

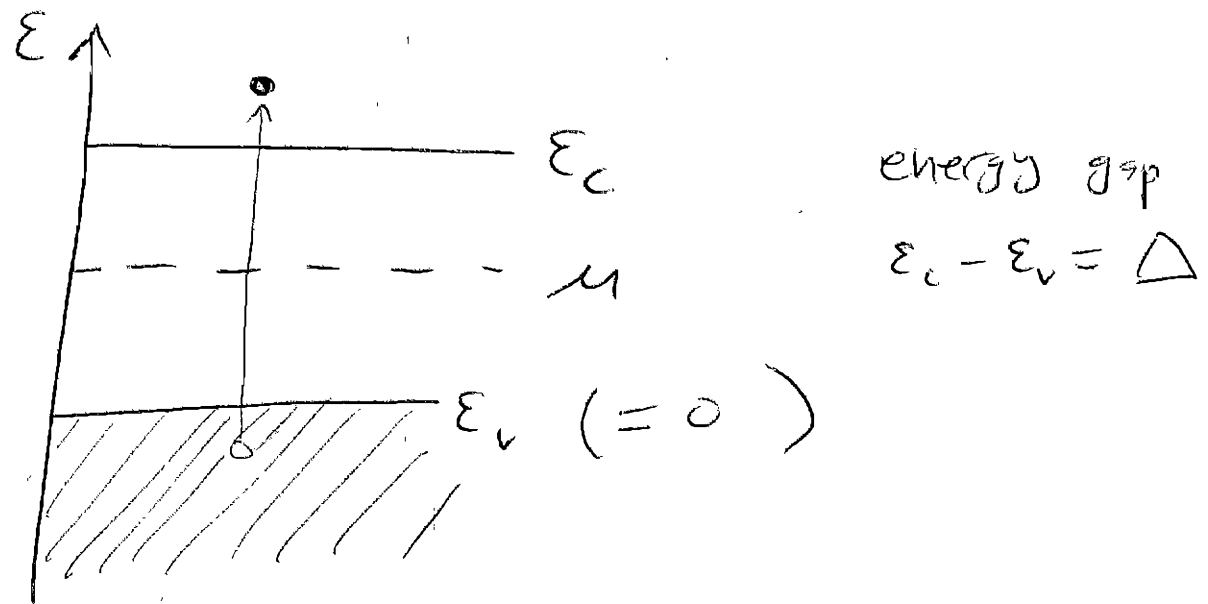
## Semiconductors II

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### Intrinsic carrier concentration

Semiconductors are often doped with special impurity atoms to alter their electrical properties. A pure semiconductor crystal, by contrast, is said to be intrinsic. An intrinsic semiconductor is an insulator at  $T=0$ , but some electrons are excited from the filled valence band into the empty conduction band at finite temperatures.

In an intrinsic semiconductor, the chemical potential  $\mu$  lies in the forbidden gap:



The probability to find an electron of energy  $\epsilon$  in the conduction band is

$$f_e(\epsilon) = \frac{1}{e^{\beta(\epsilon - \mu)} + 1} \approx e^{-\beta(\epsilon - \mu)}$$

(assuming  $\epsilon - \mu \gg k_B T$ ).

The conduction band energies

are

$$\epsilon(k) = \epsilon + \frac{\hbar^2 k^2}{2m}$$

where  $m_e$  is the effective mass in the conduction band. The

density of states in the conduction band is (per unit volume)

$$D_e(\epsilon) = \frac{1}{2\pi^2} \left( \frac{2m_e}{\hbar^2} \right)^{3/2} (\epsilon - \epsilon_c)^{1/2}$$

The concentration of thermally excited electrons in the conduction band is

$$n = \int_{\epsilon_c}^{\infty} D_e(\epsilon) f_e(\epsilon) d\epsilon$$

$$\approx \frac{1}{2\pi^2} \left( \frac{2m_e}{\hbar^2} \right)^{3/2} e^{\beta(\mu - \epsilon_c)} \int_{\epsilon_c}^{\infty} (\epsilon - \epsilon_c)^{1/2} e^{-\beta(\epsilon - \mu)} d\epsilon$$

$$n \approx 2 \left( \frac{m_e k_B T}{2\pi \hbar^2} \right)^{3/2} e^{(\mu - \epsilon_c)/k_B T}$$

Note, however that  $\mu = \mu(T)$ .

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The holes near the top of the valence band behave like particles with effective mass  $m_h$ :

$$\begin{aligned} \epsilon_h(k) &= -\epsilon_e(k) = -\left[ \epsilon_v - \frac{\hbar^2 k^2}{2m_h} \right] \\ &= -\epsilon_v + \frac{\hbar^2 k^2}{2m_h} \end{aligned}$$

$$\Rightarrow D_h(\epsilon) = \frac{1}{2\pi^2} 2 \left( \frac{2m_h}{\hbar^2} \right)^{3/2} (\epsilon_v - \epsilon)^{1/2}$$

↑  
energy of missing electron

The density of holes thermally excited in the valence band is thus

$$p = \int_{-\infty}^{\epsilon_v} D_h(\epsilon) f_h(\epsilon) d\epsilon \approx 2 \left( \frac{m_h k_B T}{2\pi \hbar^2} \right)^{3/2} e^{-\beta(\epsilon_v - \mu)}$$

The product  $np$  does not involve  $m$ :

$$np \approx 4 \left( \frac{k_B T}{2\pi \hbar^2} \right)^3 (m_e m_h)^{3/2} e^{-\beta \Delta}$$

$$\bullet n p = 4 \left( \frac{k_B T}{2\pi \hbar^2} \right)^3 (m_e m_h)^{3/2} e^{-\beta \Delta}$$

Intrinsic semiconductor :

$$n = p \equiv n_i$$

$$m_e^{3/2} e^{\beta(\mu - \epsilon_c)} = m_h^{3/2} e^{\beta(\epsilon_v - \mu)}$$

$$e^{2\beta\mu} = \left( \frac{m_h}{m_e} \right)^{3/2} e^{\beta(\epsilon_v + \epsilon_c)}$$

$$\frac{2\mu}{k_B T} = \frac{\epsilon_v + \epsilon_c}{k_B T} + \ln \left( \frac{m_h}{m_e} \right)^{3/2}$$

$$\bullet \mu = \frac{\epsilon_v + \epsilon_c}{2} + \frac{3}{4} k_B T \ln \left( \frac{m_h}{m_e} \right)$$

$$\mu = \frac{\epsilon_v + \epsilon_c}{2} \quad (\text{middle of the gap})$$

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where  $\Delta = \epsilon_c - \epsilon_v$ .

Actually, we have nowhere assumed the material is intrinsic in this derivation. All that we have assumed is that

$$\epsilon_c - \mu, \mu - \epsilon_v \gg k_B T.$$

At 300K one has

material	$n, p$
Si	$2.1 \times 10^{19} \text{ cm}^{-3}$
Ge	$2.89 \times 10^{26} \text{ cm}^{-3}$
GaAs	$6.55 \times 10^{12} \text{ cm}^{-3}$

### Intrinsic Conductivity

$$\sigma = n \frac{e^2 \tau_e}{m_e} + p \frac{e^2 \tau_h}{m_h}$$

Although  $\tau_e$  and  $\tau_h$  are dependent

on temperature due to scattering from thermally excited phonons, the main temperature dependence comes from the exponential dependence  $e^{-\Delta/2k_B T}$  of the carrier concentration.

## Impurities

Donor states  
(Go over problem set)

Pentavalent atom  
in Si, Ge

$$E_d = \frac{m_e e^4}{2 \epsilon^2 \hbar^2}$$

$\epsilon$  = static dielectric constant

$$a_d = \frac{\epsilon \hbar^2}{m_e e^2}$$

$m_e$  = electron effective mass

In general  $m_e < m$  and

$\epsilon > 1$ , so the binding energy of a donor is  $\ll$  Rydberg and

$a_d \gg$  Bohr radius. For

Ge, for example,  $\frac{m_e}{m} \frac{1}{\epsilon^2} = 4 \times 10^{-7}$ .

Crystal	$\epsilon$	$m_e/m$
diamond	5.5	—
Si	11.7	0.2
Ge	15.8	0.1
GaAs	13.13	.066

For a density  $n_d$  of donor

impurities, the donor electrons will be bound to their parent



impurities provided

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$$n_d^{-1/3} \gg a_d$$

When  $n_d^{-1/3} \sim a_d$ , the wavefunctions of neighboring

donor electrons begin to overlap, and an impurity

band of delocalized electrons forms. This

phenomenon was first described by Sir Neville Mott (c.f.

lecture on tightbinding approx.)

Such a material is known

as an n-type semiconductor, and behaves as a semiconductor.

## Acceptor states

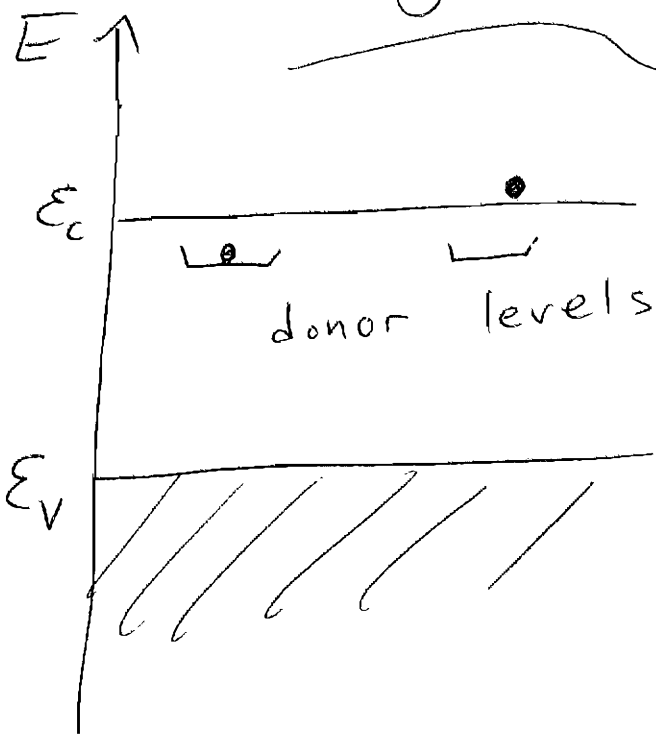
Similarly, a trivalent impurity in Si or Ge will form 4 covalent bonds with its 4 Si (Ge) neighbors, becoming a negative ion. A hole in the valence band will be bound to this negative ion:

$$E_a = \frac{m_h e^4}{2\epsilon^2 \hbar^2}$$

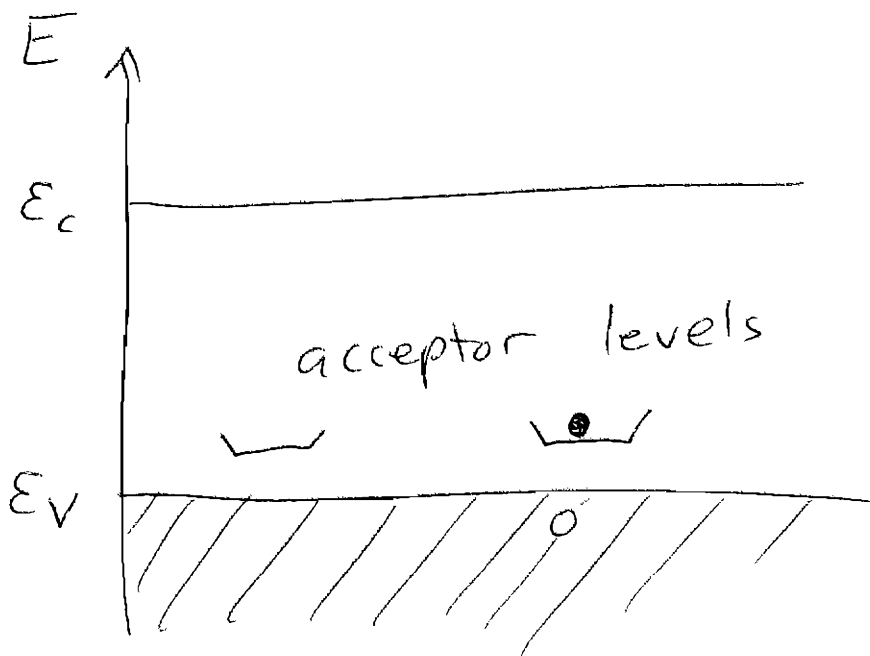
$$a_a = \frac{\epsilon \hbar^2}{m_h e^2}$$

$m_h$  = hole effective mass

For  $n_a^{-1/3} \sim a_a$  an impurity band of holes forms  $\rightarrow$  a p-type semiconductor.



n-type



p-type

$n_d =$  concentration of donor atoms

$$n_d = n_d^+ + n_d^0$$

$n_d^+ =$  concentration of ionized donor atoms

$n_d^0 =$  concentration of neutral donor atoms

$n_d^+ =$  # of electrons contributed, some of which populate the conduction band and some of which fill holes in the valence band.

Typically  $n_d^+ \gg n_i = p_i$ ,

So  $n \approx n_d^+$ .

Ex. Ge at 300K

$$n_i = 5 \times 10^{13} \text{ cm}^{-3}$$

$$\rho = 4.4 \times 10^{22} \frac{\text{atoms}}{\text{cm}^3}$$

1 ppm impurity concentration

$$= 4.4 \times 10^{16} \text{ cm}^{-3}$$

So even if only 1% of the impurities are ionized,

$$n_d^+ \sim 10 n_i.$$

$$n_d^0 = \frac{n_d}{e^{\beta(\epsilon_c - E_d - \mu)} + 1}$$

(Fermi-Dirac distribution)

$$n \approx n_d^+ = n_d - n_d^0$$

$$n \approx \frac{n_d}{e^{\beta(\mu - \epsilon_c + E_d)} + 1} \approx n_d e^{-\beta(\mu - \epsilon_c + E_d)}$$

But we know

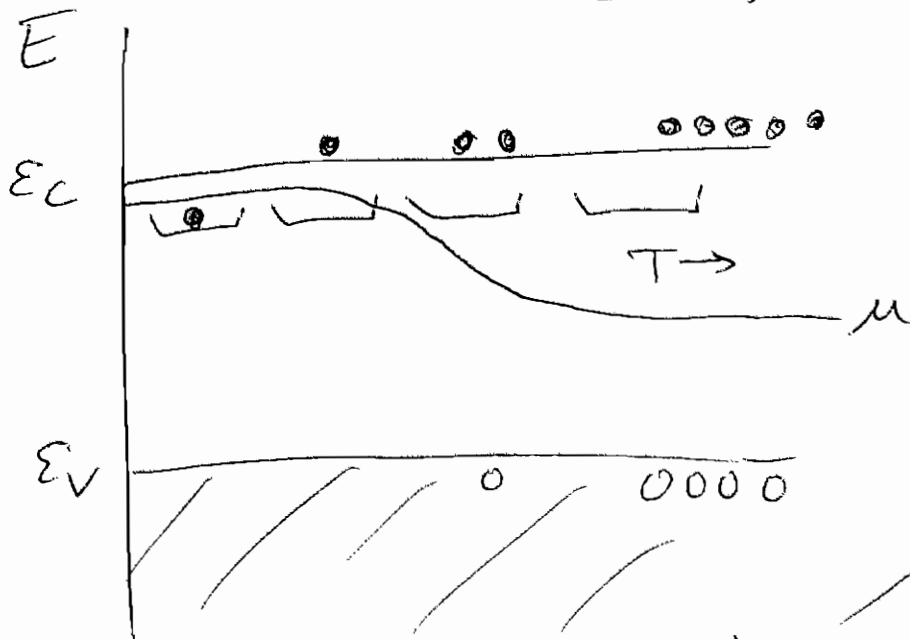
$$n = n_{0e} e^{\beta(\mu - \epsilon_c)}$$

$$\Rightarrow n_d e^{\beta(\epsilon_c - E_d - \mu)} \approx n_{0e} e^{\beta(\mu - \epsilon_c)}$$

$$\Rightarrow \mu = \epsilon_c - \frac{E_d}{2} + \frac{k_B T}{2} \ln \left( \frac{n_d}{n_{0e}(T)} \right)$$

Finally,  $n = n_{0e} e^{\beta(\mu - \epsilon_c)}$

$$\approx (n_{0e} n_d)^{1/2} e^{-\beta E_d / 2}$$



(similarly for acceptors)