Chapter 12: Semiconductors

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Contents

Semiconductors are of obvious technological importance - so much so, that a whole chapter will be dedicated to them.

Semiconductors are distinguished from metals in that they have a gap at the Fermi surface, and are distinguished from insulators in that the gap is small $\lesssim \ 1eV$. Most condensed

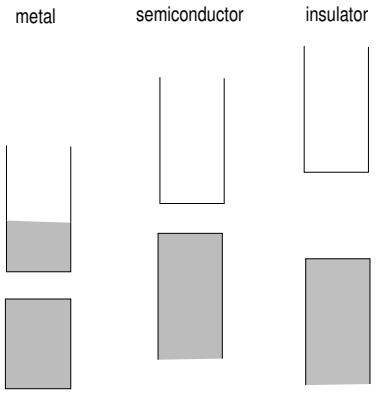

Figure 1: *There is no band gap at the Fermi energy in a metal, while there is a band gap in an insulator. Semiconductors on the other hand have a band gap, but it is much smaller than those found in insulators.*

matter physicists make the distinction on the basis of the conductivity and its temperature dependence. In the Drude model (parabolic band)

$$\sigma \ = \frac{ne^2\tau}{m^*}, \qquad \mu \ = \frac{e\tau}{m^*}, \qquad \sigma \ = ne\tau \tag{1}$$

Almost always $\frac{1}{\tau}$ increases as T increases, ie the thermal excitations increase the scattering rate and decrease the lifetime of

the quasiparticle.

For example, we have seen that $\frac{1}{\tau} \sim T$ at high temperatures due to electron-phonon interactions. In metals, n is about constant, so the temperature dependence of metals is dictated by τ.

$$\text{metals} \qquad \sigma \sim \tau \sim \frac{1}{T}, \qquad \sigma \downarrow \text{ as } T \uparrow \tag{2}$$

However, in semiconductors, the population of free carriers n is temperature dependent. The exponential always will dominate

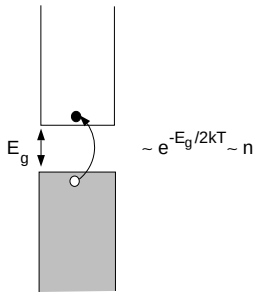

Figure 2: *This shows the temperature dependence for the excitation of electrons, thus allowing the number of free carriers to vary with changes in temperature.*

the power law dependence of τ.

$$\sigma \sim \tau n \sim \frac{1}{T} e^{-E_g/kT} \tag{3}$$

$$\sigma \uparrow \quad \text{as} \quad T \uparrow$$

The same is true for insulators, of course, except here n is so small that for all realistic purposes $\sigma \sim 0$.

1 Band Structure

Clearly the band structure of the semiconductors is crucial then for their device applications. Semiconductors fall into several categories, depending upon their composition, the simplest, *type IV* include silicon and germanium. The type refers to their valence.

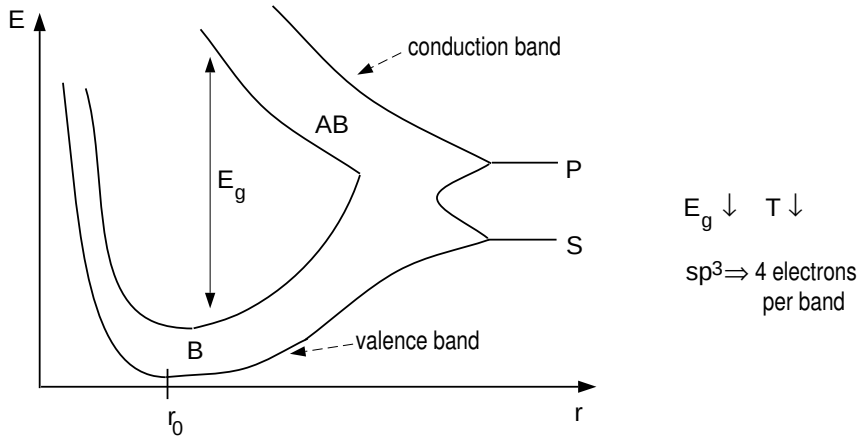

Figure 3: *Sketch of the sp^3 bands in Si vs. Si-Si separation.*

Recall that Si and Ge have a s^2p^2 atomic shell, which forms highly directional sp^3 hybrid bonds in the solid state (with tetragonal symmetry). It is the covalent bonding, or rather the splitting between the bonding and antibonding bands, that forms the gap. The band structure is also quite rich

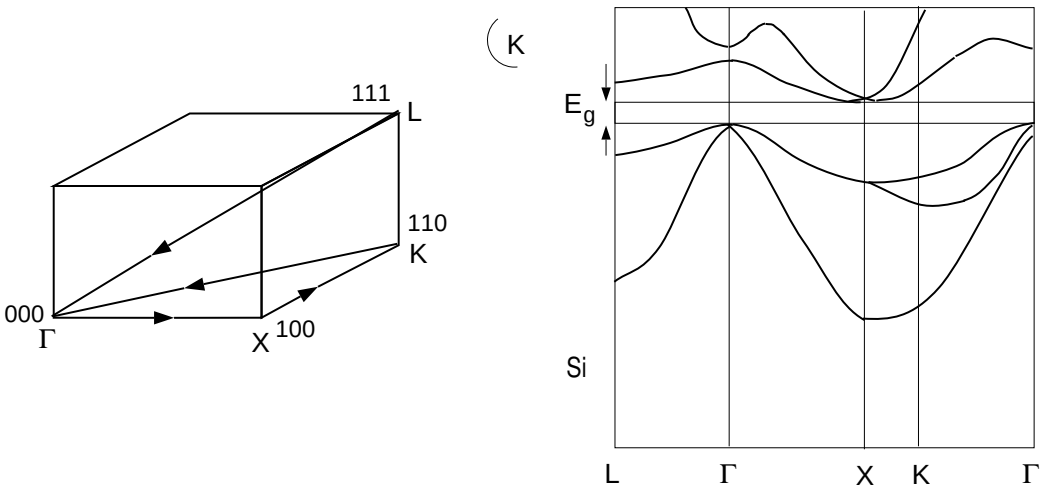

Figure 4: *Sketch of quasiparticle bands in Si (right) along the high symmetry directions (left).*

$$\frac{1}{m^*_{ij}} = \frac{1}{\hbar^2}\frac{\partial^2 E(\mathbf{k})}{\partial k_i \partial k_j} \tag{4}$$

The situation in III-V semiconductors such as GaAs is similar, in that covalent sp^3 bands still form. However, the gap is direct. For this reason GaAs makes more efficient optical devices than does either Si or Ge. A particle-hole excitation across the gap can readily recombine, emit a photon (which has essentially no momentum) and conserve momentum in GaAs; whereas, in an indirect gap semiconductor, this recombination requires the addition creation or absorption of a phonon or some other lattice excitation to conserve momentum. For the same

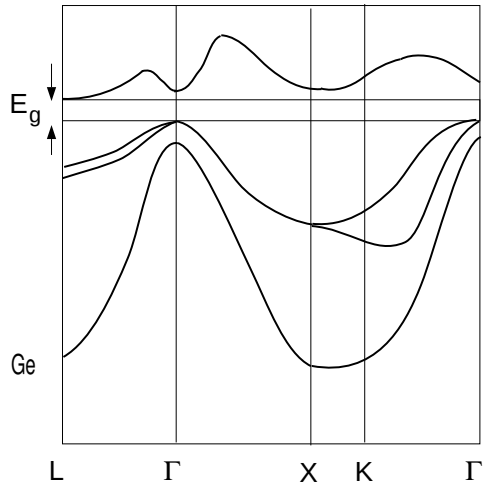

Figure 5: *Sketch of quasiparticle bands in Ge along the high symmetry directions. Note the indirect, roughly* $\Gamma \to L$*, minimum gap energy.*

reason, excitons live much longer in Si and especially Ge than they do in GaAs.

material	τ_{exciton}
GaAs	$1ns(10^{-9}s)$
Si	$19\mu s(10^{-5}s)$
Ge	$1ms(10^{-3}s)$

Table 1:

2 Charge Carrier Density in Intrinsic Semiconductors.

Both electrons and holes contribute to the conductivity with the same sign. Here the mobilities are assumed to be constant. This

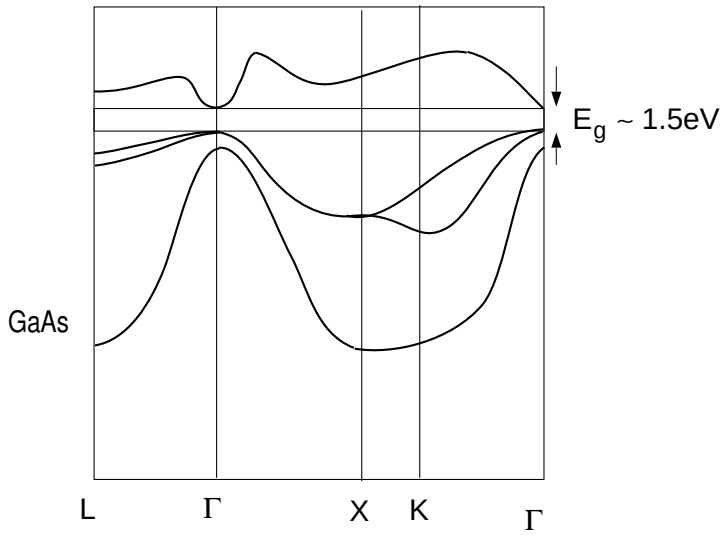

Figure 6: *Sketch of quasiparticle bands in GaAs along the high symmetry directions of the Brillouin zone. Note the direct,* $\Gamma \to \Gamma$*, minimum gap energy. The nature of the gap can be tuned with Al doping.*

is valid since for semiconductors all of the conducting carriers full near the top or bottom of bands, where $E_k \sim \frac{\hbar^2 \mathbf{k}^2}{2m_p^*}$ and the effective mass approximation is valid. Here, we found that $\mu \sim e\tau/m*$

However, as mentioned before, the carrier concentrations are highly T-dependent since all of the carriers in an intrinsic (undoped) semiconductor are thermally induced (i.e. $n = p = 0$ at $T = 0$).

$$n = \int_{E_c}^{E_{top}} D_C(E) f(E,T) dE \to \int_{E_c}^{\infty} D_C(E) f(E,T) dE \quad (5)$$

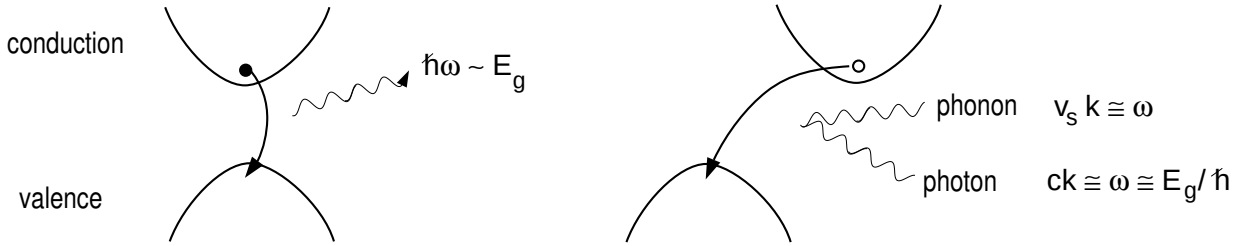

Figure 7: *A particle-hole excitation across the gap can readily recombine, emit a photon (which has essentially no momentum) and conserve momentum in a direct gap semiconductor (left) such as GaAs. Whereas, in an indirect gap semiconductor (right), this recombination requires the addition creation or absorption of a phonon or some other lattice excitation to conserve momentum.*

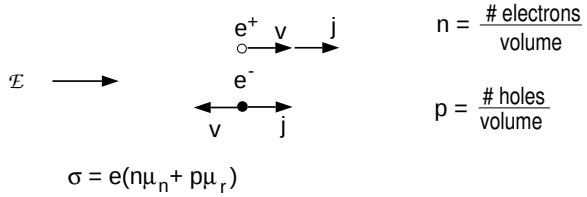

Figure 8: *The contribution of the electrons and holes to the conductivity.*

$$p = \int_{E_{bottom}}^{E_v} D_V(E)\left\{1 - f(E,T)\right\} dE \rightarrow \int_{-\infty}^{E_v} D_V(E)\left\{1 - f(E,T)\right\} dE \tag{6}$$

To proceed further we need forms for D_C and D_V. Recall that in the parabolic approximation $E_k \simeq \frac{\hbar^2 \mathbf{k}^2}{2m^*}$ we found that $D(E) = \frac{(2m^*)^{\frac{3}{2}}}{2\pi^2\hbar^3}\sqrt{E}$. Thus,

$$D_C(E) = \frac{\left(2m_n^*\right)^{\frac{3}{2}}}{2\pi^2\hbar^3}\sqrt{E - E_C} \tag{7}$$

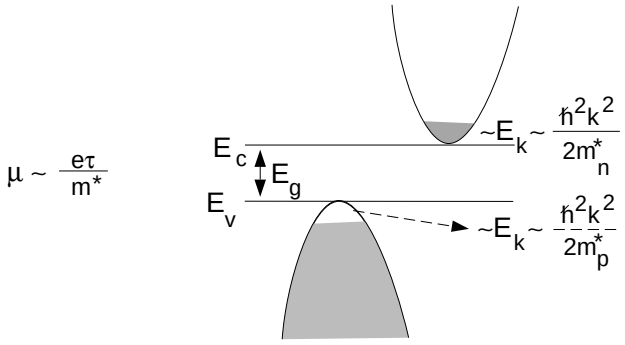

Figure 9:

$$D_V(E) = \frac{\left(2m_p^*\right)^{\frac{3}{2}}}{2\pi^2\hbar^3}\sqrt{E_V - E} \tag{8}$$

for $E > E_C$ and $E < E_V$ respectively, and zero otherwise $E_V < E < E_C$.

In an intrinsic (undoped) semiconductor $n = p$, and so E_F must lie in the band gap. However, if $m_n^* \neq m_p^*$ (ie. $D_C \neq D_V$), then the chemical potential, E_F, must be adjusted up or down from the center of the gap so that $n = p$.

Furthermore, the carriers which are induced across the gap are relatively high in energy, compared to k_BT, since typically $E_g = E_C - E_V \gg k_BT$.

$$\frac{1eV}{k_B} \sim 10000^\circ K \gg 300^\circ K \sim T \tag{9}$$

	$E_g(eV)$	$n_i(cm^{-3})(300^\circ K)$
Ge	0.67	$2.4 \times\ 10^{13}$
Si	1.1	$1.5 \times\ 10^{10}$
GaAs	1.43	$5 \times\ 10^{7}$

Table 2:

Thus, assuming that $E - E_F \gtrsim\ \frac{E_g}{2} \gg\ k_B T$

$$\frac{1}{e^{(E-E_F)/k_B T} + 1} \simeq\ \frac{1}{e^{(E-E_F)/k_B T}} = e^{-(E-E_F)/k_B T} \tag{10}$$

ie., Boltzmann statistics. A similar relationship holds for holes where $-(E - E_F) \gtrsim\ \frac{E_g}{2} \gg\ k_B T$

$$1 - \frac{1}{e^{(E-E_F)/k_B T} + 1} \simeq\ 1 - \left\{1 - e^{-(E-E_F)/k_B T}\right\} = e^{-(E-E_F)/k_B T} \tag{11}$$

since $(1 - f(E)) = f(-E)$ and $e^{(E-E_F)/k_B T}$ is small. Thus, the concentration of electrons n

$$n\ \simeq\ \frac{(2m_n^*)^{\frac{3}{2}}}{2\pi^2\hbar^3} e^{E_F/k_B T} \int_{E_C}^{\infty} \sqrt{E - E_C}\, e^{-E/k_B T} dE \tag{12}$$

$$=\ \frac{(2m_n^*)^{\frac{3}{2}}}{2\pi^2\hbar^3} (k_B T)^{\frac{3}{2}}\, e^{-\beta(E_C - E_F)} \int_0^{\infty} x^{\frac{1}{2}} e^{-x} dx \tag{13}$$

$$=\ 2\left(\frac{2\pi m_n^* k_B T}{h^2}\right)^{\frac{3}{2}} e^{-\beta(E_C - E_F)} = N_{eff}^C e^{-\beta(E_C - E_F)} \tag{14}$$

Similarly

$$p = 2\left(\frac{2\pi m_p^* k_B T}{h^2}\right)^{\frac{3}{2}} e^{-\beta(E_V - E_F)} = N_{eff}^V e^{-\beta(E_V - E_F)} \tag{15}$$

where N_{eff}^C and N_{eff}^V are the partition functions for a classical gas in 3-d and can be regarded as "effective densities of states" which are temperature-dependent. Within this interpretation, we can regard the holes and electrons statistics as classical. This holds so long as n and p are small, so that the Pauli principle may be ignored - the so called *nondegenerate limit*.

In general, in the nondegenerate limit,

$$np = 4\left(\frac{k_B T}{2\pi\hbar^2}\right)^3 \left(m_n^* m_p^*\right)^{\frac{3}{2}} e^{-\beta \mathbf{E}_g} \tag{16}$$

this, the *law of mass action*, holds for both doped and intrinsic semiconductor so long as we remain in the nondegenerate limit. However, *for an intrinsic semiconductor*, where $n = p$, it gives us further information.

$$n_i = p_i = 2\left(\frac{k_B T}{2\pi\hbar^2}\right)^{\frac{3}{2}} \left(m_n^* m_p^*\right)^{\frac{3}{4}} e^{-\beta \mathbf{E}_g/2} \tag{17}$$

However, we already have relationships for n and p involving E_C and E_V

$$n = p = N_{eff}^C e^{-\beta(E_C - E_F)} = N_{eff}^V e^{\beta(E_V - E_F)} \tag{18}$$

$$e^{2\beta E_F} = \frac{N_{eff}^V}{N_{eff}^C} e^{\beta(E_V + E_C)} \tag{19}$$

or

$$E_F = \frac{1}{2}(E_V + E_C) + \frac{1}{2} k_B T \ln\left(\frac{N_{eff}^V}{N_{eff}^C}\right) \tag{20}$$

$$E_F = \frac{1}{2}(E_V + E_C) + \frac{3}{4} k_B T \ln\left(\frac{m_p^*}{m_n^*}\right) \tag{21}$$

Thus if $m_p^* \neq m_n^*$, the chemical potential E_F in a semiconductor is temperature dependent. Recall that this T-dependence was important for the transport of a semiconductor in the presence of a thermal gradient ∇T.

3 Doping of Semiconductors

$\sigma = ne\mu$, so the conductivity depends linearly upon the doping (it may also effect μ in some materials, leading to a non-linear doping dependence). A typical metal has

$$n_{metal} \sim 10^{23}/(cm)^3 \tag{22}$$

whereas we have seen that a typical semiconductor has

$$n_{i_{SeC}} \sim \frac{10^{10}}{cm^3} \qquad \text{at} T \simeq 300^\circ K \tag{23}$$

Thus the conductivity of an intrinsic semiconductor is quite small!

To increase n (or p) to $\sim$ 10^{18} or more, dopants are used. For example, in Si the elements used as dopants have either a s^2p^1 or s^2p^3 atomic valence. Thus, in the tetrahedral bonding of Si there is either an extra electron (half bond) or an unsatisfied bond or a hole. Thus P or B will either donate or

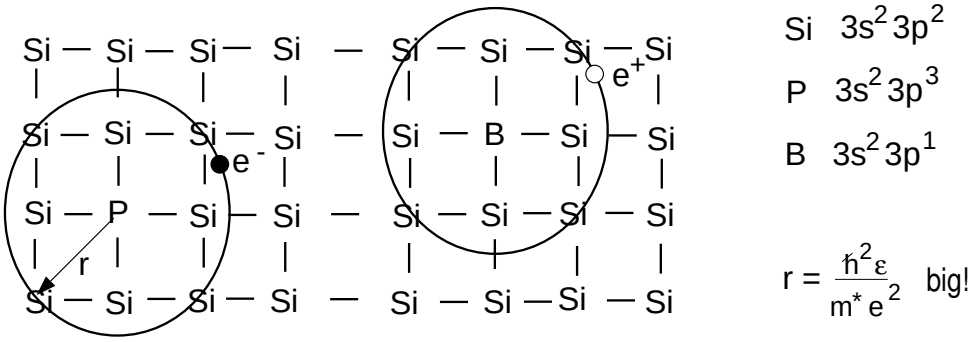

Figure 10:

absorb additional electron (with the latter called the creation of a hole). As in an exciton, these additional charges will be localized around the donor or acceptor ion. The difference is that here the donor/acceptor is fixed and may be treated as having infinite mass, thus the binding energy is given by

$$E = \frac{m^* e^4}{2\epsilon^2 \hbar^2 n^2} \tag{24}$$

$$m^* = \begin{cases} \text{hole mass acceptor}(B) \\ \text{electron mass donor}(P) \end{cases} \tag{25}$$

Again, since $\frac{m^*}{m} < 1$ and $\epsilon \sim 10$ these energies are often much less than $13.6eV$ c.f. in Si $E \sim 30MeV \sim 300°K$ or in Ge $E \sim GMeV \sim 60°K$. Thus thermal excitations will often ionize these dopant sites. In terms of energy levels

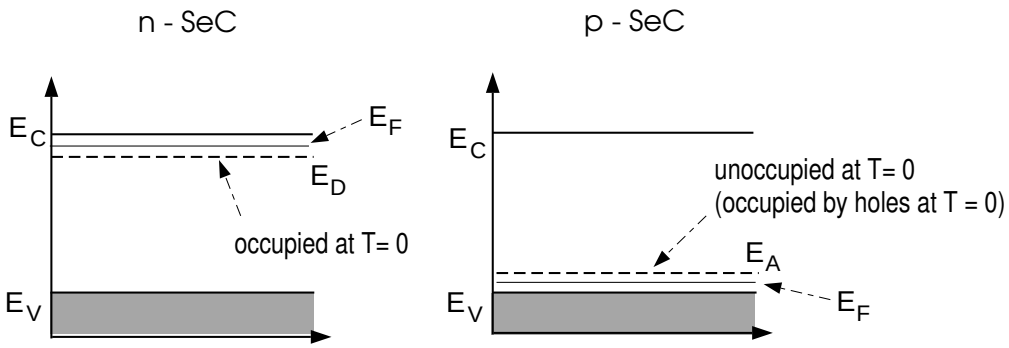

Figure 11:

4 Carrier Densities in Doped semiconductor

The law of mass action is valid so long as the use of Boltzmann statistics is valid i.e., if the degeneracy is small. Thus, even for doped semiconductor

$$np = N_{eff}^C N_{eff}^V e^{-\beta E_g} = n_i^2 = p_i^2 \tag{26}$$

Now imagine the temperature is finite so that some of the donors or acceptors are ionized. Furthermore, in equilibrium, the semi-

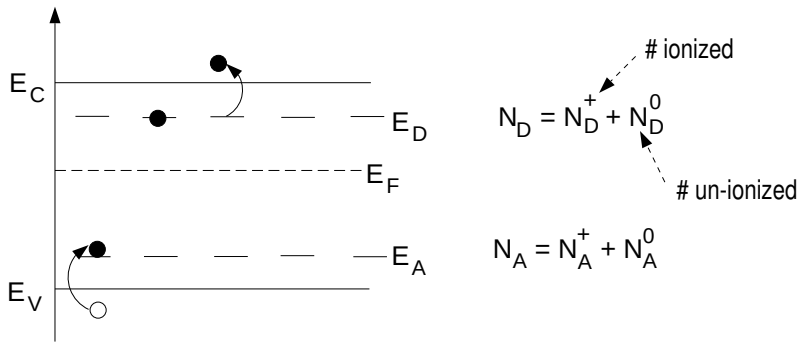

Figure 12:

conductor is charge neutral so that

$$n + N_A^- = p + N_D^+ \tag{27}$$

The probability that a donor/acceptor is occupied by an electron is determined by Fermi statistics

$$n_D = N_D^0 = N_D \frac{1}{1 + e^{\beta(E_D - E_F)}} \tag{28}$$

$$p_A = N_A^0 = N_A(1 - f(E_A)) = N_A \frac{1}{1 + e^{\beta(E_F - E_A)}} \tag{29}$$

To provide a solvable example, imagine that we have an n-type semiconductor (no p-type dopants) so that $N_A = N_A^0 = N_A^+ =$

0, then

$$n = N_{eff}^{C} e^{-\beta(E_C - E_F)} \tag{30}$$

$$N_D = N_D^0 + N_D^+ \tag{31}$$

$$N_D^0 = N_D \frac{1}{e^{\beta(E_D - E_F)} + 1} \tag{32}$$

Furthermore, charge neutrality requires that

$$n = p + N_D^+ \tag{33}$$

An excellent approximation is to assume that for a (commercially) doped semiconductor

$$N_D^+ \gg n_i \tag{34}$$

ie., many more carriers are provided by dopants than are thermally excited over the entire gap, then as $np = n_i^2$, it must be that $N_D^+ \gg p$ so that

$$n \approx N_D^+ = N_D - N_D^0 \tag{35}$$

$$n \approx N_D \left(1 - \frac{1}{e^{\beta(E_D - E_F)} + 1}\right) \tag{36}$$

If we recall that thermally induced carriers satisfy the Boltzmann equation,

$$n = N_{eff}^{C} e^{\beta(E_F - E_C)} \tag{37}$$

we can eliminate E_F in n (where $E_d = E_c - E_D$)

$$n = \frac{N_D}{1 + e^{\beta E_d} n/(N_{eff}^C)} \tag{38}$$

This quadratic equation has only one meaningful solution

$$n = \frac{2N_D}{1 + \sqrt{1 + 4\left(N_D/N_{eff}^C\right) e^{\beta E_d}}} \tag{39}$$

At low $T \ll \frac{E_d}{k_B}$

$$n \simeq \sqrt{N_D N_{eff}^C} e^{-\beta E_d} \tag{40}$$

at higher $T \gg \frac{E_d}{k_B}$

$$n = N_D \tag{41}$$

At still higher T our approximation breaks down that $N_D^+ \gg n$ since thermally excited carriers will dominate.