p-Doping limit and donor compensation in CdTe polycrystalline thin film solar cells

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ABSTRACT

Experimental evidence shows that non-shallow acceptor states defect complex $V_{Cd}-Cl_{Te}\big|^{0/-}$ and Cu substitution of Cd $Cu_{Cd}\big|^{0/-}$ play critical roles in p-doping of CdTe in CdS/CdTe thin film solar cells. In this work, two equations are presented by using graphic method, one to determine the limit of p-doping or hole density for such non-shallow acceptor levels, and another to show the quantitative relationship of n-type donor compensation of p-type acceptors in such a material.

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CdTe based solar cells have emerged in recent years as the most cost effective second generation thin film photovoltaic (PV) product by far. Despite intensive effort of research and development (R&D), however, the ratio of CdS/CdTe solar cell's lab demonstrated light to electricity conversion efficiency (16.5%) [1] vs its theoretical limit has been low, in comparison with other thin film PV technologies, such as CIGS, which has a lower theoretical limit but a higher lab demonstrated efficiency of 19.9% [2]. One of the reasons is that the hole concentration of p-CdTe keeps in the range of 10^{-14}–10^{15} cm^{-3}, instead of the desired level of 10^{16}–10^{17} cm^{-3} [3], resulting in lower junction band bending and difficulty in making ohmic contact. Both effects contribute to a lower open circuit voltage V_{OC} and therefore lower efficiency.

Traditional semiconductors, such as Si or GaAs, have a single shallow donor (for n-type) or acceptor (for p-type) impurity level, with typical activation energy ≤ 0.05 eV from the band edge. From the local charge neutrality (LCN) condition we have

$$p+N_D\frac{1}{1+g_D\exp(E_F-E_D/kT)} = n+N_A\frac{1}{1+g_A\exp(E_A-E_F/kT)} \qquad (1)$$

where n, p, E_F, E_D, E_A, N_D, N_A, g_D, and g_A are electron density, hole density, Fermi level, donor activation energy, acceptor activation energy, donor density, acceptor density, donor degeneracy, and acceptor degeneracy, respectively. For widely used tetrahedral

cubic semiconductors, such as Si, GaAs, and CdTe, $g_D=2$ due to electron spin degeneracy, and $g_A=4$ due to heavy hole and light hole in addition to spin degeneracy. For traditional non-degenerate p-type material used in electron devices and integrated circuits, Eq. (1) gives

$$p = N_V\exp\left(\frac{E_V-E_F}{kT}\right) \approx N_A\frac{1}{1+g_A\exp(E_A-E_F/kT)} \approx N_A \qquad (2)$$

under shallow doping condition

$$E_F-E_A \gg kT = 0.0259\,\text{eV} \qquad (3)$$

where N_V is the effective density of states in valence band, E_V the valence band maximum (VBM), and $T=300$ K, room temperature. The relationship of (2) and (3) are shown in Fig. 1.

As for the CdTe polycrystalline thin film in a CdS/CdTe solar cell, it is still being debated: what exactly happens during its p-doping. Yet, it is generally agreed that the Cd vacancy $V_{Cd}\big|^{0/-}$ (or the defect complex, $V_{Cd}-Cl_{Te}\big|^{0/-}$) and the impurity Cu substitution of Cd $Cu_{Cd}\big|^{0/-}$ are the responsible p-doping acceptors. Since the Cd vacancy and the defect complex have almost the same measured activation energy [4], we do not distinguish between them. High density of Cd vacancies is naturally formed—which may hinder the formation of other shallow acceptors—during the 5N CdTe crystal growth and polycrystalline CdTe thin film deposition by closed space sublimation (CSS) or other methods. The double acceptor Cd vacancy may turn to defect complex during CdCl₂ treatment of the CdS/CdTe junction at ~400 °C [1]. Cu also naturally exists

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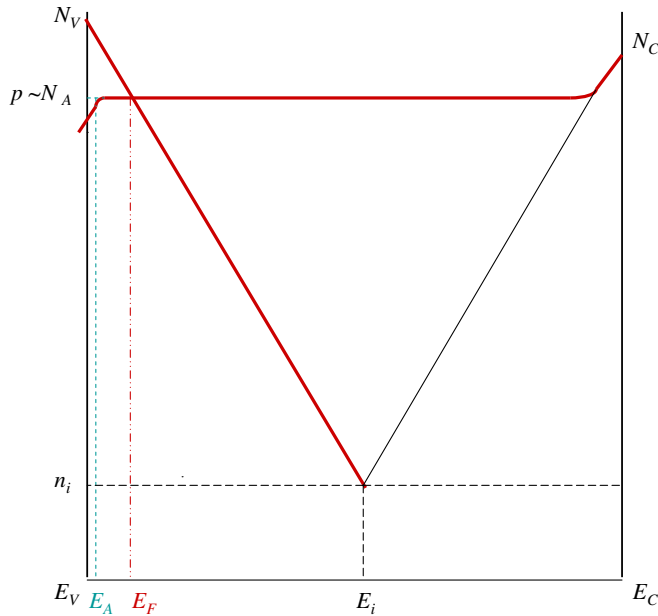 *E-mail address:* CHIN@NJIT.EDU

Fig. 1. The cross of the two solid red lines determines the Fermi level and free hole density, E_i and n_i are the intrinsic material's Fermi level and carrier density. (Density of states of y-axis is in logarithmic scale and energy of x-axis is in linear scale.)
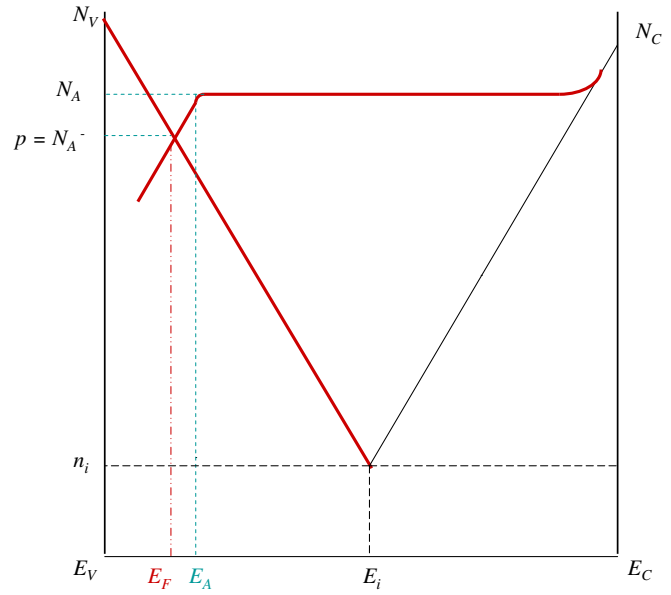

Fig. 2. Hole density p is shown as the ionized acceptor density N_A^-, which is much smaller than the acceptor density N_A.

with a concentration of 2×10^{-6} (2 ppm) or more [5] in the low cost 5N tellurium raw material, since Te is a byproduct of copper refinery, extracted from its smudge. In addition, as part of the back contact material, Cu diffuses into the CdTe thin film [6]. Apparently, the Cd vacancy and the Cu impurity are not by design or by choice, but unavoidably and conveniently involved in the p-doping of CdTe. Note that the Cu atoms, either in the raw material or diffused into the CdTe thin film during the formation of back contact, may fill in the Cd vacancy to form Cu substitution of Cd, since the difference in formation energies of $E_{V_{Cd}}$ and $E_{Cu_{Cd}}$ is in favor of the process [7]

$$E_{V_{Cd}} - E_{Cu_{Cd}} = 2.67\,\text{eV} - 1.31\,\text{eV} = 1.36\,\text{eV} \qquad (4)$$

Thus, under certain conditions Cu_{Cd} may take over V_{Cd} to become the acceptor states, responsible for the p-doping of CdTe thin film. Yet, noting that E_A of Cu_{Cd} is 0.35 eV, much larger than the normal shallow acceptor dopants, the conditions of (2) and (3) are not satisfied as shown in Fig. 2. Eq. (3) is replaced by

$$E_A - E_F \gg kT = 0.0259\,\text{eV} \qquad (5)$$

Eq. (2) is replaced by

$$p = N_V \exp\left(\frac{E_V - E_F}{kT}\right) = N_A \frac{1}{1 + g_A \exp(E_A - E_F/kT)} \approx \frac{N_A}{g_A} \exp\left(-\frac{E_A - E_F}{kT}\right) \qquad (6)$$

or

$$p \approx \sqrt{\frac{N_V N_A}{g_A}} \exp\left(-\frac{E_A - E_V}{2kT}\right) \qquad (7)$$

which is well known [8]. Interestingly, as shown in Fig. 2, Eq. (7) can be readily derived from the similarity of the two triangles in the semi-logarithmic plot of density vs energy—a graphic method—if the effect of degeneracy factor is absorbed into the activation energy E_A:

$$\frac{\ln N_V - \ln p}{E_F - E_V} = \frac{\ln N_A - \ln p}{E_A' - E_F} = \frac{1}{kT} \qquad (8)$$

which leads to (7), considering the definition [9] of

$$E_A' = E_A + kT \ln g_A \qquad (9)$$

Taking $N_V = 1.8 \times 10^{19}$ cm^{-3} [1], $N_A = 1.0 \times 10^{17}$ cm^{-3}, which is from SIMS depth profiling data [6], $g_A = 4$, and $E_A - E_V = 0.35$ eV, we have $p = 1.6 \times 10^{15}$ cm^{-3}, which is consistent with the hole density of $10^{14} - 10^{15}$ cm^{-3} from C–V measurement [4,10]. Note that the published experimental values of p of thin film CdTe are extracted from C–V measurement of the CdS/CdTe cell. However, due to the p-CdTe's Schottky barrier of the back contact, the measured C is smaller than the n–p junction's real capacitance. Therefore, our result of $p = 1.6 \times 10^{15}$ cm^{-3} is consistent with the measured hole density at the edge of the depletion region. Also note: Eq. (7) indicates that p increases at higher temperatures. This may contribute to CdS/CdTe solar cell's feature of less degradation of performance at elevated temperature.

In addition to large activation energy of acceptor states, donor compensation of acceptor, expressed as N_A–N_D, is also blamed to be one of the reasons why CdTe has low density of holes [4]. Indeed, the same Cu impurity in CdTe can also be interstitial Cu_i, playing the role of shallow donor state [7]. Just as local charge neutrality condition mandates that the dependence of p on N_A is not linear, the compensation of N_A by N_D also needs to be considered quantitatively through LCN. As shown in Fig. 3 the donor compensation of acceptor is only significant when

$$N_A > N_D > p \qquad (8)$$

When acceptors and donors of same order are both present, the LCN Eq. (1) can be expressed as

$$N_V \exp\left(\frac{E_V - E_F'}{kT}\right) + N_D \frac{1}{1 + g_D \exp(E_F' - E_D/kT)} = N_C \exp\left(\frac{E_F' - E_C}{kT}\right)$$
$$+ N_A \frac{1}{1 + g_A \exp(E_A - E_F'/kT)} \qquad (9)$$

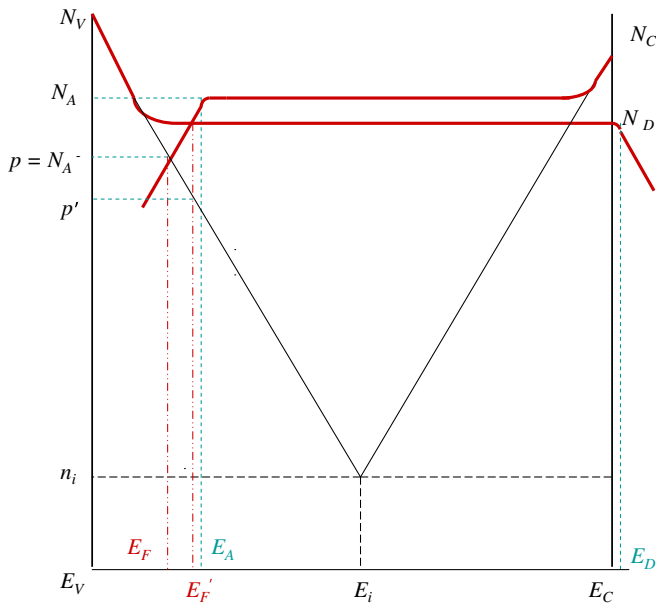Compared with the case without donor compensation, E_F is raised to E_F' and p is lowered to p'.

Fig. 3. Compensation of acceptor density N_A by donor density N_D, with $p \to p'$ and $E_F \to E'_F$.

By neglecting higher order terms or using the graphic method—the similarity of the triangles as shown in the semi-logarithmic plot of Fig. 3, we have

$$\ln N_D - \ln p \approx \ln p - \ln p' \tag{10}$$

Substituting (10) to (7), we have

$$p' \approx \frac{p^2}{N_D} = \frac{N_V N_A}{g_A N_D} \exp\left(-\frac{E_A - E_V}{kT}\right) \tag{11}$$

which shows, "surprisingly", that the result of compensation hole density p' is not the widely used $N_A - N_D$, and it does not even depend on N_A so long as the ratio of N_A/N_D is kept constant. This conclusion from the graphic method is only valid in a range that the compensation is significant—namely $N_D/N_A > 0.1$ [11]. Now we use the same numerical example discussed before: Cu_{Cd}

acceptor concentration of $N_A = 1.0 \times 10^{17}$ cm^{-3} leading to a hole density $p = 5.6 \times 10^{14}$ cm^{-3}. Now if the Cu substitutional acceptors are compensated by donor states Cu interstitial Cu_i of concentration $N_D = 1.0 \times 10^{16}$ cm^{-3}, then the hole density is lowered to $p' = 0.6 \times 10^{14}$ cm^{-3}.

In summary, we have shown that for a p-type semiconductor with non-shallow acceptor levels, such as p-CdTe with Cu_{Cd} impurities, the hole density may be a few orders lower than the acceptor concentration. Furthermore, if the acceptors are compensated by donors, such as Cu_{Cd} compensated by Cu_i in p-CdTe, the reduction of hole density is expressed by Eq. (11), very different from the often used expression of N_A–N_D [12].

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