MSE 423 Fall 2025 – Week 13

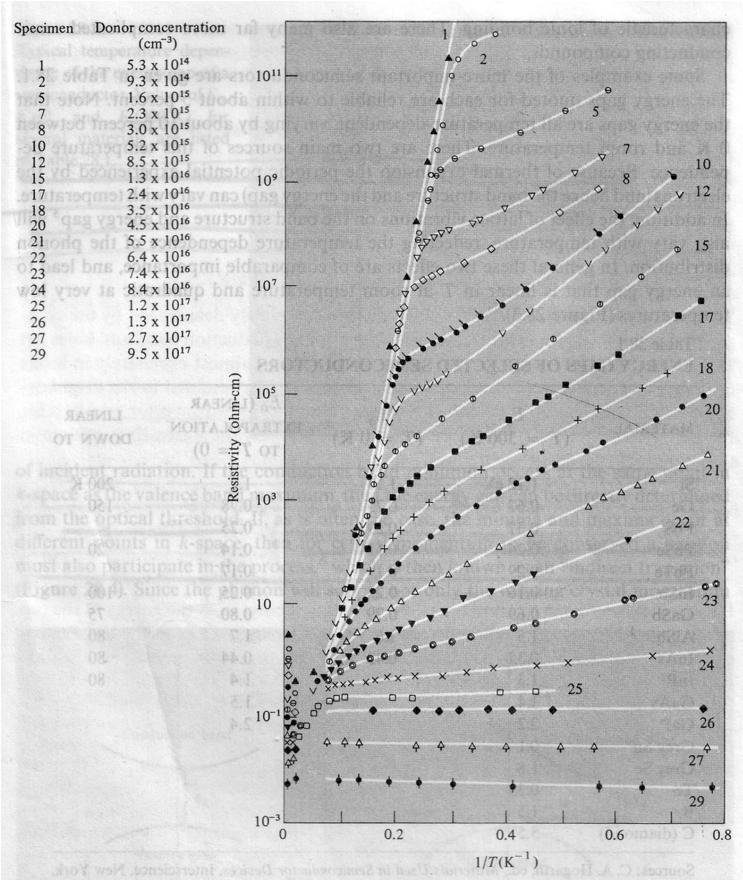
In/homogeneous semiconductors

Russell Ohl **Shockley, Bardeen, and Brattain**

Last week

- Tight-binding (LCAO for a solid)
- Bloch sums for an atomic ("exploded") crystal and for a real crystal
- From levels to bands
- How many bands are filled?
- Band structure of graphene, carbon nanotubes
- Semiconductors – basic electrical and optical properties

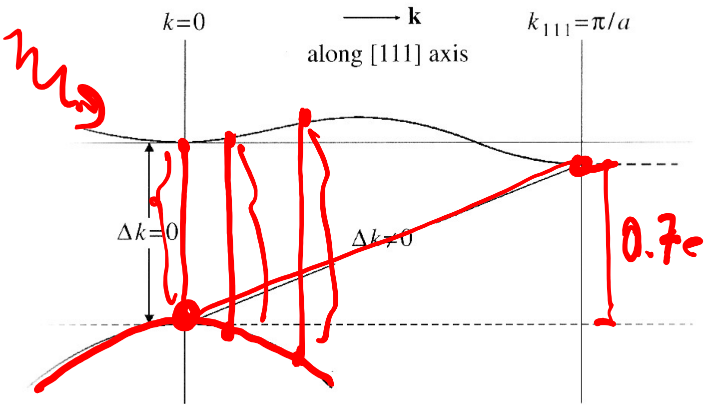
Sb-doped Germanium

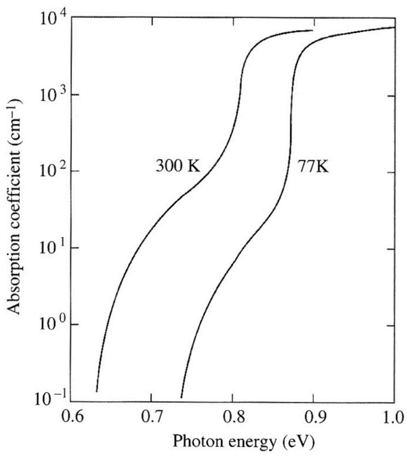


Specimen	Donor concentration (cm^{-3})
1	5.3×10^{14}
2	9.3×10^{14}
5	1.6×10^{15}
7	2.3×10^{15}
8	3.0×10^{15}
10	5.2×10^{15}
12	8.5×10^{15}
15	1.3×10^{16}
17	2.4×10^{16}
18	3.5×10^{16}
20	4.5×10^{16}
21	5.5×10^{16}
22	6.4×10^{16}
23	7.4×10^{16}
24	8.4×10^{16}
25	1.2×10^{17}
26	1.3×10^{17}
27	2.7×10^{17}
29	9.5×10^{17}

Figure 28.2
The resistivity of antimony-doped germanium as a function of $1/T$ for several impurity concentrations. (From H. J. Fritzsche, *J. Phys. Chem. Solids* **6**, 69 (1958).)

Optical absorption in Ge





Density of carriers at thermal equilibrum

DENSITY OF ELECTRONS (NEG CARRIERS) IN THE CONDUCTION BAND

$$n_c(T) = \int_{\epsilon_c}^{+\infty} d\epsilon\; g_c(\epsilon)\frac{1}{e^{(\epsilon-\mu)/k_BT}+1}$$

$\sqrt{\epsilon}$

ϵ_c (BOTTOM OF CONDUCTION

DENSITY OF HOLES (POSITIVE CARRIERS) IN THE VALENCE

$$p_v(T) = \int_{-\infty}^{\epsilon_v} d\epsilon\; g_v(\epsilon)\left(1-\frac{1}{e^{(\epsilon-\mu)/K_BT}+1}\right)$$

$$= \int_{-\infty}^{\epsilon_v} d\epsilon\; g_v(\epsilon)\left(\frac{1}{e^{(\mu-\epsilon)/K_BT}+1}\right)$$

NON-DEGENERATE

F.D. DISTR FOR EL IN THE COND IN THE NON DEG.

$$\frac{1}{e^{(\epsilon-\mu)/K_BT}\cancel{+1}} \approx e^{-(\epsilon-\mu)/K_BT},\ \epsilon > \epsilon_c$$

F.D. DISTR. FOR HOLES IN THE VALENCE.

$$\frac{1}{e^{(\mu-\epsilon)/K_BT}\cancel{+1}} \approx e^{-(\mu-\epsilon)/K_BT},\ \epsilon < \epsilon_v$$

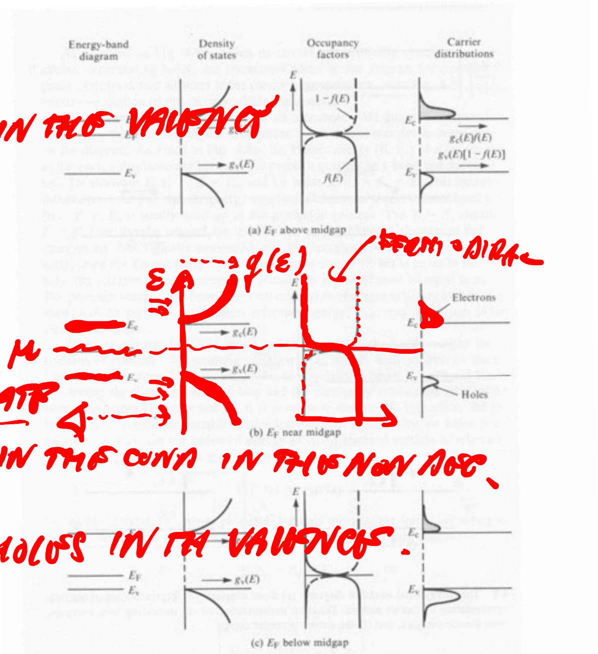


Fig. 4.7 Carrier distributions (not drawn to scale) in the respective bands when the Fermi le is positioned (a) above midgap, (b) near midgap, and (c) below midgap. Also shown in ea case are coordinated sketches of the energy-band diagram, density of states, and the occupa factors (the Fermi function and one minus the Fermi function).

Density of carriers at thermal equilibium

(non-degenerate sc)

$$n_c(T) = \int_{\epsilon_c}^{\infty} d\epsilon\; g_c(\epsilon)\frac{1}{e^{(\epsilon-\mu)/k_BT}+1}$$

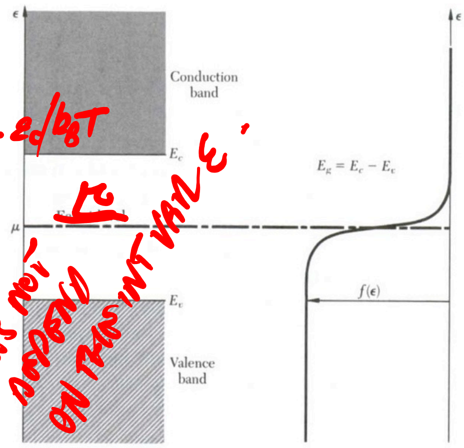
$$\approx \int_{\epsilon_c}^{\infty} d\epsilon\; g_c(\epsilon)e^{-(\epsilon-\mu)/k_BT} \cdot e^{\epsilon_c/k_BT} \cdot e^{-\epsilon_c/k_BT}$$

$$= \left\{\int_{\epsilon_c}^{\infty} d\epsilon\; g_c(\epsilon)e^{-(\epsilon-\epsilon_c)/k_BT}\right\} e^{-(\epsilon_c-\mu)/k_BT}$$

$$= N_c(T)e^{-(\epsilon_c-\mu)/k_BT}$$

DENSITY OF AVAILABLE STATES

DOES NOT DEPEND ON TRANS INT VAR ϵ'



$$p_v(T) = \int_{-\infty}^{\epsilon_v} d\epsilon\; g_v(\epsilon)\left(1-\frac{1}{e^{(\epsilon-\mu)/k_BT}+1}\right) = ... = P_v(T)e^{-(\mu-\epsilon_v)/k_BT}$$

Density of available states (isotropic effective mass)

$$g_{c,v}(\epsilon) = \sqrt{2|\epsilon - \epsilon_{c,v}|}\frac{m_{c,v}^{3/2}}{\hbar^3\pi^2}$$

$$N_c(T) = \int_{\epsilon_c}^{\infty} d\epsilon\ g_c(\epsilon)e^{-(\epsilon-\epsilon_c)/K_BT}$$

$$P_v(T) = \int_{-\infty}^{\epsilon_v} d\epsilon\ g_v(\epsilon)e^{-(\epsilon_v-\epsilon)/K_BT}$$

$$N_c(T) = \frac{1}{4}\left(\frac{2m_ck_BT}{\pi\hbar^2}\right)^{3/2}$$

$$P_v(T) = \frac{1}{4}\left(\frac{2m_vk_BT}{\pi\hbar^2}\right)^{3/2}$$

$$N_c(T) = 2.5\left(\frac{m_c}{m}\right)^{3/2}\left(\frac{T}{300K}\right)^{3/2} 10^{19}/cm^3$$

$$P_v(T) = 2.5\left(\frac{m_v}{m}\right)^{3/2}\left(\frac{T}{300K}\right)^{3/2} 10^{19}/cm^3$$

Miracle! Law of Mass Action

$$n_c(T) = N_c(T)e^{-(\epsilon_c-\mu)/K_BT}$$

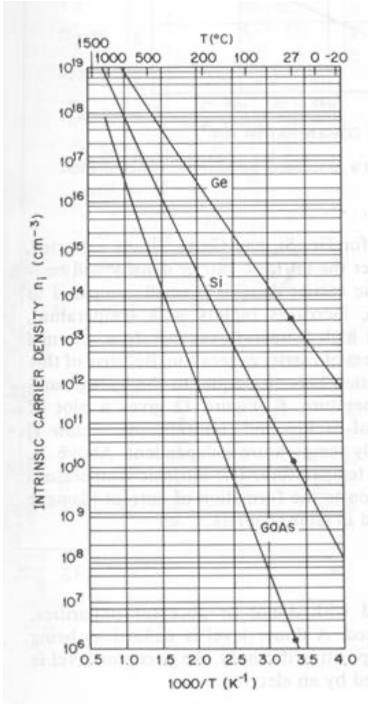
$$p_v(T) = P_v(T)e^{-(\mu-\epsilon_v)/K_BT}$$

$$\boxed{n_c(T)p_v(T)} = N_c(T)P_v(T)e^{-\frac{(\epsilon_c-\epsilon_v)}{K_BT}}$$

$$\boxed{= N_c(T)P_v(T)e^{-\frac{E_{gap}}{K_BT}}}$$

This is a property of the material (does not depend on doping)

Intrinsic case



$$n_c(T) = p_v(T) \equiv n_i(T)$$

$$n_i = \underbrace{\sqrt{n_c p_v} = \sqrt{N_c P_v}\, e^{-E_g/2k_BT}}$$

$$= 2.5\left(\frac{m_c}{m}\right)^{\frac{3}{4}}\left(\frac{m_v}{m}\right)^{\frac{3}{4}}\left(\frac{T}{300K}\right)^{\frac{3}{2}} e^{-\frac{E_g}{2K_BT}}\ 10^{19}/cm^3$$

Intrinsic case

$$\begin{cases} n_c(T) = N_c(T)e^{-(\epsilon_c-\mu)/K_BT} \\ p_v(T) = P_v(T)e^{-(\mu-\epsilon_v)/K_BT} \end{cases}$$

$$1 = \boxed{\frac{n_c(T)}{p_v(T)}} = \frac{N_c(T)}{P_v(T)} e^{2\mu/K_BT} e^{(2\epsilon_v+E_g)/K_BT}$$

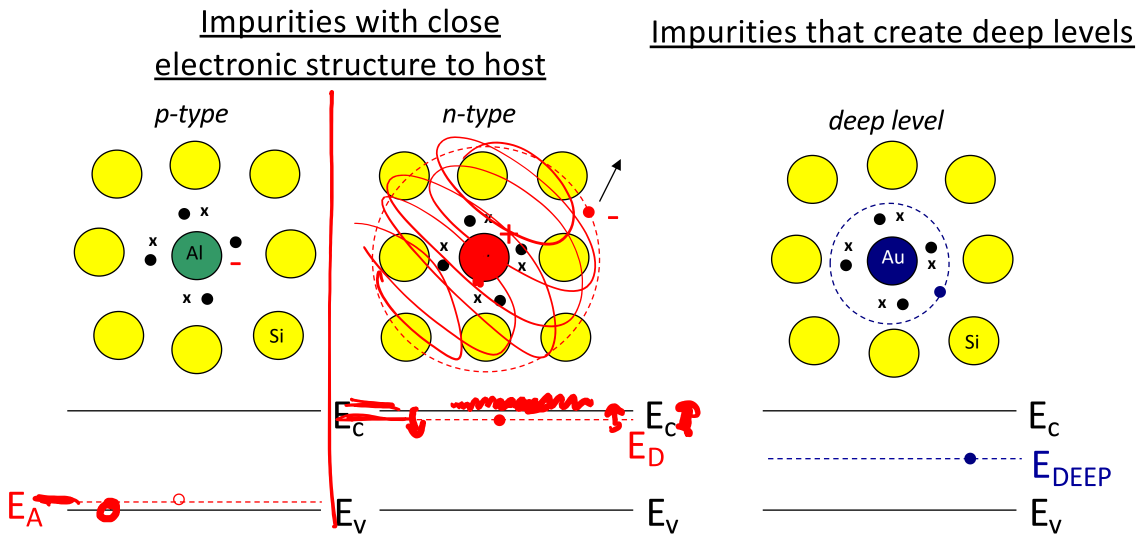
$$\mu = \mu_i = \underbrace{\epsilon_v + \frac{E_g}{2}}_{\Downarrow} + \boxed{\frac{k_BT}{2}\ln\frac{P_v(T)}{N_c(T)}}$$

$$= \epsilon_v + \frac{E_g}{2} + \frac{3}{4}k_BT\ln\left(\frac{m_v}{m_c}\right)$$

MIDDLE OF BAND GAP

Impurity levels

- Adding impurities can lead to controlled domination of one carrier type
  - n-type is dominated by electrons
  - p-type is dominated by holes
- Adding other impurities can degrade electrical properties



Impurity states as "embedded" hydrogen atoms

- Consider the weakly bound 5th electron in phosphorus as a modified hydrogen atom
- For hydrogenic donors or acceptors, we can think of the electron or hole, respectively, as an orbiting electron around a net fixed charge
- We can estimate the energy to free the carrier into the conduction band or valence band by using a modified expression for the energy of an electron in the H atom

$$E_n = \frac{me^4}{8\varepsilon_o^2 h^2 \mathrm{n}^2} = -\frac{13.6}{\mathrm{n}^2} \quad (eV)$$

$$E_n = \frac{me^4}{8\varepsilon_o^2 h^2 n^2} \xrightarrow{\frac{e^2}{\varepsilon_r}=e^2} \frac{m^* e^4}{8\varepsilon_o^2 h^2 n^2}\frac{1}{\varepsilon_r^2} = -\frac{13.6}{n^2}\frac{m^*}{m}\frac{1}{\varepsilon^2}$$

Thus, for the ground state n=1, we can see already that since $\boldsymbol{\varepsilon}$ is of the order of ~10, the binding energy of the carrier to the impurity atom is <0.1eV

Expect that many carriers are then ionized at room T:

- B acceptor in Si: 0.046 eV
- P donor in Si: 0.044 eV
- As donor in Si: 0.049

Impurity types, levels

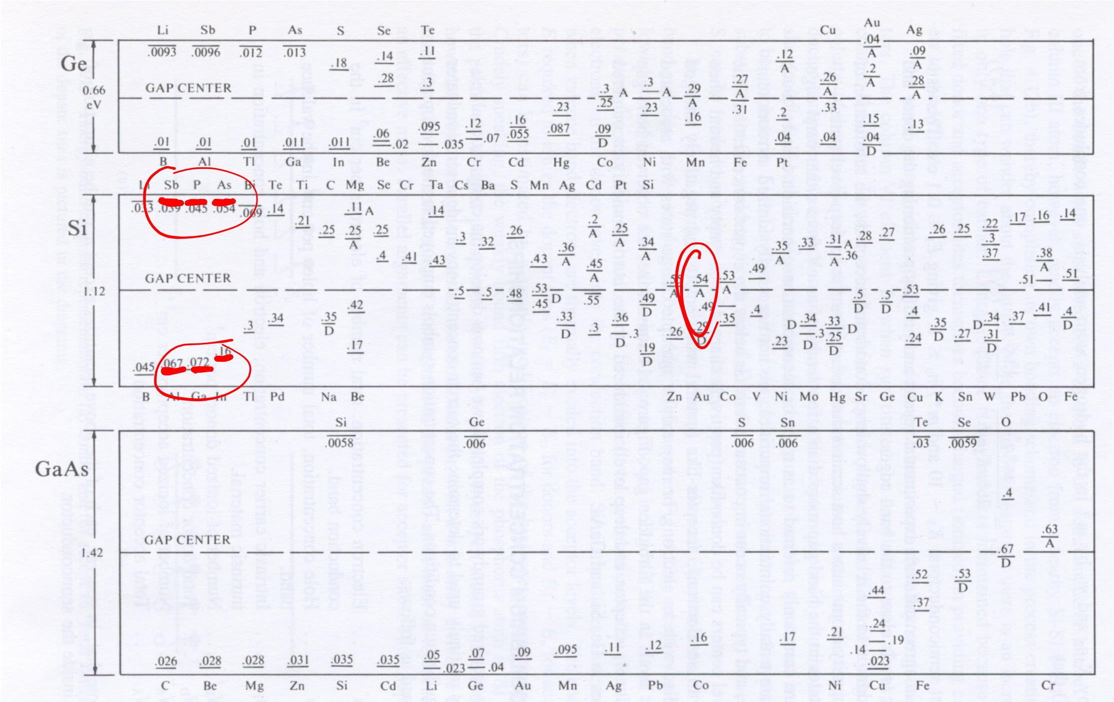
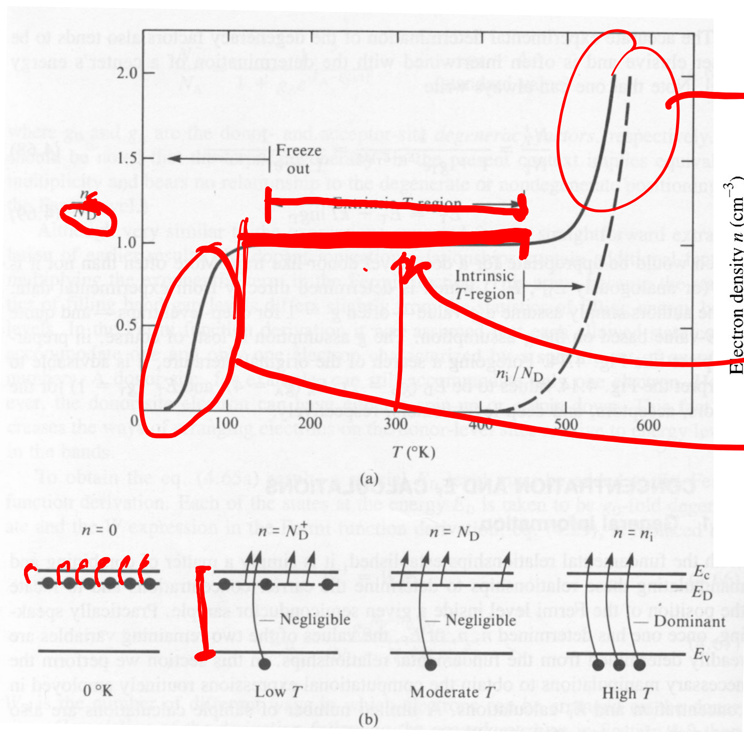
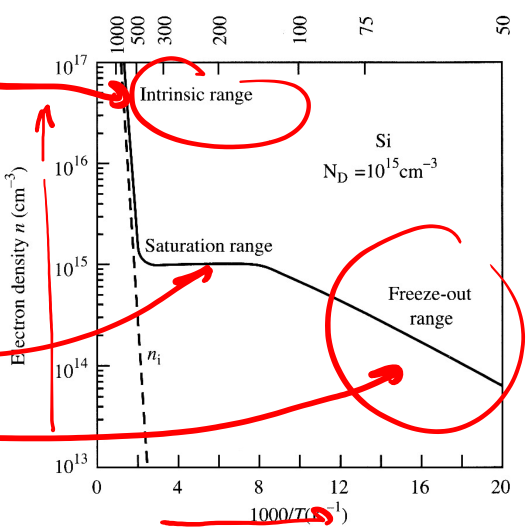


Fig. 4.14 Measured ionization energies for the most commonly encountered impurities in Ge, Si, and GaAs. The levels above midgap are referenced to E_c and are donor-like or multiply charged donors, unless marked with an A which identifies an acceptor level. The levels below midgap are referenced to E_v and are acceptor-like or multiply charged acceptors, unless marked with a D for donor level. (From Sze.[3] Reprinted with permission.)

Temperature dependence of majority carriers





Inverse T plot

Conductivity in semiconductors

Conductivity in (doped) semiconductors can be computed as in metals once we know the density of charge carriers (at every T):

MOBILITY MOBILITY

$$\sigma = n_c e \mu_e + p_v e \mu_p$$

Table 3 Carrier mobilities at room temperature, in $cm^2/V\text{-}s$

Crystal	Electrons	Holes	Crystal	Electrons	Holes
Diamond	1800	1200	GaAs	8000	300
Si	1350	480	GaSb	5000	1000
Ge	3600	1800	PbS	550	600
InSb	800	450	PbSe	1020	930
InAs	30000	450	PbTe	2500	1000
InP	4500	100	AgCl	50	—
AlAs	280	—	KBr (100 K)	100	—
AlSb	900	400	SiC	100	10–20

ELECTRONIC BANDS IN SODIUM CHLORIDE

MASS. INST. TECH. 8 AUG 1936 LIBRARY

BY

WILLIAM SHOCKLEY

B.Sc., California Institute of Technology
1932

Submitted in Partial Fulfillment of the

Requirements for the Degree of

DOCTOR OF PHILOSOPHY

from the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

1936

Signature of Author...............................

Department of Physics, May 14, 1936.

Signature of Professor
in Charge of Research.............................

?

JC SLATER

Signature of Chairman of Department
Committee on Graduate Students...................

TABLE OF CONTENTS

Equilibrium carrier densities of impure/extrinsic/doped semiconductors (simplified)

SATURATION REGIME

n-type doping: $N_d \gg \cancel{N_a}$

$$n_c \approx N_d \qquad p_v = \frac{n_i^2}{N_d}$$

$n_c p_v = n_i^2$

p-type doping: $N_a \gg \cancel{N_d}$

$$p_v \approx N_a \qquad n_c = \frac{n_i^2}{N_a}$$

$n_c p_v = n_i^2$

How does the chemical potential move?

n-type doping: $N_d \gg N_a$

$$\mu = \mu_i + k_B T \ln\left(\frac{N_d}{n_i}\right)$$

$N_{d/a} \gg n_i$

p-type doping: $N_a \gg N_d$

$$\mu = \mu_i - k_B T \ln\left(\frac{N_a}{n_i}\right)$$

Si: n and p type doping

At finite T

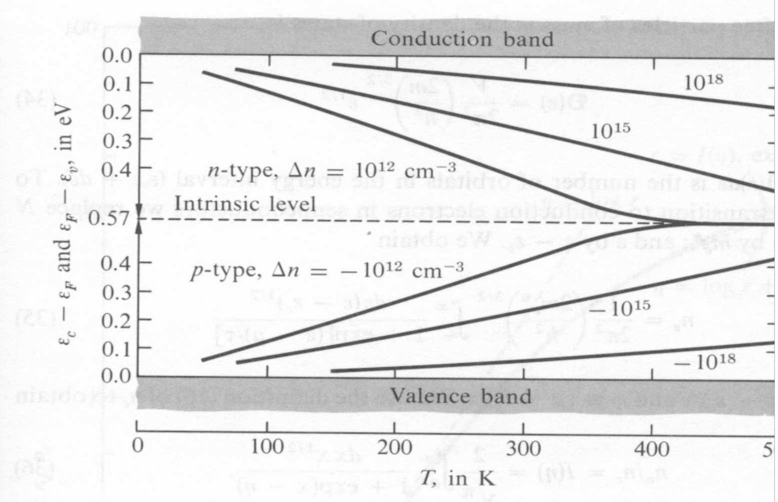


Figure 13.3 The Fermi level in silicon as a function of temperature, for various doping concentrations. The Fermi levels are expressed relative to the band edges. A small decrease of the energy gap with temperature has been neglected.

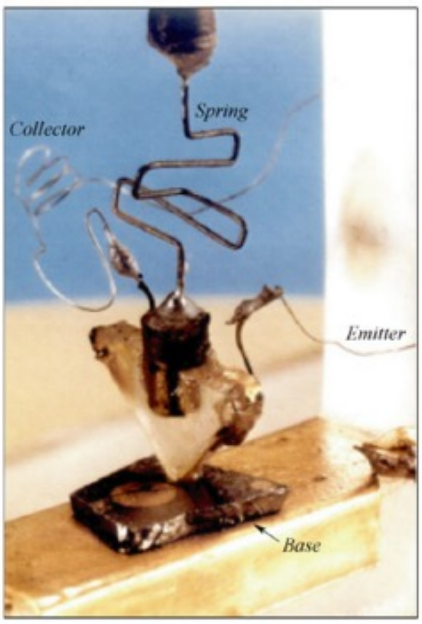
Semiconductor carrier engineering

- Silicon at room temperature ~10^{23} ATOMS / cm^3
  - n_i: ~$10^{10}cm^{-3}$
  - add $10^{16}cm^{-3}$ (~1ppm) phosphorous donors: n_c~N_d
  - $\boxed{n_c \sim 10^{16}cm^{-3}}$ $\boxed{p_v \sim 10^4}$ (n_i^2/N_d)
  - conductivity is proportional to the # of carriers leading to 6 orders of magnitude change in conductivity!

Impurities at the ppm level drastically change the conductivity (6 orders of magnitude)

Basic electronics: the transistor

The first point contact transistor
William Shockley, John Bardeen, and Walter Brattain
Bell Laboratories, Murray Hill, New Jersey (1947)



December 16, 1947 - Nobel Prize - 1956

Abrupt junction

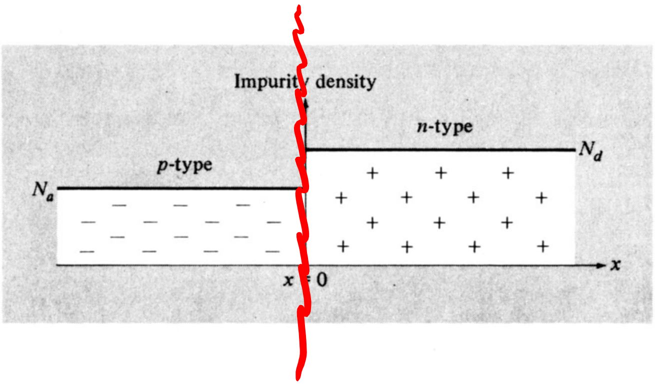


Figure 29.1
The impurity densities along a *p-n* junction in the case of an "abrupt junction," for which donor impurities dominate at positive *x*, and acceptor impurities at negative *x*. The donors are represented by (+) to indicate their charge when ionized, and the acceptors by (−). For a junction to be abrupt, the region about $x = 0$ where the impurity concentrations change must be narrow compared with the "depletion layer" in which the carrier densities are nonuniform. (Typical plots of the carrier densities are superimposed on this figure in Figure 29.3.)

The p-n junction (diode)

<u>p-type material at equilibrium</u>

$p_v \sim N_A$

$n_c \sim n_i^2/N_A$

p-TYPE

$$\boxed{\mu_p = \mu_i - k_b T \ln\left(\frac{N_A}{n_i}\right)}$$

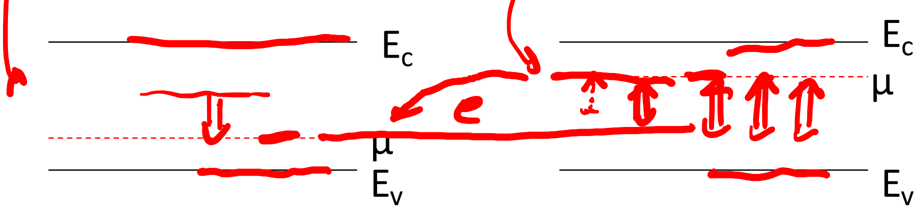
<u>n-type material at equilibrium</u>

$n_c \sim N_D$

$p_v \sim n_i^2/N_D$

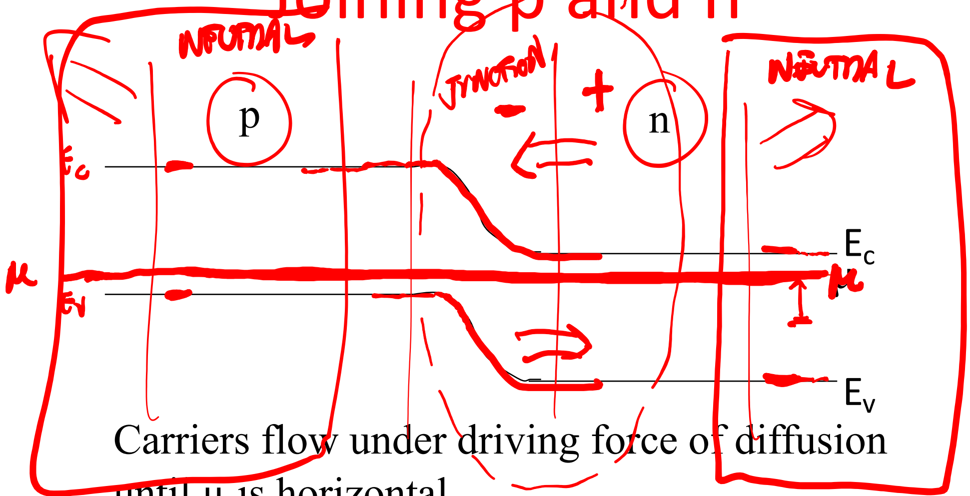
n-TYPE

$$\boxed{\mu_n = \mu_i + k_b T \ln\left(\frac{N_D}{n_i}\right)}$$

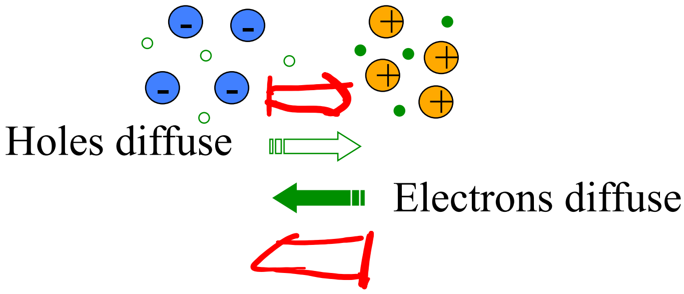


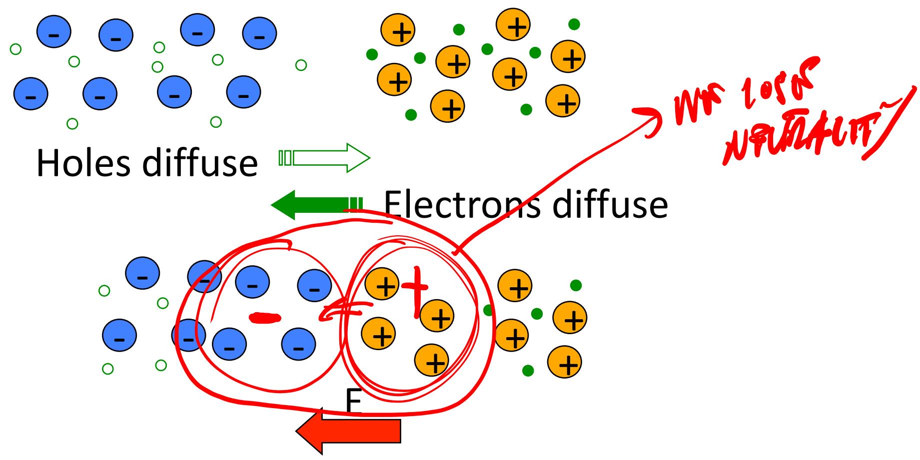
What happens when you join these together?

Joining p and n



Carriers flow under driving force of diffusion until μ is horizontal





An electric field forms due to the deviation from charge neutrality

Therefore, a steady-state balance is achieved where diffusive flux of the carriers is balanced by the drift flux

Chemical potential

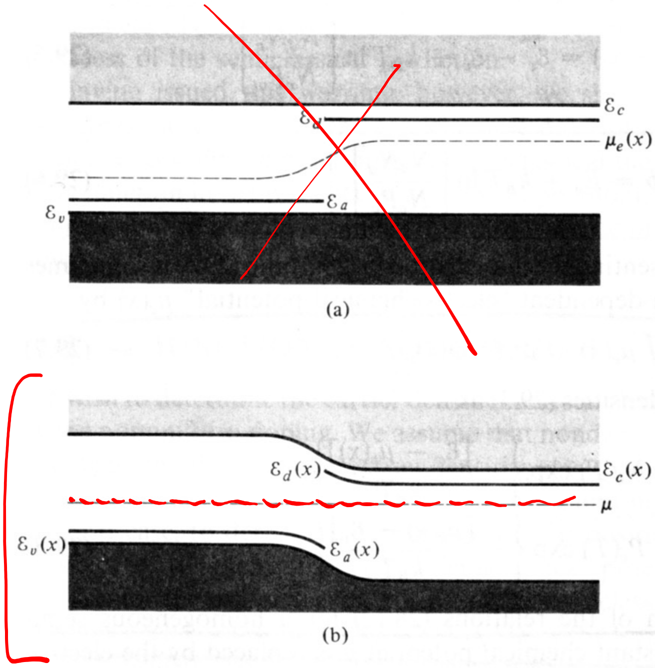


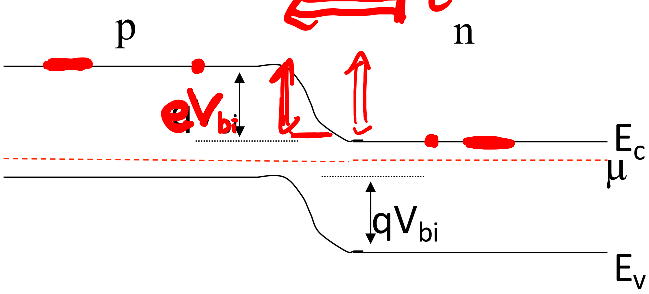
Figure 29.2
Two equivalent ways of representing the effect of the internal potential $\phi(x)$ on the electron and hole densities of a *p-n* junction. (a) The electrochemical potential $\mu_e(x) = \mu + e\phi(x)$ is plotted along the *p-n* junction. The carrier densities at any point x are those that would be found in a uniform semiconductor characterized by the fixed band and impurity energies $\mathcal{E}_c$, $\mathcal{E}_v$, $\mathcal{E}_d$, and $\mathcal{E}_a$, at a chemical potential equal to $\mu_e(x)$. (b) Here $\mathcal{E}_c(x) = \mathcal{E}_c - e\phi(x)$ is the energy of an electron wave packet localized about x formed from levels very near the conduction band minimum, and similarly for $\mathcal{E}_v(x)$. The energies of the local impurity levels are $\mathcal{E}_d(x) = \mathcal{E}_d - e\phi(x)$ and $\mathcal{E}_a(x) = \mathcal{E}_a - e\phi(x)$. The (constant) chemical potential is also shown. The carrier densities at any point x are those that would be found in a uniform semiconductor characterized by band and impurity energies equal to $\mathcal{E}_c(x)$, $\mathcal{E}_d(x)$, $\mathcal{E}_a(x)$, and $\mathcal{E}_v(x)$ at the fixed chemical potential μ.

What is the built-in voltage V_{bi}?

$$\boxed{\mu_p = \mu_i - k_b T \ln\left(\frac{N_a}{n_i}\right)} \qquad \boxed{\mu_n = \mu_i + k_b T \ln\left(\frac{N_D}{n_i}\right)}$$

$$\boxed{eV_{bi}} = \boxed{k_B T \ln\left(\frac{N_D N_A}{n_i^2}\right)} = \boxed{\mu_n - \mu_p}$$

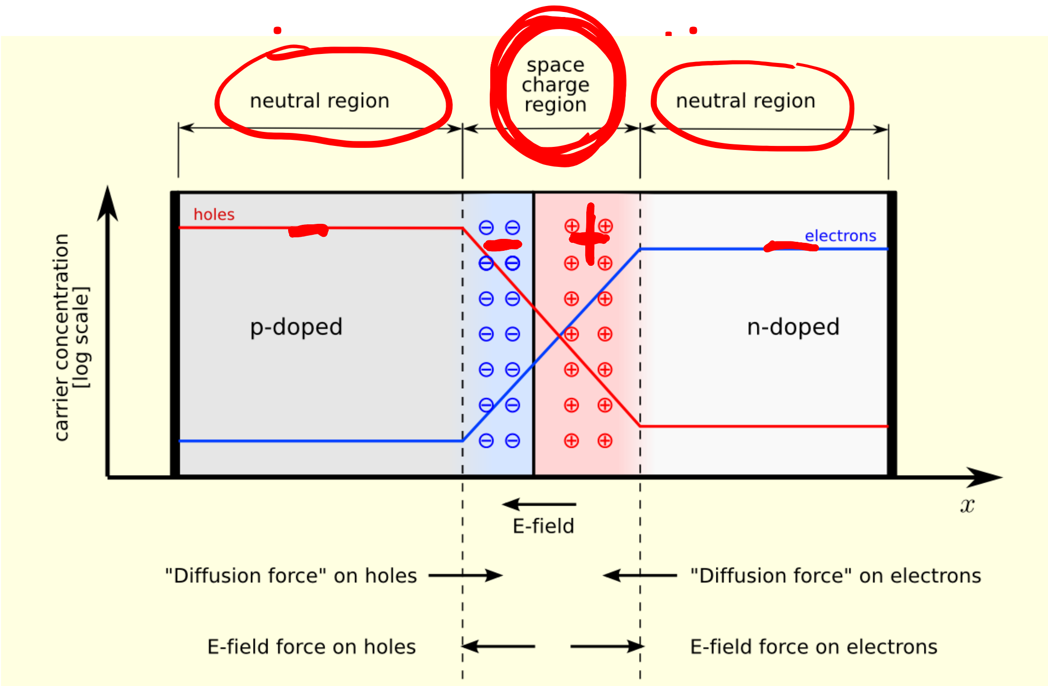
ε

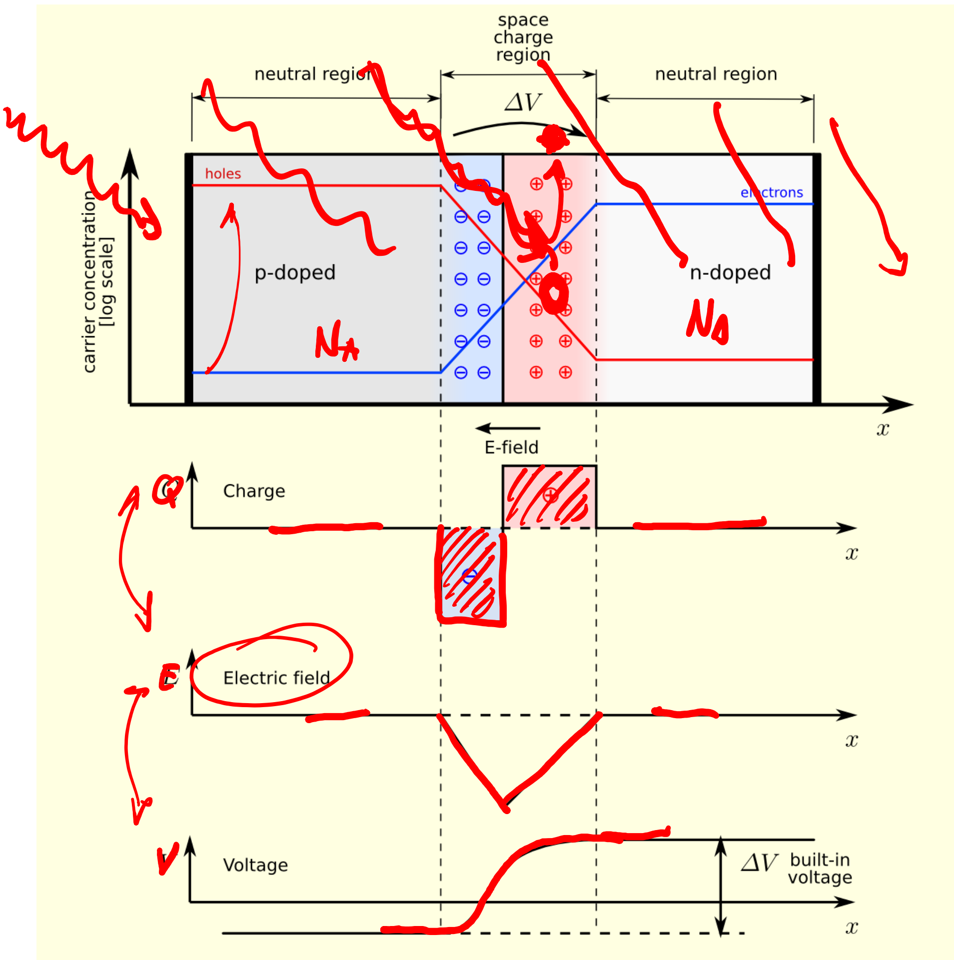


The built-in potential is also the one needed to align the Fermi levels!

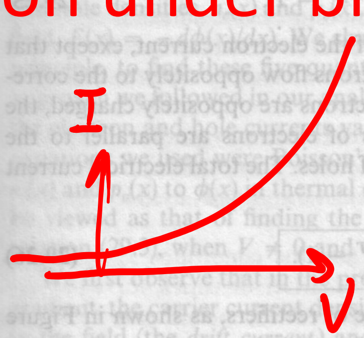
MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2025)

Carrier concentration





Operation under bias



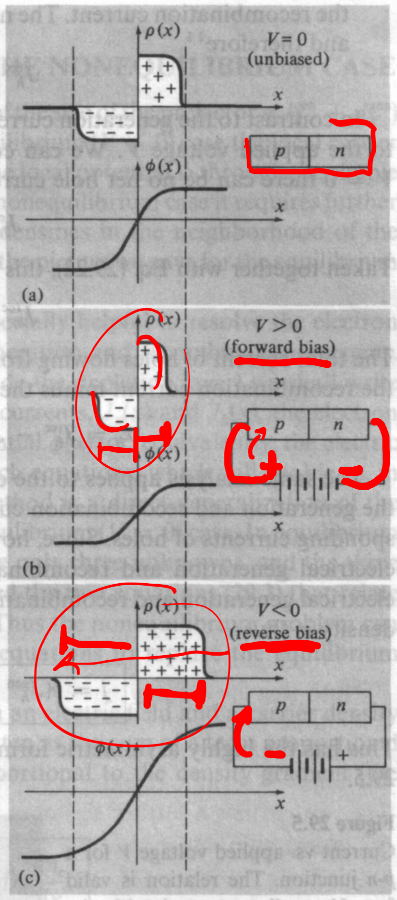


Figure 29.4
The charge density ρ and potential ϕ in the depletion layer (a) for the unbiased junction, (b) for the junction with $V > 0$ (forward bias), and (c) for the junction with $V < 0$ (reverse bias). The positions $x = d_n$ and $x = -d_p$ that mark the boundaries of the depletion layer when $V = 0$ are given by the dashed lines. The depletion layer and change in ϕ are reduced by a forward bias and increased by a reverse bias.