MTLE-6120: Advanced Electronic Properties of Materials

Intrinsic and extrinsic semiconductors

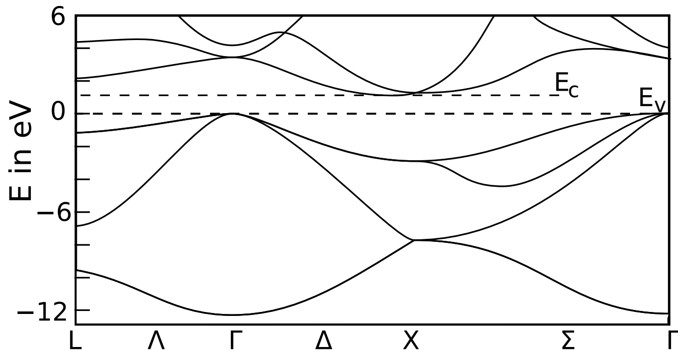
Reading:

- Kasap: 5.1 - 5.6

Band structure and conduction

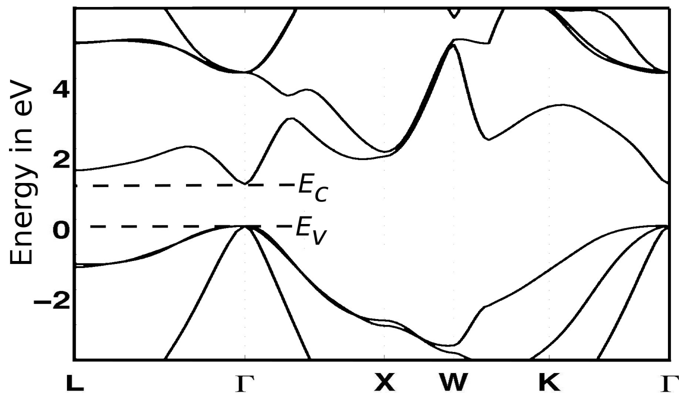
- Metals: partially filled band(s) i.e. bands cross Fermi level
- Semiconductors / insulators: each band either filled or empty ($T = 0$)
- Drude formula applicable, mobility $\mu = \frac{e\tau}{m^*}$
- Effective mass $m^* = \hbar^2[\nabla_{\vec{k}}\nabla_{\vec{k}}E_n(\vec{k})]^{-1}$ tensorial in general
- Filled band does not conduct: $e\tau \int \mathrm{d}k(m^*)^{-1} = 0$ for each band
- Metals conduct due to carriers near Fermi level $\sigma = g(E_F)e^2v_F^2\tau/3$
- Semiconductors: $g(E_F) = 0$ (will show shortly) $\Rightarrow$ no conduction at $T = 0$

Band structure of silicon (diamond-cubic semiconductor)



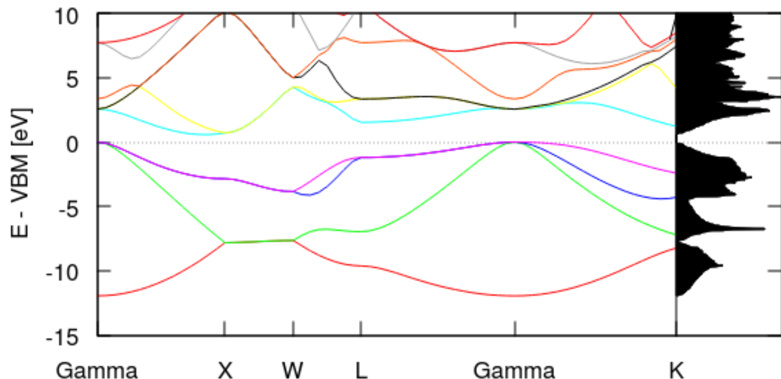
- HOMO = Valence Band Maximum (VBM) with energy E_v and LUMO = Conduction Band Minimum (CBM) with energy E_c
- HOMO-LUMO gap $E_g = E_c - E_v \approx 1.1$ eV
- HOMO and LUMO at different $\vec{k} \Rightarrow$ indirect band gap
- Diamond: similar band structure, much larger gap (≈ 5.5 eV) $\Rightarrow$ insulator
- Valence electrons/cell = 8 (even), configuration: $3s^2 3p^2$ (two Si/cell)

Band structure of GaAs (zinc-blende semiconductor)



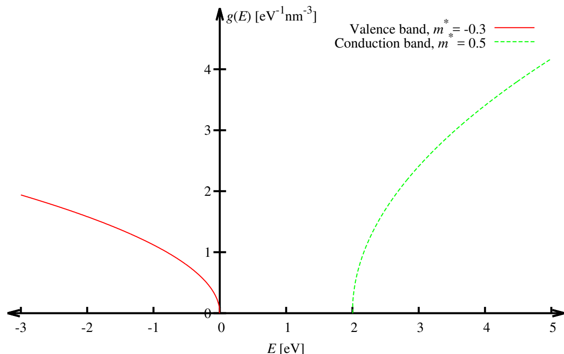
- HOMO-LUMO gap $E_g = E_c - E_v \approx 1.4$ eV
- HOMO and LUMO at same $\vec{k}$ $\quad (\Gamma) \quad \Rightarrow$ direct band gap
- Valence electrons/cell = 8 (even), configuration: Ga($4s^2 4p^1$), As($4s^2 4p^3$)

Density of states: silicon



- Can calculate numerically from band structure
- Parabolic band approximation valid for narrow energy range near gap

Density of states: parabolic-band semiconductor



- Parabolic bands near each band edge, with different effective masses
- Overall DOS reduces with reduced effective mass magnitude
- Set $E_v = 0$ conventionally (overall energy not well-defined)
- Conduction band edge $E_c = E_g$
- Where is the Fermi level?

Where is the Fermi level?

- At $T = 0$, valence band fully occupied $\Rightarrow f(E_v = 0) = 1 \Rightarrow E_F > 0$
- At $T = 0$, conduction band fully empty $\Rightarrow f(E_c = E_g) = 0 \Rightarrow E_F < E_g$
- Therefore, at $T = 0$, $0 < E_F < E_g$ i.e. Fermi level is in the band gap
- Chemical potential $\mu \to E_F$ as $T \to 0$
- In semiconductor physics, typically refer to $E_F(T)$ instead of $\mu(T)$
- Therefore, Fermi functions will be

$$f(E,T) = \frac{1}{\exp \frac{E - E_F(T)}{k_B T} + 1}$$

Where is the Fermi level at $T > 0$?

- Given Fermi level E_F and density of states $g(E)$
- Number of electrons in conduction band is $N_e = \int_{E_g}^{\infty} \mathrm{d}E g(E) f(E)$
- Number of holes in valence band is $N_h = \int_{-\infty}^{0} \mathrm{d}E g(E)(1 - f(E))$
- Total number of electrons cannot change with $T \Rightarrow N_e = N_h$

$$\int_{-\infty}^{0} \mathrm{d}E g(E)(1 - f(E)) = \int_{E_g}^{\infty} \mathrm{d}E g(E) f(E)$$

$$\int_{-\infty}^{0} \mathrm{d}E g(E) \frac{\exp \frac{E-E_F}{k_B T}}{\exp \frac{E-E_F}{k_B T} + 1} = \int_{E_g}^{\infty} \mathrm{d}E g(E) \frac{1}{\exp \frac{E-E_F}{k_B T} + 1}$$

$$\int_{-\infty}^{0} \mathrm{d}E g(E) e^{-(E_F - E)/(k_B T)} \approx \int_{E_g}^{\infty} \mathrm{d}E g(E) e^{-(E-E_F)(k_B T)}$$

$$e^{-E_F/(k_B T)} \underbrace{\int_0^{\infty} \mathrm{d}\varepsilon g(-\varepsilon) e^{-\frac{\varepsilon}{k_B T}}}_{\equiv N_v} \approx e^{(E_F - E_g)/(k_B T)} \underbrace{\int_0^{\infty} \mathrm{d}\varepsilon g(E_g + \varepsilon) e^{-\frac{\varepsilon}{k_B T}}}_{\equiv N_c}$$

Assuming $E_F, E_g - E_F \gg k_B T$, $\varepsilon \equiv$ energy from band edge

Band edge effective density of states

- Given density of states as a function of energy away from band edge

$$N_{c/v} \equiv \int_0^\infty \mathrm{d}\varepsilon g_{c/v}(\varepsilon) e^{-\frac{\varepsilon}{k_B T}}$$

- In parabolic band approximation $g(\varepsilon) = \left(\frac{\sqrt{2m^*}}{2\pi\hbar}\right)^3 4\pi\sqrt{\varepsilon}$ for both bands (but with different m^*; for tensor m^*, above defines DOS m_{eff})
- Therefore band-edge effective of density states:

$$N_{c/v} \equiv \int_0^\infty \mathrm{d}\varepsilon \left(\frac{\sqrt{2m^*_{c/v}}}{2\pi\hbar}\right)^3 4\pi\sqrt{\varepsilon} e^{-\frac{\varepsilon}{k_B T}}$$

$$= \left(\frac{\sqrt{2m^*_{c/v}}}{2\pi\hbar}\right)^3 4\pi\Gamma(3/2)(k_B T)^{3/2} = 2\left(\frac{\sqrt{2\pi m^*_{c/v} k_B T}}{2\pi\hbar}\right)^3$$

- $N_{c/v} \propto (m^*_{c/v})^{3/2}$ (steeper $g(\varepsilon)$ parabola)
- $N_{c/v} \propto T^{3/2}$ (climb higher up the $g(\varepsilon)$ parabola)

Fermi level for $T > 0$

- Charge neutrality imposes

$$N_v e^{-E_F/(k_B T)} = N_c e^{(E_F - E_g)/(k_B T)}$$

- Solve for Fermi level position:

$$E_F(T) = \frac{E_g}{2} + \frac{k_B T}{2} \ln \frac{N_v}{N_c}$$

- At $T \to 0$, E_F is exactly at the middle of the band gap
- At finite T, E_F moves away $\sim k_B T \ll E_g$ (still close to gap center)
- Which way does the Fermi level move with increasing T?
- For electrons in metals (and classical gases), $\mu \downarrow$ with $T \uparrow$
- For semiconductors, $E_F(T) \downarrow$ with $T \uparrow$ iff $N_c > N_v$
  (more DOS in positive m^* band; negative m^* pulls μ other way)

Electron and hole concentrations

- Number density of electrons $n \equiv N_e = N_c e^{-(E_g - E_F)/(k_B T)}$
- Number density of holes $p \equiv N_h = N_v e^{-E_F/(k_B T)}$
- Which one is larger? So far, they are equal: charge neutrality!
- Note product $np = N_c N_v e^{-E_g/(k_B T)} \equiv n_i^2$, independent of E_F
- Neutral pure semiconductor, $n = p = n_i$, intrinsic carrier density
- If $E_F \uparrow$, then $n \uparrow$ and $p \downarrow$ (more electrons than holes)
- If $E_F \downarrow$, then $n \downarrow$ and $p \uparrow$ (more holes than electrons)
- But $np = n_i^2$, constant in all these cases
- This is an equilibrium constant, eg. $[\mathrm{H}^+][\mathrm{OH}^-] = 10^{-14}$ M^2 in water
- How do you change E_F? Doping! (Also later, gating)

Intrinsic semiconductor thermodynamics and transport

- Fermi level far from band edges $\Rightarrow$ Boltzmann statistics in both bands
- Velocity distribution: Maxwell-Boltzmann distribution (classical gases)
- Internal energy of electrons $n \cdot (E_g + 3k_B T/2)$
- Internal energy of holes $-p \cdot (-3k_B T/2)$ (holes are missing electrons!)
- Net internal energy $n \cdot (E_g + 3k_B T/2) - p \cdot (-3k_B T/2)$
- Drude theory conductivity $\sigma = ne\mu_e + pe\mu_h$

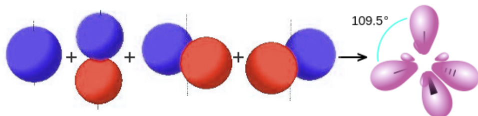
Intrinsic semiconductors: typical values at $T = 300$ K

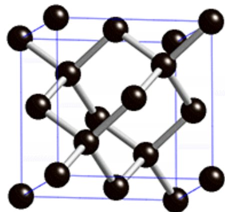
	E_g [eV]	m_e^*/m_e	m_h^*/m_e	N_c [cm-3]	N_v [cm-3]	n_i [cm-3]
Ge	0.66	0.04,0.28	1.64,0.08	1.0×10^{19}	6.0×10^{18}	2.3×10^{13}
Si	1.10	0.16,0.49	0.98,0.19	2.8×10^{19}	1.2×10^{19}	1.0×10^{10}
GaAs	1.42	0.082	0.067	4.7×10^{17}	7.0×10^{18}	2.1×10^{6}

- Note that m_{eff} for $N_{c/v}$ is an average of longitudinal / transverse values ($m_{\text{eff}} = m_L^{1/3} m_T^{2/3}$; for values see Table 5.1 in Kasap)
- N_c and N_v increase with m_{eff}
- n_i drops exponentially with increasing E_g

Diamond-cubic structure: sp^3 bonding

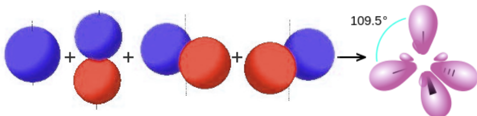
- Valence s and three p orbitals $\Rightarrow$ four sp^3 hybrid orbitals
- Orbitals point towards vertices of regular tetrahedron
- Si, C, Ge: 4 valence electrons each
- Form covalent bonds with four neighbours (8 shared electrons/atom)
- Bonding orbitals $\rightarrow$ valence band, anti-bonding orbitals $\rightarrow$ conduction band
- Tetrahedral network: FCC lattice with two atoms per cell

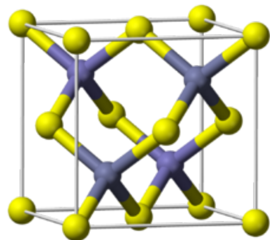




Zinc-blende structure: sp^3 bonding

- Valence s and three p orbitals $\Rightarrow$ four sp^3 hybrid orbitals
- Orbitals point towards vertices of regular tetrahedron
- Combine Ga,In (3 electrons) with As,Sb (5 electrons)
- Form covalent bonds with four neighbours (8 shared electrons/atom)
- Bonding orbitals $\rightarrow$ valence band, anti-bonding orbitals $\rightarrow$ conduction band
- Tetrahedral network: FCC lattice with two atoms per cell
- With Al and N, tend to form closely related Wurtzite structure (FCC to HCP cell)





Doping: acceptors and donors

- Extra / impurity Group III atoms: one less electron per atom
- Extra / impurity Group V atom: one extra electron per atom
- Covalent bonding theory: atoms want 8 (filled-shell) of shared electrons
- Group III 'acceptor': pick up electron from solid $\Rightarrow$ hole in valence band
- Group V 'donor': give electron to solid $\Rightarrow$ electron in conduction band

Simple picture of doping:

- Density N_a of acceptor atoms: charge $-eN_a$
- Density N_d of donor atoms: charge $+eN_d$
- Charge neutrality $-en + ep - eN_a + eN_d = 0 \Rightarrow n - p = N_d - N_a$
- Change in n and p due to shift in E_F, but $np = n_i^2$
- Solve for n and p, then find $E_F = \frac{E_g}{2} + \frac{k_B T}{2} \ln \frac{nN_v}{pN_c} = E_{F0} + \frac{k_B T}{2} \ln \frac{n}{p}$
- Even simpler picture: usually $N_d, N_a \gg n_i \Rightarrow$ either $p \gg n$ or $n \gg p$

Doping: p-type and n-type

n-type semiconductor:

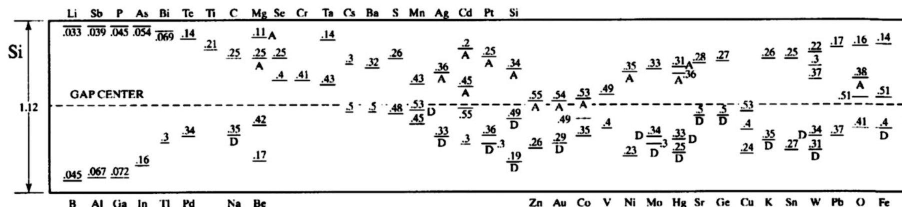
- Donor impurities dominate $N_d > 0$ ($N_a = 0$ or $< N_d$)
- Typically $N_d - N_a \gg n_i \Rightarrow n \gg p$ (since $p = n_i^2/n$)
- Therefore $n \approx N_d - N_a, p \approx n_i^2/(N_d - N_a)$
- $E_F = E_{F0} + \frac{k_B T}{2} \ln \frac{n}{p} = E_{F0} + k_B T \ln \frac{N_d - N_a}{n_i}$ (shifted $\uparrow$ towards CBM)
- Current predominantly carried by electrons

p-type semiconductor:

- Acceptor impurities dominate $N_a > 0$ ($N_d = 0$ or $< N_a$)
- Typically $N_a - N_d \gg n_i \Rightarrow p \gg n$ (since $n = n_i^2/p$)
- Therefore $p \approx N_a - N_d, n \approx n_i^2/(N_a - N_d)$
- $E_F = E_{F0} + \frac{k_B T}{2} \ln \frac{n}{p} = E_{F0} - k_B T \ln \frac{N_a - N_d}{n_i}$ (shifted $\downarrow$ towards VBM)
- Current predominantly carried by holes

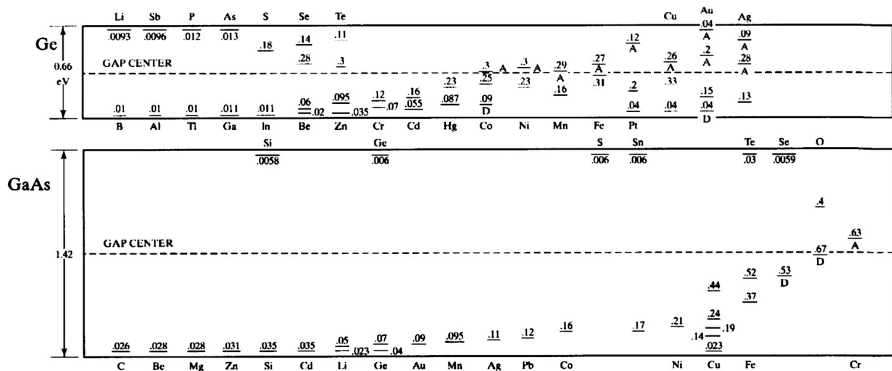
Doping: a more complete picture

- Simple picture: donor atom donates an electron, becomes positively charged
- Positively charged donor ion can bind electrons: like a hydrogen atom
- Binding energy of pseudo-hydrogenic atom $E_b = \epsilon_r^{-2} \frac{m^*}{m_e}$ Ryd ~ 0.05 eV
- Donor level: $E_d = E_c - E_b$ (electrons bound relative to CBM)
- Exact argument for acceptors and holes, with charges swapped
- Acceptor level: $E_a = E_v + E_b$ (holes bound relative to VBM)
- Levels in Si: note some impurities introduce multiple levels



Rensselaer

Dopant levels in Ge and GaAs



- For GaAs, Group II or Group VI are shallow dopants
- For GaAs, Group IV can be donor and acceptor dopants: how?

Donor charge density

- For each donor atom, degenerate donor levels typically with $g_d = 2$ (spin)
- Electron occupation: zero or one for the whole atom (repulsions)
- Probability of occupation zero $\propto 1$
- Probability of occupation one $\propto g_d \exp \frac{E_F - E_d}{k_B T}$
- Normalized probability of ionized donor (occupation zero):

$$P_d^+ = \frac{1}{1 + g_d \exp \frac{E_F - E_d}{k_B T}}$$

- Therefore number density of ionized donors:

$$N_d^+ = \frac{N_d}{1 + g_d \exp \frac{E_F - E_d}{k_B T}}$$

(which is $\approx N_d$ as long as E_F several $k_B T$ below E_d)

Acceptor charge density

- For each acceptor atom, degenerate acceptor levels typically with $g_a = 4$ (two for spin, two for dgenerate hole bands)
- Hole occupation: zero or one for the whole atom (repulsions)
- Probability of hole occupation zero $\propto 1$
- Probability of hole occupation one $\propto g_a \exp \frac{E_a - E_F}{k_B T}$ (tricky: flip energy axis when thinking in terms of holes)
- Normalized probability of ionized donor (hole occupation zero):

$$P_a^- = \frac{1}{1 + g_a \exp \frac{E_a - E_F}{k_B T}}$$

- Therefore number density of ionized acceptors:

$$N_a^- = \frac{N_a}{1 + g_a \exp \frac{E_a - E_F}{k_B T}}$$

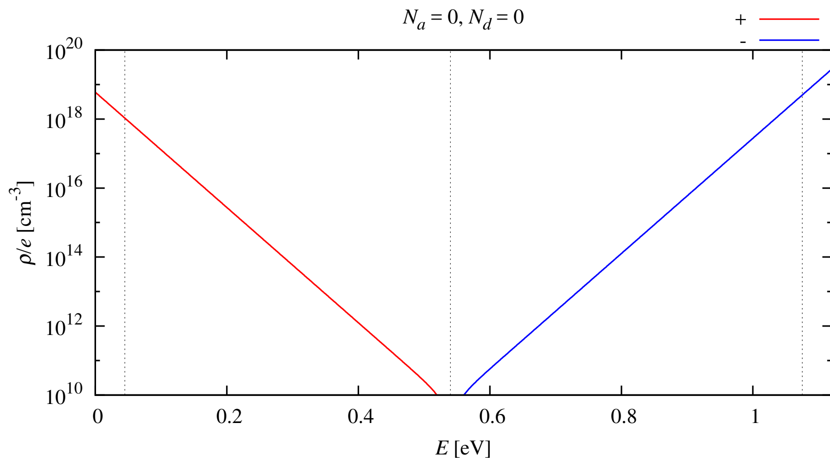
(which is $\approx N_a$ as long as E_F several $k_B T$ above E_a)

Charge neutrality

$$
\begin{aligned}
0 &= \rho(E_F) \\
&= -en + ep + eN_d^+ - eN_a^- \\
&= e\left[-\underbrace{N_c e^{-\frac{E_g - E_F}{k_B T}}}_{n} + \underbrace{N_v e^{-\frac{E_F}{k_B T}}}_{p} + \frac{N_d}{1 + g_d e^{\frac{E_F - E_d}{k_B T}}} - \frac{N_a}{1 + g_a e^{\frac{E_a - E_F}{k_B T}}} \right]
\end{aligned}
$$

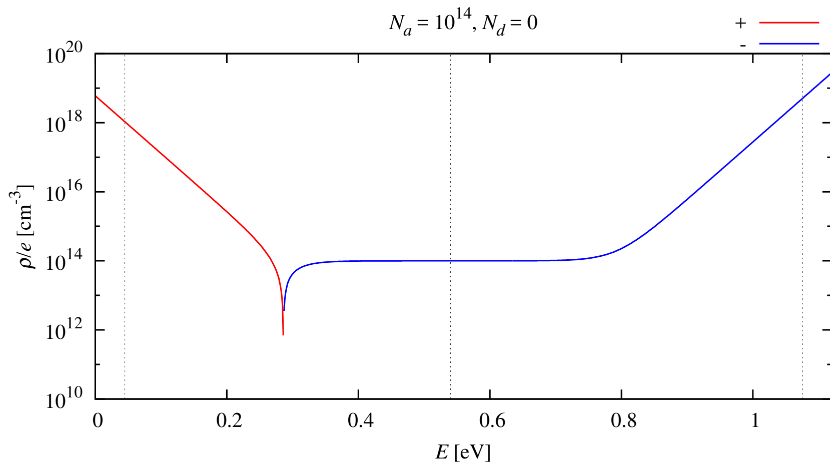
- If $N_a - N_d \gg n_i$, then $p \gg n$ (p-type)
- If $N_d - N_a \gg n_i$, then $n \gg p$ (n-type)
- Previous simple analysis holds if:
  - Net doping is stronger than n_i (one of the two regimes above), and
  - Doping is small enough that E_F is far above E_a and far below E_d (remember E_F moves up/down $\sim k_B T \ln \frac{N_{d/a}}{n_i}$)

$\rho(E_F)$: intrinsic semiconductor



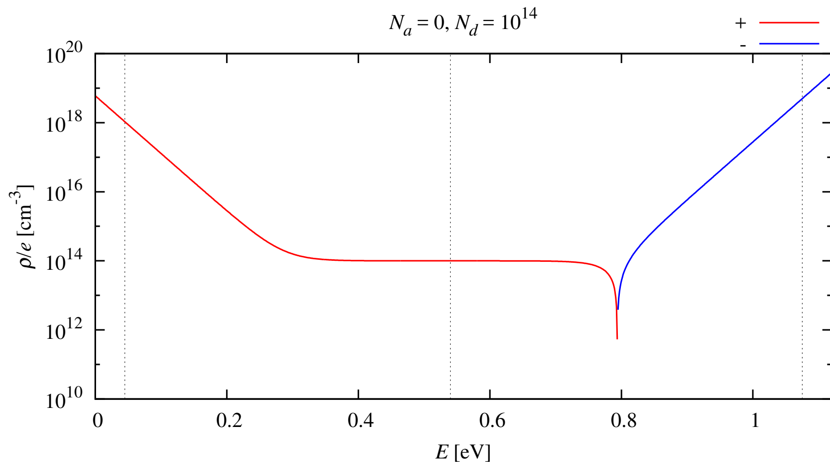
- Electrons increase with increaisng E_F (hence ρ decreases)
- Cross-over point from $+$ to $-$ is neutral E_F

$\rho(E_F)$: moderate p doping



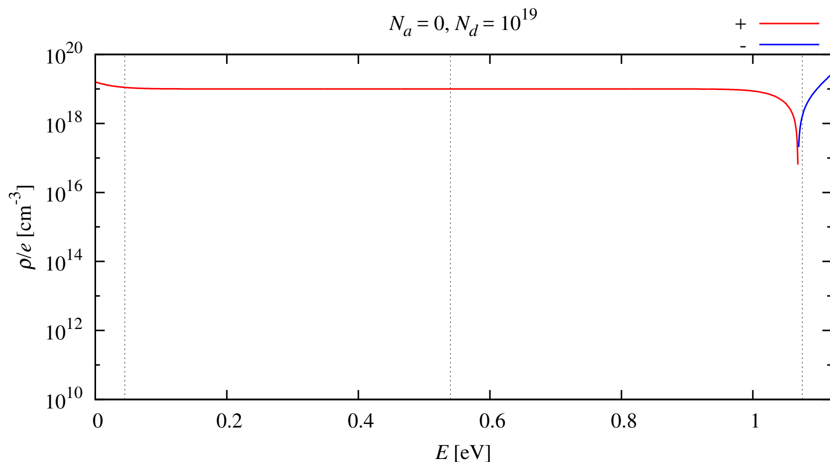
- Acceptors pull down Fermi level
- At moderate doping level, far from mid-gap and acceptor levels

$\rho(E_F)$: moderate n doping



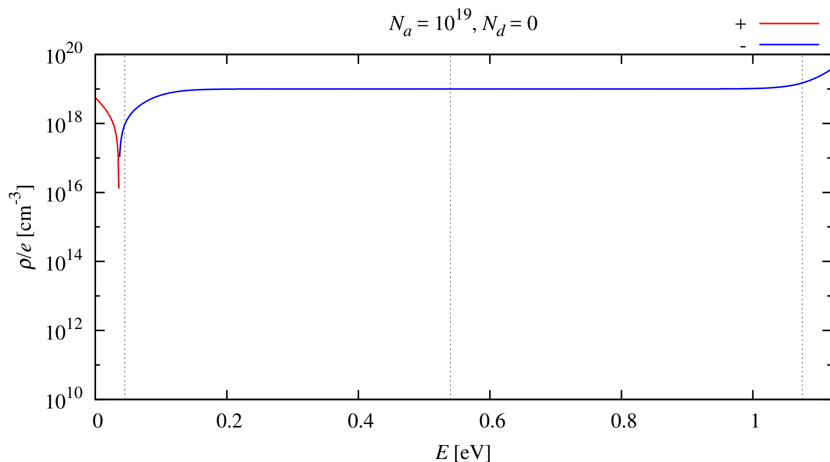
- Donors pull up Fermi level
- At moderate doping level, far from mid-gap and donor levels

$\rho(E_F)$: high n doping



- At high n doping level, approach / cross donor level
- Donors may be partially ionized (simple model no longer works)

$\rho(E_F)$: high p doping



- At high p doping level, approach / cross acceptor level
- Acceptors may be partially ionized (simple model no longer works)

Degenerate doping

- High-enough n doping: Fermi level enters conduction band (‘$n+$’)
- High-enough p doping: Fermi level enters valence band (‘$p+$’)
- One of our approximations breaks down for $n+$ case with $E_F > E_g$, $n \not\approx N_c e^{-(E_g - E_F)/(k_B T)}$ but instead

$$n \approx \frac{1}{3\pi^2} \left(\frac{\sqrt{2m^*(E_F - E_g)}}{\hbar} \right)^3$$

- Similarly, for $p+$ case with $E_F < 0$:

$$p \approx \frac{1}{3\pi^2} \left(\frac{\sqrt{2m^*(-E_F)}}{\hbar} \right)^3$$

- These are the Fermi theory expressions with $k_F = \sqrt{2m^* \varepsilon_F}/\hbar$ (where ε_F is Fermi energy relative to band edge)!
- Important: partial donor / acceptor ionization in this regime

Partial donor ionization

- Consider a p-type material ($N_d = 0$) with $E_F = E_a$ (we cross this point as we increase p-doping before getting to $p+$)
- Around this E_F, acceptors are partially ionized
- When exactly does this occur?
- Since E_F far from conduction band, neglect $n \ll p$
- Charge neutrality yields

$$N_v e^{-\frac{E_F}{k_B T}} = \frac{N_a}{1 + g_a \exp \frac{E_a - E_F}{k_B T}}$$

$$\Rightarrow \qquad N_v e^{-\frac{E_a}{k_B T}} = \frac{N_a}{1 + g_a}$$

$$\Rightarrow \qquad k_B T = \frac{E_a}{\log \frac{(1+g_a) N_v}{N_a}}$$

- Therefore, this happens for high N_a when $E_a \ll k_B T$
- But also, for $k_B T$ lower than E_a: dopant freeze-out
- Importance of shallow donor/acceptor levels! (for donors, replace $E_a \to E_g - E_d$)

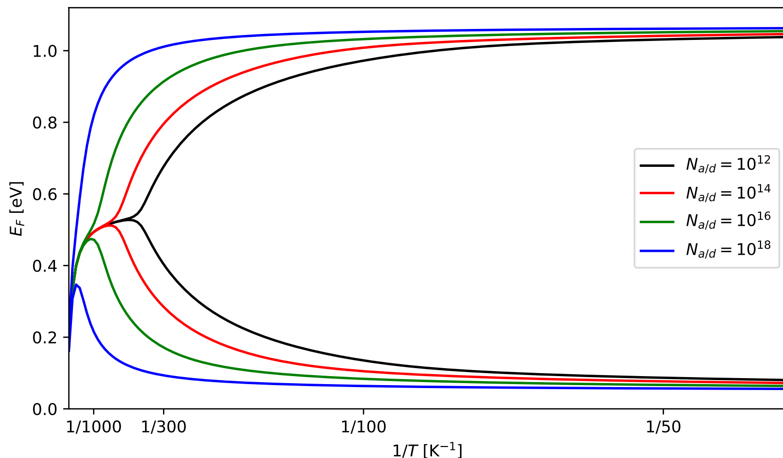
Carrier density in ionization regime

- If T much smaller than ionization threshold, neutrality:

$$
\begin{aligned}
N_v e^{-\frac{E_F}{k_B T}} &= \frac{N_a}{1 + g_a \exp \frac{E_a - E_F}{k_B T}} \\
\rightarrow \qquad N_v e^{-\frac{E_F}{k_B T}} &\approx \frac{N_a}{g_a} e^{-\frac{E_a - E_F}{k_B T}} \\
\Rightarrow E_F &= \frac{E_a}{2} + \frac{k_B T}{2} \log \frac{g_a N_v}{N_a}
\end{aligned}
$$

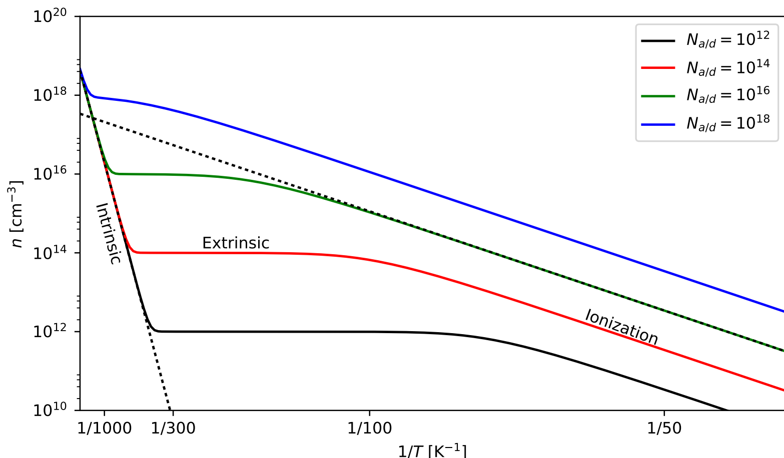
- Very similar to intrinsic case, except N_a/g_a replaces N_c
- Effective gap between valence band and acceptor level!
- In this regime, $p^2 = p \cdot N_a^- = (N_v N_a/g_a) \exp \frac{-E_a}{k_B T}$
- Similar behavior for frozen-out donors in ionization regime for n-type

Temperature dependence of E_F



- Doping dominates at low T, approach intrinsic level at high T
- At low T, Fermi level decided by donor/acceptor level
- Note using $E_{a/d} = 0.1$ eV from band edges to exaggerate effect

Temperature dependence of carrier concentration



- Ionization regime at low T upto threhsold which increases with $N_{d/a}$
- Constant concentration in extrinsic regime; threshold increases with $N_{d/a}$
- At high T, dopants don't matter: intrinsic regime

Intrinsic mobility

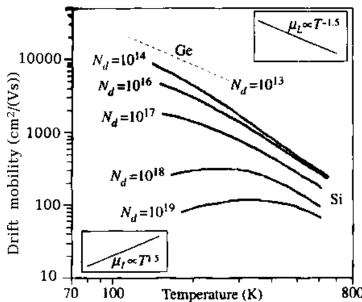
- Drude theory: mobility $\mu = e\tau/m^*$
- Typically semiconductor $m^* \sim 0.1 - 1\ m_e$, so expect higher μ than metals
- At room temperature, $\mu^e_{i\text{-Si}} \sim 1400$ cm^2/(Vs) and $\mu_{\text{Ag}} \sim 60$ cm^2/(Vs)
- Effective mass alone does not explain it!
- Remember $\tau^{-1}_{\text{e-ph}} \propto g(E)T$
- For metals, $g(E) \to g(E_F)$ since most carriers near Fermi level
- For semiconductors, carriers within few $k_B T$ of band edge where $g(E) \propto \sqrt{E}$ (and much smaller than metals)
- Averaged over carriers, $\overline{g(E)} \propto \sqrt{T}$
- Therefore, $\tau^{-1}_{\text{e-ph}} \propto T^{3/2}$ and $\mu \propto \tau \propto T^{-3/2}$

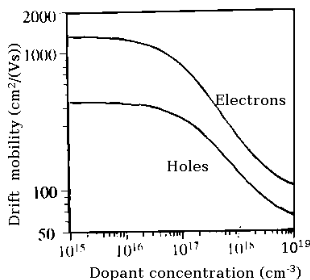
Impurity scattering

- Doped semiconductor contains ionized donors / acceptors
- Charged impurities cause electron PE $\propto 1/r$ near them
- Electrons with KE $\gg$ PE not scattered significantly
- Electrons with KE $\ll$ PE scattered most strongly
- Effective cross-section $\propto r_c^2$, where $PE(r_c) \sim KE \sim k_B T$
- Therefore $r_c \propto T^{-1}$ and cross-section $\sigma_{\text{cs}} \propto T^{-2}$
- Scattering time $\tau_I = (N_{a/d}\sigma_{\text{cs}}v)^{-1}$
- Average velocity $v \propto \sqrt{T}$
- Therefore $\tau_I \propto N_{a/d}^{-1} T^{3/2}$

Extrinsic mobility

- Intrinsic scattering $\tau_{\text{e-ph}}^{-1} \propto T^{-3/2}$
- Dopant / impurity scattering $\tau_I \propto N_{a/d}^{-1} T^{3/2}$
- Net scattering $\tau \propto \left(T^{3/2} + N_{a/d} T^{-3/2}\right)^{-1}$ (Mathiessen rule)
- Therefore mobility $\mu \propto \left(T^{3/2} + N_{a/d} T^{-3/2}\right)^{-1}$
- At high T, e-ph scattering dominates (intrinsic regime)
- At high doping concentration (or low T), impurity scattering dominates





Extrinsic conductivity

- Conductivity $\sigma = ne\mu_e + pe\mu_h$: similar dependence as n (exponentials dominate over polynomial)
- μ effect visible mainly in extrinsic regime where n is constant

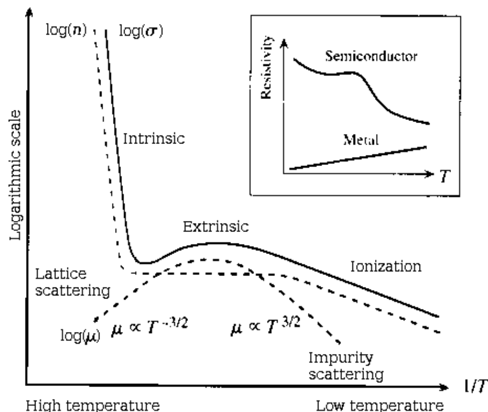
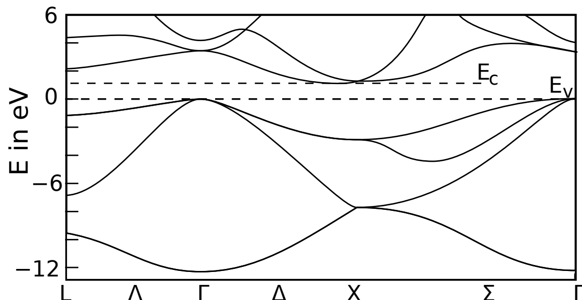


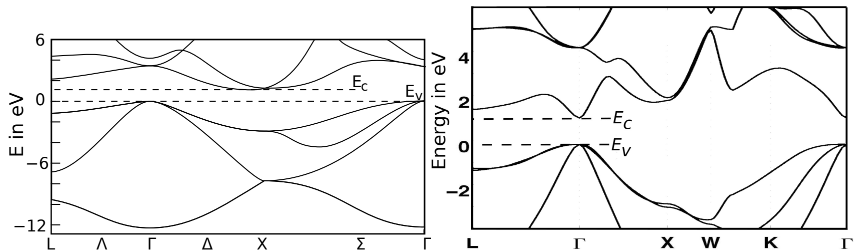
Fig. 5.20 from Kasap

Recombination



- Excite electrons and holes in semiconductor to higher energy
- e-ph scattering brings electrons and holes to band edges
- If $np > n_i^2$, equilibrium: nothing further happens
- What if you make more electron-hole pairs (eg. using light) such that $np \neq n_i^2$?
- Electrons and holes will recombine to restore equilibrium

Recombination: direct vs indirect



- Direct gap: electrons and holes at band edges at same k
- Indirect gap: band edge carriers at different k
- Which will recombine faster?
- Direct gap: momentum conservation, recombine and emit light (usually)
- Indirect gap: cannot directly recombine: momentum not conserved

Recombination mechanisms

- Recombination rate proportional to $np - n_i^2$
- Radiative / direct recombination (direct gap materials)
- Trap-assisted (Shockley-Read-Hall recombination)
  - Trap level in gap captures electron (hole), becoming $-$ ($+$) charged
  - Later captures hole (electron), becoming neutral
  - Energy from recombination emitted to phonons
  - Probability of each capture $\propto$ Boltzmann factor of trap depth from band edge
  - Net rate $\sim \operatorname{sech}^2 \frac{E_t - E_g/2}{2k_B T}$ (trap level E_t)
  - Strongest for mid-band-gap states!
- Auger recombination
  - Energy and momentum of e-h pair go to excite another e or h
  - Need e or h to excite, so rate $\propto n, p$
  - Dominates at very high carrier concentrations
- Recombination rate $= \alpha(np - n_i^2)$
- Minority carrier lifetime $= 1/(\max(n, p)\alpha)$