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Dual roles of doping and trapping of semiconductor defect levels and their ramification to thin film photovoltaics

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It is pointed out that the semiconductor localized intrinsic/impurity defect levels' dual roles for carrier doping and trapping (Shockley-Read-Hall generation-recombination) have been treated differently and inconsistently. It is proposed that instead of ionization or activation energy, transition Gibbs free energy level should be used for the dual roles of doping-trapping. To qualitatively evaluate the effectiveness of doping and of trapping, the concept of doping efficacy η_d and two types of trapping efficacy η_t and η_{SRH} are proposed. The relationship of η_d, η_t, and η_{SRH} is formulated. Various values of η_{SRH} for different types of defect levels are presented. General ramification of the proposed concepts and efficacy of trapping is explored for polycrystalline thin film solar cells. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4719046]

I. CONSISTENT AND CORRECT TREATMENT OF SEMICONDUCTOR DEFECT LEVELS' DUAL ROLES

Localized semiconductor intrinsic/impurity defects (including defect complexes) are usually classified as dopants and deep levels.[1,2] Those with ionization or activation energy level less than 0.05 eV from the band edge are (shallow) dopants, and those with greater than 0.05 eV are deep levels.[1] The dopants are necessary in most devices for doping the semiconductor with *n*- or *p*-type carriers. The deep levels may compensate the dopants, and are mostly treated as traps, also called Shockley-Read-Hall (SRH) generation-recombination centers, with negative impact on the performance of most devices. Such a classification and description of the midgap levels of defects in a semiconductor is appropriate for most widely used single crystal semiconductor materials, such as Si and GaAs, which usually has a single dominant dopant defect of shallow energy level.[1,3] The concentration of the dominant shallow dopant is usually at least one order higher than that of the other dopants and many orders higher than that of the deep levels.

The usage and importance of non-traditional semiconductor materials, such as semi insulating semiconductors,[4] wide bandgap semiconductors,[5,6] transparent conducting oxides (TCO),[7,8] as well as n-CdS and p-CdTe polycrystalline thin films used in solar cells,[9–11] have been steadily increasing. Due to either technical difficulties or process cost concerns, the non-traditional—or rather the general semiconductor—may not have clear demarcation to distinguish between shallow dopants and deep levels. Intrinsic/impurity defect levels may distribute across the bandgap fairly uniformly, and with comparable concentrations. For example, p-type CdTe polycrystalline thin film does not have any acceptor dopants according to the definition given in Ref. 1. Its double acceptor Cd vacancy levels $V_{Cd}^{(0/-)}$ and $V_{Cd}^{(-/2-)}$, Cu substitute of Cd $Cu_{Cd}^{(0/-)}$, and A-center $V_{Cd}^{(0/2-)}$-$Cl_{Te}^{(+/0)}$(a double acceptor adjacent to a single donor forming a single acceptor defect complex) have their activation energies listed as 0.13, 0.21, 0.22, and 0.14–0.17 eV, respectively. Note that except A-center,[11] due to uncertainties of experimentally measured data, here we use calculated values.[12] As all these defect levels may co-exist in CdTe, we cannot use the conventional way of calculating Fermi level and majority carrier density by using

$$\begin{cases} n = N_C \exp\left(\dfrac{E_F - E_C}{kT}\right) = N_D^+ = N_D \ \ (\text{n}-\text{type}) \\ p = N_V \exp\left(\dfrac{E_V - E_F}{kT}\right) = N_A^- = N_A \ \ (\text{p}-\text{type}) \ , \end{cases} \tag{1}$$

where N_C, N_V, N_D, N_A, E_C, E_V, and E_F are the effective density of electrons in conduction band, the effective density of holes in valence band, the donor concentration, the acceptor concentration, the conduction band minimum (CBM), the valence band maximum (VBM), and the Fermi level, respectively. $kT = 0.0259$ eV under room temperature. Invalidity of Eq. (1) is one of the reasons why the most fundamental question of any semiconductor device: "What is the dopant and its concentration in p-CdTe thin film in the n^+-CdS/*p*-CdTe solar cell?" remains a "mystery" despite commercial success and intense R&D in the area of CdTe photovoltaics (PV).

As the activation energies of the dopant levels are non-shallow, the dopants are partially ionized, and for the case of a single non-shallow donor or acceptor, Eq. (1) must be replaced by

$$\begin{cases} n = N_C \exp\left(\dfrac{E_F - E_C}{kT}\right) = N_D^+ = N_D \dfrac{1}{1 + g_D \exp\left(\dfrac{E_F - E_D}{kT}\right)} & \text{(n-type)} \\ p = N_V \exp\left(\dfrac{E_V - E_F}{kT}\right) = N_A^- = N_A \dfrac{1}{1 + g_A \exp\left(\dfrac{E_A - E_F}{kT}\right)} & \text{(p-type)}, \end{cases} \tag{2}$$

where E_D and E_A, instead of activation or ionization energy, are called transition energy levels of the donor and the acceptor, respectively, by Wei and Zhang,[12] as well as other authors. Although never directly or indirectly measured, g_D is set to be equal to 2 and $g_A = 4$ due to symmetry caused degeneracy for most widely used semiconductors of tetrahedral cubic structure, such as Si, GaAs, and CdTe.[3]

Equation (2) indicates that for (single level) defects playing the role of doping or supplying carriers their electron occupation probability is expressed as

$$\begin{cases} f_D = \dfrac{1}{1 + \dfrac{1}{g_D} \exp\left(\dfrac{E_D - E_F}{kT}\right)} \\ f_A = \dfrac{1}{1 + g_A \exp\left(\dfrac{E_A - E_F}{kT}\right)}. \end{cases} \tag{3}$$

In addition to *doping*, the defects with "non-shallow" energy levels may also be considered as "non-deep" deep-levels playing the role of *trapping*, indicated by the subscript t. However, in the equation of SRH recombination or trapping rate by a midgap defect level, Eq. (3) is usually written as[13,14]

$$f_t = \frac{1}{1 + \exp\left(\dfrac{E_t - E_F}{kT}\right)}, \tag{4}$$

which, for the sake of convenience, neglecting degeneracies g_D and g_A, does not distinguish between the donor level and acceptor level, neither does it distinguish among the multi-transition levels of deep defects.

Lack of justification and error in neglecting degeneracy or entropy of the trapping energy level in Eq. (4) are recognized by deep level transient spectroscopy (DLTS), the most effective and widely used experimental technique in measuring the energy level E_t of the trap.[15] In DLTS, after charging the traps in the depletion region with holes or electrons, the carrier emission rate by the trap is measured. Considering the emission or capture of carrier by a trap as a chemical reaction or phase transition, the trap's carrier emission rate equation used in DLTS is not based on occupancy equation (3) or (4), but based on[11,16–18]

$$f_t = \frac{1}{1 + \exp\left(\dfrac{G_t - E_F}{kT}\right)}, \tag{5}$$

where the entropy term S_t in the trap's transition Gibbs free energy level (TGFEL)

$$G_t = H_t - TS_t \tag{6}$$

as proposed by many authors,[16–18] includes "multi-phonon" induced degeneracy, but not symmetry induced degeneracy g_D and g_A (note that the difference between H_t and E_t is considered negligible).

Although seemingly Eq. (3) deals with doping by the defect level under equilibrium, Eq. (4) is used for the derivation of steady state SRH recombination through the defect level, and Eq. (5) is for transient state measurement of carrier emission rate, it is essential to note that they are all based on the same physical phenomenon—thermal occupation probability of the defect level by an electron. It is seriously inconsistent that we have three different equations describing the same physical phenomenon. It is particularly awkward for the "non-shallow non-deep" defects, such as the double acceptor transition level of Cd vacancy $V_{Cd}^{(-/2-)}$ and many other defects in thin film photovoltaic junctions. They play the dual roles of doping and trapping simultaneously in the same device. Fortunately, such an inconsistent and erroneous treatment of the doping-trapping dual roles by a transition level of a defect is easy to correct. Instead of Eqs. (3), (4), and (5), we propose to use Eq. (5) for all the three cases for all the transition levels of all the defects in their dual roles of doping and trapping. The relationship of E and G is shown in Fig. 1.

For determining the equilibrium Fermi level and majority carrier density, all transition levels of all defects must be included in the equation of local charge neutrality condition[19,20] utilizing Eq. (5), and likewise for calculating the SRH recombination current. Some levels are only effective for doping, some levels are only effective for trapping, while some other levels are effective in both doping and trapping.

II. INTRODUCTION OF DOPING AND TRAPPING EFFICACIES OF A DEFECT TRANSITION LEVEL

Apparently, the effectiveness of a transition level of a defect in semiconductor as a dopant is determined by its probability of ionization that supplies carriers. We define the efficacy of a defect level for doping

$$\eta_d = \begin{cases} \dfrac{1}{1 + \exp\left(\dfrac{E_F - G_D}{kT}\right)} & \text{(n-type dopant, donor level)} \\ \dfrac{1}{1 + \exp\left(\dfrac{G_A - E_F}{kT}\right)} & \text{(p-type dopant, acceptor level)}. \end{cases} \tag{7}$$

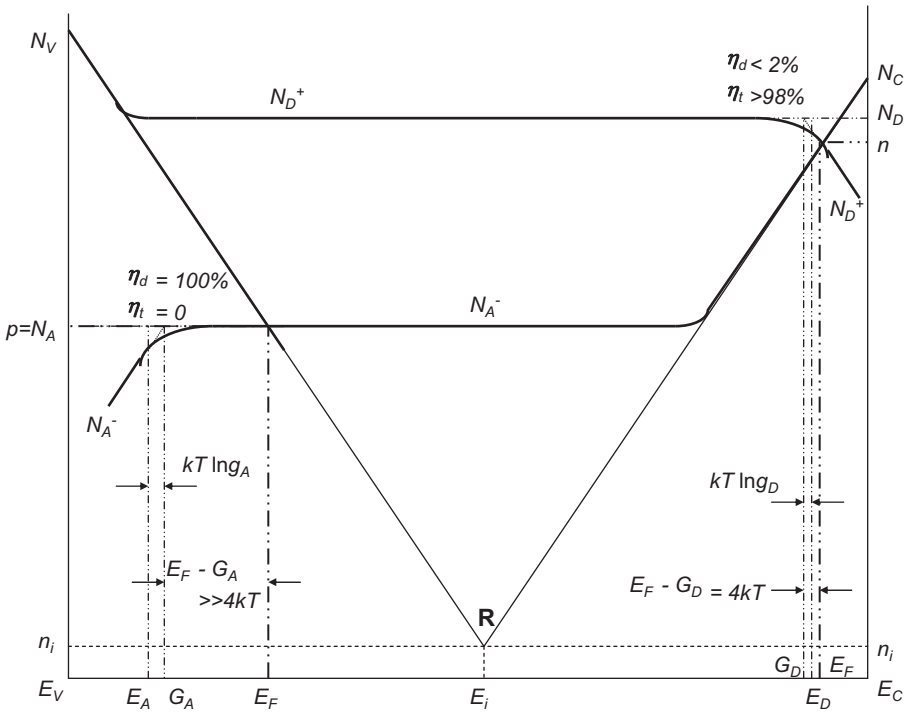


FIG. 1. An acceptor level (concentration N_A and TGFEL G_A) with $E_F - G_A \gg 4\ kT$, doping efficacy $\eta_d = 100\%$ ($p = N_A$) and trapping efficacy $\eta_t = 0$; a donor level (concentration N_D and TGFEL G_D) with $E_F - G_A = 4\ kT$, doping efficacy $\eta_d < 2\%$ ($n < 2\%\ N_D$), and trapping efficacy $\eta_t > 98\%$. Note that the Hall effect and other experimental techniques measure G_A for a p-type semiconductor and G_D for an n-type semiconductor; neither E_A and g_A nor E_A and g_A are directly measurable.

Here we only consider the single donor and single acceptor levels. Double donor, double acceptor, and amphoteric levels can be treated similarly.[20]

The defect levels playing the role of doping can play the role of trapping simultaneously, with the SRH recombination rate[3,13,14]

$$U_{SRH} = \frac{np - n_i^2}{\tau_{po}(n + n^*) + \tau_{no}(p + p^*)}, \tag{8}$$

where n, p, and n_i are the electron density, hole density, and intrinsic carrier density, respectively. τ_{no} and τ_{po} are the nominal lifetime of electron and of hole due to the SRH recombination center's capturing electrons and holes,[13,14] and defined by

$$\begin{cases} \dfrac{1}{\tau_{no}} = \sigma_n v_n N_t \\ \dfrac{1}{\tau_{po}} = \sigma_p v_p N_t. \end{cases} \tag{9}$$

Here σ_n, σ_p, v_n, and v_p are the SRH center or trap's electron capture cross section, hole capture cross section, electron thermal velocity, and hole thermal velocity, respectively. N_t is the trap or SRH recombination center transition level's concentration.

We define

$$\alpha = \sigma v = \sqrt{\sigma_n v_n \sigma_p v_p}, \tag{10}$$

$$\beta = \sqrt{\frac{\sigma_n v_n}{\sigma_p v_p}}. \tag{11}$$

First α, as the geometric average of two consecutive processes involving the capture of an electron and a hole, depicts each trap level's overall capability of SRH generation-recombination. Second, β depicts the ratio of electron capturing and hole capturing by a trap. The rate of capture of electron and that of hole by a trap level (SRH center at one of its transition level) with the same geometric size are different due to Coulomb attraction or repulsion between the trap and the carrier. Thus, we have

$$\begin{array}{ccccccc} \sigma_n^{(2+/+)} & > & \sigma_n^{(+/o)} & > & \sigma_n^{(o/-)} & > & \sigma_n^{(-/2-)} \\ \vee & & \vee & & \wedge & & \wedge \\ \vee & & & & & & \wedge \\ \sigma_p^{(2+/+)} & < & \sigma_p^{(+/o)} & < & \sigma_p^{(o/-)} & < & \sigma_p^{(-/2-)} \end{array} \tag{12}$$

and

$$\beta^{(2+/+)} \gg \beta^{(+/o)} \gg \beta^{(o/-)} \gg \beta^{(-/2-)}, \tag{13}$$

where the superscript (2+/+), (+/0), (0/−), and (−/2−) depict the double donor, single donor, single acceptor, and double acceptor transition level of the SRH center, respectively. Note that the SRH generation-recombination involves an electron generation (or capture) followed by a hole generation (or capture), and *vice versa*. The transition level of a SRH center involving two or more carriers, such as (2+/0), (0/2−), or (+/−) are negligible, since the probability of capture and emission of two carriers simultaneously is extremely low in comparison to that of one carrier. Although rules (12) and (13) have not been systematically or strictly verified by experiments, the largest reported experimental value of σ_n/σ_p is 17 000 for double donor $V_i^{(2+/+)}$, valium interstitial in Si, and the smallest measured σ_n/σ_p is 2×10^{-5} from double acceptor $Zn_{Si}^{(-/2-)}$, zinc substitute in Si.[21,22]

In addition, we define

$$\gamma = \frac{G - E_i}{kT}, \tag{14}$$

to depict the defect's TGFEL relative to the intrinsic Fermi level E_i.

In its role of trapping, a defect level's effectiveness is completely determined by the three parameters α, β, and γ. Substituting Eqs. (10) and (11) to Eq. (8) yields

$$U_{SRH} = \alpha N_t (np - n_i^2) \frac{1}{\beta(n + n^*) + \frac{1}{\beta}(p + p^*)}, \tag{15}$$

where

$$\begin{cases} n = n_i \exp\left(\dfrac{E_{F_n} - E_i}{kT}\right) = N_C \exp\left(\dfrac{E_{F_n} - E_C}{kT}\right) \\ p = n_i \exp\left(\dfrac{E_i - E_{F_p}}{kT}\right) = N_V \exp\left(\dfrac{E_V - E_{F_p}}{kT}\right), \end{cases} \tag{16}$$

n_i, E_i, E_{F_n}, and E_{F_p} being the intrinsic carrier density, intrinsic Fermi level, the quasi Fermi level of electron, and the quasi Fermi level of hole, respectively. n^* and p^* are dependent on the SRH center or trap's TGFEL, also called deep level G_t (Ref. 7)

$$\begin{cases} n^* = n_i e^{\gamma} = n_i \exp\left(\dfrac{G_t - E_i}{kT}\right) = N_C \exp\left(\dfrac{G_t - E_C}{kT}\right) \\ p^* = n_i e^{-\gamma} = n_i \exp\left(\dfrac{E_i - G_t}{kT}\right) = N_V \exp\left(\dfrac{E_V - G_t}{kT}\right). \end{cases} \tag{17}$$

To simplify the formulation of the SRH center transition level's recombination rate (8) or (15), it is usually assumed in current literature that the SRH level is "ideal" and "most effective," satisfying one or more of the following assumptions:

$$\text{Assumption 1: } \gamma = 0 \text{ or } G_t = E_i \text{ (trap's TGFEL is at midgap).} \tag{18}$$

$$\text{Assumption 2: } \beta = \frac{1}{\beta} = 1 \text{ (neglecting trap} - \text{carrier Coulomb force).} \tag{19}$$

$$\text{Assumption 3: } n = p = n_i \exp\left(\frac{V}{2kT}\right) \text{ (equal density of } n \text{ and } p \text{ in depletion region)} \tag{20}$$

where

$$V = \frac{E_{F_n} - E_{F_p}}{q} \tag{21}$$

is the bias voltage of the junction, q being 1.60×10^{-19} C, the electron's charge. For a PV junction, V is the cell's output voltage. With all the 3 assumptions, we may integrate the SRH rate equation (8) or (15) through the depletion width W to yield the widely used SRH diode equation appearing in the solar cell's J-V characteristics as dark current density[1,9–11]

$$J_{SRH}(V) = \frac{q n_i W}{2\tau_o}\left[\exp\left(\frac{qV}{2kT}\right) - 1\right], \tag{22}$$

where

$$\frac{1}{\tau_o} = \frac{1}{\sqrt{\tau_{no}\tau_{po}}} = \alpha N_t \tag{23}$$

is the nominal carrier lifetime in the depletion region, N_t being the uniformly distributed or averaged trap density.

We may define the trapping efficacy of a SRH canter transition level by comparing the defect level's effectiveness in its role as a trap with an ideal trap. The degree of ideality of a "perfect" trap depends on the observation of assumption 1, 2, and/or 3. We first define a trap's trapping efficacy by comparing with an ideal SRH center observing condition 1 only. In view of the SRH rate decrease with the denominator increase in Eq. (8) or (15), we define the trap's trapping efficacy η_t as

$$\eta_t = \begin{cases} \dfrac{n+1}{n+n^*} \approx \dfrac{\exp\left(\dfrac{E_F - G_D}{kT}\right)}{1 + \exp\left(\dfrac{E_F - G_D}{kT}\right)} & \text{(donor level trap capturing hole)} \\ \dfrac{p+1}{p+p^*} \approx \dfrac{\exp\left(\dfrac{G_A - E_F}{kT}\right)}{1 + \exp\left(\dfrac{G_A - E_F}{kT}\right)} & \text{(acceptor level trap capturing electron)} \end{cases}. \tag{24}$$

Combining Eqs. (7) and (24), we have the relationship between the doping efficacy and the trapping efficacy

$$\eta_d + \eta_t = 1. \tag{25}$$

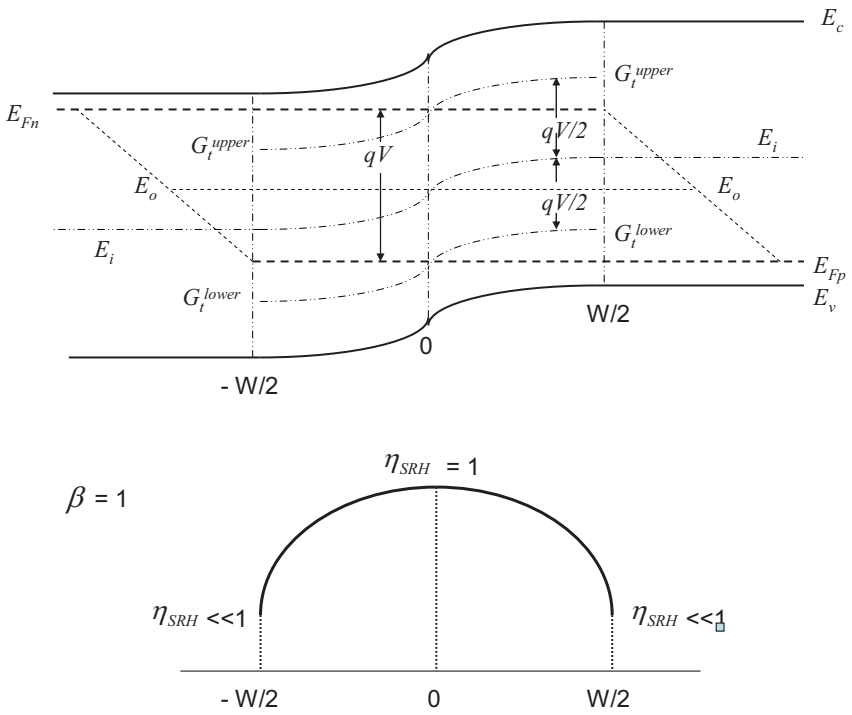


FIG. 2. Case $\beta = 1$: Defect level's trapping efficacy η_{SRH} as function of V, x, and γ in the depletion region of a symmetric n-p junction.

As shown in Fig. 1 for an acceptor level in the lower half of the band gap

$$\begin{cases} \begin{cases} \eta_d > 95\%\ (98\%) \\ \eta_t < 5\%\ (2\%) \end{cases} & \text{when} \quad E_F - G > 3kT(4kT) \\ \begin{cases} \eta_t > 95\%\ (98\%) \\ \eta_d < 5\%\ (2\%) \end{cases} & \text{when} \quad G - E_F > 3kT(4kT) \end{cases} \tag{26}$$

and for a donor level in the upper half of the band gap

$$\begin{cases} \begin{cases} \eta_d > 95\%\ (98\%) \\ \eta_t < 5\%\ (2\%) \end{cases} & \text{when} \quad G - E_F > 3kT(4kT) \\ \begin{cases} \eta_t > 95\%\ (98\%) \\ \eta_d < 5\%\ (2\%) \end{cases} & \text{when} \quad E_F - G > 3kT(4kT). \end{cases} \tag{27}$$

Considering that η_t defined by Eq. (24) refers to the capture of one type of carrier only while SRH recombination involves the capture of an electron and a hole, and also considering how Eqs. (22) and (23) are derived, we define a second type of trapping efficacy η_{SRH} by comparing the real SRH center with the ideal SRH center that observes all the 3 conditions [Eqs. (18)–(20)]

$$\eta_{SRH}(n,p,\beta,G) \equiv \frac{U_{SRH}}{U_{SRH}^{(ideal)}} = \frac{2n_i\left[\exp\left(\frac{qV}{2kT}\right)+1\right]}{\beta(n+n^*)+\frac{1}{\beta}(p+p^*)}. \tag{28}$$

Substituting Eqs. (16) and (17) to Eq. (28), the SRH center efficacy η_{SRH} can be expressed as

$$\eta_{SRH}(V,x,\beta,\gamma) = \frac{1+\exp\left(-\frac{qV}{2kT}\right)}{\left[\cosh\left(\frac{E_i(V,x)-E_o}{kT}+\ln\beta\right)+\exp\left(-\frac{qV}{2kT}\right)\cosh(\gamma+\ln\beta)\right]}, \tag{29}$$

where E_o defined by

$$E_o = \frac{E_{F_n}+E_{F_p}}{2}, \tag{30}$$

as shown in Fig. 2 for the case of a symmetric n-p junction does not follow band bending, while the intrinsic Fermi level E_i following the band bending is a function of V and x, due to space charge induced potential Φ in the depletion region

$$E_i(x) = E_i\left(\frac{W}{2}\right) + q\Phi(x). \tag{31}$$

Here we assume that the potential at the depletion region edge $W/2$ is equal to 0. The curve $E_i(x)$ crosses the horizontal line E_o at the interface $x = 0$ for a symmetrical n-p junction, but it does not cross line E_o at the interface for an asymmetrical junction.

Considering SRH recombination using Eq. (29) and summing over all the trap levels (subscript t) of all the SRH centers (subscript c) to include all their contributions to the SRH generation-recombination current, the interaction among the multiple levels of a trap being negligible[23,24] we may integrate the sum of $U_{SRH}(x)$ through the depletion width W to obtain

$$J_{SRH} = \frac{qn_i W(V)}{2\tau(V)}\left[\exp\left(\frac{qV}{2kT}\right) - 1\right], \tag{32}$$

which is similar to Eq. (22). The carrier lifetime in Eq. (32) is, however, dependent on the bias voltage V

$$\frac{1}{\tau(V)} = \frac{1}{W(V)}\int_0^W \sum_{c,t} \sigma_{ct} v N_{ct}(x)\eta_{SRHct}(V, x, \beta_{ct}, \gamma_{ct})dx, \tag{33}$$

where we assume that the multiple levels of a SRH center are independent with each other [24]. $N_{ct}(x)$ is the concentration distribution of level t of the SRH center c. σ_{ct} is the geometric average of the rates of capture of electrons and of holes of level t of the trap c, and so are β_{ct} and γ_{ct} defined.

Equation (32) maintains the same formulation of the simple SRH diode current [Eq. (22)], but by replacing Eq. (23) with a voltage dependent carrier lifetime [Eq. (33)], Eq. (31) reserves the richness and complexity of the SRH generation-recombination cast away by the three assumptions [Eqs. (18)–(20)].

Similar to our approach as presented by Eqs. (32) and (33), the complexity of SRH generation-recombination was studied by Sah *et al.*,[25] calculation using Eqs. (32) and (33) or their alike has been implemented numerically in most source codes of device simulation software packages,[26] the impact, however, of the trap's efficacy dependence on β and γ, especially in the area of photovoltaics, has not been explored. Analysis of the ramifications of the defect levels' efficacy in their roles as traps may shed new light on the performance and processing requirement of solar cells, especially polycrystalline thin film solar cells.

III. GENERAL RAMIFICATION OF EFFICACY OF THE SRH TRANSITION LEVEL TO PHOTOVOLTAICS

1. SRH generation-recombination current density without approximations [Eqs. (18)–(20)] is less than that with Eqs. (18)–(20), since the SRH level's efficacy η_{SRH} as formulated by Eq. (29) is less than 1, and is equal to 1 only when

$$\frac{E_i(V,x) - E_o}{kT} = -\ln\beta, \tag{34}$$

$$\gamma = -\ln\beta, \tag{35}$$

for all levels of all SRH centers within the depletion region. Obviously such conditions are impossible to meet. Therefore, for the same total amount of trapping levels in the depletion region

$$N_t = \frac{1}{W}\sum_{ct}\int_0^W N_{ct}(x)dx, \tag{36}$$

the ideal J_{SRH} as expressed by Eqs. (22) and (23) should be greater than the more realistic J_{SRH} as expressed by Eqs. (32) and (33). Thus, if measured diode current, either forward biased or reverse biased, is much greater than the prediction of Eqs. (22) and (23), then there are some other mechanisms deserving consideration, such as shunt resistance of the junction, surface generation-recombination at the grain boundaries of the polycrystalline thin film, and tunneling current through the interface.

2. Under reverse bias voltage with V ranging -1 to -2 V, which is used for diagnostic J-V characterization, Eq. (29) of the trap efficacy can be approximated

$$\eta_{SRH} = \frac{1}{\cosh(\gamma + \ln\beta)}, \tag{37}$$

which implies that, except in the area immediately next to the depletion region edges. the SRH generation efficacy is only determined by the charge state (double donor, donor,…) and the TGFEL of the transition level of the SRH center, independent of the bias voltage V. The SRH level's efficacy is always smaller than 1, but is equal to 1 under the condition

$$\beta = e^{-\gamma} = \exp\left(-\frac{G - E_i}{kT}\right). \tag{38}$$

Equation (38) implies that donor and double donor trapping levels in the lower part of the band gap, as well as acceptor and double acceptor trapping levels in the upper part of the band gap are more effective SRH generation centers, resulting in more reverse bias current.

3. Under forward bias voltage with $V/2kT \gg 1$, Eq. (29) may be approximated as

$$\eta_{SRH}(V, x, \beta) = \frac{1}{\cosh\left(\frac{E_i(V,x) - E_o}{kT} + \ln\beta\right)}. \tag{39}$$

As solar cells operate under forward bias, its dark current may be dominated by SRH recombination as shown in Eqs. (32) and (33). Theoretical as well as experimental study of β, the indicator of the trapping level's charging state, are still a void. Therefore, we assume 3 cases:

(a) $\beta = 1$

It is assumed that the state of electric charge of the trapping level has no effect on its capturing of electron or hole. Equation (39) is simplified

$$\eta_{SRH}(V, x, \beta) = \frac{1}{\cosh\left(\frac{E_i(V,x) - E_o}{kT}\right)}. \tag{40}$$

Trap efficacy η_{SRH} as a function of bias voltage V, location in the space charge region x, and its TGFEL is as shown in Fig. 2. Maxim $\eta_{SRH} = 1$ is at the interface $x = 0$.

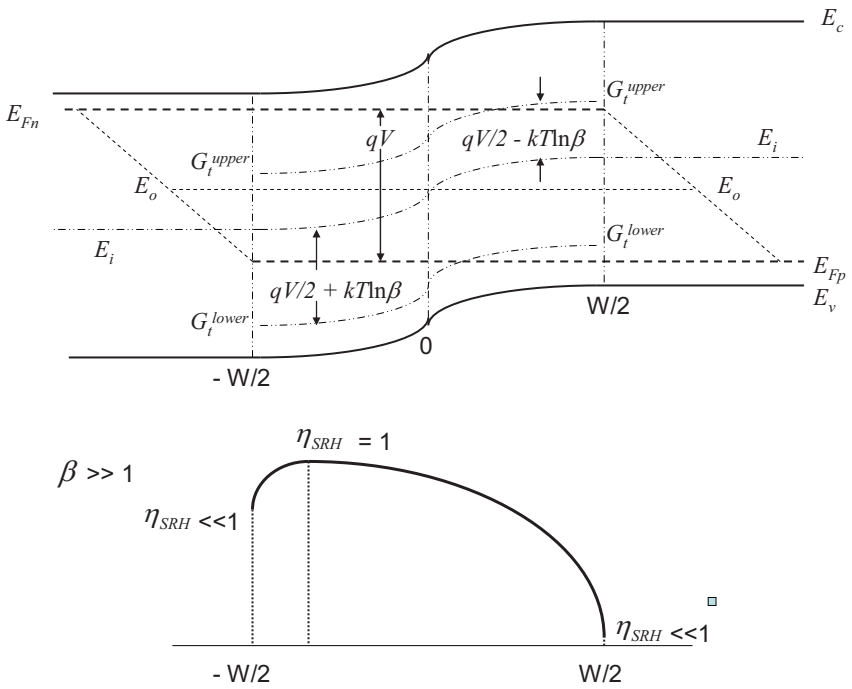


FIG. 3. Case $\beta \gg 1$: Defect level's trapping efficacy η_{SRH} as function of V, x, and γ in the depletion region of a symmetric n-p junction.

$$\eta_{SRH}\left(V, \pm\frac{W}{2}\right) = \frac{1}{2}\exp\left[-\left|\frac{E_i(V, \pm W/2) - E_o}{kT}\right|\right] \tag{41}$$

is the minimum efficacy, occurring at the depletion edges ±W/2. Since solar cells operate with output voltage V in the range 50%–70% of the junction built-in voltage V_{bi}, $\left|\frac{E_i(V,\pm W/2)-E_o}{kT}\right| \gg 1$, and therefore the minimum $\eta_{SRH} \ll 1$. Note that Eq. (40) as well as the curve of $\eta_{SRH}(x)$ as shown in Fig. 2 is only valid when the trap's TGFEL G_t is within the boundary of upper limit G_t^{upper} and lower limit G_t^{lower}

$$\begin{cases} G_t^{upper} = E_i + \dfrac{qV}{2} \\ G_t^{lower} = E_i - \dfrac{qV}{2} \end{cases} \tag{42}$$

beyond which Eq. (40) is invalid, and $\eta_{SRH} \sim 0$ for the trapping level G_t.

(b) $\beta \gg 1$ for donor and double donor trapping Equation (39) of the trapping level efficacy η_{SRH} as a function of V, x, β is shown in Fig. 3. The maxim $\eta_{SRH} = 1$ is at x, where

$$E_i(V,x) - E_o = -kT\ln\beta < 0 \text{ with } -\mathrm{W}/2 < x < 0 \ (n-\text{side of junction}). \tag{43}$$

If, however,

$$\left|E_i\left(V, -\frac{W}{2}\right) - E_o\right| < kT\ln\beta \tag{44}$$

then $\eta_{SRH} < 1$ occurring at the depletion region edge $x = -W/2$.

Equations (39) and (43), as well as the magnitude of η_{SRH} shown in Fig. 3, are valid only when the defect level's TGFEL is within the boundary of upper limit G_t^{upper} and lower limit G_t^{lower}

$$\begin{cases} G_t^{upper} = E_i - kT\ln\beta + \dfrac{qV}{2} \\ G_t^{lower} = E_i - kT\ln\beta - \dfrac{qV}{2} \end{cases} \text{ with } kT\ln\beta > 0. \tag{45}$$

Equation (39) is invalid for defect levels with TGFEL beyond the boundary. Their trapping efficacy $\eta_{SRH} \sim 0$.

(c) $\beta \ll 1$ for acceptor and double acceptor trapping level Equation (39) of the trapping level efficacy η_{SRH} as a function of V, x, β is shown in Fig. 4. The maxim $\eta_{SRH} = 1$ is at x, where

$$E_i(V,x) - E_o = -kT\ln\beta > 0 \text{ with } W/2 > x > 0 \ (p-\text{side of junction}). \tag{46}$$

If, however,

$$\left|E_i\left(V, \frac{W}{2}\right) - E_o\right| < -kT\ln\beta \tag{47}$$

then $\eta_{SRH} < 1$ occurring at the depletion region edge $x = W/2$.

Equations (39) and (46), as well as the magnitude of η_{SRH} shown in Fig. 4, are valid only when the defect level's TGFEL is within the boundary of upper limit G_t^{upper} and lower limit G_t^{lower}

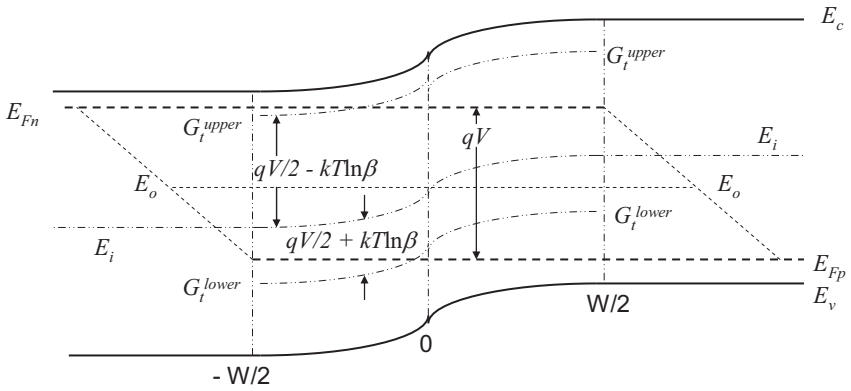
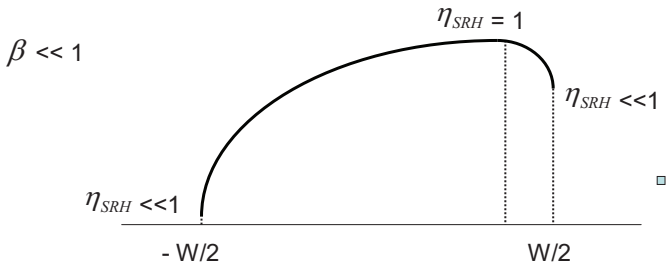


FIG. 4. Case $\beta \ll 1$ (acceptor, double acceptor): Defect level's trapping efficacy η_{SRH} as function of V, x, and γ in the depletion region of a symmetric n-p junction.



$$\begin{cases} G_t^{upper} = E_i - kT\ln\beta + \dfrac{qV}{2} \\ G_t^{lower} = E_i - kT\ln\beta - \dfrac{qV}{2} \end{cases} \text{with } kT\ln\beta < 0. \tag{48}$$

Equation (39) is invalid for defect levels with TGFEL beyond the boundary. Their trapping efficacy $\eta_{SRH} \sim 0$.

IV. CONCLUSION AND DISCUSSION

(1) We would like to emphasize that the change proposed in this work from "energy" to "free energy" is not merely semantics, as some critics would suggest. It is basic to semiconductor physics. Free energy or TGFEL involves how to treat semiconductor defect levels' dual doping-trapping roles consistently and correctly. The difference in the term of TS, which is experimentally measurable, may lead significant changes to our understanding and interpretation of experimental results in semiconductor physics. For, example, the widely used symmetry caused degeneracy $g_A = 4$ for acceptor dopant in cubic tetrahedral semiconductor induces the term of $TS = kT\ln g_A$. Yet the same acceptor defect level treated as SRH trap ignores symmetry induced entropy while involves multiple phonon induced entropy to interpret the Arrhenius plot in the Myer-Neldel rule.[16–18] Note that the optical phonon energy for Si and GaAs is 0.063 and 0.035 eV, respectively (acoustic phonon energy even lower), of comparable magnitude as $kT\ln g_A$ (0.04 eV) and the activation energy E_A (<0.05 eV for shallow acceptor). Not negligible, they are all measurable with various experimental techniques. Currently, such an inconsistent and incorrect treatment of a basic physical phenomenon—thermal occupation probability of a defect level—seems the root cause of some of the puzzling questions of semiconductor physics and its application in PV, such as whether the defect level cross section and activation energy follow the Myer-Neldel rule,[16–18] what the activation energy of $Cu_{Cd}^{(0/-)}$ is, an important acceptor level in CdTe thin film solar cells (optical experiments indicate 0.15 eV, while DLTS and other experimental techniques indicate 0.3–0.4 eV (Ref. 11 and references therein).

(2) Although the ramification of SRH trapping efficacy η_{SRH} to PV as presented in Sec. III of this work refers to the case of a symmetric n-p junction, the results, including the figures, are readily applicable to asymmetrical n-p junctions, including the abrupt n^+-p junction, wherein the band bending is only at the p-side, the n-side band bending being negligible. By taking the crossing point of an abrupt junction's p-side band bending curve and the horizontal E_o line as the interfacial $x = 0$ of a symmetrical junction, then the left side of p-band bending of an abrupt junction corresponds to the n-band bending ($x < 0$) of a symmetrical junction, while the right side corresponds to the p-band bending ($x > 0$) of a symmetrical junction. Of particular importance is the n^+-p junction in the commercially successful CdS/CdTe solar cell. Due to low cost processing, such junctions as well as other thin film solar cell junctions have high concentration (greater than $10^{17}/cm^3$) of various defect levels distributed across the band gap. It is essential to understand what type of defect levels with what TGFEL may have greater efficacy for SRH recombination, which is the dominant term in the cell's dark current density. As shown in Figs. 3 and 4, the donor and double donor level with its TGFEL in the lower part of band gap may cause more dark current than that with its TGFEL in the upper part of band gap. Oppositely, the acceptor or double acceptor level with its TGFEL in the upper part of band gap may lead to higher dark current density than that in the lower part of band gap.

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