

Local Charge Neutrality Condition, Fermi Level, and Carrier Compensation of CdTe Polycrystalline Thin Film in CdS/CdTe Solar Cells

Ken K. Chin¹ and Su-Huai Wei²

¹ Department of Physics and
Apollo CdTe Solar Energy Research Center, NJIT, Newark, NJ 07102

² National Renewable Energy Laboratory, Golden, CO 80401

ABSTRACT

In this paper we discuss the classification of localized intrinsic/impurity defect states in the band gap of semiconductors according to the charging and transition energy levels of the state being single or multiple, and according to the atomic configuration and formation of energy of the state being single or multiple. For semiconductors that have multi-level intrinsic/impurity defect states (such as Cd vacancies $V_{Cd}^{(0/-)}$ and $V_{Cd}^{(-2-)}$ in CdTe thin film), the general formulation of charge neutrality condition is given to determine the Fermi level and majority carrier density. For semiconductors that have multi-configuration intrinsic/impurity defect states (such as acceptor Cu_{Cd} and donor Cu_i in CdTe), the concept of transformation of state and self-compensation is introduced and discussed. The effect of state transformation and self-compensation on charge neutrality condition, Fermi level, and majority carrier density is explored. Numerical examples are given for CdTe to illustrate the relevance and importance of multi-level and multi-configuration intrinsic/impurity defect states for understanding the performance of CdTe thin film photovoltaics (PV).

I. Classification of Localized Intrinsic/Impurity Defect Midgap States of Semiconductors

We may classify the localized intrinsic/impurity defect midgap states in a semiconductor as

(1) Dopants and Deep Levels

Localized intrinsic/impurity defect electronic states in the bandgap of a semiconductor are usually classified as dopants and deep levels, based on the closeness of their ionization energy levels to the band edge [1-3]. They are defined as (shallow) dopants if their ionization or activation energy levels are less than 0.05 eV from the band edge, and as deep levels if greater than 0.05 eV [2]. The dopant dopes the semiconductor, determining its type (n or p), Fermi level, and majority carrier density. The deep levels may compensate the doping level of the dopants, but are mostly treated as Shockley-Read-Hall (SRH) generation-recombination centers, with negative impact on the performance of most devices, including solar cells. Such a classification and description of the midgap states in a semiconductor is appropriate for most widely used semiconductor materials, such as Si and GaAs, which is usually intentionally doped with a single dominant dopant state of shallow energy level [1, 2], and inadvertently incorporated with undesired deep levels with concentration at least one order lower than that of the dopant. It is widely quoted in the literature

$$\left\{ \begin{array}{ll} \text{For n - type} & n \approx N_D^+ \approx N_D \quad \text{or} \quad n \approx N_D - N_A \quad \text{with compensation by acceptors} \\ \text{For p - type} & p \approx N_A^- \approx N_A \quad \text{or} \quad p \approx N_A - N_D \quad \text{with compensation by donors} \end{array} \right. \quad (1)$$

where n and p are the electron and hole density, and $N_D, N_D^+, N_A,$ and N_A^- are the concentrations of donors, ionized donors, acceptors, and ionized acceptors, respectively.

(2) Shallow Dopants and Non-shallow Dopants

Classification of intrinsic/impurity defect states as dopants and deep levels based on equation (1) may not be appropriate for wide bandgap materials, including CdTe, which may lack of fully ionized shallow dopants [4 – 8]. Following the Fermi-Dirac statistics, the probabilities of ionization of a donor state and of an acceptor state are referred to the Fermi level E_F

$$\begin{cases} N_D^+ = N_D \frac{1}{1 + g_D \exp\left(\frac{E_F - E_D}{kT}\right)} \\ N_A^- = N_A \frac{1}{1 + g_A \exp\left(\frac{E_A - E_F}{kT}\right)} \end{cases} \quad (2)$$

where g_D and g_A the degeneracy of the donor and acceptor states, respectively [9]. $g_D = 2$ due to spin degeneracy, and g_A depends on the material. For tetrahedral semiconductors, such as Si, GaAs, and CdTe, $g_A = 4$; in addition to spin degeneracy, acceptor has the heavy hole and light hole degeneracy [1]. $kT = 0.0259$ eV. By introducing

$$\begin{cases} E_D' = E_D - kT \ln g_D \\ E_A' = E_A + kT \ln g_A \end{cases} \quad (3)$$

the ionization or activation probability of the states can be simplified as

$$\begin{cases} N_D^+ = N_D \frac{1}{1 + \exp\left(\frac{E_F - E_D'}{kT}\right)} \\ N_A^- = N_A \frac{1}{1 + \exp\left(\frac{E_A' - E_F}{kT}\right)} \end{cases} \quad (4)$$

Thus,

{	Donor	{	Shallow	$E_D' - E_F > 3kT$	$> 95\%$	ionized	(5)
		Non - shallow	$E_F - E_D' > 3kT$	$< 5\%$	ionized		
{	Acceptor	{	Shallow	$E_F - E_A' > 3kT$	$> 95\%$	ionized	
		Non - shallow	$E_A' - E_F > 3kT$	$< 5\%$	ionized		

As shown in Fig. 1, the activation energy of the donor state D is closer to the band edge than that of the acceptor state A. Yet the acceptor state is fully ionized with $p = N_A$, and the donor state is only partially ionized with $n \ll N_D$.

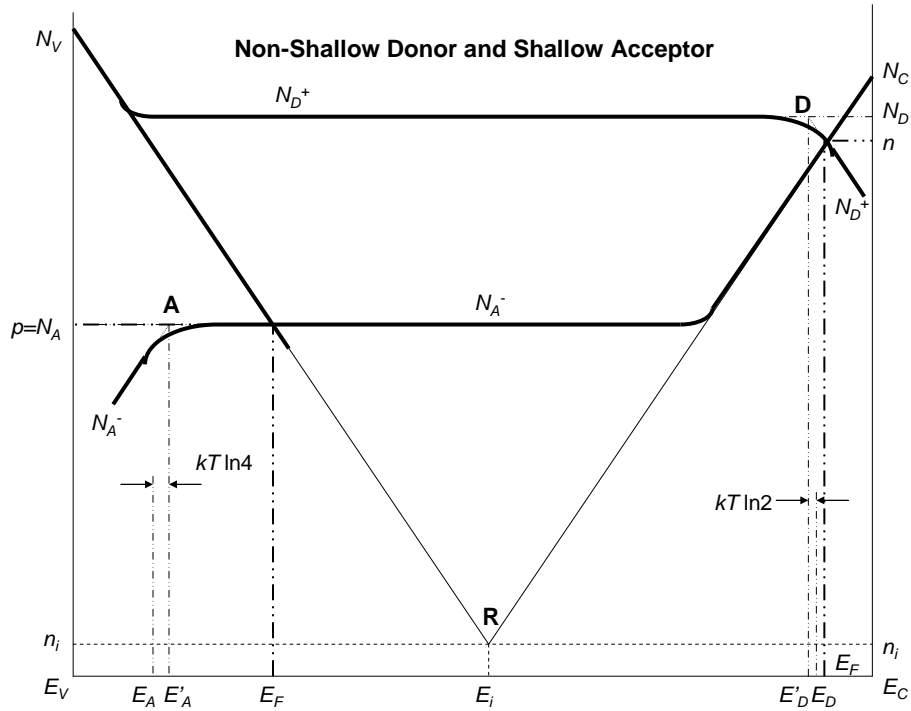


Fig. 1 Fully activated acceptor state A and partially activated donor state D

(3) Single-Level and Multi-Level States

Wei and Zhang [4] propose to use “transition energy level” instead of “state” to describe the transition between two charge states of a localized intrinsic/impurity defect. For example, an acceptor state is an intrinsic/impurity defect with a transition (o/-) — from empty or neutral to occupied or negatively charged with an electron. A double acceptor is an intrinsic/impurity defect with two possible transitions: (o/-) and (-/2-). Therefore, a localized intrinsic/impurity defect may have only a single transition level, or multiple transition levels. The local charge neutrality (LCN) condition of a semiconductor with only single-level states is

$$\begin{aligned}
N_V \exp\left(\frac{E_V - E_F}{kT}\right) + \sum_i N_{D_i} \frac{1}{1 + \exp\left(\frac{E_F - E'_{D_i}}{kT}\right)} \\
= N_C \exp\left(\frac{E_F - E_C}{kT}\right) + \sum_j N_{A_j} \frac{1}{1 + \exp\left(\frac{E'_{A_j} - E_F}{kT}\right)}
\end{aligned} \tag{6}$$

where E_V and E_C are the valence band maximum (VBM) and conduction band minimum (CBM), N_V and N_C the effective hole density in the valence band and the effective electron density in the conduction band. From equation (6), by using numerical or graphic method, we can solve the Fermi level, and with it the majority carrier density [9].

Divalent states — double donors and double acceptors, and amorphetic states — as donor if the host semiconductor is doped n-type and as acceptor if the host is doped p-type are the two most common multi-level states. We may also have amorphetic divalent states, such as the impurity complex $FeGa$ or $FeIn$ in Si [10], or even amorphetic multi-valent states as the general case of multi-level states (Fig. 2).

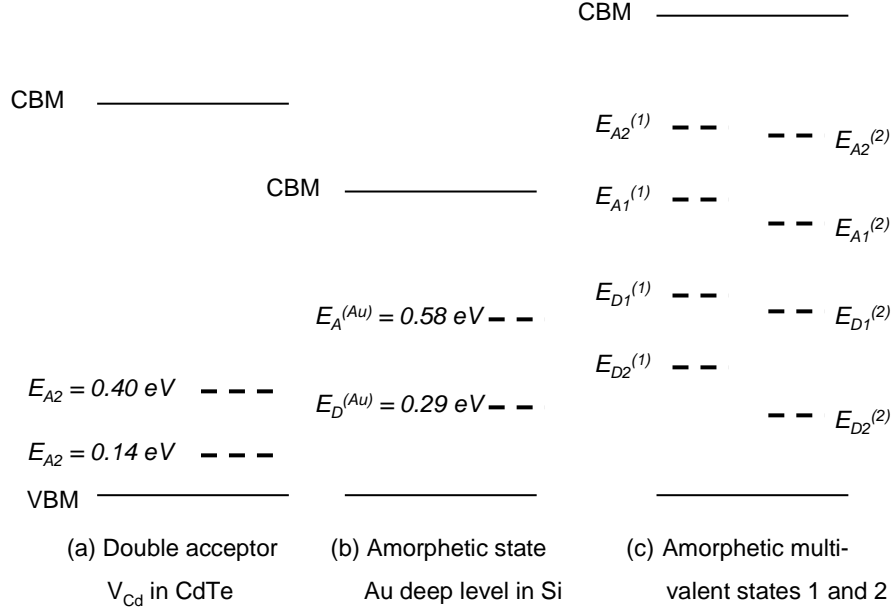


Fig. 2 Examples of multi-level intrinsic/impurity defect state

The generalized formulation of LCN equation of a semiconductor with any types of states — single-level and multi-level — is expressed as [11]

$$\begin{aligned}
 & N_V \exp\left(\frac{E_V - E_F}{kT}\right) + \sum_i N_i \left[1 + \exp\left(\frac{E_F - E'_{D1_i}}{kT}\right) \right]^{-1} \left\{ 1 + \left[1 + \exp\left(\frac{E_F - E'_{D2_i}}{kT}\right) \right]^{-1} \right\} \\
 & = N_C \exp\left(\frac{E_F - E_C}{kT}\right) + \sum_i N_i \left[1 + \exp\left(\frac{E'_{A1_i} - E_F}{kT}\right) \right]^{-1} \left\{ 1 + \left[1 + \exp\left(\frac{E'_{A2_i} - E_F}{kT}\right) \right]^{-1} \right\}
 \end{aligned} \tag{7}$$

When state N_i can only be positively ionized, then it acts only as donor state, and its corresponding term at the right side of (7) does not exist. Similarly, for a state acting only as acceptor, its corresponding term at the left side of (7) does not exist. When a state N_i can only be singly ionized, then the terms of double ionization with E'_{D2_i} or E'_{A2_i} disappear.

(4) States of Single Atomic Configuration and Multiple Atomic Configurations

The divalent and amorphous states, such as V_{Cd} in CdTe and Au in Si, have multiple transition energy levels, but a single atomic configuration with the same energy of formation. There is another category of multi-level states, the multiple transition energy levels of which are due to multiple atomic configurations. For example, an impurity I may have atomic configuration a with transition energy level E_a , and atomic configuration b with transition energy level E_b . The equilibrium ratio of occupation of the impurity I in configuration a and b is determined by Boltzmann distribution

$$\frac{N_a}{N_b} = \exp\left(-\frac{\Delta H_a - \Delta H_b}{kT}\right) \quad (8)$$

where ΔH_a and ΔH_b are the energies of formation of the configuration a and b , respectively.

Note that the transition from a to b , or vice versa, may incur an energy barrier to overcome, and the ratio of N_a vs. N_b may be in a metastable state, different from (8). Therefore, in this work we treat the impurity I with configuration a and configuration b as two independent states, not related to each other. The uncertainty of N_a/N_b may impose severe challenges to the processing, stability, reliability, and proper operation of the device made of a semiconductor material with such multi-configurational intrinsic/impurity defect states. An elevated temperature may trigger the change from one configuration to the other: from a shallow donor state to a deep level trap, from a donor state to an acceptor state, etc.

II. Challenge of PV of CdTe — a Polycrystalline Semiconductor Thin Film with Multiple, Non-Shallow, Multi-Level, and Multi-Configurational Dopants and Compensators

Among many challenges facing the attempted improvement of efficiency of CdTe photovoltaics, the most fundamental one is the lack of basic understanding of the material. The most basic question — what localized intrinsic/impurity defect states are responsible for the p-

doping of the CdTe polycrystalline thin film in a CdS/CdTe junction solar cell [4 – 10] — is still being debated. The calculated acceptor states close to the VBM is shown in Fig. 3 [4].

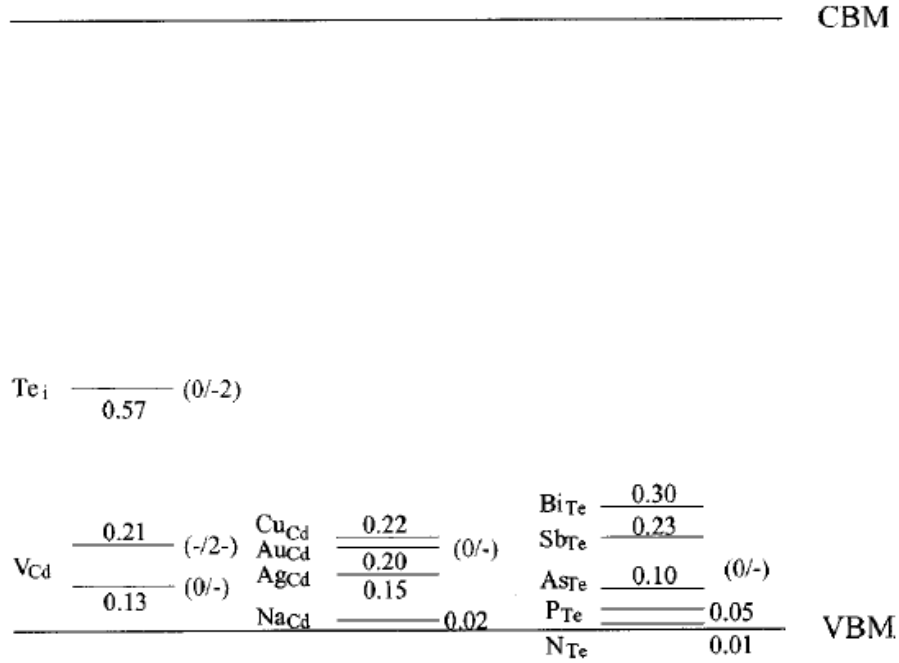


Fig. 3 Calculated Defect and Impurity Acceptor States in CdTe

The first candidate of probable or available p-dopant is the Cd vacancy, a double acceptor state. Cd vacancies are energetically favorable, and therefore naturally exist in CdTe thin films. The second group of probable p-dopants is noble metal substitutional of Cd (excluding Na_{Cd} , Na is a notoriously volatile impurity prohibited in any semiconductor device), especially Cu_{Cd} . Since the low cost 5N tellurium raw material may have up to 2×10^{-6} (2 ppm) Cu impurity content [6]. In addition, as part of the back contact material, Cu diffuses into the CdTe thin film [8]. The third group on the right side of the figure, the V-column substitutes of Te is impossible to incorporate in CdTe thin film. Instead of substituting the anion, the 5th column impurity atoms fall into the cation vacancies. Not shown in Fig. 3, the last but not least probable p-dopant is the defect complex $V_{Cd}^{2-} - Cl_{Te}^+ |^{0/-}$, a single acceptor due to compensation of the double acceptor V_{Cd}^{2-}

by an adjacent single donor $Cl_{Te}^{+/o}$. The transition energy levels of the three probable p-dopants of CdTe thin film used in solar cells are listed in Table 1.

	E_A (eV) Calculated [4]	E_A (eV) Hall	E_A (eV) DLTS	E_A (eV) LTPL+ OMR, EPR	E_A (eV) Assigned
$Cu_{Cd} ^{0/-}$	0.22	0.3-0.4	0.35		0.35
$V_{Cd} ^{0/-}$	0.13	0.15			0.14
$V_{Cd} ^{-/2-}$	0.21	0.6-0.9		<0.47	0.40
$V_{Cd}^{2-} - Cl_{Te}^{+/o} ^{0/-}$	0.10	0.14-0.17	0.12	0.12	0.12

Table 1 Three probable p-dopants of CdTe polycrystalline thin film. The experimentally measured data using Hall effects and DLTS [5] should be E'_A instead of ionization energy E_A

$$V_{Cd}^{o/2-} - Cl_{Te}^{+/o} \Rightarrow V_{Cd}^{2-} - Cl_{Te}^{+}|^{o/-} \quad (\text{defect complex})$$

With the first criterion of classification as discussed in the previous section, none of the three intrinsic/impurity defect states are qualified as dopants. They are all “deep levels”. To avoid such awkwardness, we use the second classification — all the three are probable dopants. Yet, they may be non-shallow, with multi-level transitions, and multiple atomic configurations.

(1) Critical Doping Level of Dopant

The first probable p-dopant listed in Table 1 is the acceptor state Cu substitute of Cd , a non-shallow p-type dopant, as well as a non-deep Shockley-Read-Hall (SRH) recombination center, which causes dark current, detrimental to the performance of CdTe solar cell. Considering the uncertainty and discrepancy of the experimental data — Hall effect measurement renders $E' = 0.3 \sim 0.4$ eV, and deep level transient spectroscopy (DLTS) gives 0.35 eV — as well as the difficulty to interpret the data, we must assign the activation energy level based on our information and weighted compromise between calculated and experimental data.

In this work, we use 0.35 eV as the activation energy of the *Cu* substitute acceptor. The second probable dopant double acceptor V_{Cd} has assigned first ionization energy 0.14 eV, and second ionization energy of 0.40 eV, which is a weighted compromise between the calculated value, the more reliable LTPL (low temperature photoluminescence), OMR (optical magnetic resonance) and EPR (electron paramagnetic resonance) data, and the lesser reliable Hall data. For the vacancy-substitute defect complex $V_{Cd}^{2-} - Cl_{Te}^+$, a single acceptor, we use 0.12 eV, which is in good agreement from calculated and experimental data.

Defining the critical doping level p_c of a dopant when its activation energy E'_A is equal to Fermi level E_F

$$p_c = N_V \exp\left(\frac{E_V - E'_A}{kT}\right) = N_A^- = \frac{1}{2} N_A \quad (9)$$

When desired hole density p is much smaller than p_c , we have $p \sim N_A$; when desired hole density p is much greater than p_c , we have $p \ll N_A$. High dopant concentration implies high solubility, which may not be easy to obtain. Therefore, a dopant with small activation energy is usually pursued. For Cu_{Cd} , we have $p_c = 2.4 \times 10^{13} \text{ cm}^{-3}$, and for V_{Cd} and $V_{Cd}^{2-} - Cl_{Te}^+$, $p_c = 8.1 \times 10^{16} \sim 1.8 \times 10^{17} \text{ cm}^{-3}$. By the consideration of p_c , V_{Cd} and defect complex $V_{Cd}^{2-} - Cl_{Te}^+$ are better p-dopants than Cu_{Cd} .

(2) Compensation of Cu Acceptors by Cu Donors

Similar to acceptor p-dopants, transition energy levels of donor n-dopants (Fig. 4) are also calculated using first principles [4]. Self compensation occurs when an intrinsic/impurity defect acceptor p-dopant transforms to a donor n-compensator. A prominent example is the Cu impurity's two atomic configurations: the substitutional Cu_{Cd} as p-dopant acceptor and the interstitial Cu_i as donor and compensator. The transition energy levels and energies of formation of the two states are listed in table 2.

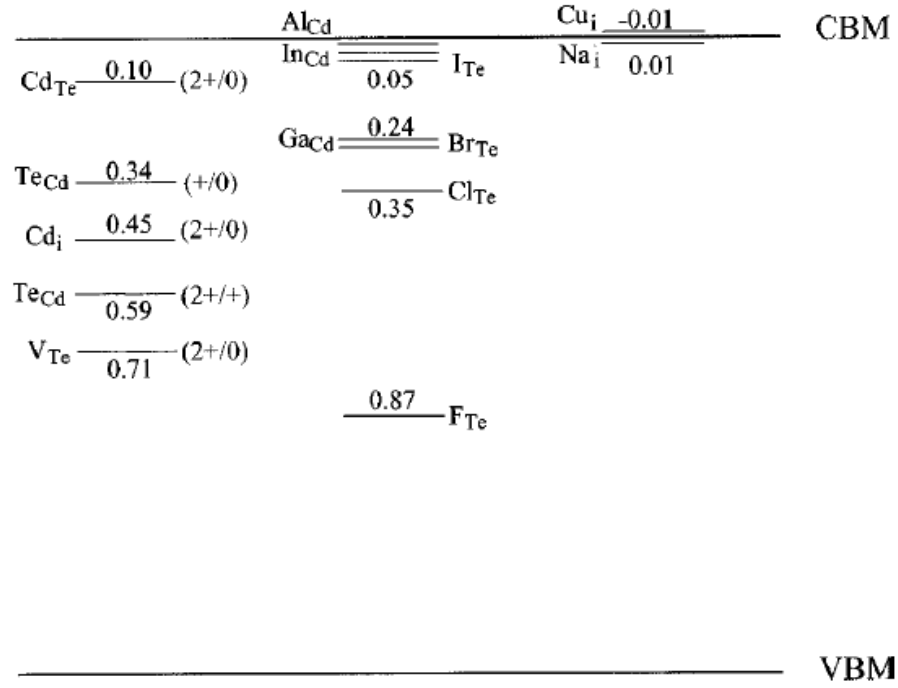


Fig. 4 Calculated Donor States of Defects and Impurities in CdTe

	Symbol	Assigned energy level	Energy of Formation
Non-shallow acceptor	$Cu_{Cd} ^{0/-}$	0.35 eV (experimental)	1.31 eV (calculated)
Shallow donor	$Cu_i ^{+/0}$	0.01 eV (calculated)	2.19 eV (calculated)

Table 2 Transition energy levels and formation energies of multi-configuration Cu impurity states, the energy of formation of Cu_i being the average of 2.14 eV for Cu_i close to anion and 2.24 eV for Cu_i close to cation [4]

The compensation of Cu substitute acceptor by Cu interstitial donor can be solved by single-level LCN equation (6) using graphic method as shown in Fig. 5 [12]. Without donor compensation, we have hole density p due to non-shallow dopant Cu_{Cd} expressed as [5, 9]

$$p \approx \sqrt{N_V N_{Cu_{cd}}} \exp\left(-\frac{E'_{Cu_{cd}} - E_V}{2kT}\right) \ll N_{Cu_{cd}} \quad (10)$$

With compensation of donor Cu_i , E_F is raised to E_F' and p is lowered to p' . From the similarity of the triangles as shown in the semi-logarithmic plot of Fig. 4, we have

$$\ln N_{Cu_{cd}} - \ln p \approx \ln p - \ln p' \quad (11)$$

Substituting (11) to (10), we have

$$p' \approx \frac{p^2}{N_{Cu_i}} = \frac{N_V N_{Cu_{cd}}}{N_{Cu_i}} \exp\left(-\frac{E'_{Cu_{cd}} - E_V}{kT}\right) \quad (12)$$

which shows, “surprisingly”, that the result of compensated hole density p' is not the widely quoted equation (1) $N_A - N_D$, or $N_{Cu_{cd}} - N_{Cu_i}$. p' does not even depend on $N_{Cu_{cd}}$ so long as the ratio of $N_{Cu_{cd}} / N_{Cu_i}$ is kept a constant. This conclusion from the graphic method is only valid in a range that the compensation is significant — namely $1 > N_D / N_A > 0.1$ [12]. Compensation of p-doping of acceptor Cu_{cd} by donor Cu_i not only reduces the hole density, considering the uncertainty of the ratio of $N_{Cu_{cd}} / N_{Cu_i}$, the processing of CdTe solar cell may be very sensitive to the temperature, and the performance of the solar cell may also be not reliable due to elevated temperatures. The compensation of p-doping is another setback of Cu impurity as a p-dopant.

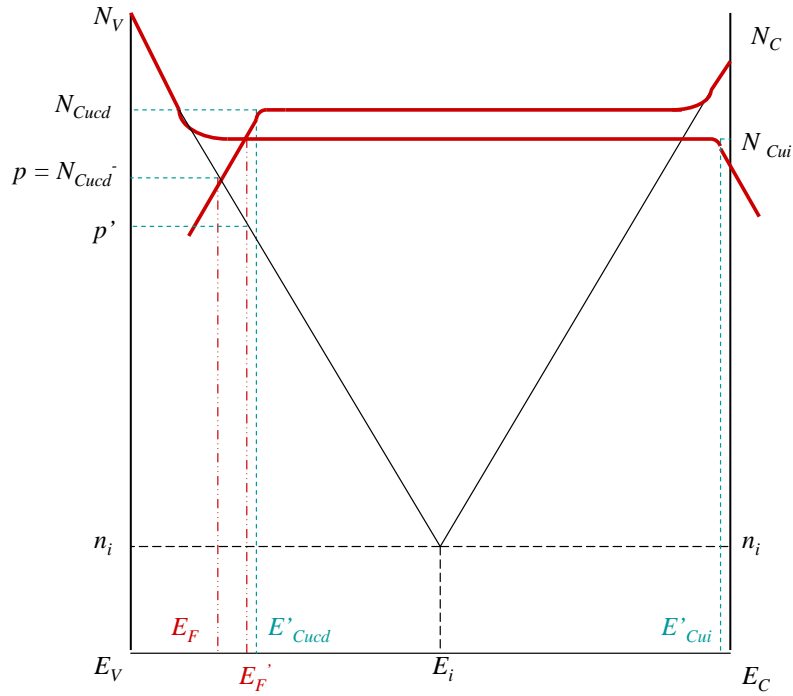


Fig 5 Compensation of acceptor density N_{CuCd} by donor density N_{Cui} , with $E_F \rightarrow E'_F$ and $p \rightarrow p'$

(3) Disadvantage of Double Acceptor V_{Cd}

Cd vacancy V_{Cd} in CdTe is a double acceptor, with its first ionization energy almost identical as that of the vacancy-substitute defect complex $V_{Cd}^{2-} - Cl_{Te}^+$. Therefore, V_{Cd} and defect complex $V_{Cd}^{2-} - Cl_{Te}^+$ can also be viewed as the same defect of different configurations. V_{Cd} turns into a defect complex or co-dopant by compensating a double acceptor V_{Cd} by a single donor Cl_{Te} , which is adjacent to the Cd vacancy. The role of the adjacent Cl_{Te} is two folds: it modifies the first activation energy level of V_{Cd} , and it eliminates the second ionization of V_{Cd} . The first role is minor, but the second role may turn the undesired p-dopant V_{Cd} to the desired p-dopant vacancy-substitute defect complex $V_{Cd}^{2-} - Cl_{Te}^+$. Fig. 6 is a plot of the LCN equation (7) of CdTe with the double acceptor V_{Cd} as its only dopant. For three different concentrations of the Cd

vacancies $N_A^{(1)} > N_A^{(2)} > N_A^{(3)}$, the graph shows clearly the invalidity of equation (1), since $p/N_A^{(1)} \ll 1$, $p/N_A^{(2)} \sim 1$, and $p/N_A^{(3)} \sim 2$. The level or percentage of the dopant activation depends not only on the activation energy, but also on the concentration. It is obvious that the contribution of being “double” acceptors to the level of hole density is a factor ≤ 2 , insignificant for doping, which is evaluated in logarithmic scale. The second ionization energy level, however, is deeper than E_F for the case $N_A^{(1)}$ and $N_A^{(2)}$. The second ionization state may be effective as undesired SRH recombination centers, or deep level traps. For the case $N_A^{(3)}$, which is lower than the doping level of any device, the level of second ionization, as that of the first ionization, plays virtually no roles. Therefore, as p-dopant, the double acceptor V_{Cd} is not as good as the defect complex, single acceptor $V_{Cd}^{2-} - Cl_{Te}^+$, which, as listed in Table 1, has almost the identical first transition energy level, but without second ionization.

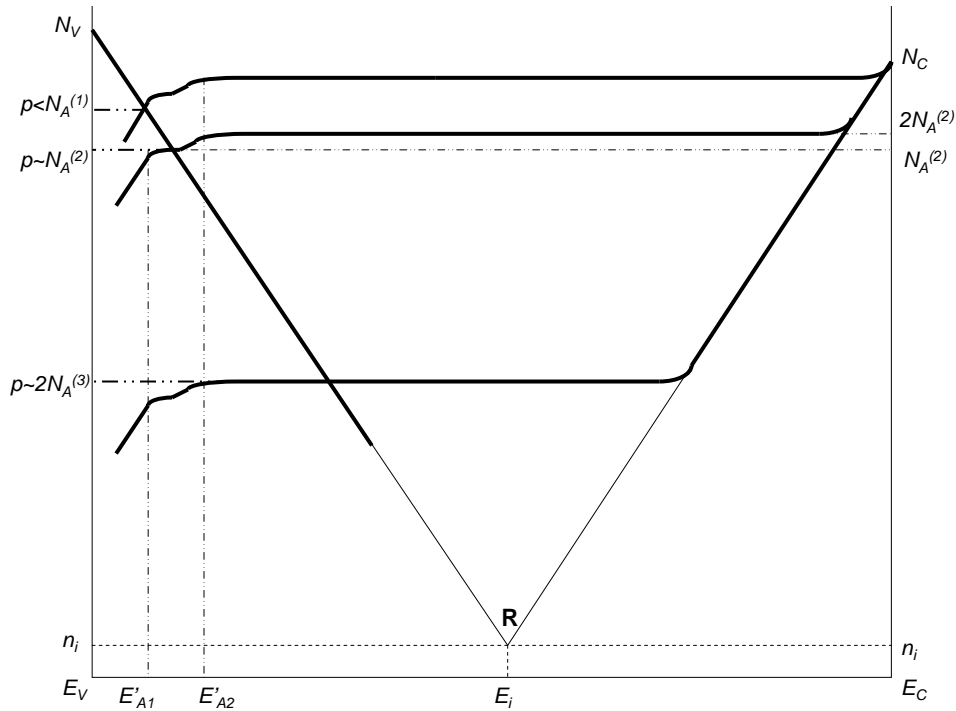


Fig. 6 Three different concentrations of Cd vacancy acceptors that can be doubly ionized

In conclusion, we have discussed CdTe thin film used in solar cells as a semiconductor with multiple, non-shallow, multi-level, and multi-configurational dopants. The advantages and disadvantages of the three most probable p-dopants are compared. It is concluded that the vacancy-substitute defect complex $V_{Cd}^{2-} - Cl_{Te}^{+}$ may be the best possible p-dopants for CdTe PV. The authors acknowledge helpful discussions with Tim Gessert of NREL and Jim Sites of Colorado State University. The work is partially supported by the grant from Apollo Solar Energy, Inc., the sponsor of the Apollo CdTe Solar Energy Research Center, NJIT.

REFERENCES

- [1] S. Sze, "Physics of Semiconductor Devices," 2nd Edition, Wiley, New York, 1981.
- [2] P. Blood and J. W. Orton, "The Electrical Characterization of Semiconductors: Majority Carriers and Electron States," Academic Press, 1992.
- [3] J. W. Orton and P. Blood, "The Electrical Characterization of Semiconductors: Measurement of Minority Carrier Properties," Academic Press, 1990.
- [4] Su-Huai Wei and S. B. Zhang, "Chemical Trends of Defect Formation and Doping Limit in II-VI Semiconductors: The Case of CdTe", *Phys. Rev. B* **66**, 15521 (2002)
- [5] Fred Seymour, "Studies of Electronic States Controlling the Performance of CdTe Solar Cells", Ph.D. (Materials Science) Thesis, Colorado School of Mines, p. 35, 2005.
- [6] Raw Material Specifications, Apollo Solar Energy (ASOE), Inc.
- [7] Xuanzhi Wu, "High-Efficiency Polycrystalline Thin-Film Solar Cells," *Solar Energy* **77**, 803-814 (2004).
- [8] T. A. Gessert, W. K. Metzger, P. Dippo, S. E. Asher, R. G. Dhere, and M. R. Young, "Dependence of Carrier Lifetime on Copper-contacting Temperature and ZnTe:Cu Thickness in CdS/CdTe Thin Film Solar Cells," *Thin solid Films* **517**, 2370-2373 (2009).
- [9] Ken K. Chin, submitted to *International Journal of Electronics*.
- [10] D. Macdonald and L. J. Geerligs, "Recombination activity of interstitial iron and other transition metal point defects in p- and n-type crystalline silicon," *Appl. Phys. Lett.* **85**, No. 18 (2004).
- [11] Ken K. Chin, submitted to *IEEE Transaction on ED*.

[12] Ken K. Chin, “p-Doping Limit and Donor Compensation in CdTe Polycrystalline Thin Film Solar Cells,” Solar Energy Materials and Solar Cells, May 31, 2010.