Carrier Statistics
Doping

EECS 320

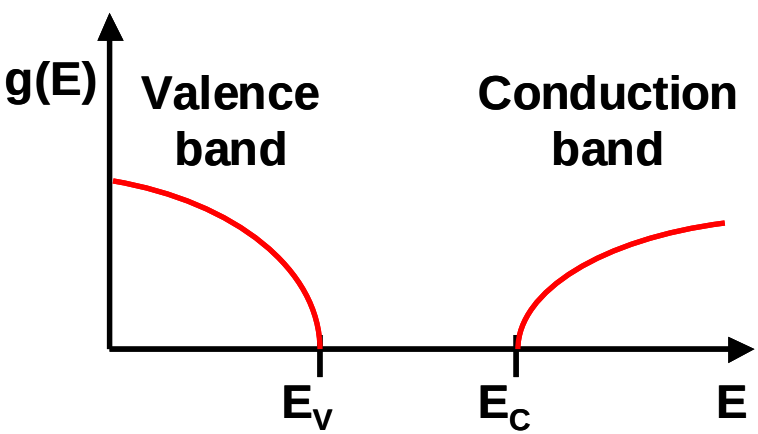
Introduction to Semiconductor Devices

Review g(E) and f(E)

Density Of States

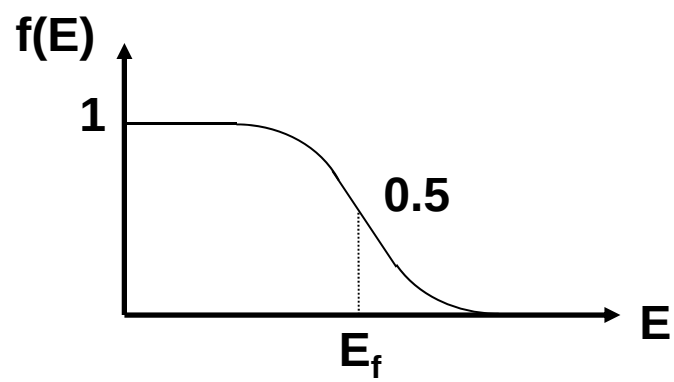
$$g_c(E) = \frac{m_n^* \sqrt{2m_n^*(E - E_c)}}{\pi^2 \hbar^3}$$

$$g_v(E) = \frac{m_p^* \sqrt{2m_p^*(E_v - E)}}{\pi^2 \hbar^3}$$

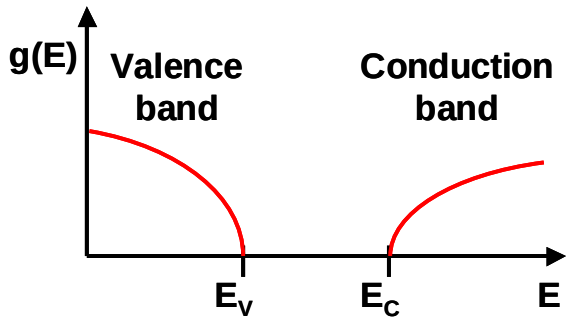


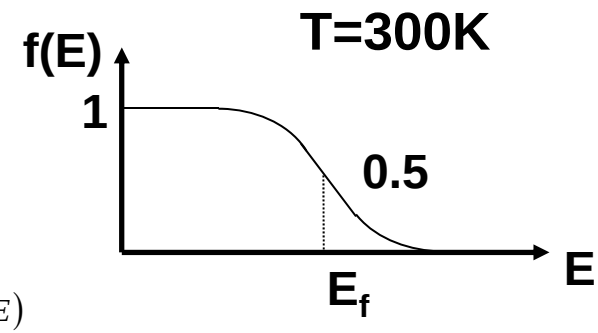
Fermi-Dirac Statistics

$$f(E) = \frac{1}{1 + e^{(E - E_f)/kT}}$$

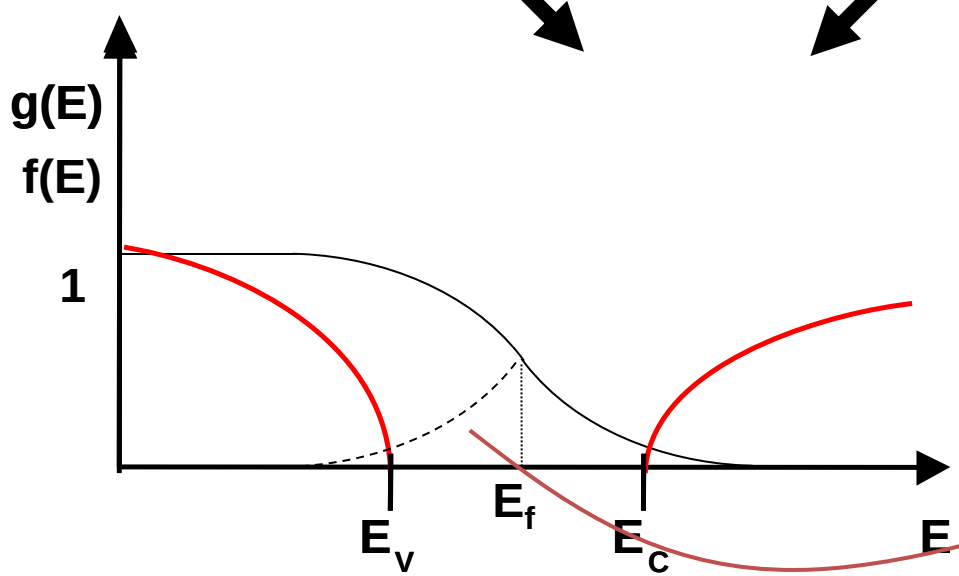


Review g(E) and f(E)





$$n(E) = g_C(E) f(E)$$



$$p(E) = g_V(E)[1 - f(E)]$$

Determining Carrier Density

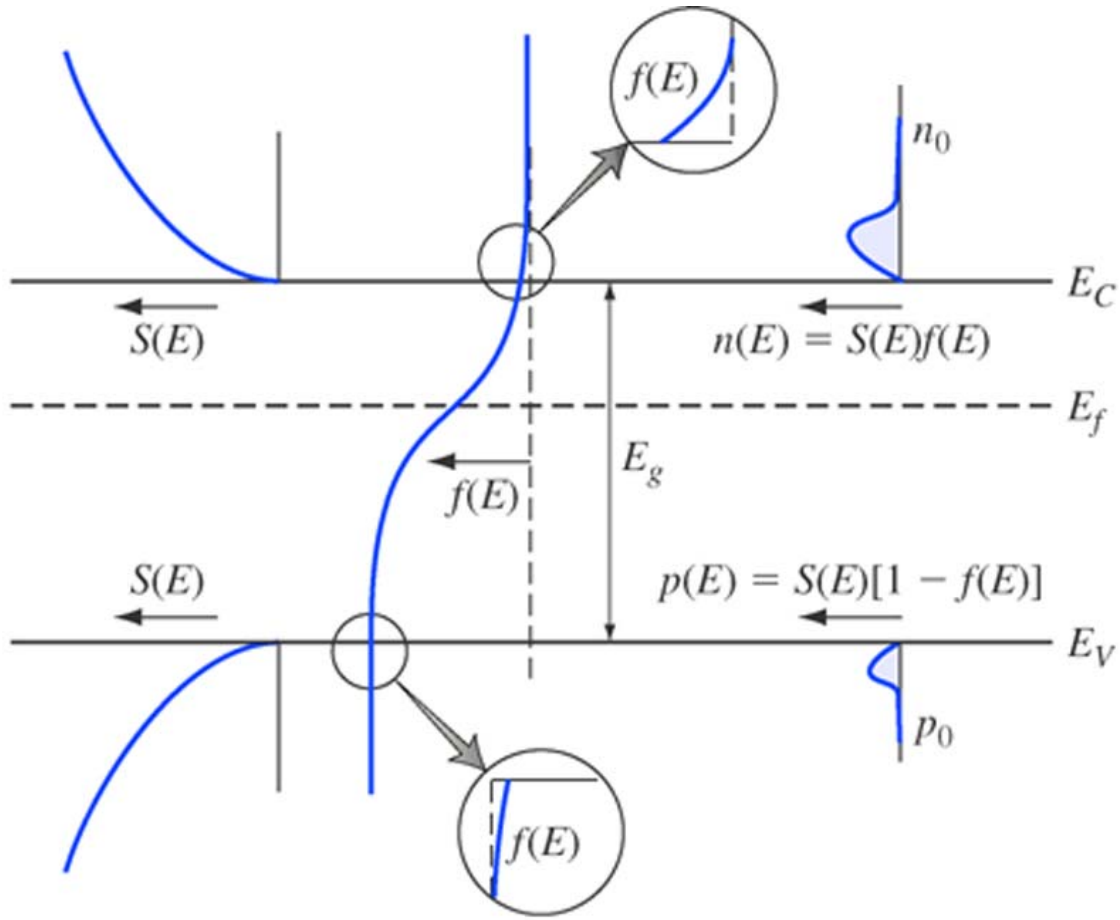
Density of states x Occupation probability

$$n(E) = g_C(E) f(E)$$

$$n = \int_{E_C}^{\infty} g_C(E) f(E)\, dE$$

$$p(E) = g_V(E)[1 - f(E)]$$

$$p = \int_{-\infty}^{E_V} g_V(E)[1 - f(E)]\, dE$$



Carrier Density (Quantitative)

Density of states x Occupation probability

$$n(E) = g_C(E)\, f(E)$$

$$n = \int_{E_C}^{\infty} g_C(E)\, f(E)\, dE$$

$$\text{for } E - E_f >> kT, \quad f(E) \approx e^{-(E-E_f)/kT} \qquad \textit{Boltzmann Approximation}$$

$$n = \int_{E_C}^{\infty} \frac{m_n^* \left[2m_n^*(E-E_c)\right]^{1/2}}{\pi^2 \hbar^3} e^{-(E-E_f)/kT}\, dE$$

$$n = \int_{E_C}^{\infty} \frac{m_n^* \left[2m_n^* (E - E_c) \right]^{1/2}}{\pi^2 \hbar^3} e^{-\left(E - E_f\right)/kT} \quad dE$$

$$\eta \equiv \left(E - E_c\right)/kT \rightarrow d\eta = \left(kT\right) dE$$

$$\frac{\left(E - E_f\right)}{kT} = \eta + \frac{\left(E_c - E_f\right)}{kT}$$

$$n = \frac{m_n^* \left[2m_n^* \right]^{1/2}}{\pi^2 \hbar^3} \int_0^{\infty} \left(kT\eta\right)^{1/2} e^{-\eta} e^{-\left(E_c - E_f\right)/kT} \quad \left(kT\right) d\eta$$

$$= \frac{m_n^* \left[2m_n^* \right]^{1/2}}{\pi^2 \hbar^3} \left(kT\right)^{3/2} e^{-\left(E_c - E_f\right)/kT} \int_0^{\infty} \eta^{1/2} e^{-\eta} \; d\eta$$

$$= \frac{m_n^* \left[2m_n^* \right]^{1/2}}{\pi^2 \hbar^3} \left(kT\right)^{3/2} e^{-\left(E_c - E_f\right)/kT} \frac{\sqrt{\pi}}{2}$$

$$= 2\left(\frac{m_n{}^* kT}{2\pi\hbar^2} \right)^{3/2} e^{-\left(E_c - E_f\right)/kT}$$

$$= N_C e^{-\left(E_c - E_f\right)/kT}$$

Carrier Density (Quantitative)

Density of states x Occupation probability

$$n(E) = g_C(E) f(E) \qquad p(E) = g_V(E)[1 - f(E)]$$

$$n = \int_{E_C}^{\infty} g_C(E) f(E)\, dE \qquad p = \int_{-\infty}^{E_V} g_V(E)[1 - f(E)]\, dE$$

$$\text{for } E - E_f >> kT, \quad f(E) \approx \exp\left(\frac{-(E - E_f)}{kT}\right)$$

(Boltzmann approximation)

$$\boxed{n = 2\left(\frac{m_n^* kT}{2\pi\hbar^2}\right)^{3/2} \exp\left(\frac{E_f - E_C}{kT}\right)} \qquad \boxed{p = 2\left(\frac{m_p^* kT}{2\pi\hbar^2}\right)^{3/2} \exp\left(\frac{E_V - E_f}{kT}\right)}$$

N_C, N_V – Effective Density of States

Constant terms that fall out of the integral representing density of states in a material

$$N_C = 2\left(\frac{m_n^* kT}{2\pi\hbar^2}\right)^{3/2} \qquad N_V = 2\left(\frac{m_p^* kT}{2\pi\hbar^2}\right)^{3/2}$$

Factoring out constants,

$$N_{C,V} = 2.5\times10^{19}\left(\frac{m_{n,p}^*}{m_0}\right)^{3/2}\left(\frac{T}{300}\right)^{3/2}\ \text{cm}^{-3}$$

For Boltzmann approximation,

$$\boxed{n = N_C \exp\left(\frac{E_f - E_C}{kT}\right)} \qquad \boxed{p = N_V \exp\left(\frac{E_V - E_f}{kT}\right)}$$

Carrier Density – Without Boltzmann Approx.

When Boltzmann approx. is not valid, math is messy

$$n = \sqrt{2}\frac{\left(m_n^*\right)^{3/2}}{\pi^2\hbar^3}\int_{E_C}^{\infty}\frac{\sqrt{E-E_C}}{1+e^{\left(E-E_f\right)/kT}}dE \qquad \eta = \frac{\left(E-E_C\right)}{kT}, \eta_C = \frac{\left(E_f-E_C\right)}{kT}$$

$$n = \sqrt{2}\frac{\left(m_n^* kT\right)^{3/2}}{\pi^2\hbar^3}\int_0^{\infty}\frac{\eta^{1/2}}{1+e^{\eta-\eta_C}}d\eta = N_C\frac{2}{\sqrt{\pi}}F_{1/2}\left(\eta_C\right)$$

Obtain $F_{1/2}$ numerically, look up tables, etc

Alternatively, use Joyce-Dixon or other approximations (typically these are power series expansions)

$$\eta_C = \frac{\left(E_f-E_C\right)}{kT} = \ln\left(\frac{n}{N_C}\right) + 2^{-3/2}\left(\frac{n}{N_C}\right), \quad -1 \le \eta_C \le 6$$

Joyce-Dixon approximation

Better Than Joyce Dixon

$$\mathcal{F}_{1/2}(\eta) \equiv \frac{2}{\sqrt{\pi}} F_{1/2}(\eta)$$

$$\mathcal{F}_{1/2}(\eta) \simeq \left[e^{-\eta} + \xi(\eta) \right]^{-1}$$

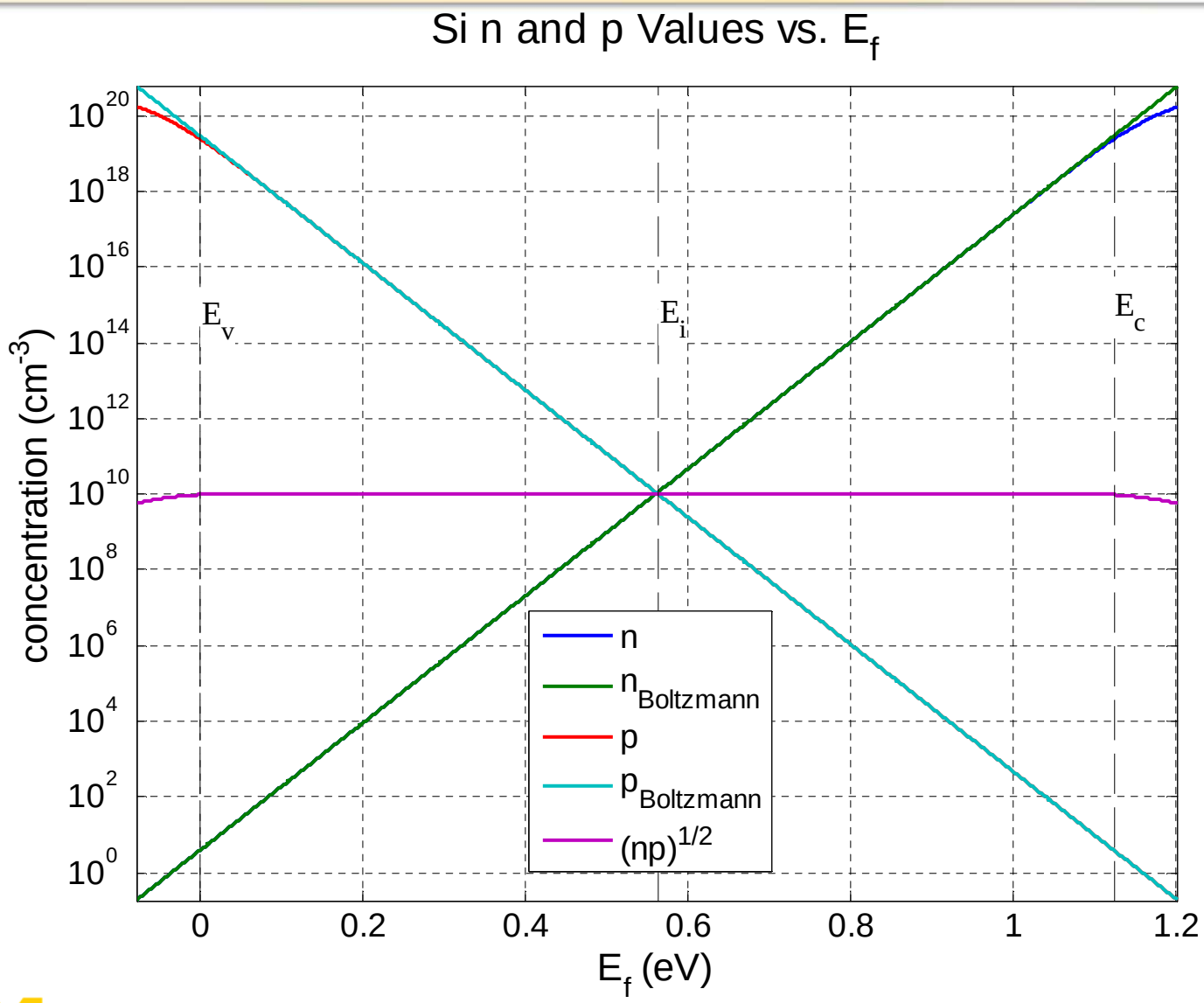
$$where \quad \xi(\eta) = 3\sqrt{\pi/2} \left[\eta + 2.13 + \left(\left| \eta - 2.13 \right|^{2.4} + 9.6 \right)^{5/12} \right]^{-3/2}$$

$$\eta \simeq \frac{\ln(u)}{1-u^2} + \frac{\left(3u\sqrt{\pi}/4\right)^{2/3}}{1 + \left[0.24 + 1.08\left(3u\sqrt{\pi}/4\right)^{2/3} \right]^{-2}}$$

$$where\ u \equiv F_{1/2}(\eta)$$

both expression have a maximum error of $\sim \pm 0.5$

Si Electron and Hole Populations



$$n = N_c \mathcal{F}_{1/2}(\eta_c) \quad \eta_c = \frac{(E_f - E_C)}{kT}$$

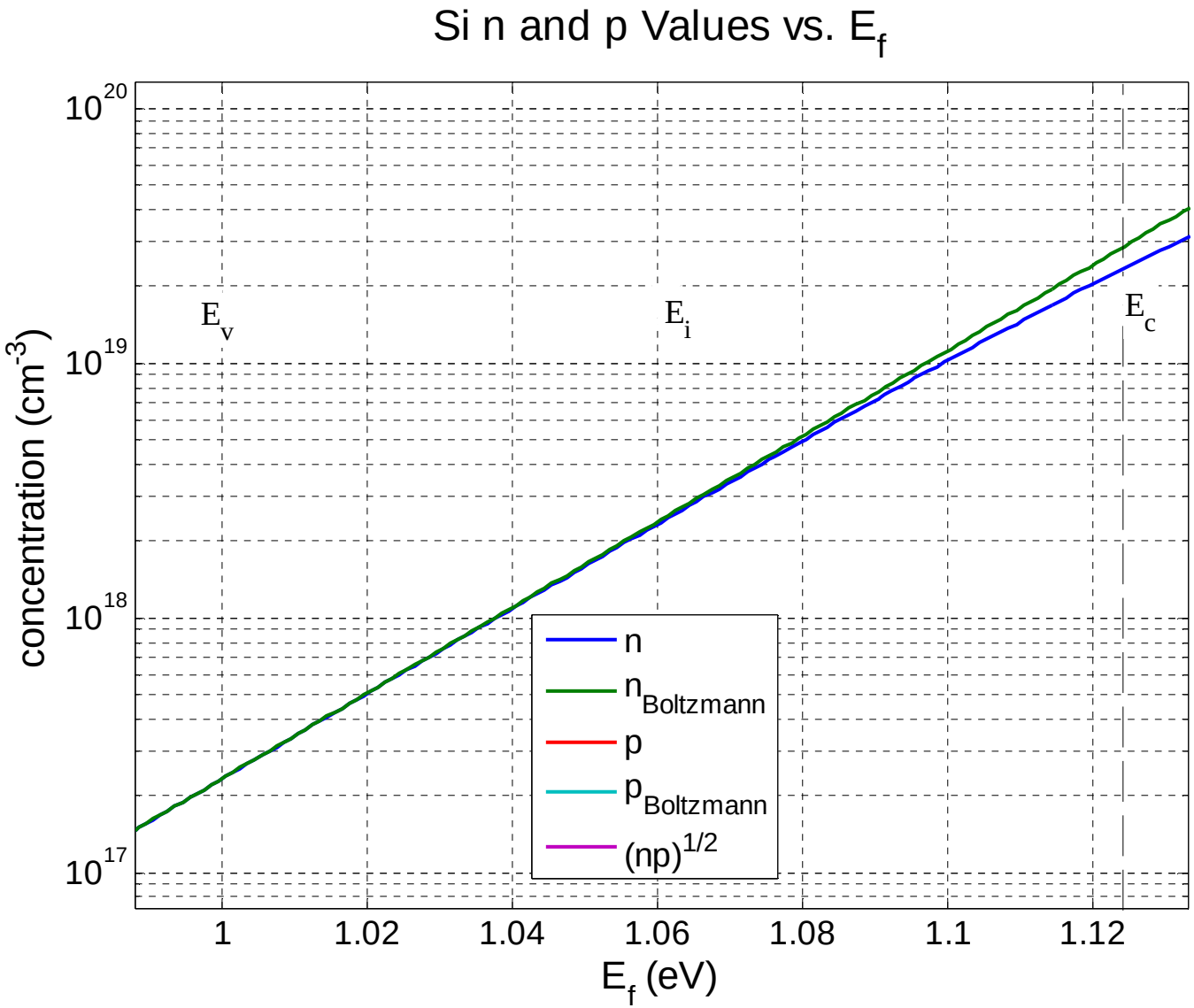
$$p = N_v \mathcal{F}_{1/2}(\eta_v) \quad \eta_v = \frac{(E_v - E_f)}{kT}$$

$$np = N_c N_v \mathcal{F}_{1/2}(\eta_c)\mathcal{F}_{1/2}(\eta_v)$$

(from M.A. Green, J. Appl. Phys. vol. 67, pp. 2944-2954)

At T=300K

$$\left.\begin{aligned} N_c &= 2.86x10^{19}\,cm^{-3} \\ N_v &= 3.10x10^{19}\,cm^{-3} \\ E_g &= 1.1242eV \\ n_i &= 1.07x10^{10}\,cm^{-3} \end{aligned}\right\}$$

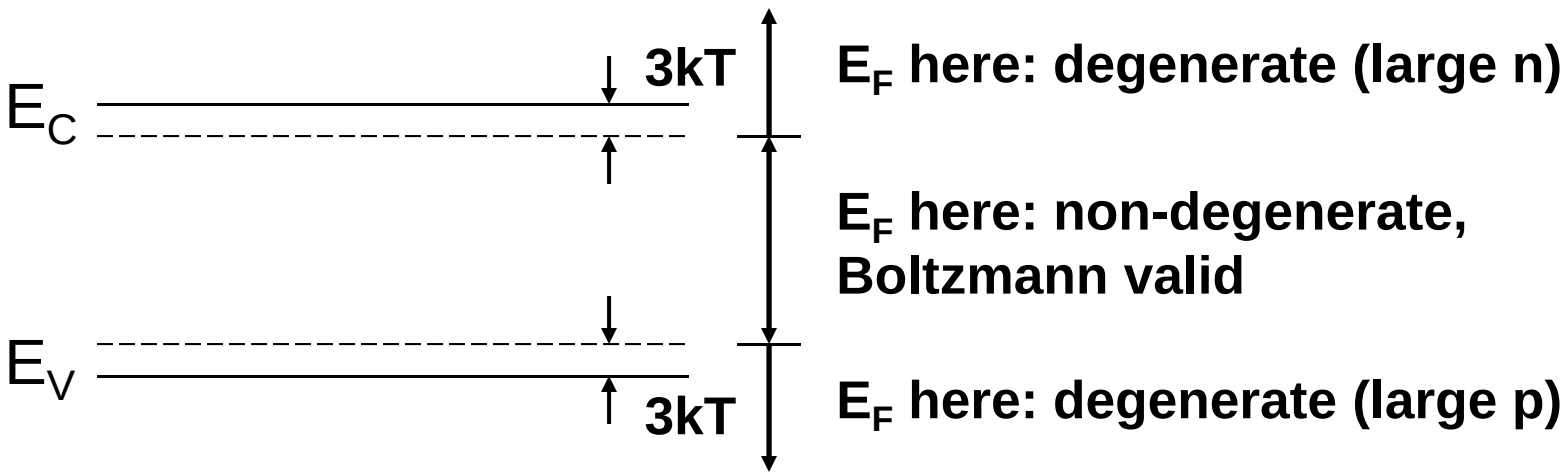

Si n and p Values vs. E_f
10^{20}
10^{19}
10^{18}
10^{17}
concentration (cm^{-3})
E_v
E_i
E_c
n
$n_{Boltzmann}$
p
$p_{Boltzmann}$
$(np)^{1/2}$
1
1.02
1.04
1.06
1.08
1.1
1.12
E_f (eV)

Degenerate versus Non-Degenerate

Define where Boltzmann approximation is valid

For $E_V + 3kT < E_f < E_C - 3kT$, Boltzmann approximation is accurate

Semiconductor is said to be "non-degenerate"



Calculations Of n/p and E_f

Note that either n (p) or E_f relative to E_C (E_V) is known

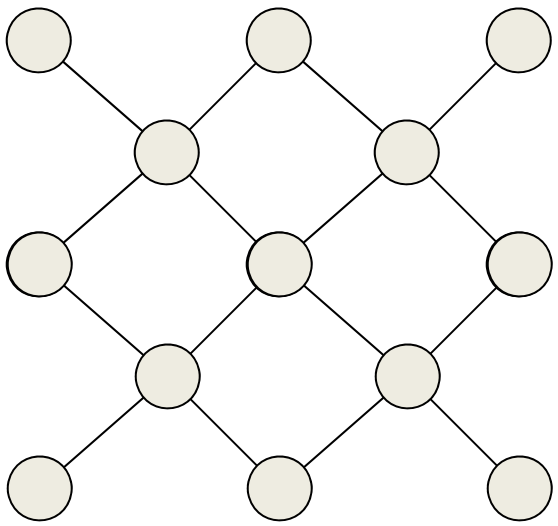
- Determine if semiconductor is degenerate, or assume and then check answer
- Use appropriate expression based on degenerate/non-degenerate

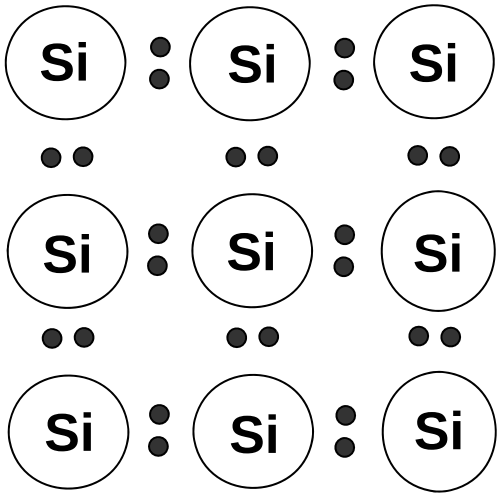
Calculate Fermi energy position for silicon (300K) with $n=10^{16}$ cm^{-3}

Calculate n in silicon (300K) when E_f-E_C=-3kT,
and p in silicon (300K) when E_f-E_V=3kT
(transition to degenerate)

Are n and p the same? Why or why not?

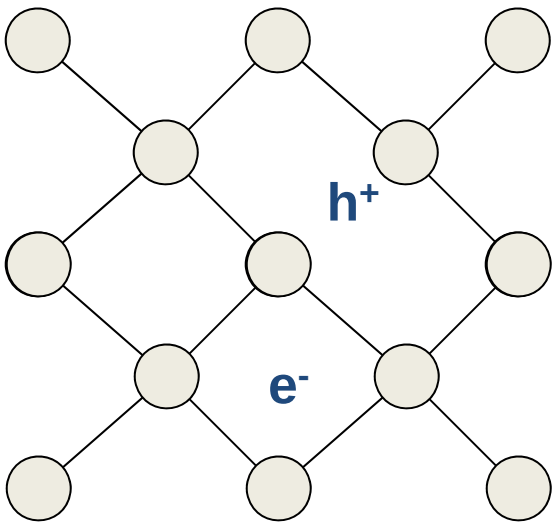
Intrinsic Silicon at 0K

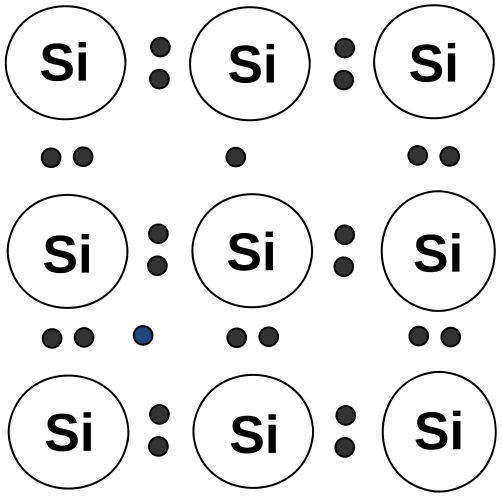




- n=p=0
- Fermi Level is at the middle of the bandgap

Intrinsic Silicon at 300K





- $n=p=n_i$
- Fermi level is near the middle of the bandgap
- We would like to selectively alter n, p. Why?

Intrinsic Semiconductor

Carrier density in pure semiconductor

- The product of n and p gives:

$$np = 4\left(\frac{kT}{2\pi\hbar^2}\right)^3 \left(m_e^* m_h^*\right)^{3/2} \exp\left(-\frac{E_G}{kT}\right)$$

$$np = N_C N_V \exp\left(-\frac{E_G}{kT}\right)$$

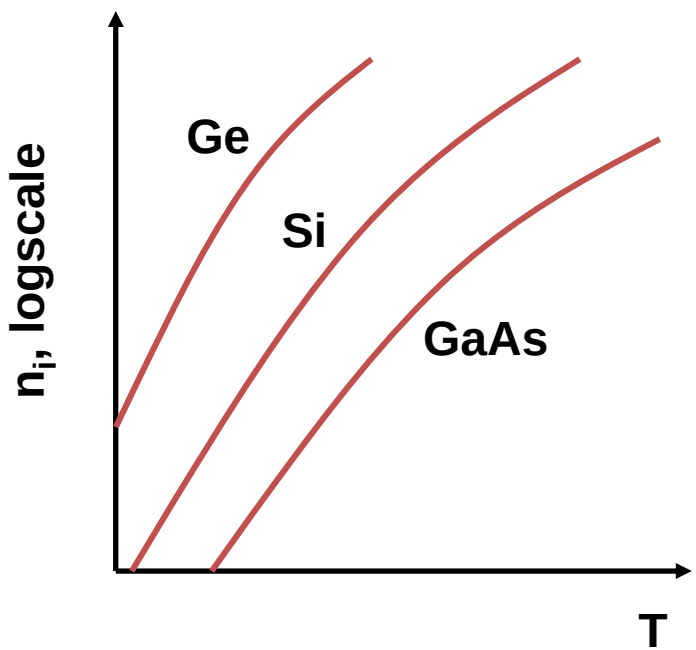
- The intrinsic concentrations are then given by:

$$n_i = p_i = 2\left(\frac{kT}{2\pi\hbar^2}\right)^{3/2} \left(m_e^* m_h^*\right)^{3/4} \exp\left(-\frac{E_G}{2kT}\right)$$

- Dependent on material parameters (effective mass and bandgap) and temperature

Intrinsic Carrier Concentration

Intrinsic concentration shows temperature dependence



Why is n_i temperature dependent?

What is n_i at T=0 K?

Why does n_i vary with material, what causes the variation?

Fermi Energy For Intrinsic Semiconductor

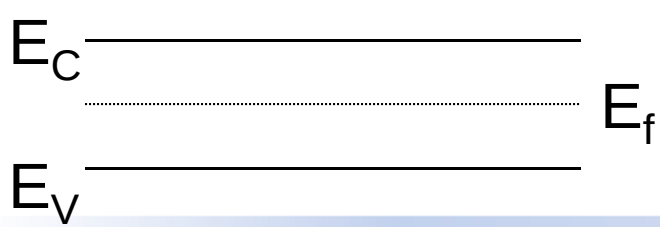
- Let us now determine the Fermi level position, and evaluate the validity of the Boltzmann approximation

$$n = 2\left(\frac{m_n^* kT}{2\pi\hbar^2}\right)^{3/2} \exp\left(\frac{E_f - E_C}{kT}\right) \qquad p = 2\left(\frac{m_p^* kT}{2\pi\hbar^2}\right)^{3/2} \exp\left(\frac{E_V - E_f}{kT}\right)$$

Set equal, solve for $E_f = E_i$

$$E_i = \frac{E_C + E_V}{2} + \frac{3}{4} kT \ln\left(\frac{m_h^*}{m_e^*}\right)$$

- The Fermi energy lies near the middle of the bandgap, shifts depending on effective mass and temperature



Doping

Intrinsic material

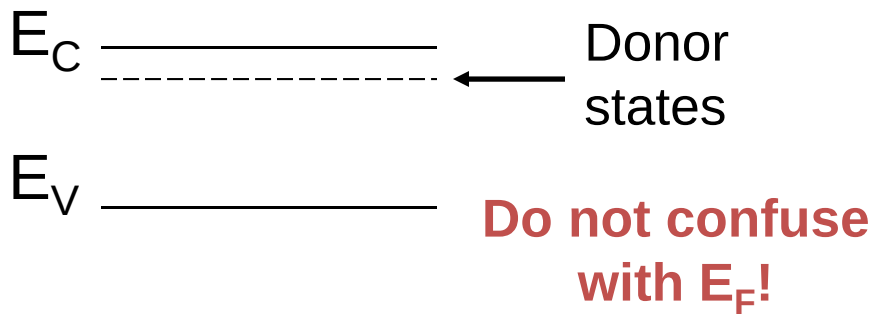
- $n=p=n_i$
- Carrier density is fixed for given material and T
- We would like to selectively alter n, p

Q: How do we alter n, p in a semiconductor?

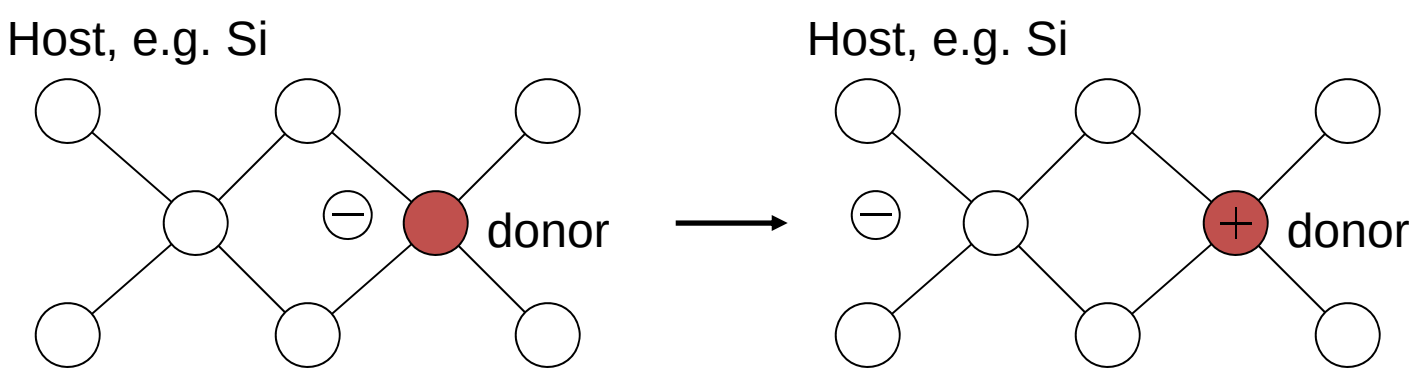
A: Provide substitutional impurity that provides an additional electron or hole.

Donors

- Donors – impurity atoms that provide additional electrons.
- A net concentration of donors provides a higher electron concentration than intrinsic material
- "n-type" material

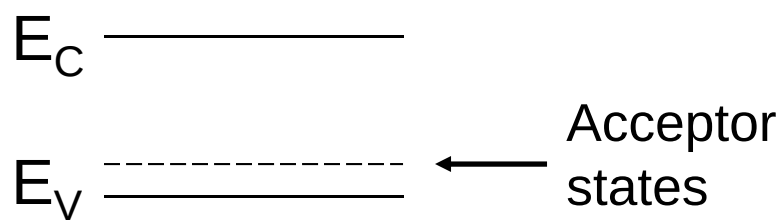


"Activated" donor



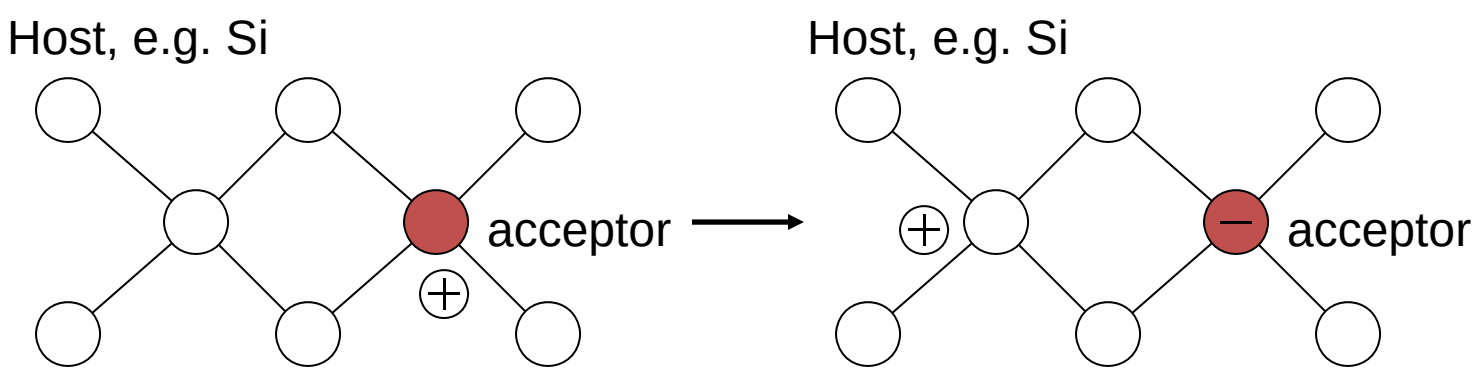
Acceptors

- Acceptors – impurity atoms that have fewer electrons
- Increase hole concentration relative to intrinsic material
- "p-type" material



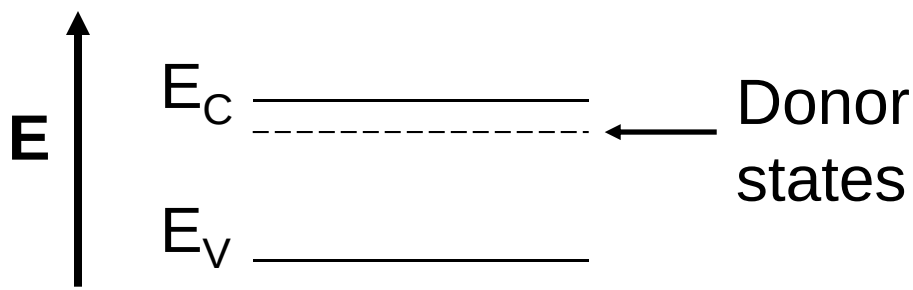
Do not confuse with E_F!

"Activated" acceptor

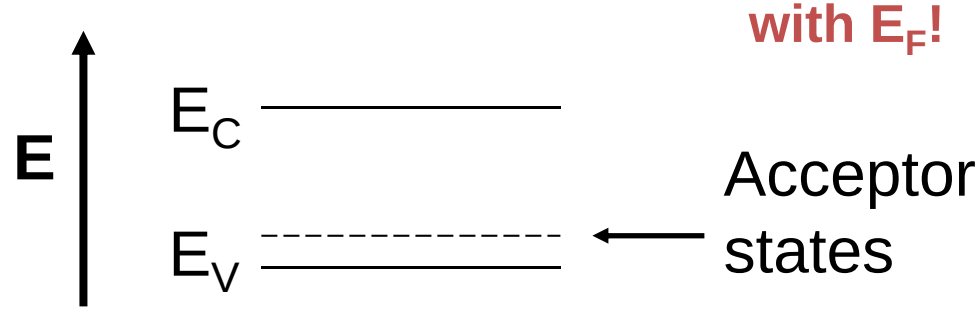


Activation Energies for Dopants

- Activation energies are typically shown in reference to the relevant band edge (valence band for acceptors, conduction band for donors)
- The difference between the donor/acceptor state and the band edge (in eV) is the activation energy

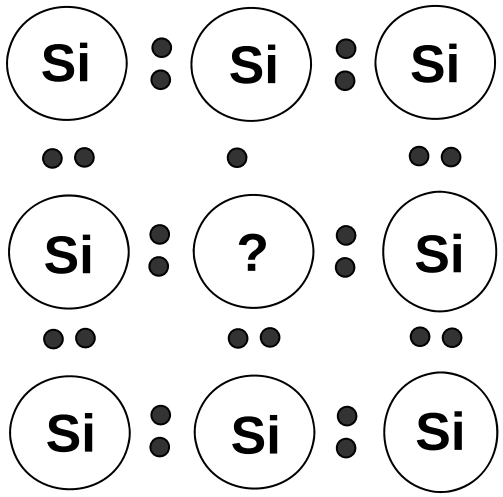


Do not confuse with E_F!

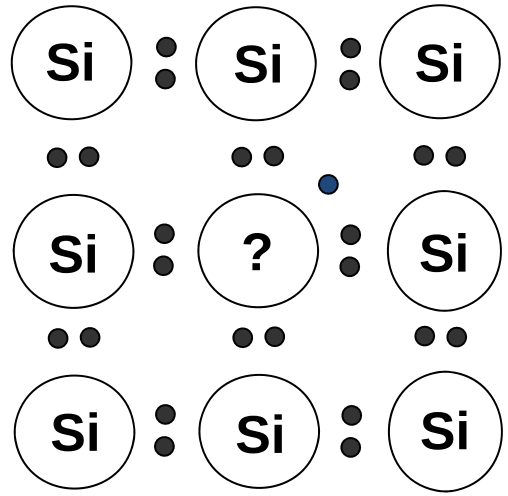


What makes a good dopant?

Acceptor



Donor



- For acceptors, need element with only 3 valence electrons
- For donors, need element with 5 valence electrons
- Since only "activated" dopants contribute carriers, want a low activation energy. Room temperature?
- Many other concerns

Periodic Table Of Elements

PERIODIC CHART OF THE ELEMENTS

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	INERT GASES
1 H 1.00797																1 H 1.00797	2 He 4.0026
3 Li 6.939	4 Be 9.0122											5 B 10.811	6 C 12.0112	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.183
11 Na 22.9898	12 Mg 24.312											13 Al 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.909	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.905	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.30
55 Cs 132.905	56 Ba 137.34	✳57 La 138.91	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	‡89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 ? (271)	111 ? (272)	112 ? (277)						

Numbers in parenthesis are mass numbers of most stable or most common isotope.

Atomic weights corrected to conform to the 1963 values of the Commission on Atomic Weights.

The group designations used here are the former Chemical Abstract Service numbers.

✳ Lanthanide Series

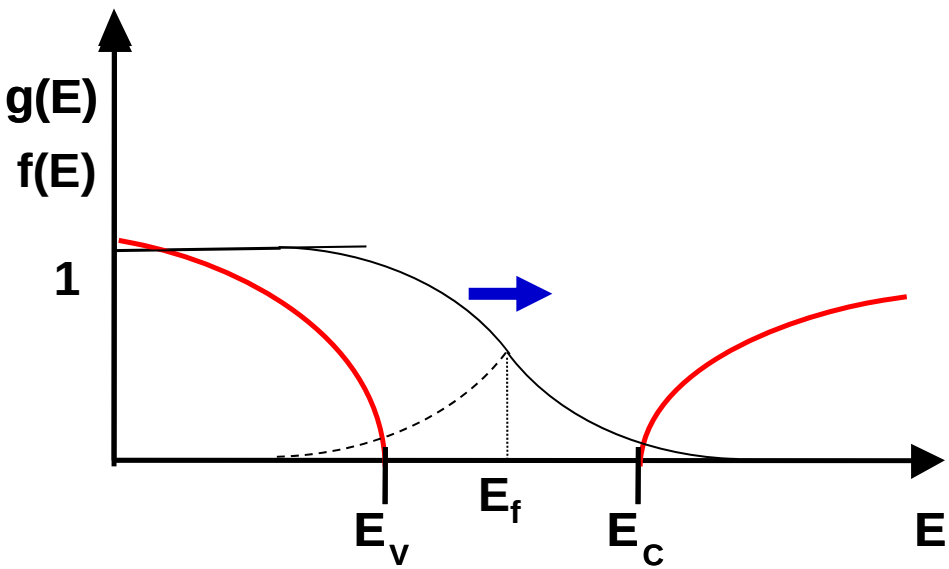
58 Ce 140.12	59 Pr 140.907	60 Nd 144.24	61 Pm (147)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.924	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.97

‡ Actinide Series

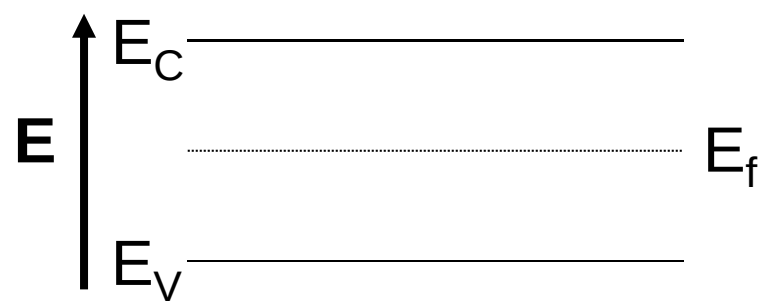
90 Th 232.038	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (256)	103 Lr (257)

Fermi Level for Doped Semiconductors

n-type semiconductors have excess electrons in the conduction band, therefore the probability of finding an electron in the conduction band increases, so the Fermi level moves to a higher energy

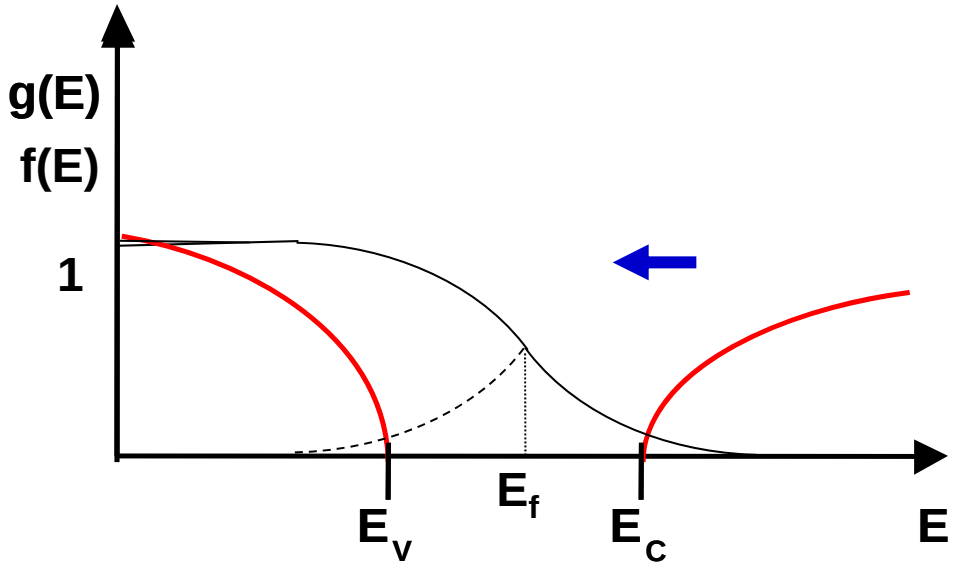


n-type Band Diagram

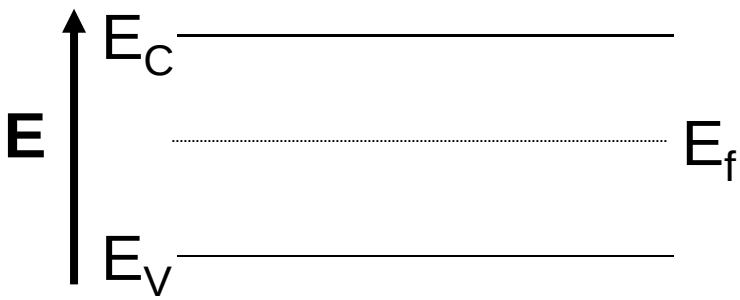


Fermi Level for Doped Semiconductors

p-type semiconductors have excess holes in the valence band, therefore the probability of finding an electron in the valence band decreases, so the Fermi level moves to a lower energy



p-type Band Diagram



Fermi Energy From Carrier Density

n, p may be determined from Fermi energy
OR
Fermi energy may be determined from n, p

$$n = N_C \exp\left(\frac{E_f - E_C}{kT}\right) \qquad p = N_V \exp\left(\frac{E_V - E_f}{kT}\right)$$

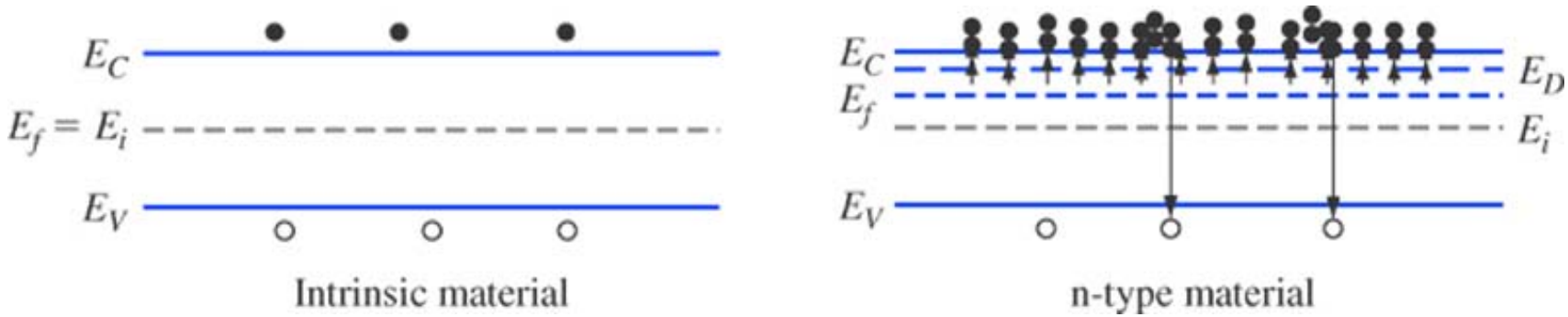
$$n = n_i \exp\left(\frac{E_f - E_i}{kT}\right) \qquad p = n_i \exp\left(\frac{E_i - E_f}{kT}\right)$$

$$E_C - E_f = -kT \ln\left(\frac{n}{N_C}\right) \qquad E_f - E_V = -kT \ln\left(\frac{p}{N_V}\right)$$

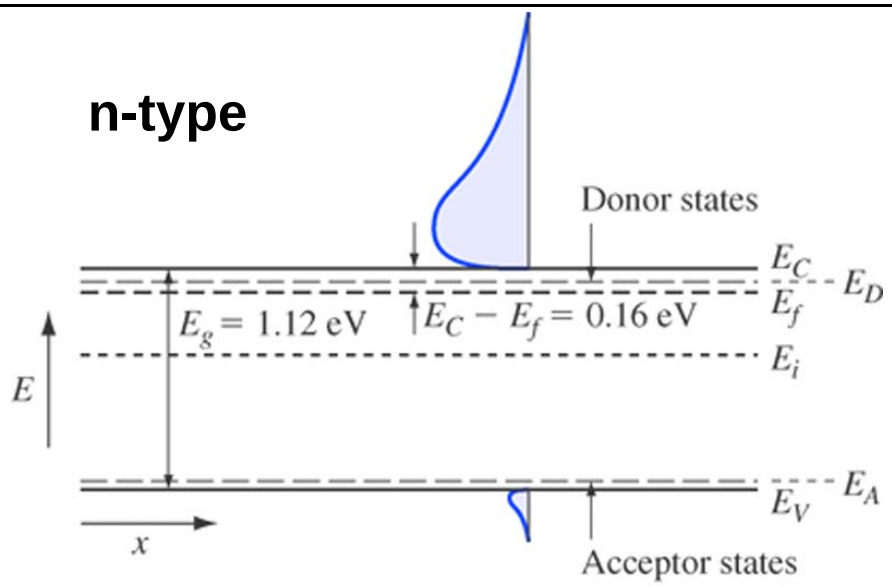
$$E_f - E_i = kT \ln\left(\frac{N_D}{n_i}\right) \qquad E_i - E_f = kT \ln\left(\frac{N_A}{n_i}\right)$$

Doping

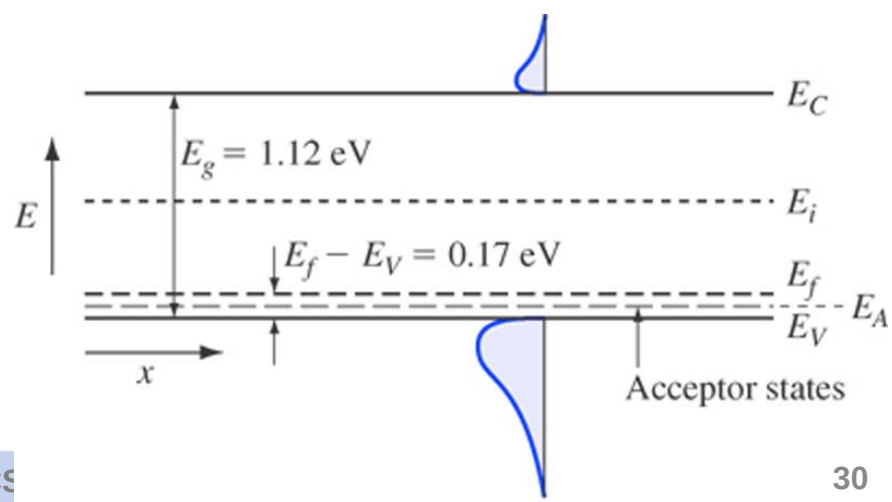
Add impurities to provide electron states near the conduction band or valence band to increase n or p



n-type

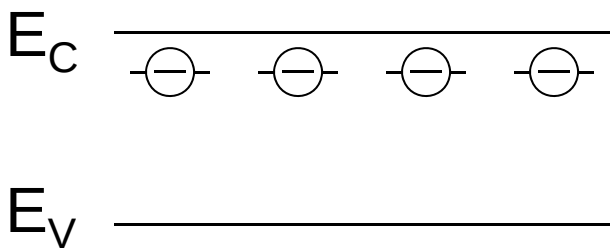


p-type

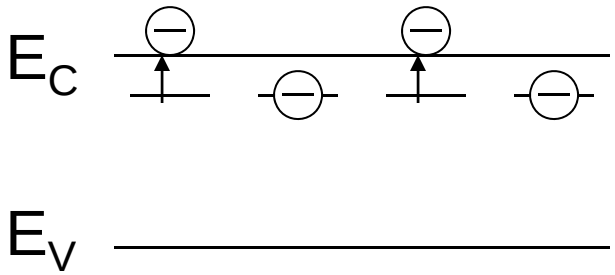


Ionization Of Dopants

Finite temperature needed to ionize dopants



At low temperature, electrons frozen to dopant site (freeze-out)



At elevated temperatures, electrons gain enough energy to jump into conduction band

For "good dopant" majority of dopants ionized at room temperature

What does this picture look like for p-type material?

Fermi Energy From Carrier Density

Dopants are activated according to binding energy and temperature

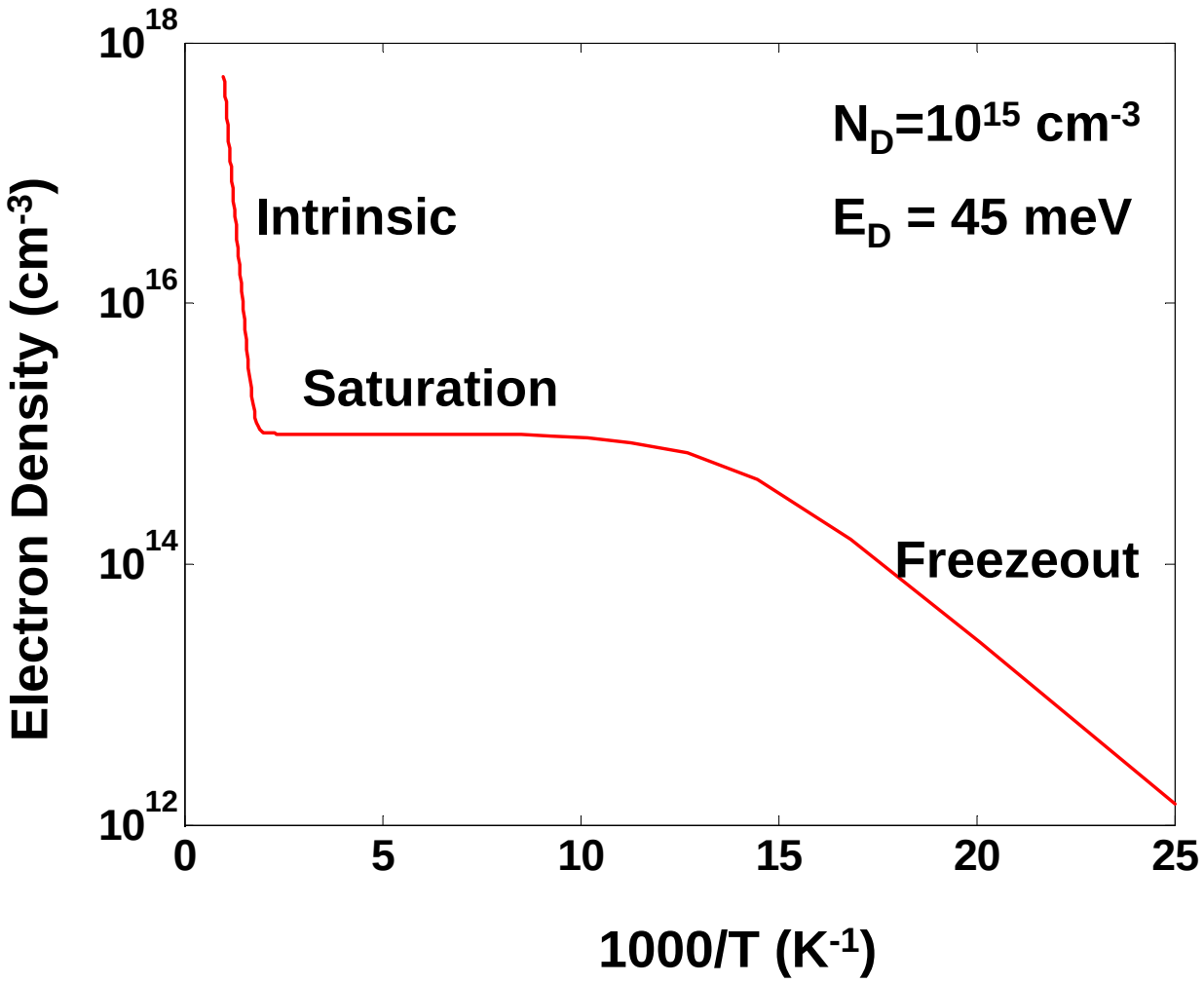
$$\frac{N_D^+}{N_D} = \frac{1}{1 + g_D e^{(E_f - E_D)/kT}} \qquad g_D = 2$$

$$\frac{N_A^-}{N_A} = \frac{1}{1 + g_A e^{(E_A - E_f)/kT}} \qquad g_A = 4$$

g_i are degeneracy factors

- Spin up, spin down for donors
- Spin up, spin down, heavy hole, light hole for acceptors
- E_D, E_A are binding energies

Temperature-Dependence Of Carrier Density



Space Charge Density

- General:

$$\rho = q\left(p - n + N_D^+ - N_A^-\right)$$

- All are function of E_f
- In equilibrium we will have no <u>net</u> space charge:

$$\rho = q\left(p - n + N_D^+ - N_A^-\right) = 0$$

$$p - n + N_D^+ - N_A^- = 0$$

Equilibrium, Nondegenerate Case

$$p - n + N_D^+ - N_A^- = 0$$

$$N \equiv N_D^+ - N_A^-$$

$$\frac{n_i^2}{n} - n + N = 0$$

$$n_i^2 - n^2 + nN = 0$$

$$n^2 - nN - n_i^2 = 0$$

$$n = \frac{N}{2} \pm \left[\left(\frac{N}{2} \right)^2 + n_i^2 \right]^{1/2} = \frac{\left(N_D^+ - N_A^- \right)}{2} \pm \left[\left(\frac{\left(N_D^+ - N_A^- \right)}{2} \right)^2 + n_i^2 \right]^{1/2}$$

Only + root applies, why?

$$p = \frac{\left(N_A^- - N_D^+ \right)}{2} + \left[\left(\frac{\left(N_A^- - N_D^+ \right)}{2} \right)^2 + n_i^2 \right]^{1/2}$$

Relationships For Carrier Density

Charge Neutrality

$$p + N_D^+ = n + N_A^-$$

Mass-action law

$$np = n_i^2$$

Carrier Density

$$n = \frac{N_D - N_A}{2} + \sqrt{\left(\frac{N_D - N_A}{2}\right)^2 + n_i^2}$$

$$p = \frac{N_A - N_D}{2} + \sqrt{\left(\frac{N_A - N_D}{2}\right)^2 + n_i^2}$$

Example Calculations

Si at 300K constants from M.A. Green (J. Appl. Phys. Vol 76, pp 2944-2954)

$N_c = 2.86x10^{19} cm^{-3} \quad N_V = 3.10x10^{19} cm^{-3} \quad E_g = 1.1242eV$