Effect of shallow secondary impurities on the hopping activation energy in semiconductors

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We consider the low-temperature conductivity of heavily doped semiconductors which proceeds via thermally activated hopping of carriers between impurity sites. We investigate a model of an n-type semiconductor with the density of the primary donor dopant (N_D), shallower secondary donors (N_d), and compensating acceptors (N_A). We calculate the hopping activation energy ε_3 for low compensation in the limit as the temperature $T \rightarrow 0$. We extend a Shklovskii-Efros model [*Electronic Properties of Doped Semiconductors* (Springer, New York, 1984)] by including N_d and find ε_3 to be a very sensitive function of N_d/N_A.

When a semiconductor, such as silicon, is doped heavily with impurities, it is possible to pass from the regime where the impurities can be considered as isolated to the regime where there is a small interaction between the impurities.[1-5] In the case of common p-type and n-type dopants (P, As, B, Al, Ga, In) this regime starts at doping densities greater than 5×10^{16} cm^{-3}, depending on the ionization energy of the impurity.[6] If the semiconductor is compensated then some of the majority dopant atoms will have an empty electronic level. Motion of charge carriers from filled to empty electronic states on neighboring impurities occurs at sufficiently high doping densities. For low compensation, current is carried by the empty electronic state which is analogous to a hole in the valence band. This hopping motion is thermally activated with the activation energy ε_3. The problem has been dealt with to varying degrees of approximation by several authors.[1-5] For a comprehensive review, one should consult Shklovskii and Efros (SE).[1] Usually, existing treatments consider the majority dopant of one electrical type and compensation with impurities of opposite electrical type. But in real semiconductors, one invariably finds shallow secondary impurities of the same electrical type as the primary majority dopant. The only published account of the effect of secondary impurities on the hopping activation energy is that by Price[7] who, however, did not consider the zero- and two-impurity complexes discussed below. This problem assumes a new relevance as a novel blocked-impurity-band infrared detector[8] exploits the hopping conduction mechanism to sweep out hopping charges from the active device area, thus eliminating charging effects that plague ordinary extrinsic detectors. It is the purpose of this work[9] to include the effect of the secondary dopants in calculating the hopping energy ε_3.

We assume a random distribution of impurities throughout the semiconductor bulk. The semiconductor is heavily doped with majority donors of density N_D, which is below the density at which metallic conduction occurs.

An isolated majority impurity has energy E_D. There are shallower secondary donors of density N_d and energy E_d. The donors are compensated with acceptors with density N_A. We consider the case in the limit as $T \rightarrow 0$ with $N_d < N_A \ll N_D$ and $E_D < \mu < E_d$, where μ is the Fermi level. All acceptors and all secondary donors are ionized and there are no free thermally generated carriers. The conservation of charge leads to

$$N_D^+ + N_d = N_A \ , \tag{1}$$

where N_D^+ is the density of ionized majority donors.

Because of their small numbers, acceptors and residual donors are on the average far apart. Hence, each acceptor is most probably surrounded solely by majority donors. An ionized acceptor repels the electrons on its surrounding donors. Thus, the ionized majority donors will usually be found near acceptors.

Acceptors and local ionized donors form complexes. A "0-complex" occurs when no donor is ionized around a given acceptor. A "1-complex" is an acceptor–ionized-donor pair. A "2-complex" is a grouping of an acceptor and two ionized donors. One can show that complexes higher than two will not form.[1]

0-complexes are negatively charged, and 2-complexes have a positive charge, but 1-complexes are neutral. Therefore, the charge balance equation, Eq. (1), may be recast into

$$N_2(\mu) + N_d = N_0(\mu) \ , \tag{2}$$

where $N_2(\mu)$ is the density of two complexes, $N_0(\mu)$ the density of 0-complexes, and μ is the Fermi energy.

The hopping activation energy:

$$\varepsilon_3 = \mu - E_D \ . \tag{3}$$

Figure 1 is an energy diagram which shows ionized shallow secondary donors and acceptors, and a distribution of majority dopant electronic levels. These levels depend

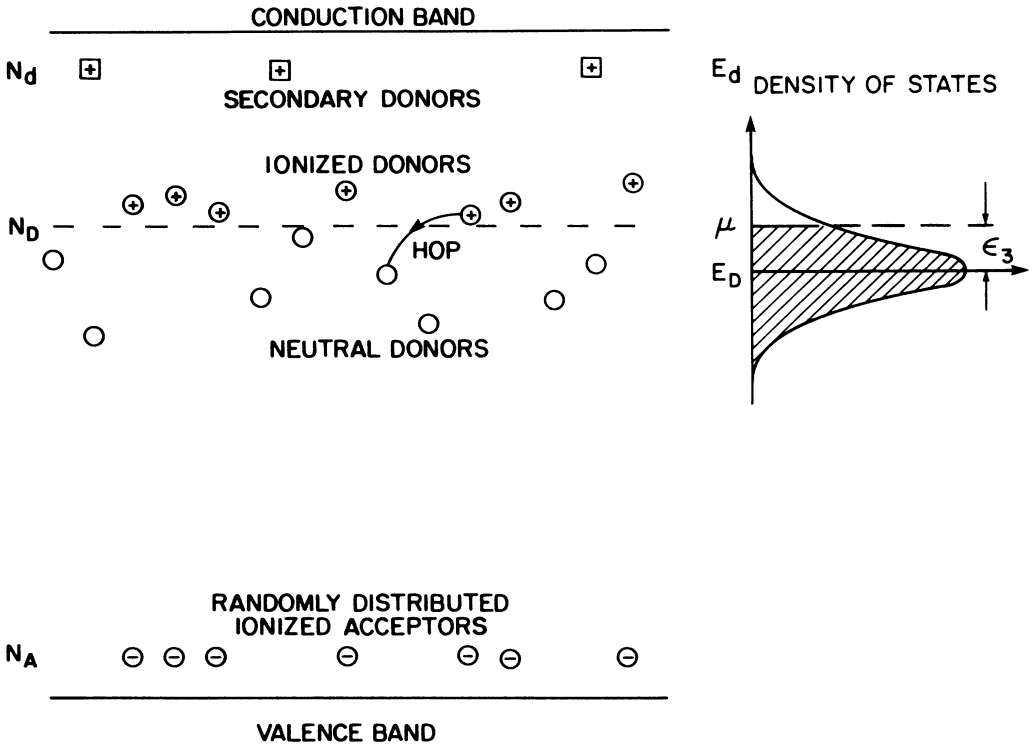

FIG. 1. Electron energy diagram showing the energy-level distribution for shallow secondary donors, primary majority donors, and compensating acceptors.

on the local environment of the particular donor, i.e., on the presence of ionized acceptors and donors in its vicinity. The width of the resulting "impurity band" is not significantly affected by the overlap of electronic wave functions on neighboring donors, in the doping regime relevant to this work. Electrons are filled up to μ and the density of states is sharply peaked at E_D, making $\varepsilon_3=\mu-E_D$ the activation energy for the onset of hopping motion. From this point on we reference E_D to zero.

The density of 0-complexes is[1]

$$N_0(\mu)=N_A e^{-z^3} ,$$

where (4)

$$z=(4\pi/3)^{1/3}\frac{e^2}{K\mu}N_D^{1/3} ,$$

e is the charge of an electron and K is the dielectric constant.

An approximation for the density of 2-complexes is[1]

$$N_2(\mu)\approx 7.14\times 10^{-4}z^6 N_A , \quad (5)$$

which is an overestimate by only 1 or 2%.

Altogether, Eqs. (2), (4), and (5) give

$$e^{-z^3}=7.14\times 10^{-4}z^6+N_d/N_A , \quad (6)$$

which can be used to find z, and from z to find $\mu, N_0(\mu)$ and $N_2(\mu)$.

Figure 2 shows N_0 and N_2 as a function of N_d/N_A. N_2/N_A decreases rapidly from the maximum value of 0.013 towards zero as N_d approaches N_A and N_0/N_A increases almost linearly from its minimum value of 0.013 (see the inset). The explanation is as follows. For high secondary doping, $N_d\simeq N_A$, so N_d rather than N_D is compensated. This results in no ionized majority donors, so that acceptors form 0-complexes, and not 1-complexes or 2-complexes, i.e., $N_2\to 0$. In the opposite limit, $N_d\to 0$, we recover the limit $N_2(\mu)=N_0(\mu)=0.013N_A$ described in SE.

Figure 3 shows $\mu=\varepsilon_3$ as a function of N_d/N_A. At $N_d/N_A=0$, we find $\mu=0.99\mu_0$, as in SE, where

$$\mu_0=e^2N_D^{1/3}/K . \quad (7)$$

The Fermi level increases rapidly towards the energy of the secondary donor level as secondary donors are added, and electrons from the secondary donors fill states in the impurity band of the primary donors, Fig. 1.

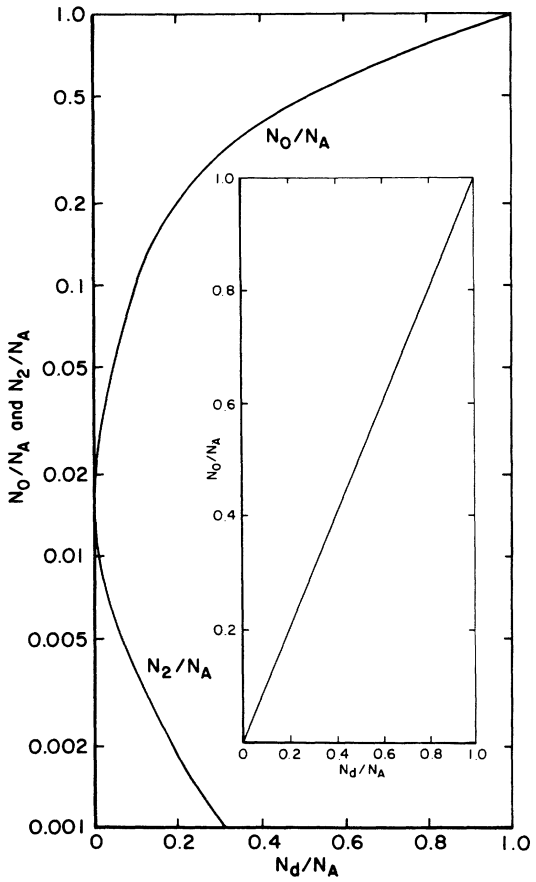

FIG. 2. The ratios of the number of two- and zero-donor complexes to the number of acceptors as a function of the secondary donor-to-acceptor ratio.

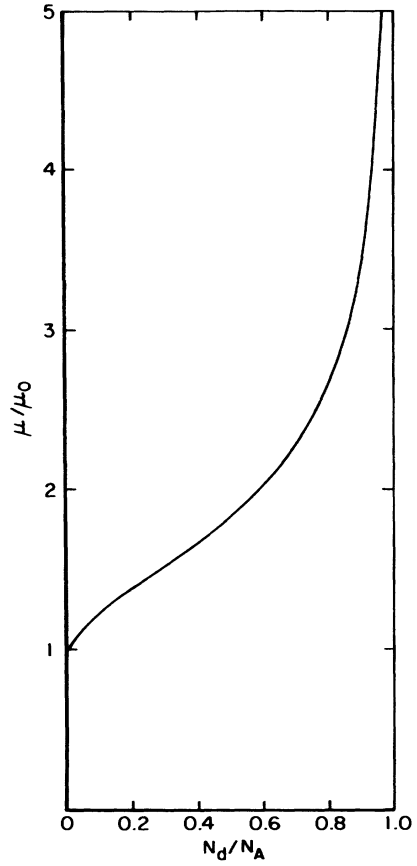

FIG. 3. The hopping activation energy (or equivalently the Fermi energy) as a function of the secondary donor-to-acceptor ratio.

In conclusion, we have shown that secondary impurities which are shallower than the primary majority dopant in a heavily doped semiconductor, have a large effect on the Fermi level, and hence, on the hopping activation energy.

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[9]Preliminary results of this work were presented at the 1986 Spring Meeting of the Ohio APS Section of the American Physical Society [Bull Am. Phys. Soc. **31**, 1778 (1986)].