Band bending within inhomogeneously doped semiconductors with multilevel impurities. I. Theory

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Based on the theory of carrier statistics under thermal equilibrium, a method for calculating band bending and concentration profiles of a multilevel impurity center in its individual charge states within a semiconductor inhomogeneously doped with the impurity by solving the Poisson equation has been proposed. The boundary conditions used are as follows: the sample as a whole and everywhere outside the doped layer are kept electrically neutral. Discussions as to whether the multisteplike barrier might exist in this type of doping layer and the significance of the calculation are made. [S0163-1829(96)03220-1]

I. INTRODUCTION

In principle, statistics allows us to determine the population of impurity levels in semiconductors. For cases in which an impurity may exist in different charge states and is doped inhomogeneously, the problem becomes more complex and to our knowledge has not yet been solved, even though it has been of concern for a long time. We shall develop a numerical calculation scheme for dealing with the subject, and some general features of the band bending in these cases will be drawn. This is important for assigning charge states of impurities in the samples used in the experiment and even for designing devices that contain this kind of impurity.

In the case where an impurity forms only one local energy level within the forbidden gap of the substrate, the band bending (barrier) within the doping layer can, in principle, be calculated by integrating the Poisson equation[1]

$$\frac{d^2V(x)}{dx^2}=-\frac{\rho(x)}{\epsilon}, \tag{1}$$

where $V(x)$ denotes potential variation along the x direction, ρ is charge density, and ϵ is the dielectric constant of the material. When the profile of the ionized impurity density can be written in an analytic form, this kind of problem can be solved without difficulty, providing proper boundary conditions corresponding to the profile are used. For example, the solutions for abrupt or linearly graded p-n junctions are well known.

Some impurities, such as $3d$ group transition metal elements Fe, Ni, and Cr, etc., may exist in multicharge states after being doped into semiconductors. For an example, it is generally believed that Ni substitutes Ga in GaP and it may exist in three different charge states: Ni(d^9), Ni(d^8), and Ni(d^7).[2] Correspondingly, two levels, Ni(d^8/d^7) and Ni(d^9/d^9) are formed within the forbidden gap E_g. Referring to the Ga ions that have been substituted, nickel ions in the three charge states are overfilled by 2, 1, and 0 electrons, respectively. For convenience, when the number of the overfilled electrons is j, we denote the charge states as $j-$, and the levels as $j-/(j-1)-$. Generally speaking, for an impurity T that may exist in charge states T^{j-} with $j=m,m-1,\ldots,1,0,-1,\ldots,-n$, the charge states can be denoted as $T^{m-},T^{(m-1)-},\ldots,T^{-},T^{0},T^{+},\ldots,T^{n+}$, totally $m+n+1$ states, then $m+n$ levels $T[m-/(m-1)-],\ldots,T[(n-1)+/n+]$ will be formed. Some of these levels may be located within E_g of the substrate.

For this kind of impurity, solving Eq. (1) will present some problems. In some cases, the doping profile is inhomogeneous, for example, in the cases of doping by thermal diffusion or ion implantation currently used in technology. Because electron occupancy of the charge states $j-$ of the impurity, f^{j-}, depends on the distance between the corresponding impurity level and Fermi level and the former keeps a constant distance from the band edge, the integrated function $\rho(x)$ on the right side of Eq. (1) is a function of $V(x)$ on the left side of the same equation. Therefore, solving Eq. (1) becomes a self-consistent problem. It has no analytic solution in principle.

The behavior of $3d$ metal impurities in semiconductors is of concern for both theoretical and applied aspects.[2,3] Since the 1980's, the theory of $3d$ electronic states in semiconductors has progressed extensively.[3–6] It has been suggested that the energy levels of $3d$ impurities can be used as a reference to determine the band offsets in quantum wells and superlattices.[7]

Generally speaking, $3d$ impurities may have important influences on optical, electrical, and magnetic properties of materials. These effects are restricted by charge states of the impurities in the materials. Then, determination of charge states of the impurities and their profiles within the doping layer in a specific sample is very important. With regard to some physical measurements, such as deep level transient spectroscopy, optical absorption, electron magnetic resonance, and Mössbauer spectroscopy, etc., explanation of experimental results depends strongly on the assignments for charge states of the impurity in the sample. Thus, the calculations of the band bending and concentration profiles of a multilevel impurity within a specific doped layer is a significant task.

The relevant theoretical basis will be described briefly in Sec. II. The theoretical model used in this work will be drawn in Sec. III. Then in Sec. IV, the problem with a

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multisteplike band bending that may occur within the doping layer will be discussed. The final section will provide the concluding remarks.

II. THEORETICAL BASIS

A. Charge density

Assume that both a donor D and an acceptor A are doped into a semiconductor, and both D and A may exist in multicharge states. The corresponding multilevel E_{Di} ($i=1,2,\ldots,n$) and E_{Aj} ($j=1,2,\ldots,m$) are formed in the forbidden gap. The doping profiles are assumed to be homogeneous in both directions y and z but inhomogeneous in the x direction. Then the charge density at x can be written as

$$\rho(x)=p(x)-n(x)-\sum_{j=1}^{m}\rho_{Aj}(x)+\sum_{i=1}^{n}\rho_{Di}(x), \tag{2}$$

where p and n are the concentrations of electron in the conduction band (CB) and that of hole in the valence band (VB), respectively. From general semiconductor statistics, it is known that

$$n(x)=N_C\exp\{[E_F(x)-E_C(x)]/kT\} \tag{3}$$

and

$$p(x)=N_V\exp\{[E_V(x)-E_F(x)]/kT\}. \tag{4}$$

In these expressions, the following notations are used: N_C and N_V are effective densities of states in the CB and VB; E_C and E_V are the bottom of the CB and top of the VB, respectively; E_F is the Fermi level, which is a constant in a thermal equilibrium system; ρ_{Aj} is the contribution to the total charge density (absolute value) from the j-fold ionized acceptor and ρ_{Di} is that from the i-fold ionized donor. They may be expressed as

$$\rho_{Aj}(x)=jn_{Aj}(x), \tag{5}$$

$$\rho_{Di}(x)=in_{Di}(x), \tag{6}$$

where n_{Aj} is the concentration of the j-fold ionized acceptor and n_{Di} is that of the i-fold ionized donor. In the case that more than one acceptor and/or donor are doped, the corresponding terms should be added into Eq. (2). When only one impurity is doped into a semiconductor, and the impurity forms several acceptor and donor levels within E_g, the last two terms on the right side of Eq. (2) represent the contributions from the acceptor and donor levels of the impurity center, respectively. For this situation, Milnes[8] has proved that if N is the total density of the impurity center, then electron occupancy of the jth acceptor level is equal to

$$f(E_{Aj})\equiv\left(\frac{n_{Aj}}{N}\right)=\frac{(1/2)^j\left\{\prod_{p=1}^{j}\exp[(E_{Ap}-E_F)/kT]\right\}}{D}, \tag{7}$$

and that of the ith donor level is equal to

$$f(E_{Di})\equiv\left(\frac{n_{Di}}{N}\right)=\frac{(1/2)^i\left\{\prod_{q=1}^{i}\exp[(E_{Dq}-E_F)/kT]\right\}}{D} \tag{8}$$

with

$$D=1+\sum_{k=1}^{m}(1/2)^k\left[\prod_{p=1}^{k}\exp\left(\frac{E_F-E_{Ap}}{kT}\right)\right]+\sum_{l=1}^{n}(1/2)^l\left[\prod_{q=1}^{l}\exp\left(\frac{E_{Dq}-E_F}{kT}\right)\right]. \tag{9}$$

Profile $N(x)$ is determined by the doping technology. From Eqs. (7) and (8), we obtain

$$n_{Aj}=Nf(E_{Aj}), \tag{10}$$

$$n_{Di}=Nf(E_{Di}). \tag{11}$$

It is worthwhile to note that both expressions of $f(E_{Aj})$ and $f(E_{Di})$, Eq. (7) and (8), contain E_F; on the other hand E_{Aj} and E_{Di} are defined with respect to the band edges E_C and E_V. Thus, $n_{Aj}(x)$ and $n_{Di}(x)$ depend on both $N(x)$ and $E_C(x)-E_F$. E_F will be taken as the zero point of energy in the calculations described below.

Substituting Eqs. (3)–(8) into Eq. (2), a general expression of $\rho(x)$ can be obtained.

B. Poisson equation

Substituting Eq. (2) into the Poisson equation (1), the specific equation that we need to solve is obtained.

Due to inhomogeneous doping, a space charge region (SCR) is built up in the sample, then a band bending occurs and a barrier is formed. A simple example for the situation is the junction region of a p-n junction. Within a homogeneously doped region, no space charge occurs and the energy band is still flat. Electrical neutrality should be satisfied everywhere within the region. This region will be called the electrical neutral region (ENR) hereafter. Taking E_C within ENR as the zero point of potential V, then

$$E_C(x)=-qV(x). \tag{12}$$

Thus, the Poisson equation (1) can be rewritten as

$$\frac{d^2E_C(x)}{dx^2}=\frac{\rho(x)q}{\epsilon}. \tag{13}$$

As described above, if $\rho(x)$ on the right side of the equation and $E_C(x)$ on the left side are dependent upon each other, solving Eq. (13) will become a self-consistent problem. In general, it cannot be done analytically and a numerical solution will be called for.

When a reverse bias V_R is applied on the sample, the system will be turned into nonequilibrium. In this case, the quasi-Fermi levels E_F^n and E_F^p for electron and hole subsystems, respectively, can be used instead of E_F. It is assumed that both E_F^n and E_F^p are kept at their own constant values within the barrier region, and $E_F^p-E_F^n=|V_r|$. Thus, the discussions about the Poisson equation and $\rho(x)$ made above can be maintained to be correct. With regard to calculations of occupancies of the impurity levels, E_F^n or E_F^p will be used depending on with which band, CB or VB, the level exchanges carriers.

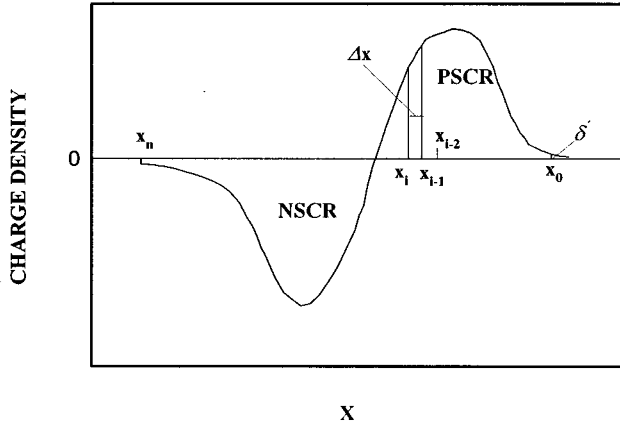

FIG. 1. A schematic profile of space charges within a space-charge region.

III. CALCULATION SCHEME

A. SCR and boundary conditions

In the case that the doping profile is inhomogeneous, especially when the impurity induces more than one level, the shape of SCR and the band bending may be very complicated. But in any case, the positive space charges always exist within some regions, forming positive SCR's (PSCR's); and the negative space charges exist within other regions, forming negative SCR's (NSCR's). For the sake of brievity, only the cases in which one PSCR and one NSCR are formed in a sample will be treated below (see Fig. 1). It is not difficult to deal with the cases in which more than one PSCR and NSCR occur along a similar line.

To satisfy the requirement for keeping electrical neutrality within the sample as a whole, the absolute value of the total charge in PSCR and that in NSCR should be equal to each other. The condition of electrical neutrality should also be valid everywhere within the ENR's. We shall restrict ourselves to the case in which only one maximum occurs on the doping profile. Actually, total impurity concentration profiles formed by the current doping technologies such as ion implantation and thermal diffusion belong to this case. For ion implantation, the profile of total concentration of the implanted ion $N(x)$ is a Gaussian distribution. For thermal diffusion with a constant source the $N(x)$ is an error function complement distribution. Both of them have only one maximum. In this sort of case, any form of distribution may have a tail region within which $N(x)$ slowly tends to its value in the neighboring homogeneously doped region. At the same time, the space-charge density $\rho(x)$ gradually approaches zero. In practical problems, when the absolute value of $\rho(x)$ becomes smaller than a certain value $\delta=|\rho(x_0)|$ (see Fig. 1), very light doping has only a negligible effect on the material. Of course, there is a point x_n on the opposite side of the SCR, where $\rho(x_n)=-\rho(x_0)$. Therefore, it is reasonable to take the region (x_n,x_0) as the SCR in the case shown in Fig. 1, and the areas outside the region will be regarded as ENR's. This approximation may be called the "tail cutoff approximation."

Considering the fact that electrical neutrality will be kept within the sample as a whole and everywhere in ENR's, under the tail cutoff approximation, the boundary conditions needed for solving Eq. (13) can be obtained as

$$\varepsilon(x)|_{x>x_0}=0, \tag{14}$$

$$\varepsilon(x)|_{x<x_n}=0, \tag{15}$$

$$E_C(x)|_{x>x_0}=E_C(x_0)\equiv E_{C0}, \tag{16}$$

$$E_C(x)|_{x<x_n}=E_C(x_n)\equiv E'_{C0}, \tag{17}$$

$$\int_{x_0}^{x_n}\rho(x)dx=0, \tag{18}$$

where ε is electric field, E_{C0} in Eq. (16) and E'_{C0} in Eq. (17) are the values of E_C within the regions $x\geqslant x_0$ and $x\leqslant x_n$, respectively.

B. Iterative equation

For convenience in computer calculation, SCR (x_0,x_n) is divided into small enough n equal segments (x_n,x_{n-1}), $(x_{n-1},x_{n-2}),\ldots,(x_i,x_{i-1}),\ldots,(x_2,x_1),(x_1,x_0)$; the length of such a segment is Δx. Integrating Eq. (13) from x_0 to x_i, we get

$$\left.\frac{dE_C(x)}{dx}\right|_{x_i}\simeq\left.\frac{dE_C(x)}{dx}\right|_{x_{i-1}}+\frac{q\rho(x_i)}{\epsilon}\Delta x. \tag{19}$$

Integrating twice gives

$$E_C(x_i)\simeq 2E_C(x_{i-1})-E_C(x_{i-2})+\frac{q\rho(x_i)}{\epsilon}(\Delta x)^2. \tag{20}$$

The expression of $\rho(x_i)$ is given by Eq. (2). Noting that $\rho(x_i)=\rho(E_C(x_i))$, when the values of E_C at two points x_{i-1} and x_{i-2} within (x_n,x_0), $E_C(x_{i-1})$ and $E_C(x_{i-2})$ can be determined, $E_C(x_i)$ can be calculated using Eq. (20) numerically. Following an iteration using the same equation, a set of values $E_C(x_0),E_C(x_1),E_C(x_2),\ldots,E_C(x_n)$, denoted as $\{E_C(x_i)\}$, may be obtained. That is just the band bending within the whole SCR.

From the boundary conditions Eqs. (16) and (17), it can be seen that $E_C(x_0)=E_{C0}$, which may be determined from equlibrium statistics in the ENR $x\geqslant x_0$, and $E_C(x_n)=E'_{C0}$ may be calculated in the ENR $x\leqslant x_n$ in the same way. Due to the continuity of $E_C(x)$ the latter value E'_{C0} should be equal to the asymptotic value of $E_C(x_i)$ when $x_i\rightarrow x_n$, i.e., $E_C(x_n)=E'_{C0}$. This requirement can be used as a criterion for judging the feasibility of the calculated $\{E_C(x_i)\}$.

During the first step of the calculation, i was taken to be 2, then $E_C(x_{i-2})=E_C(x_0)$ was known and a tentative value of $E_C(x_{i-1})=E_C(x_i)$, denoted as $E_C^{(1)}(x_1)$, was chosen to be substituted into Eq. (20). Thus a value of $E_C^{(1)}(x_2)$ could be obtained using the relation between $E_C(x_i)$ and $\rho(x_i)$ expressed through Eqs. (2)–(11). During the second step, taking $i=3$ and substituting the values $E_C^{(1)}(x_2)$ and $E_C^{(1)}(x_1)$ into Eq. (20) as $E_C(x_{i-1})$ and $E_C(x_{i-2})$, respectively, a value $E_C^{(1)}(x_3)$ could be obtained. Following an iterative calculation, a set of values $E_C^{(1)}(x_0)$ $[=E_C(x_0),E_C^{(1)}(x_1),E_C^{(1)}(x_2),\ldots,E_C^{(1)}(x_n)]$, denoted as

$\{E_C^{(1)}(x_i)\}$ could be obtained. By checking the asymptotic behavior of $\{E_C^{(1)}(x_i)\}$ when $x_i \to x_n$ and the difference between its asymptotic value (when $x_i \to x_n$) and E'_{C0}, the feasibility of the solution $\{E_C^{(1)}(x_i)\}$ can be judged. If it does not satisfy the conditions given in the preceding paragraph, a new tentative value of $E_C(x_1)$, $E_C^{(2)}(x_1)$, should be chosen. Then a new set of $\{E_C^{(2)}(x_i)\}$ would be obtained in the same way as described above. If the calculation was carried out p times, following the same method, until the asymptotic behavior of $\{E_C^{(p)}(x_i)\}_{x_i \to x_n}$ was good enough and the difference between its asymptotic value and E'_{C0} was smaller than a predesigned critical value δ, then $\{E_C^{(p)}(x_i)\}$ is a reasonable approximate solution of the band bending $\{E_C(x_i)\}$.

C. Profiles of impurity charge state concentrations and space-charge density

As mentioned above, the band bending $\{E_C(x_i)\}$ in a SCR can be calculated by using the iterative equation (20). Inserting the values of $\{E_C(x_i)\}$ into Eqs. (3), (4), (7), and (8), the profiles $\{n(x_i)\}$, $\{p(x_i)\}$, $\{n_{Aj}(x_i)\}$, and $\{n_{Di}(x_i)\}$ can be calculated. Substituting them into Eq. (2), the profile of space-charge density $\{\rho(x_i)\}$ can be obtained. Integrating $\{\rho(x_i)\}$ within the region between x_0 and x_n, the result should be equal to zero as expected from Eq. (18). In practice, an integration smaller than a certain value depending on the error level of the calculation can be accepted. Otherwise, it implies that the x_0 used is not far enough from the surface and a new x_0 point should be chosen. In principle, the x_0 point should be chosen as far as possible from the surface, but if it is too far away from the surface error accumulation during the integration may blur the result.

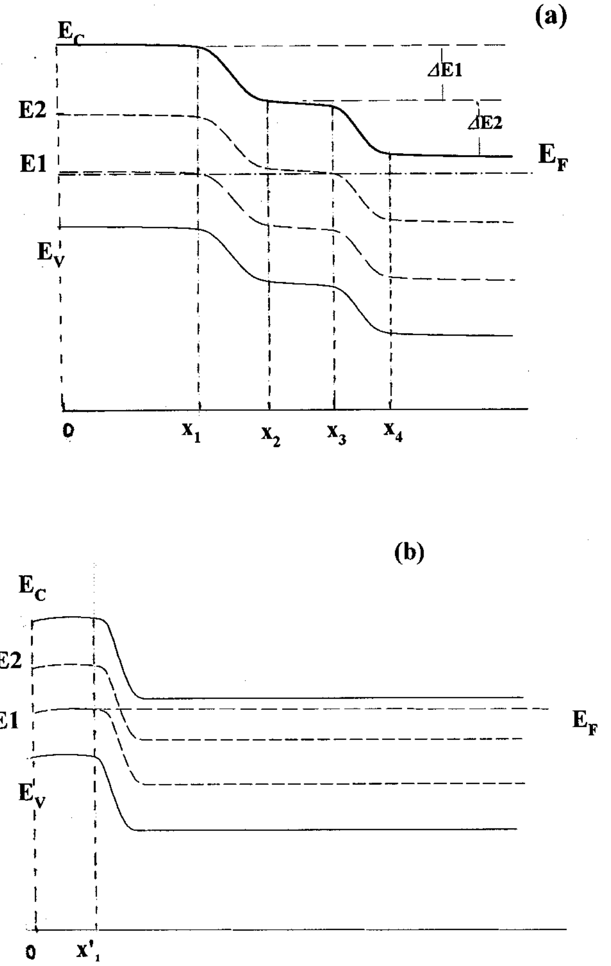

FIG. 2. Schematic band bendings: (a) Multisteplike band bending, (b) Single-step-like band bending.

IV. CLASSIFICATION OF BAND BENDING

The calculation scheme described in the preceding section has been used in the cases of Ni-implanted n-GaP under the different conditions. The details will be reported in Ref. 9. In GaP, Ni substituted Ga, Ni_{Ga}, may exist in three different charge states, with $j=0$, 1, and 2. Consequently, two impurity levels $E1$ and $E2$ are formed within the E_g, $E1$ is a single acceptor level A_1, $E2$ is a twofold acceptor level A_2. So the calculation scheme is suitable for the system. In the calculation, the following parameters were used: $E1=E_V+0.62$ eV,[10] $E2=E_C-0.82$ eV,[11] and $E_{Ga}=2.26$ eV. The typical calculated band bendings are shown in Fig. 2. From the results, the following types of band bending can be classified.

A. Multisteplike band bending

When dopant concentration in a sample is high enough and annealed sufficiently, the typical calculated band bending is like that shown in Fig. 2(a). A layer near the surface [the region $(0,x_1)$] becomes p type, because E_F is located nearer to VB than to CB within the layer. Additionally, there is a rather wide transition region [the region (x_1,x_4)] from the p-type layer to the n-type substrate, since impurity concentration varies slowly as the depth increases. Then two steps appear on the $E_C(x)$. Within the plateau region between the two steps (x_2,x_3), E_F is located far away from both band edges (E_C and E_V), so this region becomes a high resistivity layer (i layer). The whole sample is actually a p-i-n structure. The p-i step is caused by transition from Ni(d^7) to Ni(d^8), and the i-n step is result of the transition from Ni(d^8) to Ni(d^9). Within the i layer, E_F is located near level Ni(d^8/d^9), and the distance between them varies quite slowly. The height of the first step, $\Delta E1$, is approximately equal to the difference between levels Ni(d^9/d^8) and Ni(d^8/d^7), $E2-E1$,

$$\Delta E1 \simeq E2-E1=E(d^9/d^8)-E(d^8/d^7)$$

$$=E_g-0.82 \text{ eV}-0.62 \text{ eV}=0.81 \text{ eV}.$$

The height of the second step, $\Delta E2$, is approximately equal to the difference between E_F in the neutral n layer and level $E(d^9/d^8)$. That is,

$$\Delta E2 \simeq E_D-E2=(E_C-0.104 \text{ eV})-(E_C-0.82 \text{ eV})$$

$$=0.716 \text{ eV}.$$

Within the region where the total concentration of the $3d$ impurity N is high enough E_F is pinned approximately at $E1$. This region forms the first plateau on $E_C(x)$,$(0,x_1)$ in Fig. 2(a). As $N(x)$ decreases, $E_C(x)$ reduces related to E_F. On the second plateau, (x_2,x_3) in Fig. 2(a), E_F is pinned approximately at $E2$. After that $E_C(x)$ reduces again, and goes to its value in the next ENR, E_{C0}. Within the ENR E_F

is located approximately at $E_{C0}-E_D$. Therefore, the heights of the two steps on $E_C(x)$ are approximately equal to $E2-E1, E_D-E2$ in order as described above. Generally speaking, an impurity may create k levels in the E_g: m acceptor levels $(A_m, A_{m-1},\ldots,A_1)$ and n donor levels $(D_1, D_2,\ldots,D_n)$, with $m+n=k$. For the samples that were n type before doping with the impurity, as long as the doping concentration is high enough and annealed sufficiently, m steps will appear on $E_C(x)$. Every step corresponds to a transition between two adjacent charge states of the impurity, E_F is pinned at $E_{\Lambda j}$ within the plateau ahead of the jth step and pinned at $E_{A(j+1)}$ within the next plateau. For the last step, its ''next plateau'' is just the ENR in the substrate, in which E_F is pinned approximately at E_D. Thus the heights of the first to mth steps should be approximately equal to $\Delta E1 \simeq E_{A2}-E_{A1}$, $\Delta E2 \simeq E_{A3}-E_{A2},\ldots,\Delta Ej \simeq E_{A(j+1)} - E_{Aj},\ldots,\Delta E(m-1) \simeq E_{Am}-E_{A(m-1)}$, $\Delta Em \simeq E_D - E_m$ in order. For the samples that were p type before the doping, and with a high enough doping level, $E_C(x)$ will behave in a similar way. The heights of the steps should be approximately equal to $\Delta E1 \simeq E_{D1}-E_{D2}$, $\Delta E2 \simeq E_{D2} - E_{D3},\ldots$, $\Delta Ei \simeq E_{Di}-E_{D(i+1)},\ldots$, $E(n-1) \simeq E_{D(n-1)} - E_{Dn}$, $\Delta En \simeq E_{Dn}-E_A$, in order, where E_A is the background shallow acceptor level.

In the case that the sample was p type before the doping, a similar discussion can be made, the only difference is that VB should be used instead of CB and vice versa in the description above.

Generally speaking, when the doping concentration is so high that the near-surface layer reverses its type and $N(x)$ reduces very quickly as depth x increases, the multisteplike band bending described in the preceding paragraph will disappear, resulting in the formation of a single p-n junction, which has a single-step-like band bending.

B. Single-step-like band bending

When the dopant's concentration in a sample is high enough and its profile is steep enough (for example, the sample is implanted heavily and annealed insufficiently) $N(x)$ concentrates in a thin layer near the surface. In this case, $N(x)$ reduces very quickly as depth x increases. In this case, the calculated band bending is like that shown in Fig. 2(b). E_F in the layer near the surface is located nearer to VB than to CB, resulting in the layer being p type. The little protrusion within the layer is caused by the Gaussian profile of the implanted ions. For x larger than a certain value (x_1' in the figure), $E_C(x)$ reduces quickly. Because $N(x)$ is already not high enough to control E_F there, the i layer in the case described in the preceding paragraph cannot appear now. Thus only one p-n junction is formed. In the usual situation, this sort of structure may be dealt with as a simple p-n junction.

C. Other cases

When the doping level is very low so that E_F does not vary a great deal within the whole sample, the problem will be simplified. In an n-type sample, the impurity will exist in the charge state in which the number of electrons occupied on the center is the largest. In a p-type sample, a similar situation will happen, but a hole should be used instead of an electron in the description above. In this sort of case, the impurity mainly acts as a compensator, but does not cause any obvious band bending.

V. CONCLUSIONS

A scheme used for calculating band bending and profiles of different charge states of a multilevel impurity, $n_{Aj}(x)$ [or $n_{Di}(x)$], within a layer inhomogeneously doped with the impurity has been proposed. The scheme is based on the theory of carrier statistics under thermal equilibrium and carried out by solving the Poisson equation iteratively. Its solution has improved the understanding of semiconductor statistics. As to the applied aspect, it allows us to analyze some relevant problems quantitatively, then some new insights can be given (see Ref. 9).

Several typical cases of band bending within a layer doped inhomogeneously with a multilevel impurity have been classified. Particularly, multisteplike band bending appearing in the samples doped heavily and annealed sufficiently has been discussed in detail. The question as to whether it can be used for some special purposes, for example, in some device design, will be left for consideration.

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