
\tag{9}
$$

The chemical potential of Cd (μ_{Cd}) does not appear in the equations. The concentration of negative charge induced by Cd vacancies is

$$N_{V_{Cd}}^{-} = n_{V_{Cd}}(-) + 2n_{V_{Cd}}(2-). \tag{10}$$

Solving Eq. (5) self-consistently, we can get the Fermi energy and carrier concentrations. For example, we find $E_f = 0.112$ eV, $p_0 = 2.53 \times 10^{17}$ cm^{-3} when $N_{V_{Cd}} = 10^{18}$ cm^{-3} and $E_f = 0.245$ eV, $p_0 = 1.48 \times 10^{15}$ cm^{-3} when $N_{V_{Cd}} = 10^{15}$ cm^{-3} at room temperature ($T = 300$ K). Note that as $N_{V_{Cd}}$ decreases, E_f approaches its intrinsic value (0.792 eV) as expected. In that case, all the Cd vacancies are doubly ionized.

Next, we consider how dopants interact with each other in a multidopant system. As an example, we dope Cu into the CdTe system which initially has Cd vacancies. Cu can form either Cu$_{Cd}$ or Cu$_i$. For Cu$_{Cd}$, the formation energy of various charged states is given by

$$
\begin{aligned}
\Delta H_f(\mathrm{Cu_{Cd}},0) &= \Delta E(\mathrm{Cu_{Cd}},0) + \mu_{Cd} - \mu_{Cu} \\
\Delta H_f(\mathrm{Cu_{Cd}},-) &= \Delta H_f(\mathrm{Cu_{Cd}},0) + \epsilon_{\mathrm{Cu_{Cd}}}(0/-) - E_f.
\end{aligned}
\tag{11}
$$

Due to the existence of Cd vacancy, there are $N_{Cd} - N_{V_{Cd}} \approx N_{Cd}$ possible sites left, where N_{Cd} is the number of total Cd sites. The population is given by

$$n_{\mathrm{Cu_{Cd}}}(q) \propto g_q N_{Cd} e^{-\Delta H_f(\mathrm{Cu_{Cd}},\, q)/k_BT}, \tag{12}$$

where g_q is the degeneracy of charged q state. In this case, $g_0 = 4$ and $g_- = 1$ due to the spin and light/heavy hole degeneracy. Note that g_0 for the double acceptor V$_{Cd}$ is different from g_0 for the single acceptor Cu$_{Cd}$. For Cu$_i$, the formation energy of various charged states is given by

$$
\begin{aligned}
\Delta H_f^{a(c)}(\mathrm{Cu_i},0) &= \Delta E^{a(c)}(\mathrm{Cu_i},0) - \mu_{Cu}, \\
\Delta H_f^{a(c)}(\mathrm{Cu_i},+) &= \Delta H_f^{a(c)}(\mathrm{Cu_i},0) + E_f - \epsilon_{\mathrm{Cu_i}}(0/+).
\end{aligned}
\tag{13}
$$

TABLE I. The calculated formation energies of neutral defects at $\mu_i = 0$ and transition energy levels (measured from VBM) of various dopant states involved. All the values in the table are from Ref. 20.

Formation energy (eV)		Transition energy level (eV)	
$\Delta E(\mathrm{V_{Cd}},0)$	2.67	$\epsilon_{V_{Cd}}(0/-)$	0.13
		$\epsilon_{V_{Cd}}(-/2-)$	0.21
$\Delta E(\mathrm{Cu_{Cd}},0)$	1.31	$\epsilon_{\mathrm{Cu_{Cd}}}(0/-)$	0.22
$\Delta E(\mathrm{Cu_i},0)$	2.14^a (2.24^c)	$\epsilon_{\mathrm{Cu_i}}(0/+)$	1.51

The a and c denote two kinds of interstitial sites: surrounded with cation and anion, which have N_i^a and N_i^c possible sites, respectively. We can absorb the formation energy difference into the prefactor and the population can be given by

$$n_{\mathrm{Cu_i}}(q) = n_{\mathrm{Cu_i}}^a(q) + n_{\mathrm{Cu_i}}^c(q) \propto g_q N_i e^{-\Delta H_f(\mathrm{Cu_i},\, q)/k_BT}, \tag{14}$$

where $N_i = N_i^a + N_i^c \exp[(\Delta H_f^a - \Delta H_f^c)/k_BT] = N_i^a(1 + \exp[-0.1\ \mathrm{eV}/k_BT])$ and $\Delta H_f = \Delta H_f^a$. In this case, $g_0 = 2$ and $g_+ = 1$ due to the spin degeneracy. The formation energy of these defects is shown in Fig. 1.

Since there are Cd vacancies in the system, Cu can occupy these vacancy sites, which is labeled as Cu$_V$. Note that because the formation energy of Cu$_V$

$$\Delta E(\mathrm{Cu_V},0) = \Delta E(\mathrm{Cu_{Cd}},0) - \Delta E(\mathrm{V_{Cd}},0) = -1.36\ \mathrm{eV} \tag{15}$$

is strongly negative, Cu will occupy Cd vacancies to form Cu$_V$ spontaneously until no Cd vacancies are available. Therefore, when the concentration of Cu $N_{Cu} < N_{V_{Cd}}$, we only need to consider V$_{Cd}$ and Cu$_V$. In this case, if the number of Cu in the system is N_{Cu}, we have $n_{\mathrm{Cu_V}} = N_{Cu}$ [$n_{\mathrm{Cu_V}} = n_{\mathrm{Cu_V}}(0) + n_{\mathrm{Cu_V}}(-)$ denotes the total concentration of Cu$_V$; similar notations are used also for other defects] and $n_{V_{Cd}} = N_{V_{Cd}} - N_{Cu}$. In general, if the formation energies of several dopants are comparable, the simplification above is

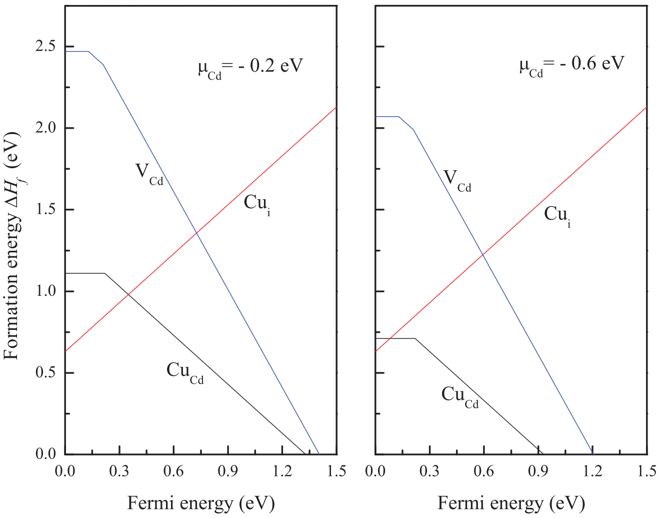

FIG. 1. (Color online) The formation energy of involved defects as a function of Fermi energy at both Cd-rich ($\mu_{Cd} = -0.2$ eV) and poor cases ($\mu_{Cd} = -0.6$ eV). In the plots, $\mu_{Cu} = 0$ eV. The lines cross at positions where Fermi energy may be pinned.

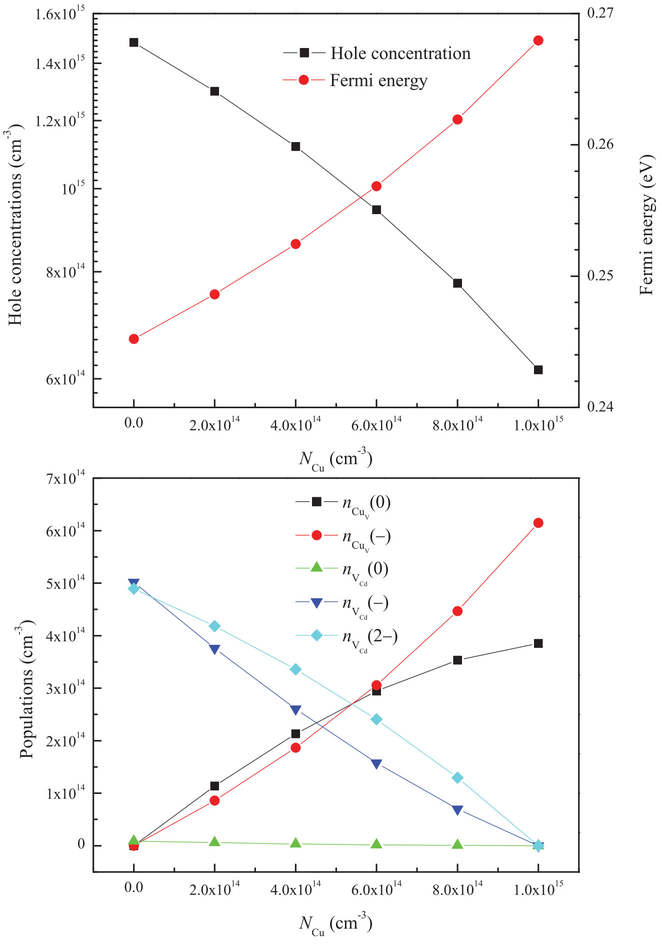

FIG. 2. (Color online) The top panel is the hole concentration (black square) and Fermi energy (red dot) versus N_{Cu} and the bottom one is the populations of defects at various charged states. At very low Cu concentration, all Cu go to vacancy sites. The hole concentration decreases as Cu density increases. In this calculation, initial Cd vacancy concentration is $N_{V_{\mathrm{Cd}}} = 10^{15}$ cm^{-3}, $\mu_{\mathrm{Cd}} = -0.2$ eV and $T = 300$ K. The result here does not depend on the chemical potential of Cd.

not valid. In that case, all the dopants have to be treated equally.[21–23] However, in our case, the formation energy of $\mathrm{Cu_V}$ is much lower than others. The test calculations show that the error induced by the simplification in this system is negligible. Assuming initially $N_{V_{\mathrm{Cd}}} = 10^{15}$ cm^{-3} and $T = 300$ K, solving Eq. (5) self-consistently, we obtain the concentration of holes and the populations of defects at various charged states, which are plotted in Fig. 2. Because the transition energy level of $\mathrm{Cu_V}$, which is the same as that of $\mathrm{Cu_{Cd}}$, is higher than that of $\mathrm{V_{Cd}}$, as the concentration of Cu increases the concentration of hole decreases. This result does not depend on the chemical potential of Cd. This explains why initially the system turns from a poor p-type to a poorer p-type when the Cu is introduced at a very low concentration.

Next, we add more Cu into the system. Since when $N_{\mathrm{Cu}} > N_{V_{\mathrm{Cd}}}$ all the Cd vacancies are transformed into $\mathrm{Cu_V}$ ($n_{\mathrm{Cu_V}} = N_{V_{\mathrm{Cd}}}$ and $n_{V_{\mathrm{Cd}}} = 0$), the problem is equivalent to dope CdTe with Cu and the system already contains $N_{V_{\mathrm{Cd}}}$ $\mathrm{Cu_{Cd}}$ defects with no Cd vacancies. We only need to consider $\mathrm{Cu_{Cd}}$ and $\mathrm{Cu_i}$. If we dope N'_{Cu} more Cu into the system, i.e., $N_{\mathrm{Cu}} = N'_{\mathrm{Cu}} + N_{V_{\mathrm{Cd}}}$, then

$$N'_{\mathrm{Cu}} = n_{\mathrm{Cu_{Cd}}}(0) + n_{\mathrm{Cu_{Cd}}}(-) + n_{\mathrm{Cu_i}}(0) + n_{\mathrm{Cu_i}}(+). \qquad (16)$$

The populations of various Cu defects in CdTe are given by

$$\begin{aligned}
n_{\mathrm{Cu_V}}(0) &= N_{V_{\mathrm{Cd}}} \frac{4}{4 + e^{-(\epsilon_{\mathrm{Cu_{Cd}}}(0/-)-E_f)/k_BT}}\\
n_{\mathrm{Cu_V}}(-) &= N_{V_{\mathrm{Cd}}} \frac{e^{-(\epsilon_{\mathrm{Cu_{Cd}}}(0/-)-E_f)/k_BT}}{4 + e^{-(\epsilon_{\mathrm{Cu_{Cd}}}(0/-)-E_f)/k_BT}}\\
n_{\mathrm{Cu_{Cd}}}(0) &= N'_{\mathrm{Cu}} \frac{4N_{\mathrm{Cd}} e^{-\Delta H_f(\mathrm{Cu_{Cd}},0)/k_BT}}{f_d} \qquad (17)\\
n_{\mathrm{Cu_{Cd}}}(-) &= N'_{\mathrm{Cu}} \frac{N_{\mathrm{Cd}} e^{-\Delta H_f(\mathrm{Cu_{Cd}},0)/k_BT} e^{-(\epsilon_{\mathrm{Cu_{Cd}}}(0/-)-E_f)/k_BT}}{f_d}\\
n_{\mathrm{Cu_i}}(0) &= N'_{\mathrm{Cu}} \frac{2N_i e^{-\Delta H_f(\mathrm{Cu_i},0)/k_BT}}{f_d}\\
n_{\mathrm{Cu_i}}(+) &= N'_{\mathrm{Cu}} \frac{N_i e^{-\Delta H_f(\mathrm{Cu_i},0)/k_BT} e^{-(E_f-\epsilon_{\mathrm{Cu_i}}(0/+))/k_BT}}{f_d},
\end{aligned}$$

where the denominator

$$\begin{aligned}
f_d = {}& N_{\mathrm{Cd}} e^{-\Delta H_f(\mathrm{Cu_{Cd}},0)/k_BT}\left(4 + e^{-(\epsilon_{\mathrm{Cu_{Cd}}}(0/-)-E_f)/k_BT}\right)\\
&+ N_i e^{-\Delta H_f(\mathrm{Cu_i},0)/k_BT}\left(2 + e^{-(E_f-\epsilon_{\mathrm{Cu_i}}(0/+))/k_BT}\right). \qquad (18)
\end{aligned}$$

In the equations above, the chemical potential of Cu disappears because only Cu impurity is considered here. However, the results depend on chemical potential of Cd because of the formation of $\mathrm{Cu_{Cd}}$. Solving Eq. (5) with $N_A^- = n_{\mathrm{Cu_V}}(-) + n_{\mathrm{Cu_{Cd}}}(-)$ and $N_D^+ = n_{\mathrm{Cu_i}}(+)$ self-consistently, we can get the hole concentration as well as the concentration of dopants at various forms and charge states.

III. RESULTS AND DISCUSSIONS

Since the formation energy and populations of defects depend on the chemical potential of Cd, we will first investigate its effect on carrier concentration. Under the Cd-rich growth condition ($\mu_{\mathrm{Cd}} \sim 0$), the formation energy of $\mathrm{Cu_i}(+)$ in a p-type sample (i.e., the Fermi energy is close to VBM) is smaller than that of $\mathrm{Cu_{Cd}}$, so Cu prefers to go to the interstitial sites which compensate the p-type dopants. Therefore, the hole concentration will keep decreasing as Cu concentration increases. However, under Cd-poor condition, $\mu_{\mathrm{Cd}} \sim \Delta H(\mathrm{CdTe}) = -0.8$ eV (Ref. 20), the formation energy of $\mathrm{Cu_i}$ is larger than that of $\mathrm{Cu_{Cd}}$ and Cu prefers to be at the substitutional site as an acceptor. Therefore, the hole concentration increases. To verify it, we perform calculations with μ_{Cd} equal to -0.2 eV and -0.6 eV, and the results are plotted in Figs. 3 and 4, respectively. In Fig. 3, the chemical potential of Cd is -0.2 eV (Cd-rich case). The hole concentration decreases and the Fermi energy increases monotonically as most Cu go to interstitial sites. Since the Fermi energy is far away from the VBM, almost all Cu impurities are ionized. The fact that ionized $\mathrm{Cu_i}$ are more than $\mathrm{Cu_{Cd}}$ explains the dropping of the hole concentration. As N_{Cu} increases, the Fermi energy is eventually pinned at a position at which equal amounts of substitutional Cu and interstitial Cu are formed, and the hole concentration keeps

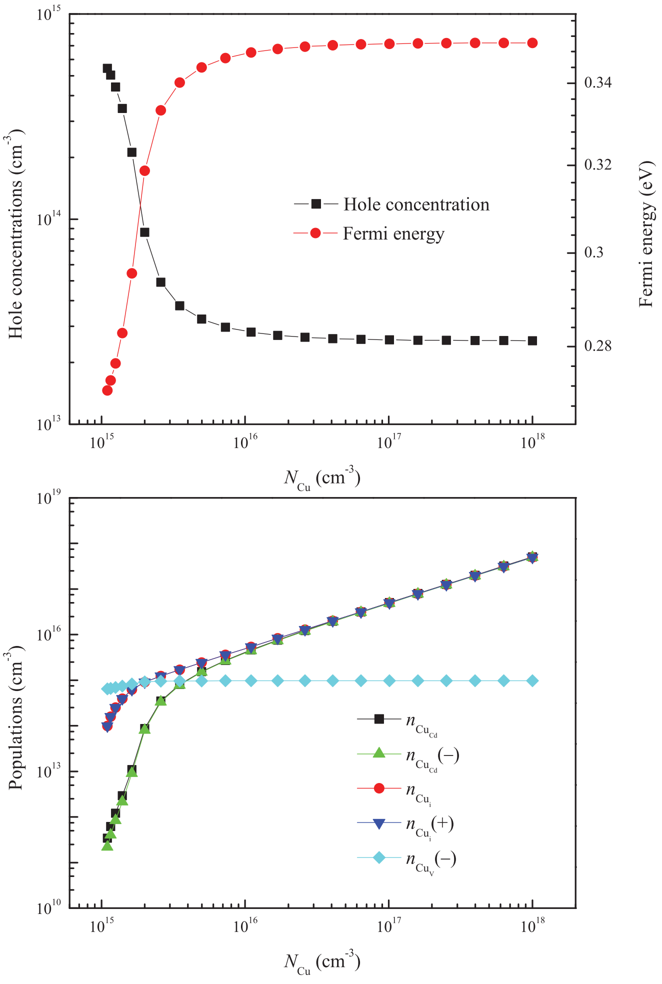

FIG. 3. (Color online) The top panel is the hole concentration (black square) and Fermi energy (red dot) versus N_{Cu} and the bottom one is the populations of defects at various charged states. In the calculation, $T = 300$ K and $\mu_{\mathrm{Cd}} = -0.2$ eV. The hole concentration decreases monotonically and eventually the Fermi energy is pinned. Cu prefers $\mathrm{Cu_i}$. Almost all the Cu defects are ionized. The concentration of ionized $\mathrm{Cu_i}$ is larger than that of $\mathrm{Cu_{Cd}}$, which explains the deceasing of the hole concentration.

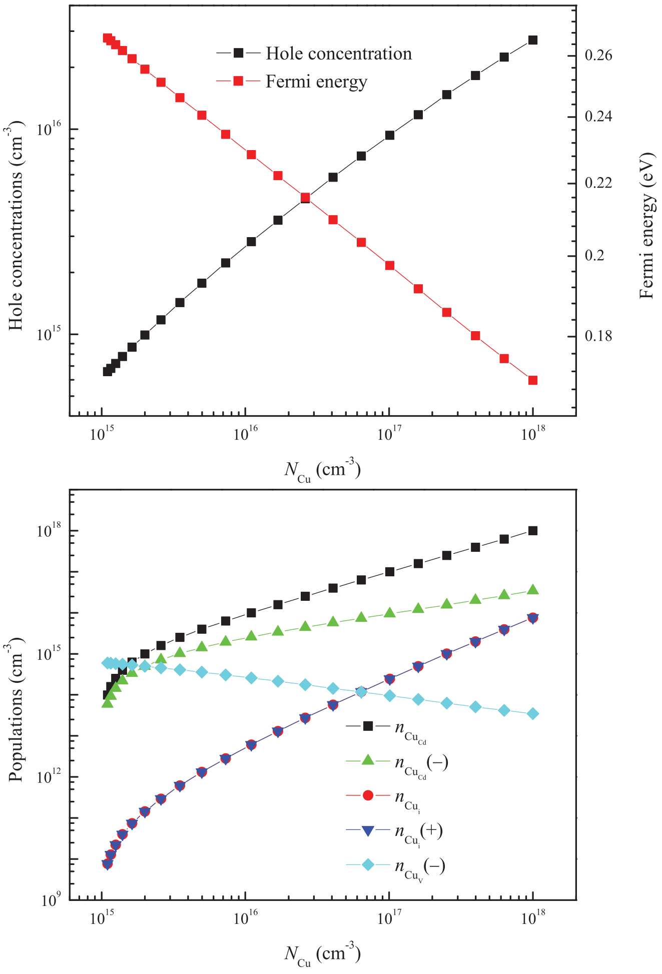

FIG. 4. (Color online) The top panel is the hole concentration (black square) and Fermi energy (red dot) versus N_{Cu} and the bottom one is the populations of defects at various charged states. In the calculation, $T = 300$ K and $\mu_{\mathrm{Cd}} = -0.6$ eV. The hole concentration increases monotonically. Cu prefers $\mathrm{Cu_{Cd}}$. All the $\mathrm{Cu_i}$ are ionized, but only a small portion of $\mathrm{Cu_{Cd}}$ is ionized. The concentration of ionized $\mathrm{Cu_{Cd}}$ is larger than that of $\mathrm{Cu_i}$, which explains the increasing of the hole concentration.

unchanged. In Fig. 4, the chemical potential of Cd is -0.6 eV (Cd poor case). The concentration of hole increases as most Cu go to the substitutional site and the Fermi energy decreases monotonously. Since the Fermi energy is close to VBM, only a part of $\mathrm{Cu_{Cd}}$ is ionized but all $\mathrm{Cu_i}$ are ionized. However, because Cu prefers $\mathrm{Cu_{Cd}}$ sites, the concentration of ionized $\mathrm{Cu_{Cd}}$ is still larger than that of $\mathrm{Cu_i}$, which explains the increasing of holes. Similar to the Cd-rich case, the Fermi energy will also be eventually pinned above the VBM (Fig. 1) as N_{Cu} increases and the hole concentration will stop increasing. It is clear from the above analysis that the behavior of Cu doping depends sensitively on the chemical potential of Cd. With a low μ_{Cd}, one may observe a turning from poor p-type to better p-type, which eventually saturates. However, the turning from better p-type to insulating is not observed under these equilibrium doping conditions.

In realistic experiments, incorporation of Cu is usually done at a high temperature such as 600 K and the sample is then quenched to room temperature (300 K) for measuring the carrier density. In this case, the populations of $\mathrm{Cu_{Cd}}$ ($n_{\mathrm{Cu_{Cd}}}$) and $\mathrm{Cu_i}$ ($n_{\mathrm{Cu_i}}$) should be calculated at doping temperature and the hole concentration should be calculated at the measuring temperature. Since the formation energy of ionized defects also depend on the Fermi energy, we have to do self-consistent calculations twice: first, self-consistently calculating the populations of $\mathrm{Cu_{Cd}}$ and $\mathrm{Cu_i}$ at doping temperature and then, assuming the impurity has difficulty to change its sites preference at low temperature, keeping the impurity populations fixed and calculating the hole concentration at measuring temperature self-consistently. We have performed the calculations with $\mu_{\mathrm{Cd}} = -0.2$ eV and $\mu_{\mathrm{Cd}} = -0.6$ eV, respectively. The results are shown in Figs. 5 and 6, respectively. They both show a clear peak of hole concentration, which is in agreement with the experiments—turning from poor p-type to better p-type and then to poor p-type again. At high temperature (600 K), due to the large intrinsic excitation, the Fermi energy is closer

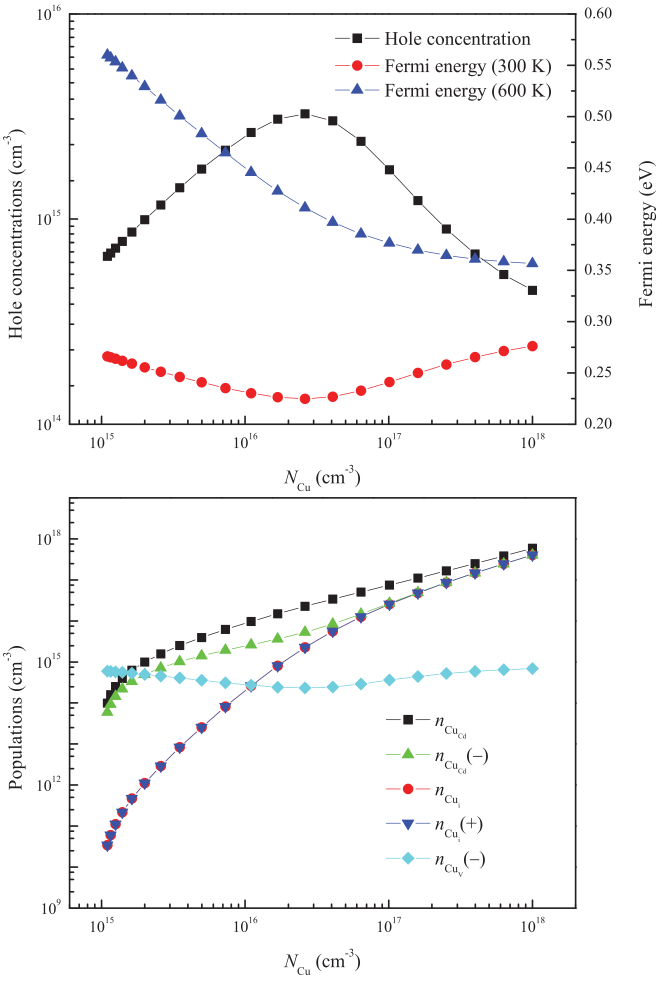

FIG. 5. (Color online) The top panel is the hole concentration (black square) and Fermi energies at growing (blue triangle) and measuring (red dot) temperature versus N_{Cu} and the bottom one is the populations of defects at various charged states at measuring temperature. In the calculation, the populations of Cu_{Cd} and Cu_i are calculated self-consistently at 600 K and hole concentration is calculated self-consistently at 300 K. $\mu_{Cd} = -0.2$ eV. A clear peak of hole concentration has been built up.

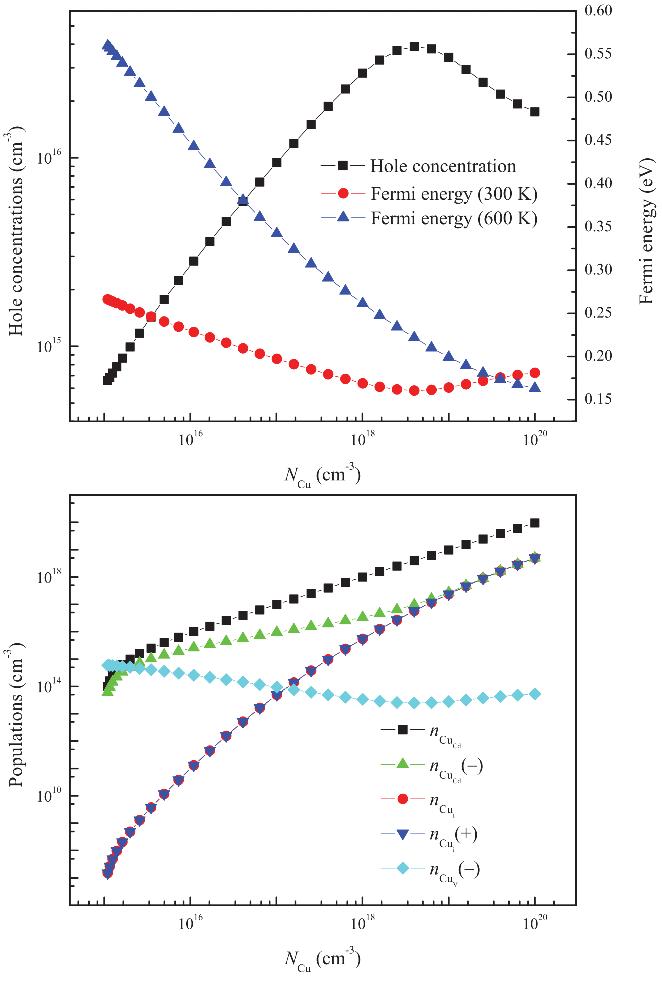

FIG. 6. (Color online) The top panel is the hole concentration (black square) and Fermi energies at growing (blue triangle) and measuring (red dot) temperature versus N_{Cu} and the bottom one is the populations of defects at various charged states at measuring temperature. In the calculation, the populations of Cu_{Cd} and Cu_i are calculated self-consistently at 600 K and hole concentration is calculated self-consistently at 300 K. $\mu_{Cd} = -0.6$ eV. A clear peak of hole concentration has been built up.

to the middle of the band gap, especially at low dopant concentration. Since the formation energy of ionized Cu_{Cd} is lower than that of Cu_i at high Fermi energy, Cu will go to the substitutional site and the Fermi energy keeps dropping. This explains the increase of hole concentration. However, as more Cu are doped into the system, the Fermi energy at high temperature tends to be pinned and the hole concentration at high temperature does not change. In both Cd-rich and Cd-poor cases, Cu prefers Cu_{Cd} which are partially ionized, whereas all the Cu_i are ionized. When the system is quenched to room temperature, because the Fermi energy is lowered at low temperature, closer to VBM, the ratio of ionized Cu_{Cd} decreases but the ratio of ionized Cu_i is not affected (Figs. 5 and 6). In this case, increasing Cu concentration increases the Fermi energy, which explains the decrease of hole concentration at room temperature. In another word, the difference between the concentrations of ionized Cu_{Cd} and Cu_i at room temperature ($n_{Cu_{Cd}}(-) - n_{Cu_i}(+)$) determines the peak position. The peak value of hole concentration increases and the peak appears at higher Cu doping level, as μ_{Cd} decrease, therefore, becoming more Cd poor. Combining this peak with the dropping of hole concentration in Fig. 2 (top panel), the puzzling effect—turning from a poor p-type, to a poorer p-type, to a better p-type, and to poor p-type again—can be understood by the interaction between Cu impurities and Cd vacancies in the system.

IV. CONCLUSION

In conclusion, in this paper, we described how to derive carrier concentration as a function of Fermi energy and dopant concentration in a multidopant and multitransition energy level system. By analyzing the competition between the dominant defects V_{Cd}, Cu_{Cd}, and Cu_i using the concept described in this paper, we have successfully explained why the properties of the CdTe thin film show such puzzling changes—turning from a poor p-type, to a poorer p-type, to a better p-type, and to poor p-type again when the Cu doping level is gradually increased. The model proposed here can be applied to other multidopant and multitransition energy level systems.

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