A new method for calculation of majority carrier compensation in photovoltaics

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Abstract: In thin film solar cells, the semiconductor materials usually contain multiple impurity/defect states as donor or acceptor dopants. The local charge neutrality (LCN) condition determines the equilibrium Fermi (EF) level and concentration of electrons and holes. However, the equation of LCN is a transcendental equation of EF. It is impossible to find its analytical solution and we can only solve it by graphic or numerical method. A simple approximate graphic method (GM) used for estimation of majority carrier compensation of semiconductors with multiple donors and acceptors was proposed by Chin. By introducing the concept of ranking the dopants and the wrapping step function, dopants concentration and Fermi level could be obtained easily. In this paper, we analyze the graphic method and propose a new numeric graphic method (NGM) based on GM. In addition, comparison of NGM with NM and analytics of the accuracy of GM are presented. With numerical calculation, some procedures of GM extending the application of GM are improved.

Key words: doping II–VI; semiconductors; defect
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1. Introduction

The performance of an intrinsic semiconductor would be improved when the semiconductor is implanted by donors or acceptors impurities, such as silicon with phosphorous which raise its conductivity over 10 orders of magnitude[1]. For traditional semiconductors with a single shallow donor (for n-type) or acceptor (for p-type) impurity level, all the impurities are ionized[2]. The concentration of majority carriers in non-degenerate p-type and n-type material are presented, respectively.

$$p = N_{\mathrm{V}} \exp \frac{E_{\mathrm{V}} - E_{\mathrm{F}}}{kT} \approx N_{\mathrm{A}} \frac{1}{1 + g_{\mathrm{A}} \exp \frac{E_{\mathrm{V}} - E_{\mathrm{F}}}{kT}} \approx N_{\mathrm{A}}, \quad (1)$$

$$n = N_{\mathrm{C}} \exp \frac{E_{\mathrm{F}} - E_{\mathrm{C}}}{kT} \approx N_{\mathrm{D}} \frac{1}{1 + g_{\mathrm{D}} \exp \frac{E_{\mathrm{F}} - E_{\mathrm{D}}}{kT}} \approx N_{\mathrm{D}}. \quad (2)$$

The above approximations are under the shallow doping condition.

$$E_{\mathrm{F}} - E_{\mathrm{A}} \gg kT = 0.026\,\mathrm{eV}, \quad (3)$$

$$E_{\mathrm{D}} - E_{\mathrm{F}} \gg kT = 0.026\,\mathrm{eV}, \quad (4)$$

where n, p, N_{C}, N_{V}, N_{D}, N_{A}, E_{C}, E_{V} and E_{F} are the electron density, hole density, the effective density of states in the conduction band, the effective density of states in the valence band, the shallow donor concentration, the shallow acceptor concentration, the conduction band minimum (CBM), the valence maximum (VBM), and Fermi level, respectively.

Non-traditional semiconductors, e.g. semi-insulating semiconductors[3], or p-CdTe polycrystalline film[4–6] were widely used in thin film photovoltaic products in recent years. Some unexpected impurity atoms were unavoidably introduced into semiconductors during processing. So it is very difficult to determine the Fermi level, majority carrier density, and semiconductors' type. Under this complex situation, the LCN condition is used to determine the thermal equilibrium electrons and holes concentrations as a function of the impurity concentration. According to the fact that the density of negative charges equates to the density of positive charges, we get

$$p + N_{\mathrm{D}}^{+} = n + N_{\mathrm{A}}^{-}, \quad (5)$$

where N_{D}^{+} denotes the ionized concentration of the donor dopant and N_{A}^{-} the concentration of the acceptor dopant. Assuming donor concentration N_{D} and acceptor concentration N_{A} are known, we can obtain:

$$N_{\mathrm{D}}^{+} = N_{\mathrm{D}} \frac{1}{1 + g_{\mathrm{D}} \exp \frac{E_{\mathrm{F}} - E_{\mathrm{D}}}{kT}}, \quad (6)$$

$$N_{\mathrm{A}}^{-} = N_{\mathrm{A}} \frac{1}{1 + g_{\mathrm{A}} \exp \frac{E_{\mathrm{A}} - E_{\mathrm{F}}}{kT}}, \quad (7)$$

where g_{D} and g_{A} are the degeneracy of the donor and acceptor states, respectively. $g_{\mathrm{D}} = 2$ due to spin, while g_{A} depends on the material. For the tetrahedral semiconductors, such as Si, GaAs, or CdTe, $g_{\mathrm{A}} = 4$.

According to Equations (1), (2), (5)–(7), the condition of local charge neutrality (LCN) can be replaced by:

$$N_{\mathrm{V}} \exp \frac{E_{\mathrm{A}} - E_{\mathrm{F}}}{kT} + N_{\mathrm{D}} \frac{1}{1 + g_{\mathrm{D}} \exp \frac{E_{\mathrm{F}} - E_{\mathrm{D}}}{kT}} =$$

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$$N_{\rm C}\exp\frac{E_{\rm F}-E_{\rm C}}{kT}+N_{\rm A}\frac{1}{1+g_{\rm A}\exp\frac{E_{\rm A}-E_{\rm F}}{kT}}. \quad (8)$$

Equation (8) is a transcendental equation and it is impossible to find an analytical solution. However, we can solve the equation using graphical or numerical methods.

A simple approximate graphic method (GM) for estimation of the approximate solution was proposed in Reference [7], which introduced the concept of ranking dopants and compensator according to their doping and compensation levels, respectively. Then the approximate concentration and Fermi level could be calculated easily. In this paper, we analyze the graphic method and propose a new numeric-graphic method (NGM) based on GM. In addition, comparison of NGM with numerical method (NM) is presented as well.

2. Solution of LCN equation

2.1. Graphic method

In GM plots each state is represented by a point in the plane of $\ln N$(N dopant concentration) versus $E_{\rm F}$ and then solutions are found using the intersecting points. Under certain conditions, the acceptor and donor levels are much larger than the normal shallow acceptor dopants, Equations (1) and (2) are replaced by

$$p=N_{\rm V}\exp\frac{E_{\rm V}-E_{\rm F}}{kT}=N_{\rm A}\frac{1}{1+g_{\rm A}\exp\frac{E_{\rm A}-E_{\rm F}}{kT}}$$
$$\approx\frac{N_{\rm A}}{g_{\rm A}}\exp\left(-\frac{E_{\rm A}-E_{\rm F}}{kT}\right), \quad (9)$$

$$n=N_{\rm C}\exp\frac{E_{\rm F}-E_{\rm C}}{kT}=N_{\rm D}\frac{1}{1+g_{\rm D}\exp\frac{E_{\rm F}-E_{\rm D}}{kT}}$$
$$\approx\frac{N_{\rm D}}{g_{\rm D}}\exp\left(-\frac{E_{\rm F}-E_{\rm D}}{kT}\right), \quad (10)$$

Using Equations (9) and (10), we can deduce

$$p\approx\sqrt{\frac{N_{\rm V}N_{\rm A}}{g_{\rm A}}}\exp\left(-\frac{E_{\rm A}-E_{\rm V}}{2kT}\right), \quad (11)$$

$$n\approx\sqrt{\frac{N_{\rm C}N_{\rm D}}{g_{\rm D}}}\exp\left(-\frac{E_{\rm C}-E_{\rm D}}{2kT}\right), \quad (12)$$

By introducing

$$\begin{cases}E'_{\rm A}=E_{\rm A}+kT\ln g_{\rm A},\\ E'_{\rm D}=E_{\rm D}-kT\ln g_{\rm D}.\end{cases} \quad (13)$$

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

$$\begin{cases}N_{\rm D}^{+}=N_{\rm D}\dfrac{1}{1+\exp\frac{E_{\rm F}-E'_{\rm D}}{kT}},\\ N_{\rm A}^{-}=N_{\rm A}\dfrac{1}{1+\exp\frac{E'_{\rm A}-E_{\rm F}}{kT}}.\end{cases} \quad (14)$$

As shown in Figure 1, the terms of the LCN equation are almost a straight line except around $|E_{\rm D}-E_{\rm F}|<mkT$ and

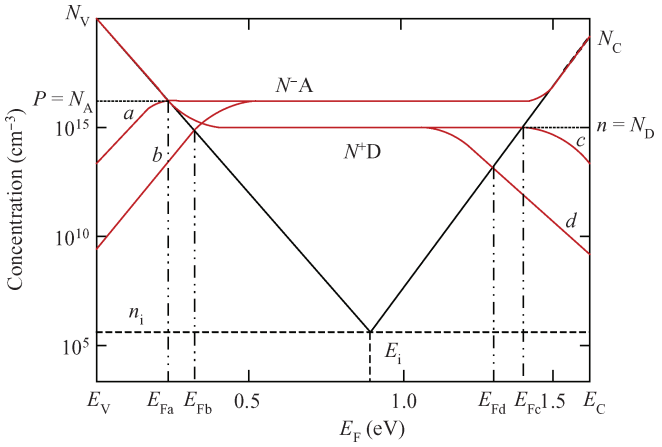

Figure 1. (Color online) A single shallow acceptor dopant without compensation in semiconductor. Red curves represent minor carrier concentration plus ionized acceptor or donor density. Curve a: $E_{\rm A}=0.10$ eV, $N_{\rm A}=1\times10^{16}$ cm^{-3}; curve b: $E_{\rm A}=0.35$ eV, $N_{\rm A}=1\times10^{16}$ cm^{-3}; curve c: $E_{\rm D}=1.5$ eV, $N_{\rm A}=1\times10^{15}$ cm^{-3}; curve d: $E_{\rm D}=1.10$ eV, $N_{\rm A}=1\times10^{15}$ cm^{-3}.

$|E_{\rm A}-E_{\rm F}|<mkT$ ($m=3$–5), then we classify the intrinsic/impurity defects as shallow and non-shallow donor or acceptor for the wide bandgap materials such as CdTe. Thus,

$$\begin{cases}n\approx N_{\rm D}^{+}\approx N_{\rm D}, \text{ Shallow donor},\\ p\approx N_{\rm A}^{+}\approx N_{\rm A}, \text{ Shallow acceptor},\\ n\approx\sqrt{\frac{N_{\rm C}N_{\rm D}}{g_{\rm D}}}\exp\left(-\frac{E_{\rm C}-E_{\rm D}}{2kT}\right), \text{ Nonshallow donor},\\ p\approx\sqrt{\frac{N_{\rm V}N_{\rm A}}{g_{\rm A}}}\exp\left(-\frac{E_{\rm A}-E_{\rm V}}{2kT}\right), \text{ Nonshallow acceptor}.\end{cases} \quad (15)$$

2.2. Numeric-graphic method

NGM based on GM is presented in this section to estimate the precision of GM's results. GM obtains solutions by plotting each term of the LCN equation in a semi-logarithmic coordinate. Following the procedure of GM, NGM plots each state by computer in the plane of concentration versus Fermi energy level and calculates the intersecting point by computer. Basically, NGM is a graphic method based on numerical calculation.

2.3. Numerical method

NM considers all terms of Equation (5), which is a transcendental equation, and calculates its solution using a numerical method, e.g. the bisection method, Newton's iteration. If $N_{\rm C}$, $N_{\rm V}$, $N_{\rm D}$, $N_{\rm A}$, $E_{\rm C}$, $E_{\rm V}$ and T are all given, $E_{\rm F}$ of any precision can be found after iterations. Substituting $E_{\rm F}$ into Equations (1) and (2), majority concentration will be obtained.

In this paper, the bisection method which is a simple and robust root-finding algorithm is adopted. A numerical calculation was performed by bisecting the interval of [$E_{\rm V}$, $E_{\rm C}$] and exact $E_{\rm F}$ was calculated. Then majority carrier concentration will be obtained by replacing $E_{\rm F}$ in Equations (1) and (2).

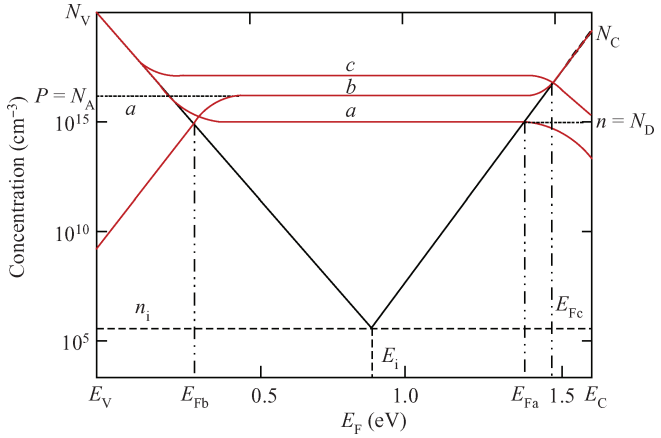

Figure 2. (Color online) A single donor dopant compensated by a single acceptor ($E_A = 0.35$ eV, $N_A = 1 \times 10^{16}$ cm^{-3}). Curve b depicts the ionized acceptor density; curves a and c are ionized donor density with two different doping concentration ($E_D = 1.50$ eV, $N_D = 1 \times 10^{15}$ cm^{-3} for curve a; $E_D = 1.50$ eV, $N_D = 1 \times 10^{17}$ cm^{-3} for curve c).

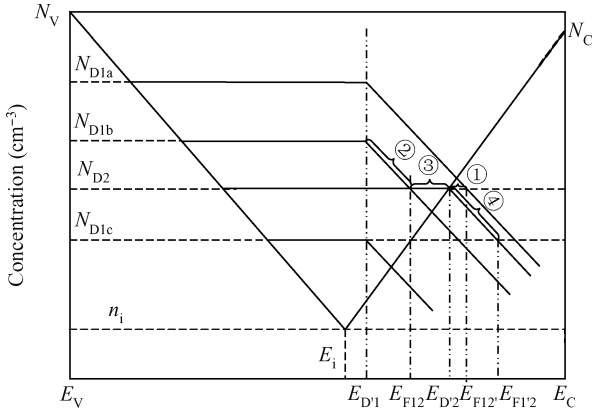

Figure 3. Formation of wrapping step function when $E_{D'1}$ and $E_{D'2}$ are far away from each other. Intervals 1, 2, 3 and 4 are used to estimate the closeness of N_{D1} and N_{D2} which determine forming the wrapping step function.

3. Experiment and analysis

3.1. Single dopant

Traditional semiconductors, e.g. Ge or Si, have a shallow impurity level which has a distance of less than 3–5 kT to the edge of conduction or valance band (conduction band for donor level in n-type semiconductor, and valance band for acceptor level in p-type semiconductor).

As shown in Figure 1, shallow acceptor state A_1 with ionization energy of 0.10 eV, which is so close to the valance band (less than 3 kT), is shallow and fully ionized. GM gives the result of majority carrier concentration $p \approx N_A^- \approx N_A$. Figure 1 demonstrates the situation of non-shallow impurity levels, which are high or low more than 3–5 kT to the edge of the conduction or valance band (conduction band for donor level in n-type semiconductor, and valance band for acceptor level in p-type semiconductor).

To see the precision of approximation results got by GM, calculations of E_F and the majority carrier concentration using NGM and NM are done. NM considers all terms together in the LCN equation, and gets the exact result. From the calculation results shown in Table 1, we can know that NGM and NM get almost the same results for a single dopant in the semiconductor, since NGM just neglect the minority carrier of many orders less than the ionized acceptor.

3.2. Single dopant compensated by single compensator

Assuming a p-type semiconductor with an acceptor dopant compensated by a donor compensator and $N_D < N_A$, N_D are fully ionized, compared with N_A^+. From the data in Table 1, NGM gets the same result with NM.

Similarly, we would have a similar situation as $N_D > N_A$. However, this situation unavoidably happens when compensation has a higher concentration than the dopant needed. As described in Figure 2, the material will become n-type while E_D is higher than E_i.

In addition, there are also cases like non-shallow donor dopant compensated by acceptor compensator with different ionization energy. We note that the minority carrier and compensator concentration are of orders less than the majority carrier concentration and ionized dopant concentration, when the compensator concentration is far smaller than dopant. While the minority carrier and majority carrier are of orders less than the dopant and compensator concentrations, as compensator concentration is far bigger than dopant concentration. So neglecting the minority carrier and compensator, or the minority carrier and majority carrier can be valid. This is the reason why NGM and NM can get almost the same results.

3.3. Multiple dopants

In order to graphically estimate compensation of multiple dopants by multiple compensators, Reference [7] established some procedures of which the most important step is to get a good wrapping step function formed by ranking dopants according to its majority carrier density calculated or the curve on the semi-logarithmic plane, neglecting ionization of the dopant with concentration far below the others and the ionization energy higher than the others.

It is hard to form a good wrapping step function while there are too many donor compensator states or the states are too close. Figures 3 and 4 show what happens when concentration or activation energy of states are too close.

To find how close states can influence the forming of wrapping step function, let us assume there are only two donors D_1 and D_2 described by their concentration and ionization energy in the semiconductor. Figure 3 describes the case $E_{D2} \gg E_{D1}$ ($E_{D2} - E_{D1} > 6\,kT$). For simplification, let N_{D2} be a constant, and vary N_{D1} to find the influence of the relationship between N_{D1} and N_{D2} on forming the wrapping step function.

We note that the ionized curve is a straight line for $|E_D - E_F| > 3$–$5\,kT$. As shown in Figure 3, if the intersecting point of two ionized curves is near to $E_{D'1}$ or $E_{D'2}$ within 3–5 kT, that means N_{D1} and N_{D2} are too close to form a good wrapping step function, since $N_{D1} + N_{D2}$ is comparable to N_{D1} and N_{D2} of which neither can be negligible under this condition. Let us see the N_{D1b} and N_{D2} curve, around the crossing point as shown in Figure 3, N_{D1b} is partially ionized and N_{D2} is fully

Table 1. Fermi level and majority carrier concentration calculated by NGM and NM respectively.

Dopant state	Fermi level (eV)		Majority carrier concentration (cm^{-3})	
	NGM	NM	NGM	NM
$E_A = 0.10$ eV $N_A = 1 \times 10^{16}$ cm^{-3}	0.194	0.196	$P =$ 1.00×10^{16}	$P =$ 9.12×10^{16}
$E_A = 0.35$ eV $N_A = 1 \times 10^{16}$ cm^{-3}	0.289	0.290	$P =$ 2.44×10^{16}	$P =$ 2.41×10^{16}
$E_D = 1.50$ eV $N_D = 1 \times 10^{15}$ cm^{-3}	1.235	1.235	$n =$ 2.70×10^{12}	$n =$ 2.70×10^{16}
$E_D = 1.10$ eV $N_D = 1 \times 10^{15}$ cm^{-3}	1.265	1.265	$n =$ 8.55×10^{12}	$n =$ 8.54×10^{12}
$E_A = 0.35$ eV $N_A = 1 \times 10^{16}$ cm^{-3} $E_D = 1.50$ eV $N_D = 1 \times 10^{15}$ cm^{-3}	0.326	0.331	$P =$ 5.94×10^{12}	$P =$ 5.06×10^{12}
$E_A = 0.35$ eV $N_A = 1 \times 10^{16}$ cm^{-3} $E_D = 1.50$ eV $N_D = 1 \times 10^{17}$ cm^{-3}	1.495	1.483	$n =$ 6.19×10^{16}	$n =$ 5.93×10^{16}

ionized. Using the approximation introduced above, let N_{D1b} equal N_{D2},

$$\frac{N_{D1}}{g_{D1}} \exp \frac{E_{D1} - E_F}{kT} = N_{D2}. \tag{16}$$

Simplifying Equation (16), we have

$$E_{F12} = E_{D1} + kT \ln \frac{N_{D1}}{g_{D1} N_{D2}}. \tag{17}$$

For the condition of N_{D1a} and N_{D1b}, let $E_{F12'}$, be the intersecting point of N_{D1a} and extended line of N_{D2} and $E_{F1'2}$ intersecting point extend line of N_{D1c} and N_{D2} instead, although they do not have a crossing point with N_{D2}. Similar to Equation (17), we can obtain that

$$E_{F12'} = E_{D1} + kT \ln \frac{N_{D1}}{g_{D1} N_{D2}}, \tag{18}$$

$$E_{F1'2} = E_{D1} + kT \ln \frac{N_{D1}}{g_{D1} N_{D2}}. \tag{19}$$

As analyzed above, the intersecting point of two ionized curves could not be near to E_{D1} or E_{D2} within mkT (m = 3–5), which means the intervals 1, 2, 3 and 4 demonstrated in Figure 3 should be broader than mkT, namely,

$$\begin{cases} E_{F1'2} - E_{D'2} > mkT \\ E_{F12} - E_{D'1} > mkT \\ E_{D'2} - E_{F12} > mkT \\ E_{F1'2} - E_{D'2} > mkT \end{cases} \Rightarrow$$

$$\ln \frac{N_{D1}}{N_{D2}} > \frac{1}{kT}(E_{D2} - E_{D1}) + m, \tag{20}$$

$$m + \ln g_{D1} < \ln \frac{N_{D1}}{N_{D2}} < \frac{1}{kT}(E_{D2} - E_{D1}) - m, \tag{21}$$

$$\ln \frac{N_{D1}}{N_{D2}} < -m, \tag{22}$$

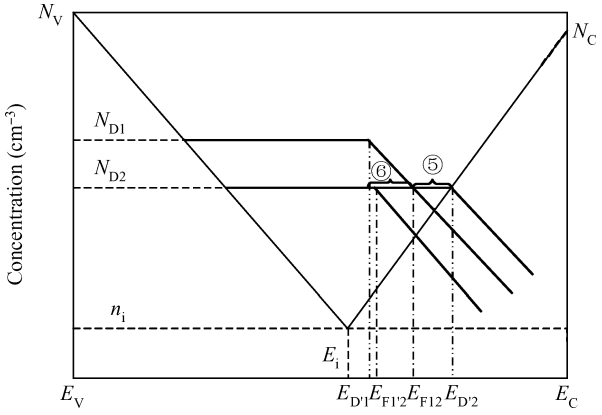

Figure 4. Formation of wrapping step function when $N_{D'1}$ and $N_{D'2}$ are far away from each other. Intervals 5 and 6 are used to estimate the closeness of E_{D1} and E_{D2} which determine formation of the wrapping step function.

The value of m reveals the tolerance of the graphic method and usually equals to 3. To make GM be valid for a more general case, m should have the value of 2, even 1 can be tolerated. From Equations (20) and (22), we can see that no matter where the Fermi level lies, N_{D1}^+ predominate, as the contribution from N_{D2}^+ can be negligible when $N_{D1} \gg N_{D2}$. If N_{D1} is no longer higher or lower than N_{D2}, WSF can also be obtained only if N_{D1}/N_{D2} is between the range of Equation (21).

Now let us consider the second case shown in Figure 4 when $N_{D1} \gg N_{D2}$ (usually $\ln(N_{D1}/N_{D2}) > 3$). N_{D2}^+ can be neglected for $E_F < E_{D1}$. Care must be taken, in forming the wrapping step function for $E_F > E_{D2}$. Let E_{D1} be constant, and vary E_{D2} to find how E_{D1} and E_{D2} are far from each other can form a good wrapping step function. Using the same analytic method above, we know the intervals 5 and 6 shown in Figure 4 should be broader than 3–5 kT, that is,

$$\begin{cases} E_{D'2} - E_{F12} > mkT \\ E_{F12'} - E_{D'2} > mkT \end{cases} \Rightarrow$$

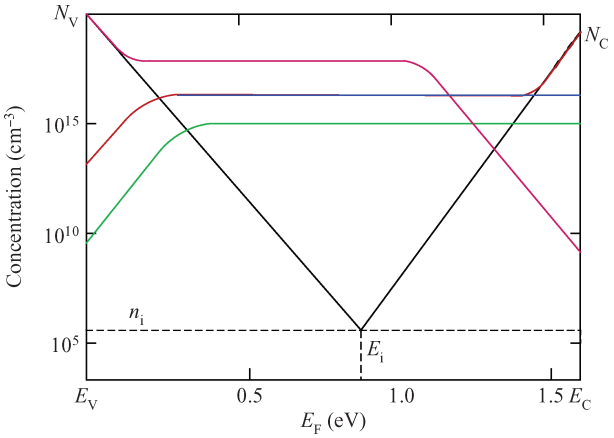

Figure 5. (Color online) A single donor dopant compensated by two acceptor compensators whose doping concentrations are far away from each other. Blue line represents the ionized acceptor density N_{A1}^-; green line, the ionized acceptor density N_{A2}^-; red line, the total ionized acceptor density plus electron density and purple line, the ionized donor density N_D^+. Since N_{A1}^- and the total ionized acceptor are almost equivalent, they overlap in the plane concentration versus E_F.

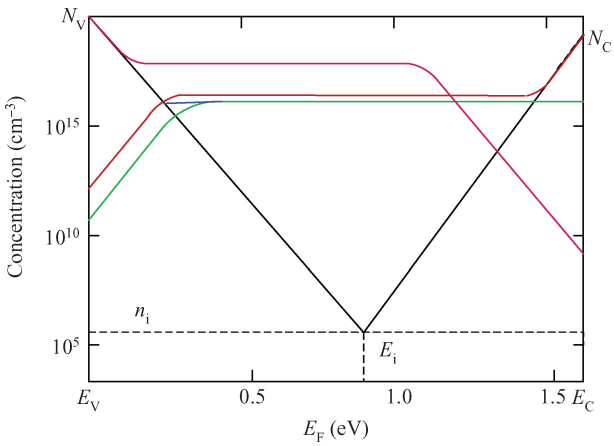

Figure 6. (Color online) A single donor dopant compensated by two acceptor compensators whose doping concentrations are equivalent.

$$E_{D2} - E_{D1} > kT\left(\ln\frac{N_{D1}}{N_{D2}} + m\right), \tag{23}$$

$$E_{D2} - E_{D1} < kT\left(\ln\frac{N_{D1}}{N_{D2}} - m\right). \tag{24}$$

First, we discuss the situation of Equation (23). As D2 has a smaller ionization energy than D1, D2 ionizes more electrons than D1, although N_{D1} is higher than N_{D2}. In this case, the wrapping step function is trustworthy since N_{D1}^+ can be neglected for $E_F > E_{D2}$. The second situation occurs when Equation (24) N_{D1}^+ will predominate since N_{D2}^+ is much smaller than N_{D1}^+ no matter where the Fermi level lies between E_V and E_C. So it will be a good approximation during forming the wrapping step function by neglecting N_{D1}^+.

Figures 5 and 6 are two examples of a single donor dopant ($N_{D1} = 1 \times 10^{17}$ cm^{-3}, $E_{D1} = 1.1$ eV) compensated by two different acceptor compensators: (a) $N_{A1} = 1 \times 10^{16}$ cm^{-3}, $E_{A1} = 0.15$ eV; $N_{A2} = 1 \times 10^{15}$ cm^{-3}, $E_{A2} = 0.30$ eV; (b) $N_{A1} = 1 \times 10^{16}$ cm^{-3}, $E_{A1} = 0.15$ eV; $N_{A2} = 1 \times 10^{16}$ cm^{-3}, and $E_{A2} = 0.30$ eV. For the case shown in Figure 5, GM neglects N_{A1} and forms a good wrapping step function, then get $E_F = 1.18$ eV, $n = 2.9 \times 10^{11}$ cm^{-3}, which is very close to NM's results $E_F = 1.14$ eV, $n = 5.9 \times 10^{10}$ cm^{-3}. For the case b shown in Figure 6, the wrapping step function is dubious because N_{A1} and N_{A2} are too close. If we adopt higher N_{A1} to represent the wrapping step function, then we would get GM's results $E_F = 1.18$ eV, $n = 2.9 \times 10^{11}$ cm^{-3}, which is so different with NM's results $E_F = 1.12$ eV, $n = 2.9 \times 10^{10}$ cm^{-3}.

To make GM be valid for the more general case, improvement must be introduced. For the case b, two N_A are so close that the lower one cannot be neglected. We can calculate the new $N_A = N_{A1} + N_{A2}$ numerically instead of N_{A1}, and form a new wrapping step function. Using the new NA', we have improved GM's results $E_F = 1.16$ eV, $n = 1.46 \times 10^{11}$ cm^{-3}, which is close to NM's results and can be trusted.

4. Conclusion

In conclusion, we have discussed the LCN equation used to calculate the Fermi level and majority carriers concentration in semiconductors in detail. A graphical method and a numerical method for finding solutions to the LCN equation are presented and a new Graphic-numeric method for estimating the accuracy of the graphic method is also introduced. This new method numerically calculates the sum of contribution of two states without neglecting the lower one and gets a new wrapping step function.

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