Local charge neutrality condition, Fermi level and majority carrier density of a semiconductor with multiple localized multi-level intrinsic/impurity defects

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Abstract: For semiconductors with localized intrinsic/impurity defects, intentionally doped or unintentionally incorporated, that have multiple transition energy levels among charge states, the general formulation of the local charge neutrality condition is given for the determination of the Fermi level and the majority carrier density. A graphical method is used to illustrate the solution of the problem. Relations among the transition energy levels of the multi-level defect are derived using the graphical method. Numerical examples are given for p-doping of the CdTe thin film used in solar panels and semi-insulating Si to illustrate the relevance and importance of the issues discussed in this work.

Key words: multi-level defects; defect complex; intrinsic; impurity; semiconductor; Fermi level; majority carrier density

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1. Introduction

All localized electronic states in the bandgap of semiconductors due to intrinsic or impurity defects (including defect complexes), which may be incorporated naturally or through doping procedures, play the roles of intended carrier doping and mostly unintended carrier compensation and recombination. According to the role of the defect, it is called dopant (donor or acceptor) or (deep level) recombination center. The energy level of the former is close to the band edge, $\leqslant 0.05$ eV. That of the deep levels is greater than 0.05 eV[1−4]. In most semiconductor devices, the concentration of dopants is much higher than that of the traps. When calculating the Fermi level and majority carrier density we usually only consider shallow dopants (although the term of carrier compensation by deep levels is used, it is often not well defined), and when calculating the recombination current we only consider deep-level traps. Such a description, classification and treatment of midgap defect states are appropriate for widely used traditional semiconductor (such as Si, GaAs and InP) materials and devices.

Due to application requirements, technical difficulties and/or cost consideration, non-traditional semiconductor materials, such as semi-insulating semiconductors[5, 6], wide bandgap semiconductors[7, 8], transparent conducting oxides (TCO)[9, 10], as well as the CdTe polycrystalline thin films used in solar cells[11−14], the desired dopants may not be shallow and the unwanted generation-recombination centers or traps may not be deep. Localized midgap states of various activation energies and comparable concentrations may coexist in such materials. A well-known example is Cu_{Cd}, the Cu substitution of Cd in CdTe thin film, with a calculated activation energy of 0.22 eV[15] and an experimentally measured value 0.3–0.4 eV[13]. Cu_{Cd} is a non-shallow p-type dopant, as well as a non-deep trap. For such materials, it is appropriate to include all localized states as dopants (or compensators) when determining the Fermi level and carrier concentration, and to treat all states equally, not distinguishing between dopants and deep levels.

2. Local charge neutrality (LCN) condition of a semiconductor with multiple single-level donors and acceptors

For a non-degenerate semiconductor with multiple single-level dopants, including all intended or unintended n- and p-dopants, as well as all deep levels, either as compensators or as ineffective dopants, its Fermi level and majority carrier density can be calculated by using the local charge neutrality (LCN) condition[16]:

$$N_{\mathrm{V}} \exp \frac{E_{\mathrm{V}} - E_{\mathrm{F}}}{kT} + \sum_i \frac{N_{\mathrm{D}_i}}{1 + g_{\mathrm{D}_i} \exp \dfrac{E_{\mathrm{F}} - E_{\mathrm{D}_i}}{kT}} = N_{\mathrm{C}} \exp \frac{E_{\mathrm{F}} - E_{\mathrm{C}}}{kT} + \sum_j \frac{N_{\mathrm{A}_j}}{1 + g_{\mathrm{A}_j} \exp \dfrac{E_{\mathrm{A}_j} - E_{\mathrm{F}}}{kT}}, \quad (1)$$

where the left side includes the positively charged hole and ionized donor densities, and the right side includes the negatively charged electron and ionized acceptor densities. N_{C}, N_{V}, N_{D}, N_{A}, E_{C}, E_{V} and E_{F} are the effective density of states in the conduction band, the effective density of states in the valence band, the donor concentration (summed over i, or all the single donors), the acceptor concentration (summed over j, or all the single acceptors), the conduction band minimum (CBM), the

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valence band maximum (VBM), and the Fermi level, respectively. The most efficient way to solve Eq. (1) for the Fermi level and the majority carrier density—the result of compensation of dopants (donor or acceptor) by compensators (acceptor or donor)—is by using the graphical method[16].

For E_D and E_A, Wei and Zhang[15], as well as other authors, use the term transition energy level, instead of the widely used ionization or activation energy of the donor and acceptor, respectively. The transition energy level is defined as the Fermi energy at which the enthalpies of formation of an intrinsic/impurity defect of two different charges, such as $\Delta H_{\rm D}^{(+)}$ and $\Delta H_{\rm D}^{(0)}$ for an empty and occupied donor and $\Delta H_{\rm A}^{(0)}$ and $\Delta H_{\rm A}^{(-)}$ for an empty and occupied acceptor, are equal, and the transition occurs between the two charged states.

$$\begin{cases} E_{\rm A} = E_{\rm A}^{(0/-)} = \Delta E_{\rm A}^{(-)} - \Delta E_{\rm A}^{(0)} = E_{\rm F}, \\ \qquad \text{when } \Delta E_{\rm A}^{(0)} = \Delta E_{\rm A}^{(-)}(E_{\rm F}) = \Delta E_{\rm A}^{(-)} - E_{\rm F}, \\ E_{\rm D} = E_{\rm D}^{(+/0)} = \Delta E_{\rm D}^{(0)} - \Delta E_{\rm D}^{(+)} = E_{\rm F}, \\ \qquad \text{when } \Delta E_{\rm D}^{(0)} = \Delta E_{\rm D}^{(+)}(E_{\rm F}) = \Delta E_{\rm D}^{(+)} + E_{\rm F}, \end{cases} \tag{2}$$

where $\Delta E_{\rm D}^{(0)}$ and $\Delta E_{\rm A}^{(0)}$ of the neutral occupied donor and empty acceptor, as well as $\Delta E_{\rm D}^{(+)}$ and $\Delta E_{\rm A}^{(-)}$ of their charged counterparts, are Fermi level independent. They are defined and obtained by using first principles calculation[15].

The values of $g_{\rm D}$ and $g_{\rm A}$, depending on the configuration and symmetry of the defects, can be calculated by using Boltzmann statistics[2, 16, 17] for each donor and acceptor. For most widely used semiconductors of tetrahedral cubic structure, such as Si, GaAs and CdTe, $g_{\rm D} = 2$ and $g_{\rm A} = 4$.

3. Occupancy and ionization of double acceptors and double donors

The usefulness of Eq. (1) is limited, since many "dopants" and "deep levels" have multiple transition energy levels among their multiple charge states. Well-known examples are: the Cd vacancy $V_{\rm Cd}$ a double acceptor with calculated transition energy levels of 0.13 eV and 0.21 eV from the VBM[15]; the antisite double donor $\rm Te_{Cd}$, with calculated transition energy levels of 0.34 eV and 0.59 eV from the CBM[15]; and the Au impurity in Si, an amphoteric defect, which is a donor in p-type Si and an acceptor in n-type Si, with reported experimental value of $E_{\rm D} = 0.29$ eV, and $E_{\rm A} = 0.58$ eV, from the VBM[1, 6, 18]. Note that the ionization probability as well as the contribution to the fixed-charge density by multi-level defects given in Refs. [15, 19, 20] is only an approximation and valid under special conditions. The general and exact formulations of the occupancies of various charge states of single- and multi-level defects are given as follows.

As shown in Fig. 1, a single acceptor has one transition energy level $E_{\rm A}^{(0/-)}$ between the two charge states (0) and (−), with degeneracy $g_{\rm A}^{(0)}$ and $g_{\rm A}^{(-)}$, depending on the configuration and symmetry of the defect and the host semiconductor's valence band. For semiconductors with cubic tetrahedral symmetry, $g_{\rm A}^{(0)} = 4$ and $g_{\rm A}^{(-)} = 1$, respectively[2, 17, 18]. A double acceptor has three transition energy levels, $E_{\rm AA}^{(0/-)}$, $E_{\rm AA}^{(0/2-)}$

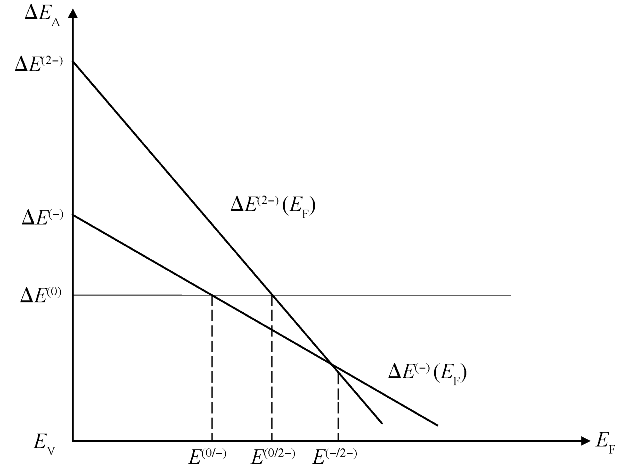

Fig. 1. The transition energy level is defined as the Fermi energy when the two charge states have the same energy of formation. For a single acceptor, two charge states, (0) and (−), have one transition energy level $E_{\rm A}^{(0/-)}$, usually called the ionization or activation energy $E_{\rm A}$ of the acceptor. For a double acceptor, denoted by the subscript AA, three charge states, (0), (−) and (2−), have three transition energy levels, $E_{\rm AA}^{(0/-)}$, $E_{\rm AA}^{(0/2-)}$, and $E_{\rm AA}^{(-/2-)}$. Note that ΔE of the charge state (0) is independent of the Fermi level, while ΔE of the charge states (−) and (2−) are dependent on the Fermi level, with slope −1 and −2, respectively. Note that from similarity of the triangles it is readily verified that $E_{\rm AA}^{(0/2-)} = \frac{1}{2}\left(E_{\rm AA}^{(0/-)} + E_{\rm AA}^{(-/2-)}\right)$. Since the figure is valid for both single acceptors and double acceptors, the subscripts A and AA are omitted.

and $E_{\rm AA}^{(-/2-)}$, among the three charge states (0), (−) and (2−), with degeneracy $g_{\rm AA}^{(0)}$, $g_{\rm AA}^{(-)}$, and $g_{\rm AA}^{(2-)}$, depending on the configuration and symmetry of the double acceptor and the host semiconductor. For the semiconductor with cubic tetrahedral symmetry, $g_{\rm AA}^{(0)} = 6$, $g_{\rm AA}^{(-)} = 4$, and $g_{\rm AA}^{(2-)} = 1$, respectively, which are obtained using the same argument as a single acceptor. By using Boltzmann statistics, a single acceptor has occupation probabilities as functions of the Fermi level.

$$P_{\rm A}^{(0)} = \frac{g_{\rm A}^{(0)} \exp\left(-\dfrac{\Delta E_{\rm A}^{(0)}}{kT}\right)}{g_{\rm A}^{(0)} \exp\left(-\dfrac{\Delta E_{\rm A}^{(0)}}{kT}\right) + g_{\rm A}^{(-)} \exp\left(-\dfrac{\Delta E_{\rm A}^{(-)}(E_{\rm F})}{kT}\right)} = \frac{1}{1 + \dfrac{g_{\rm A}^{(-)}}{g_{\rm A}^{(0)}} \exp\dfrac{E_{\rm F} - E_{\rm A}}{kT}}, \tag{3}$$

$$P_{\rm A}^{(-)} = \frac{g_{\rm A}^{(-)} \exp\left(-\dfrac{\Delta E_{\rm A}^{(-)}(E_{\rm F})}{kT}\right)}{g_{\rm A}^{(0)} \exp\left(-\dfrac{\Delta E_{\rm A}^{(o)}}{kT}\right) + g_{\rm A}^{(-)} \exp\left(-\dfrac{\Delta E_{\rm A}^{(-)}(E_{\rm F})}{kT}\right)} = \frac{1}{1 + \dfrac{g_{\rm A}^{(0)}}{g_{\rm A}^{(-)}} \exp\dfrac{E_{\rm A} - E_{\rm F}}{kT}}, \tag{4}$$

where $E_A = E_A^{(0/-)} = \Delta E_A^{(-)} - \Delta E_A^{(0)}$. Apparently, $P_A^{(0)} + P_A^{(-)} = 1$. Equations (3) and (4) are consistent with the ionization.

For a double acceptor, the occupation probabilities of the charge states of (0), (−) and (2−) are

$$P_{AA}^{(0)} = \frac{g_{AA}^{(0)} \exp\left(-\frac{\Delta E_{AA}^{(0)}}{kT}\right)}{g_{AA}^{(0)} \exp\left(-\frac{\Delta E_{AA}^{(0)}}{kT}\right) + g_{AA}^{(-)} \exp\left(-\frac{\Delta E_{AA}^{(-)}(E_F)}{kT}\right) + g_{AA}^{(2-)} \exp\left(-\frac{\Delta E_{AA}^{(2-)}(E_F)}{kT}\right)}$$

$$= \frac{\frac{g_{AA}^{(0)}}{g_{AA}^{(2-)}} \exp \frac{2\left(E_{AA}^{(0/2-)} - E_F\right)}{kT}}{1 + \frac{g_{AA}^{(-)}}{g_{AA}^{(2-)}} \exp \frac{E_{AA}^{(-/2-)} - E_F}{kT} + \frac{g_{AA}^{(0)}}{g_{AA}^{(2-)}} \exp \frac{2\left(E_{AA}^{(0/2-)} - E_F\right)}{kT}}, \quad (5)$$

$$P_{AA}^{(-)} = \frac{g_{AA}^{(-)} \exp\left(-\frac{\Delta E_{AA}^{(-)}(E_F)}{kT}\right)}{g_{AA}^{(0)} \exp\left(-\frac{\Delta E_{AA}^{(0)}}{kT}\right) + g_{AA}^{(-)} \exp\left(-\frac{\Delta E_{AA}^{(-)}(E_F)}{kT}\right) + g_{AA}^{(2-)} \exp\left(-\frac{\Delta E_{AA}^{(2-)}(E_F)}{kT}\right)}$$

$$= \frac{\frac{g_{AA}^{(-)}}{g_{AA}^{(2-)}} \exp \frac{E_{AA}^{(-/2-)} - E_F}{kT}}{1 + \frac{g_{AA}^{(-)}}{g_{AA}^{(2-)}} \exp \frac{E_{AA}^{(-/2-)} - E_F}{kT} + \frac{g_{AA}^{(0)}}{g_{AA}^{(2-)}} \exp \frac{2\left(E_{AA}^{(0/2-)} - E_F\right)}{kT}}, \quad (6)$$

$$P_{AA}^{(2-)} = \frac{g_{AA}^{(2-)} \exp\left(-\frac{\Delta E_{AA}^{(2-)}(E_F)}{kT}\right)}{g_{AA}^{(0)} \exp\left(-\frac{\Delta E_{AA}^{(0)}}{kT}\right) + g_{AA}^{(-)} \exp\left(-\frac{\Delta E_{AA}^{(-)}(E_F)}{kT}\right) + g_{AA}^{(2-)} \exp\left(-\frac{\Delta E_{AA}^{(2-)}(E_F)}{kT}\right)}$$

$$= \frac{1}{1 + \frac{g_{AA}^{(-)}}{g_{AA}^{(2-)}} \exp \frac{E_{AA}^{(-/2-)} - E_F}{kT} + \frac{g_{AA}^{(0)}}{g_{AA}^{(2-)}} \exp \frac{2\left(E_{AA}^{(0/2-)} - E_F\right)}{kT}}, \quad (7)$$

where $P_{AA}^{(0)} + P_{AA}^{(-)} + P_A^{(2-)} = 1$.

Similarly, as shown in Fig. 2, a single donor has one transition energy level, $E_D^{(+/0)}$, between the two charge states, (0) and (+). As in the case of a single acceptor, $g_D^{(0)}$ and $g_D^{(+)}$ depend on the configuration and symmetry of the donor defect as well as the host semiconductor's conduction band. For semiconductors with cubic tetrahedral symmetry, $g_D^{(0)} = 2$ and $g_D^{(+)} = 1$, respectively[2, 17, 18], which are obtained using the same argument as a single acceptor. A double donor has three transition energy levels $E_{DD}^{(+/0)}$, $E_{DD}^{(2+/0)}$ and $E_{DD}^{(2+/+)}$ among the three charge states (0), (+) and (2+), with degeneracy $g_{DD}^{(0)}$, $g_{DD}^{(+)}$, and $g_{DD}^{(2+)}$, depending on the configuration and symmetry of the double donor and the host semiconductor's conduction band. For semiconductors with cubic tetrahedral symmetry, $g_{DD}^{(0)} = 1$, $g_{DD}^{(+)} = 2$ and $g_{DD}^{(2+)} = 1$, respectively, by using the same argument as used for the double acceptor.

$$P_D^{(0)} = \frac{g_D^{(0)} \exp\left(-\frac{\Delta E_D^{(0)}}{kT}\right)}{g_D^{(0)} \exp\left(-\frac{\Delta E_D^{(0)}}{kT}\right) + g_D^{(+)} \exp\left(-\frac{\Delta E_D^{(+)}(E_F)}{kT}\right)} = \frac{1}{1 + \frac{g_D^{(+)}}{g_D^{(0)}} \exp \frac{E_D^{(+/0)} - E_F}{kT}}, \quad (8)$$

$$P_{\mathrm{D}}^{(+)} = \frac{g_{\mathrm{D}}^{(+)} \exp\left(-\frac{\Delta E_{\mathrm{D}}^{(+)}(E_{\mathrm{F}})}{kT}\right)}{g_{\mathrm{D}}^{(0)} \exp\left(-\frac{\Delta E_{\mathrm{D}}^{(0)}}{kT}\right) + g_{\mathrm{D}}^{(+)} \exp\left(-\frac{\Delta E_{\mathrm{D}}^{(+)}(E_{\mathrm{F}})}{kT}\right)} = \frac{1}{1 + \frac{g_{\mathrm{D}}^{(0)}}{g_{\mathrm{D}}^{(+)}} \exp\frac{E_{\mathrm{F}} - E_{\mathrm{D}}^{(+/0)}}{kT}}. \tag{9}$$

Again, $P_{\mathrm{D}}^{(+)} + P_{\mathrm{D}}^{(0)} = 1$, and Eqs. (8) and (9) are consistent with the single-level donor ionization probability in Eq. (1). For a double donor, the occupancies of the charge states of (0), (+) and (2+) are

$$\begin{aligned} P_{\mathrm{DD}}^{(0)} &= \frac{g_{\mathrm{DD}}^{(0)} \exp\left(-\frac{\Delta E_{\mathrm{DD}}^{(0)}}{kT}\right)}{g_{\mathrm{DD}}^{(0)} \exp\left(-\frac{\Delta E_{\mathrm{DD}}^{(0)}}{kT}\right) + g_{\mathrm{DD}}^{(+)} \exp\left(-\frac{\Delta E_{\mathrm{DD}}^{(+)}(E_{\mathrm{F}})}{kT}\right) + g_{\mathrm{DD}}^{(2+)} \exp\left(-\frac{\Delta E_{\mathrm{DD}}^{(2+)}(E_{\mathrm{F}})}{kT}\right)} \\ &= \frac{\frac{g_{\mathrm{DD}}^{(0)}}{g_{\mathrm{DD}}^{(2+)}} \exp\frac{2\left(E_{\mathrm{F}} - E_{\mathrm{DD}}^{(2+/0)}\right)}{kT}}{1 + \frac{g_{\mathrm{DD}}^{(+)}}{g_{\mathrm{DD}}^{(2+)}} \exp\frac{E_{\mathrm{F}} - E_{\mathrm{DD}}^{(2+/+)}}{kT} + \frac{g_{\mathrm{DD}}^{(0)}}{g_{\mathrm{DD}}^{(2+)}} \exp\frac{2\left(E_{\mathrm{F}} - E_{\mathrm{DD}}^{(2+/0)}\right)}{kT}}, \end{aligned} \tag{10}$$

$$\begin{aligned} P_{\mathrm{DD}}^{(+)} &= \frac{g_{\mathrm{DD}}^{(+)} \exp\left(-\frac{\Delta E_{\mathrm{DD}}^{(+)}(E_{\mathrm{F}})}{kT}\right)}{g_{\mathrm{DD}}^{(0)} \exp\left(-\frac{\Delta E_{\mathrm{DD}}^{(0)}}{kT}\right) + g_{\mathrm{DD}}^{(+)} \exp\left(-\frac{\Delta E_{\mathrm{DD}}^{(+)}(E_{\mathrm{F}})}{kT}\right) + g_{\mathrm{DD}}^{(2+)} \exp\left(-\frac{\Delta E_{\mathrm{DD}}^{(2+)}(E_{\mathrm{F}})}{kT}\right)} \\ &= \frac{\frac{g_{\mathrm{DD}}^{(+)}}{g_{\mathrm{DD}}^{(2+)}} \exp\frac{E_{\mathrm{F}} - E_{\mathrm{DD}}^{(2+/+)}}{kT}}{1 + \frac{g_{\mathrm{DD}}^{(+)}}{g_{\mathrm{DD}}^{(2+)}} \exp\frac{E_{\mathrm{F}} - E_{\mathrm{DD}}^{(2+/+)}}{kT} + \frac{g_{\mathrm{DD}}^{(0)}}{g_{\mathrm{DD}}^{(2+)}} \exp\frac{2\left(E_{\mathrm{F}} - E_{\mathrm{DD}}^{(2+/0)}\right)}{kT}}, \end{aligned} \tag{11}$$

$$\begin{aligned} P_{\mathrm{DD}}^{(2+)} &= \frac{g_{\mathrm{DD}}^{(2+)} \exp\left(-\frac{\Delta E_{\mathrm{DD}}^{(2+)}(E_{\mathrm{F}})}{kT}\right)}{g_{\mathrm{DD}}^{(0)} \exp\left(-\frac{\Delta E_{\mathrm{D}}^{(0)}}{kT}\right) + g_{\mathrm{DD}}^{(+)} \exp\left(-\frac{\Delta E_{\mathrm{DD}}^{(+)}(E_{\mathrm{F}})}{kT}\right) + g_{\mathrm{DD}}^{(2+)} \exp\left(-\frac{\Delta E_{\mathrm{DD}}^{(2+)}(E_{\mathrm{F}})}{kT}\right)} \\ &= \frac{1}{1 + \frac{g_{\mathrm{DD}}^{(+)}}{g_{\mathrm{DD}}^{(2+)}} \exp\frac{E_{\mathrm{F}} - E_{\mathrm{DD}}^{(2+/+)}}{kT} + \frac{g_{\mathrm{DD}}^{(0)}}{g_{\mathrm{DD}}^{(2+)}} \exp\frac{2\left(E_{\mathrm{F}} - E_{\mathrm{DD}}^{(2+/0)}\right)}{kT}}, \end{aligned} \tag{12}$$

where $P_{\mathrm{DD}}^{(0)} + P_{\mathrm{DD}}^{(+)} + P_{\mathrm{DD}}^{(2+)} = 1$.

4. Occupancy and ionization of amphoteric and higher-valent defects

The amphoteric defect, denoted by the subscript DA, as shown in Fig. 3 has three transition energy levels among its three charge states (+), (0) and (−), with degeneracy $g_{\mathrm{DA}}^{(+)}$, $g_{\mathrm{DA}}^{(0)}$, and $g_{\mathrm{DA}}^{(-)}$, dependent on the configuration and symmetry of the defect. Their occupation probabilities are

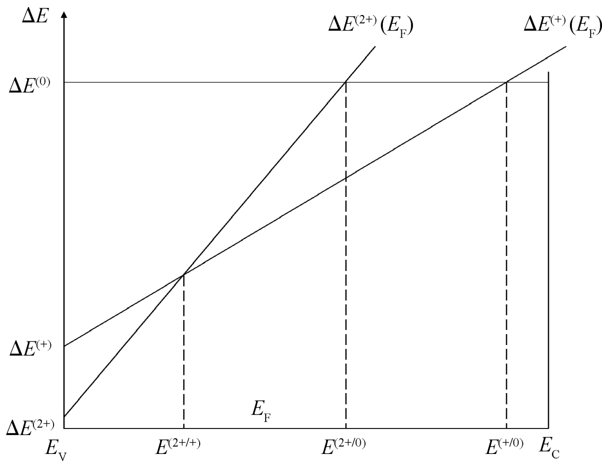

Fig. 2. For a single donor, two charge states, (+) and (0), have one transition energy level $E_{\rm D}^{(+/0)}$, usually called the ionization or activation energy $E_{\rm D}$ of the donor. For a double donor, three charge states, (2+), (+) and (0), have three transition energy levels $E_{\rm DD}^{(2+/+)}$, $E_{\rm DD}^{(2+/0)}$, and $E_{\rm DD}^{(+/0)}$. Note that ΔE of the charge state (0) is independent of Fermi energy, while ΔE of charge states (+) and (2+) are dependent on the Fermi level, with slope +1 and +2, respectively. Similarly, as in Fig. 1, $E_{\rm DD}^{(2+/0)} = \frac{1}{2}\left(E_{\rm DD}^{(+/0)} + E_{\rm DD}^{(2+/+)}\right)$. Since the figure is valid for both single donors and double donors, the subscript D and DD are omitted.

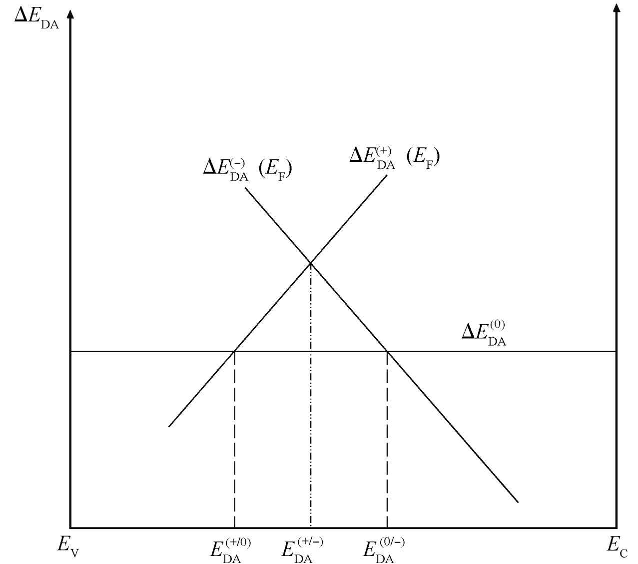

Fig. 3. An amphoteric defect has three transition energy levels among three charge states, (+), (0), and (−). Similar to the double acceptor and the double donor, the amphoteric defect has $E_{\rm DA}^{(+/-)} = \frac{1}{2}\left(E_{\rm DA}^{(+/0)} + E_{\rm DA}^{(0/-)}\right)$.

$$\begin{aligned}
P_{\rm DA}^{(+)} &= \frac{g_{\rm DA}^{(+)}\exp\left(-\dfrac{\Delta E_{\rm DA}^{(+)}(E_{\rm F})}{kT}\right)}{g_{\rm DA}^{(+)}\exp\left(-\dfrac{\Delta E_{\rm DA}^{(+)}(E_{\rm F})}{kT}\right) + g_{\rm DA}^{(0)}\exp\left(-\dfrac{\Delta E_{\rm DA}^{(0)}}{kT}\right) + g_{\rm DA}^{(-)}\exp\left(-\dfrac{\Delta E_{\rm DA}^{(-)}(E_{\rm F})}{kT}\right)} \\
&= \frac{\dfrac{g_{\rm DA}^{(+)}}{g_{\rm DA}^{(0)}}\exp\dfrac{E_{\rm DA}^{(+/0)} - E_{\rm F}}{kT}}{\dfrac{g_{\rm DA}^{(+)}}{g_{\rm DA}^{(0)}}\exp\dfrac{E_{\rm DA}^{(+/0)} - E_{\rm F}}{kT} + 1 + \dfrac{g_{\rm DA}^{(-)}}{g_{\rm DA}^{(0)}}\exp\dfrac{E_{\rm F} - E_{\rm DA}^{(0/-)}}{kT}} \\
&= \frac{1}{1 + \dfrac{g_{\rm DA}^{(0)}}{g_{\rm DA}^{(+)}}\exp\dfrac{E_{\rm F} - E_{\rm DA}^{(+/0)}}{kT} + \dfrac{g_{\rm DA}^{(-)}}{g_{\rm DA}^{(+)}}\exp\dfrac{2\left(E_{\rm F} - E_{\rm DA}^{(+/-)}\right)}{kT}},
\end{aligned} \tag{13}$$

$$\begin{aligned}
P_{\rm DA}^{(0)} &= \frac{g_{\rm DA}^{(0)}\exp\left(-\dfrac{\Delta E_{\rm DA}^{(0)}}{kT}\right)}{g_{\rm DA}^{(+)}\exp\left(-\dfrac{\Delta E_{\rm DA}^{(+)}(E_{\rm F})}{kT}\right) + g_{\rm DA}^{(0)}\exp\left(-\dfrac{\Delta E_{\rm DA}^{(0)}}{kT}\right) + g_{\rm DA}^{(-)}\exp\left(-\dfrac{\Delta E_{\rm DA}^{(-)}(E_{\rm F})}{kT}\right)} \\
&= \frac{1}{\dfrac{g_{\rm DA}^{(+)}}{g_{\rm DA}^{(0)}}\exp\dfrac{E_{\rm DA}^{(+/0)} - E_{\rm F}}{kT} + 1 + \dfrac{g_{\rm DA}^{(-)}}{g_{\rm DA}^{(0)}}\exp\dfrac{E_{\rm F} - E_{\rm DA}^{(0/-)}}{kT}},
\end{aligned} \tag{14}$$

$$P_{\rm DA}^{(-)} = \frac{g_{\rm DA}^{(-)}\exp\left(-\dfrac{\Delta E_{\rm DA}^{(-)}(E_{\rm F})}{kT}\right)}{g_{\rm DA}^{(+)}\exp\left(-\dfrac{\Delta E_{\rm DA}^{(+)}(E_{\rm F})}{kT}\right) + g_{\rm DA}^{(0)}\exp\left(-\dfrac{\Delta E_{\rm DA}^{(0)}}{kT}\right) + g_{\rm DA}^{(-)}\exp\left(-\dfrac{\Delta E_{\rm DA}^{(-)}(E_{\rm F})}{kT}\right)}$$

$$
= \frac{\dfrac{g_{\mathrm{DA}}^{(-)}}{g_{\mathrm{DA}}^{(0)}} \exp \dfrac{E_{\mathrm{F}} - E_{\mathrm{DD}}^{(0/-)}}{kT}}{\dfrac{g_{\mathrm{DA}}^{(+)}}{g_{\mathrm{DA}}^{(0)}} \exp \dfrac{E_{\mathrm{DA}}^{(+/0)} - E_{\mathrm{F}}}{kT} + 1 + \dfrac{g_{\mathrm{DA}}^{(-)}}{g_{\mathrm{DA}}^{(0)}} \exp \dfrac{E_{\mathrm{F}} - E_{\mathrm{DA}}^{(0/-)}}{kT}}
$$

$$
= \frac{1}{1 + \dfrac{g_{\mathrm{DA}}^{(0)}}{g_{\mathrm{DA}}^{(-)}} \exp \dfrac{E_{\mathrm{DA}}^{(0/-)} - E_{\mathrm{F}}}{kT} + \dfrac{g_{\mathrm{DA}}^{(+)}}{g_{\mathrm{DA}}^{(-)}} \exp \dfrac{2\left(E_{\mathrm{DA}}^{(+/-)} - E_{\mathrm{F}}\right)}{kT}}. \tag{15}
$$

It is readily verified that $P_{\mathrm{DA}}^{(+)} + P_{\mathrm{DA}}^{(0)} + P_{\mathrm{DA}}^{(-)} = 1$. Trivalent and higher order defects do exist, but there is very little experimental data available. The 10 transition energy levels of a quadravalent, or amphoteric double donor–double acceptor among its five charge states are shown in Fig. 4. In general, a defect or defect complex with m charge states has $(m-1)m/2$ transition energy levels among them.

5. LCN condition of a semiconductor with multiple multi-level defects

The usefulness of Eq. (1) is limited, since many “dopants”, especially “deep levels”, have multi-level transitions. In the progressively more complicated semiconductor materials we must consider single and double donors, single and double acceptors, and amphoteric defects (single donor or single acceptor). The general form of the LCN condition of such a material is expressed as

$$
\begin{aligned}
& N_{\mathrm{V}} \exp \frac{E_{\mathrm{V}} - E_{\mathrm{F}}}{kT} + \sum_i N_{\mathrm{D}_i} \frac{1}{1 + \dfrac{g_{\mathrm{D}_i}^{(0)}}{g_{\mathrm{D}_i}^{(+)}} \exp \dfrac{E_{\mathrm{F}} - E_{\mathrm{D}_i}}{kT}} \\
& + \sum_l N_{\mathrm{DD}_l} \frac{\dfrac{g_{\mathrm{DD}_l}^{(+)}}{g_{\mathrm{DD}_l}^{(2+)}} \exp \dfrac{E_{\mathrm{F}} - E_{\mathrm{DD}_l}^{(2+/+)}}{kT} + 2}{1 + \dfrac{g_{\mathrm{DD}_l}^{(+)}}{g_{\mathrm{DD}_l}^{(2+)}} \exp \dfrac{E_{\mathrm{F}} - E_{\mathrm{DD}_l}^{(2+/+)}}{kT} + \dfrac{g_{\mathrm{DD}_l}^{(0)}}{g_{\mathrm{DD}_l}^{(2+)}} \exp \dfrac{2\left(E_{\mathrm{F}} - E_{\mathrm{DD}_l}^{(2+/0)}\right)}{kT}} \\
& + \sum_s N_{\mathrm{DA}_s} \frac{1}{1 + \dfrac{g_{\mathrm{DA}_s}^{(0)}}{g_{\mathrm{DA}_s}^{(+)}} \exp \dfrac{E_{\mathrm{F}} - E_{\mathrm{DA}_s}^{(+/0)}}{mkT} + \dfrac{g_{\mathrm{DA}_s}^{(-)}}{g_{\mathrm{DA}_s}^{(+)}} \exp \dfrac{2\left(E_{\mathrm{F}} - E_{\mathrm{DA}_s}^{(+/-)}\right)}{kT}} \\
& = N_{\mathrm{C}} \exp \frac{E_{\mathrm{F}} - E_{\mathrm{C}}}{kT} + \sum_j N_{\mathrm{A}_j} \frac{1}{1 + \dfrac{g_{\mathrm{A}_j}^{(0)}}{g_{\mathrm{A}_j}^{(-)}} \exp \dfrac{E_{\mathrm{A}_j} - E_{\mathrm{F}}}{kT}} \\
& + \sum_m N_{\mathrm{AA}_m} \frac{\dfrac{g_{\mathrm{AA}_m}^{(-)}}{g_{\mathrm{AA}_m}^{(2-)}} \exp \dfrac{E_{\mathrm{AA}_m}^{(-/2-)} - E_{\mathrm{F}}}{kT} + 2}{1 + \dfrac{g_{\mathrm{AA}_m}^{(-)}}{g_{\mathrm{AA}_m}^{(2-)}} \exp \dfrac{E_{\mathrm{AA}_m}^{(-/2-)} - E_{\mathrm{F}}}{kT} + \dfrac{g_{\mathrm{AA}_m}^{(0)}}{g_{\mathrm{AA}_m}^{(2-)}} \exp \dfrac{2\left(E_{\mathrm{AA}_m}^{(0/2-)} - E_{\mathrm{F}}\right)}{kT}} \\
& + \sum_s N_{\mathrm{DA}_s} \frac{1}{1 + \dfrac{g_{\mathrm{DA}_s}^{(0)}}{g_{\mathrm{DA}_s}^{(-)}} \exp \dfrac{E_{\mathrm{DA}_s}^{(0/-)} - E_{\mathrm{F}}}{kT} + \dfrac{g_{\mathrm{DA}_s}^{(+)}}{g_{\mathrm{DA}_s}^{(-)}} \exp \dfrac{2\left(E_{\mathrm{DA}_s}^{(+/-)} - E_{\mathrm{F}}\right)}{kT}},
\end{aligned} \tag{16}
$$

where the first two terms of the left side and of the right side are the same as in Eq. (1). The third term of the left side is the sum of the positive fixed-charge density due to double donors (summed over l) and the third term of the right side is the sum of the

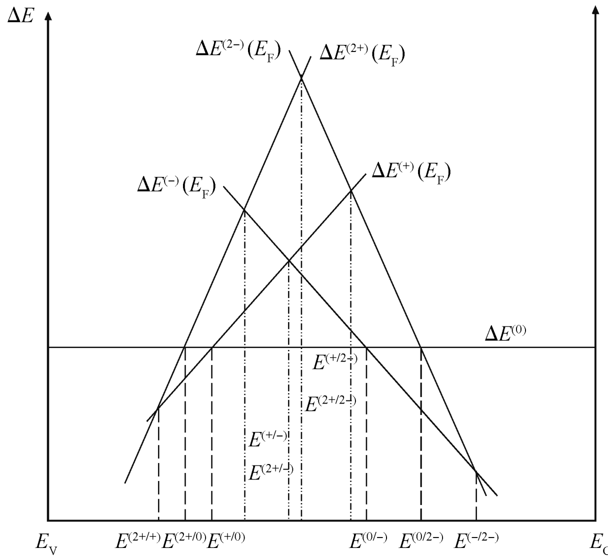

Fig. 4. A quadravalent double donor/double acceptor defect or defect complex has 10 transition energy levels, $E^{(+/0)}$, $E^{(2+/0)}$, $E^{(2+/+)}$ (as a double donor), $E^{(0/-)}$, $E^{(0/2-)}$, $E^{(-/2-)}$ (as a double acceptor) and $E^{(2+/-)}$, $E^{(+/-)}$, $E^{(2+/2-)}$ and $E^{(+/2-)}$ among its five charge states $\Delta E^{(2+)}$, $\Delta E^{(+)}$, $\Delta E^{(0)}$, $\Delta E^{(-)}$, $\Delta E^{(2-)}$.

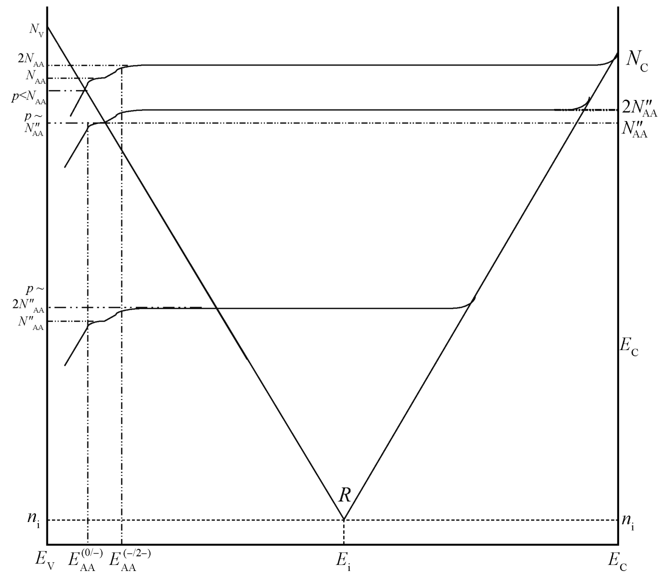

Fig. 5. Three different concentrations $N_{\rm AA} > N'_{\rm AA} > N''_{\rm AA}$ of the same double acceptor (for example a CD vacancy in CdTe) with transition energy level $E^{(0/-)}$ for first ionization and $E^{(-/2-)}$ for second ionization. The hole density of the three cases are $p/N_{\rm AA} \ll 1$, $p'/N'_{\rm AA} \approx 1$, $p''/N''_{\rm AA} \approx 2$, respectively. The straight lines of hole concentration and of electron concentration cross at R, yielding the intrinsic Fermi energy $E_{\rm F}$ and the intrinsic carrier density $n_{\rm i}$.

negative fixed-charge density due to double acceptors (summed over m). The fourth term of the left side is the sum (over s) of the positive fixed-charge density due to amphoteric defects functioning as donors. The fourth term of the right side is the sum (over s) of the negative fixed-charge density due to amphoteric defects functioning as acceptors.

It is interesting to note that under the condition

$$E_{\rm DA}^{(+/0)} - E_{\rm F} > 3kT, \tag{17}$$

the amphoteric defect functions mostly as an ionized donor and the fourth term on the right side—the amphoteric defect functioning as an ionized acceptor—is negligible. However, if

$$E_{\rm F} - E_{\rm DA}^{(0/-)} > 3kT, \tag{18}$$

the amphoteric defect functions mostly as an ionized acceptor, and the fourth term on the left side—the amphoteric defect functioning as an ionized donor—is negligible. Under the condition of

$$\begin{cases} E_{\rm F} - E_{\rm DA}^{(+/0)} < 3kT, \\ E_{\rm DA}^{(0/-)} - E_{\rm F} < 3kT, \end{cases} \tag{19}$$

the amphoteric defect functions as a donor as well as an acceptor, and neither the fourth terms on the right side nor on the left side can be neglected. However, under the condition of

$$\begin{cases} E_{\rm F} - E_{\rm DA}^{(+/0)} > 3kT, \\ E_{\rm DA}^{(0/-)} - E_{\rm F} > 3kT, \end{cases} \tag{20}$$

the fourth terms on both the right side and the left side are negligible. The amphoteric defect is mostly not ionized.

As in the case of a semiconductor with multiple single-level defects, to solve the Fermi level and the majority carrier density of a semiconductor with multiple multi-level defects, the best approaches are the graphical method[21] and the mixed graphical-numerical method[22], respectively. Here we give two simple examples of the utilization of Eq. (18). Figure 5 can be graphically obtained by substituting the given parameters in Eq. (18) with $E_{\rm F}$ in linear scale as the x-axis, and the carrier concentration in logarithmic scale as the y-axis. Figure 5 involves only the hole concentration—the first term of the left side and the double acceptor density—one item of the third term of the right side. Such a p-type semiconductor may have its hole density p ranging from far less than $N_{\rm AA}$ to $2N_{\rm AA}$.

The compensation of an amphoteric donor-acceptor of an n-type semiconductor is shown in Fig. 6. A similar plot can be made for the graphical solution of the compensation of a p-type semiconductor by amphoteric defects.

A particularly interesting application of the general LCN condition (16) is the case of the p-doping of CdTe, one of the commercially most successful semiconductor materials for photovoltaics. It is generally agreed that $\rm Cu_{Cd}$, the Cu impurity substitute of Cd, is the dominant p-doping single acceptor[12, 15, 20] for CdTe polycrystalline thin film. In addition to $\rm Cu_{Cd}$, CdTe is also incorporated with a cadmium vacancy $\rm V_{Cd}$, a double acceptor and Cu interstitial $\rm Cu_i$, a shallow donor. The interplay of these three intrinsic/impurity states (multi-level $\rm V_{Cd}$ and self-compensating $\rm Cu_{Cd}$ and $\rm Cu_i$) makes the material poor p-type, good p-type, insulating or n-type, depending on the CdTe thin film processing temperature[19, 20, 23]. Since the experimental data of the energies of formation and transition energy levels of the aforesaid three states are unreliable and controversial, they are determined by first principles calculation[15, 24]. By substituting the calculated transition energy levels into Eq. (16) we get the Fermi energy and doping level of CdTe at a certain temperature, which agree with experimentally

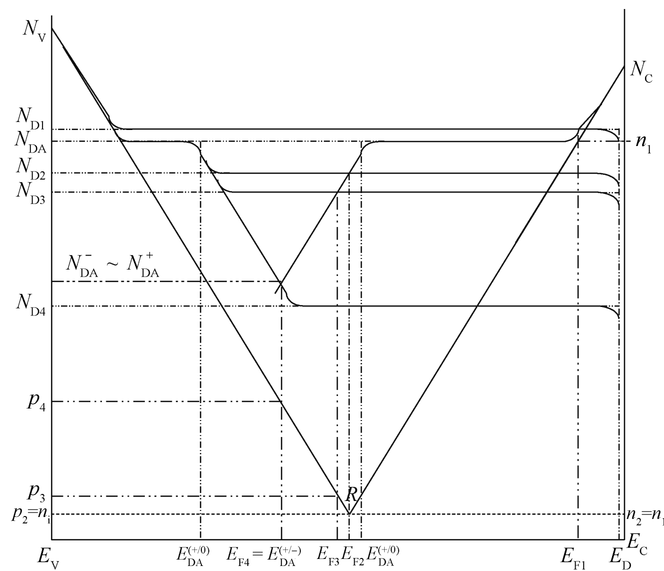

Fig. 6. Four n-type semiconductors with the same shallow single donors of transition energy level $E_{\rm D}$, but different concentrations ($N_{\rm D1} > N_{\rm D2} > N_{\rm D3} > N_{\rm D4}$) are compensated by the amphoteric defect with concentration of $N_{\rm DA}$ and transition energy level $E^{(+/0)}$ and $E^{(0/-)}$ (for example, a Au impurity in Si). For $N_{\rm D1} > N_{\rm DA}$, the amphoteric defects, behaving as deep-level acceptors of transition energy level $E_{\rm DA}^{(0/-)}$, compensate the n-type semiconductor, rendering an electron density of n_1, which is determined by $N_{\rm D1}$ and $N_{\rm DA}$, independent of the depth ($E_{\rm DA}^{(+/0)}$ and $E_{\rm DA}^{(0/-)}$) of the amphoteric defect. For n-type dopant level of $N_{\rm D2}$, $N_{\rm D3}$, and $N_{\rm D4}$, all less than the amphoteric defect density $N_{\rm DA}$, the result is dominated by the amphoteric defect as deep levels, ranging from very low n, to insulating ($N_{\rm D2}$), and very low p ($N_{\rm D3}$ and $N_{\rm D4}$).

measured Fermi level and p-doping values[23].

6. Conclusion

In summary, we have presented the general form of the LCN condition of semiconductors with multiple single-level and multi-level defects. The author acknowledges helpful discussions with Professor H. Kroemer of University of California, Santa Barbara, S. Wei of National Renewable Energy Lab, J. Sites of Colorado State University, and T. Ohno and R. Collins of Colorado School of Mines.

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