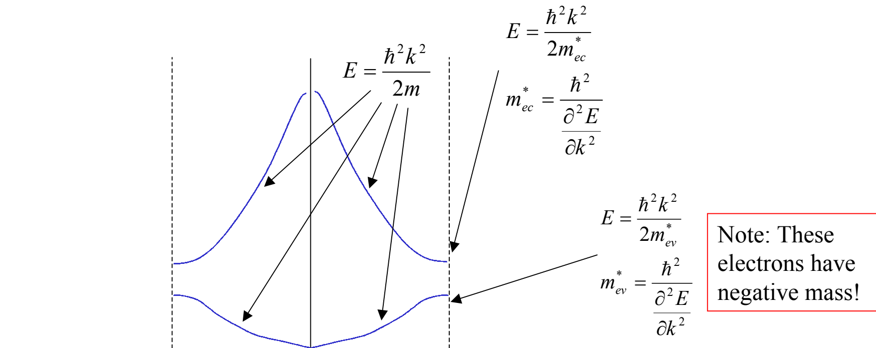
Properties of non-free electrons

- Electrons near the diffraction condition are not approximated as free
- Their properties can still be viewed as free e- if an ‘effective mass’ m* is used



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Band Gap Energy Trends

IV / III-V / II-VI*

II B	III	IV	V	VI
	B	C	N	O
	Al	Si	P	S
Zn	Ga	Ge	As	Se
Cd	In	Sn	Sb	Te

MP (°K)	Eg (eV)	a_o A
	6 / 10	3.56 / 3.16
1685 / 1770	1.1 / 3	5.42 / 5.46
1231 / 1510 / ?	0.72 / 1.35/ ?	5.66 / 5.65 / ?
508 / 798 / ?	0.08 /0.18 / 1.45	6.45 / 6.09 / ?

* Fill in as many of the question marks as you can.

Note Trends:

1. As descend column, MP decreases as does Eg while a_o increases.
2. As move from IV to III-V to II-VI compounds become more ionic, MP and Eg increase while a_o tends to decrease

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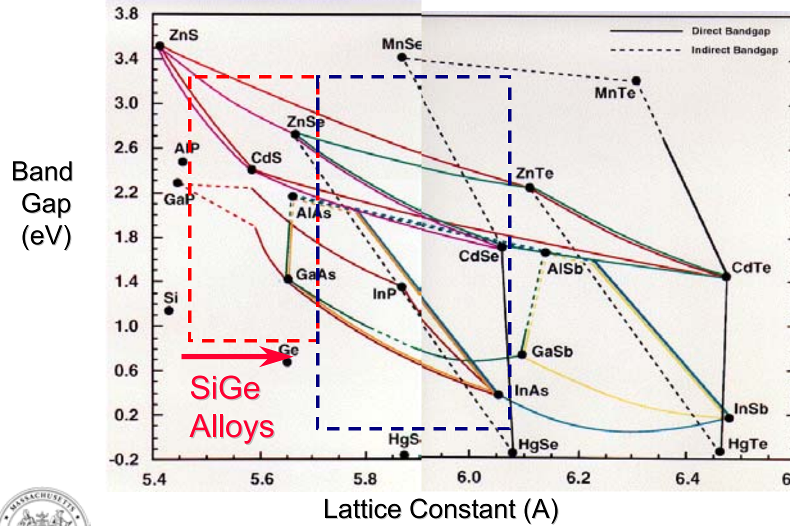
Trends in III-V and II-VI Compounds

Larger atoms, weaker bonds, smaller U, smaller E_g, higher μ, more costly!



Energy Gap and Mobility Trends

Material	Eg(eV)°K	µn(cm²/V·s)
GaN	3.39	150
AlAs	2.3	180
GaP	2.4	2,100
GaAs	1.53	16,000
InP	1.41	44,000
InAs	0.43	120,000
InSb	0.23	1,000,000

Remember that: $\mu = \frac{e\tau}{m^*}$ and $\frac{1}{m^*} = \frac{1}{h^2}\frac{\partial^2 E}{\partial k^2}$

Metals and Insulators

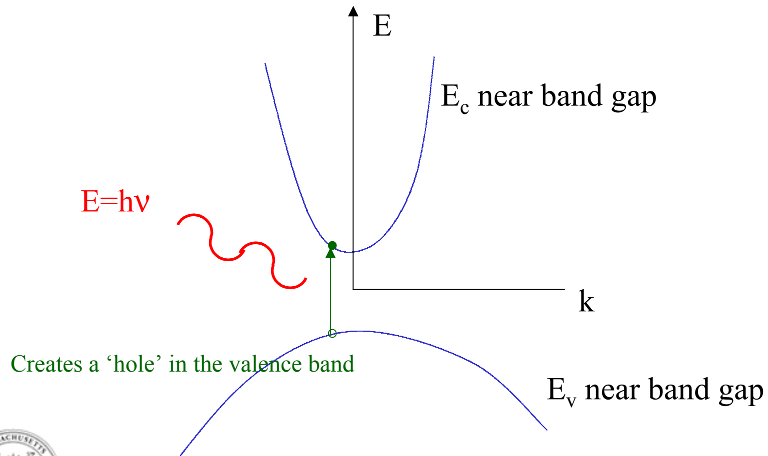
- E_F in mid-band area: free e-, *metallic*
- E_F near band edge
  - E_F in or near kT of band edge: *semimetal*
  - E_F in gap: *semiconductor*
- E_F in very large gap, *insulator*

Semiconductors

- Intermediate magnitude band gap enables free carrier generation by three mechanisms
  - photon absorption
  - thermal
  - impurity (i.e. doping)
- Carriers that make it to the next band are free carrier- like with mass, m*

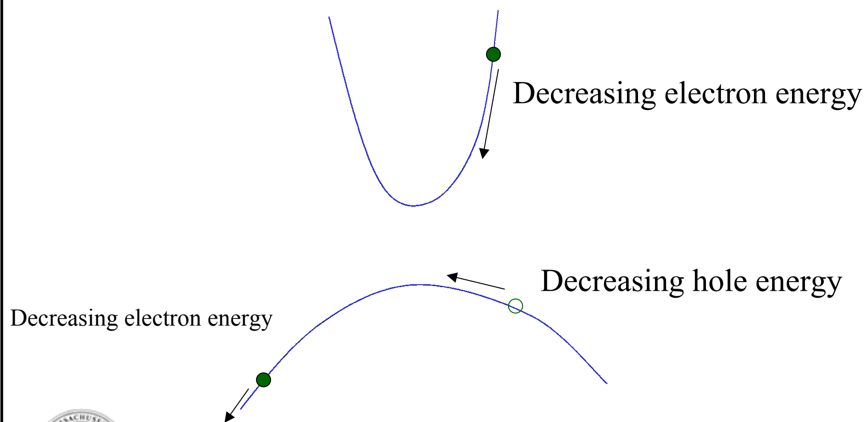
Semiconductors: Photon Absorption

- When $E_{light}=h\nu>E_g$, an electron can be promoted from the valence band to the conduction band



Holes and Electrons

- Instead of tracking electrons in valence band, more convenient to track missing electrons, or 'holes'
- Also removes problem with negative electron mass: since hole energy increases as holes 'sink', the mass of the hole is positive as long as it has a positive charge



Conductivity of Semiconductors

- Need to include both electrons and holes in the conductivity expression

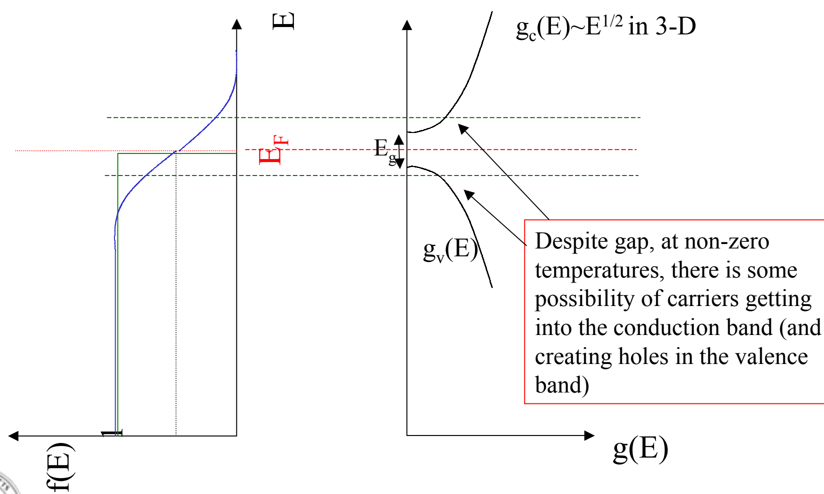
$$\sigma = ne\mu_e + pe\mu_h = \frac{ne^2\tau_e}{m_e^*} + \frac{pe^2\tau_h}{m_h^*}$$

p is analogous to n for holes, and so are τ and m*

Note that in both photon stimulated promotion as well as thermal promotion, an equal number of holes and electrons are produced, i.e. n=p

Thermal Promotion of Carriers

- We have already developed how electrons are promoted in energy with T: Fermi-Dirac distribution
- Just need to fold this into picture with a band-gap



Density of Thermally Promoted of Carriers

Number of electrons per volume in conduction band

$$n = \int_{E_c}^{\infty} f(E) g(E) dE$$

Density of electron states per volume per dE

Fraction of states occupied at a particular temperature

$$f(E) = \frac{1}{e^{\frac{(E-E_F)}{k_b T}} + 1} \approx e^{-\frac{(E-E_F)}{k_b T}} \quad \text{when } (E - E_F) >> k_b T$$

$$g_c(E) = \frac{1}{2\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{\frac{3}{2}} (E - E_g)^{\frac{1}{2}} \longrightarrow n = \frac{1}{2\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{\frac{3}{2}} e^{\frac{E_F}{k_b T}} \int_{E_g}^{\infty} (E - E_g)^{\frac{1}{2}} e^{\frac{-E}{k_b T}} dE$$

Since $\int_0^{\infty} x^{\frac{1}{2}} e^{-x} dx = \frac{\sqrt{\pi}}{2}$, then $n = 2\left(\frac{m_e^* k_b T}{2\pi\hbar^2}\right)^{\frac{3}{2}} e^{\frac{E_F}{k_b T}} e^{\frac{-E_g}{k_b T}}$

N_C (the term $2\left(\frac{m_e^* k_b T}{2\pi\hbar^2}\right)^{\frac{3}{2}}$)

$$n = N_C e^{\frac{E_F - E_g}{k_b T}}$$

Density of Thermally Promoted of Carriers

- A similar derivation can be done for holes, except the density of states for holes is used
- Even though we know that n=p, we will derive a separate expression anyway since it will be useful in deriving other expressions

$$g_v(E) = \frac{1}{2\pi^2}\left(\frac{2m_h^*}{\hbar^2}\right)^{\frac{3}{2}} (-E)^{\frac{1}{2}} \longrightarrow p = \int_{-\infty}^{0} f_h(E) g_v(E) dE, \quad \text{where } f_h = 1 - f(E)$$

$$p = 2\left(\frac{m_h^* k_b T}{2\pi\hbar^2}\right)^{\frac{3}{2}} e^{\frac{-E_F}{k_b T}}$$

$$p = N_v e^{\frac{-E_F}{k_b T}}$$

Thermal Promotion

- Because electron-hole pairs are generated, the Fermi level is approximately in the middle of the band gap
- The law of mass action describes the electron and hole populations, since the total number of electron states is fixed in the system

$$n = p \text{ gives } E_F = \frac{E_g}{2} + \frac{3}{4} k_b T \ln\left(\frac{m_h^*}{m_e^*}\right)$$

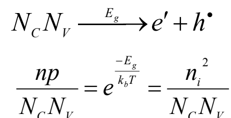
Since m_e* and m_h* are close and in the ln term, the Fermi level sits about in the center of the band gap

$$p \text{ or } n = n_i = 2\left(\frac{k_b T}{2\pi\hbar^2}\right)^{\frac{3}{2}} \left(m_e^* m_v^*\right)^{\frac{3}{4}} e^{\frac{-E_g}{2k_b T}}$$

Law of Mass Action for Carrier Promotion

$$n_i^2 = np = 4\left(\frac{k_b T}{2\pi\hbar^2}\right)^3 \left(m_e^* m_h^*\right)^{\frac{3}{2}} e^{\frac{-E_g}{k_b T}} \quad ; \qquad n_i^2 = N_C N_V e^{\frac{-E_g}{k_b T}}$$

- Note that re-arranging the right equation leads to an expression similar to a chemical reaction, where E_g is the barrier.
- $N_C N_V$ is the density of the reactants, and n and p are the products.



$$N_C N_V \xrightarrow{E_g} e' + h^\bullet$$

$$\frac{np}{N_C N_V} = e^{\frac{-E_g}{k_b T}} = \frac{n_i^2}{N_C N_V}$$

- Thus, a method of changing the electron or hole population without increasing the population of the other carrier will lead to a dominant carrier type in the material.
- Photon absorption and thermal excitation produce only pairs of carriers: *intrinsic semiconductor.*
- Increasing one carrier concentration without the other can only be achieved with impurities, also called doping: *extrinsic semiconductors.*

Intrinsic Semiconductors

- Conductivity at any temperature is determined mostly by the size of the band gap
- All intrinsic semiconductors are insulating at very low temperatures

Recall: $$\sigma = ne\mu_e + pe\mu_h = \frac{ne^2\tau_e}{m_e^*} + \frac{pe^2\tau_h}{m_h^*}$$

$$\sigma_{\text{int}} = n_i e(\mu_e + \mu_h) \propto e^{\frac{-E_g}{2k_bT}}$$ ← This can be a measurement for E_g

For Si, Eg=1.1eV, and let μ_e and μ_h be approximately equal at 1000cm^2/V-sec (very good Si!).

$\sigma \sim 10^{10}$cm^{-3}*1.602x10^{-19}*1000cm^2/V-sec=1.6x10^{-6} S/m, or a resistivity ρ of about 10^6 ohm-m max.

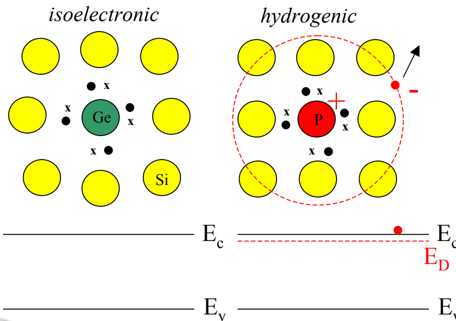
- One important note: No matter how pure Si is, the material will always be a poor insulator at room T.
- As more analog wireless applications are brought on Si, this is a major issue for system-on-chip applications.

Extrinsic Semiconductors

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

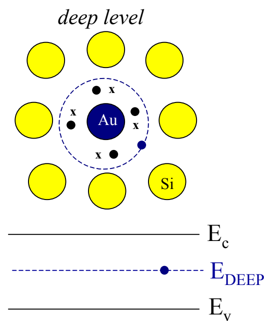
<u>Impurities with close electronic structure to host</u>

isoelectronic *hydrogenic*



<u>Impurities with very different electronic structure to host</u>

deep level



Hydrogenic Model

- 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

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

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

- Thus, for the ground state n=1, we can see already that since ε is on the order of 10, the binding energy of the carrier to the center is <0.1eV
- Expect that many carriers are then thermalize at room T
- Experiment:
  - B acceptor in Si: .046 eV
  - P donor in Si: 0.044 eV
  - As donor in Si: 0.049

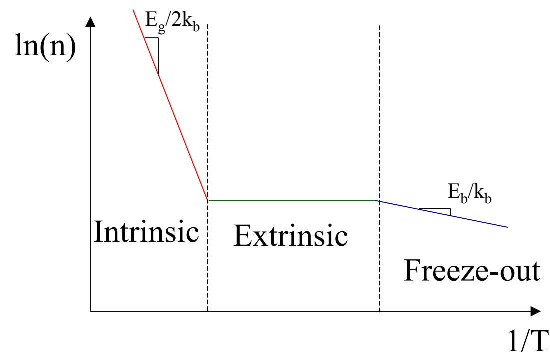
The Power of Doping

- Can make the material n-type or p-type: Hydrogenic impurities are nearly fully ionized at room temperature
  - n_i^2 for Si: ~10^{20}cm^{-3}
  - Add 10^{18}cm^{-3} donors to Si: n~N_d
  - n~10^{18}cm^{-3}, p~10^2 (n_i^2/N_d)
- Can change conductivity drastically
  - 1 part in 10^7 impurity in a crystal (~10^{22}cm^{-3} atom density)
  - 10^{22}*1/10^7=10^{15} dopant atoms per cm^{-3}
  - n~10^{15}, p~$10^{20}/10^{15}$~10^5
    σ/σ_i~(p+n)/2n_i~n/2n_i~10^5!

Impurities at the ppm level drastically change the conductivity (5-6 orders of magnitude)

Expected Temperature Behavior of Doped Material (Example:n-type)

- 3 temperature regimes



Contrasting Semiconductor and Metal Conductivity

$$\sigma = \frac{ne^2\tau}{m}$$

- Semiconductors
  - changes in n(T) can dominate over τ
  - as T increases, conductivity increases
- Metals
  - n fixed
  - as T increases, τ decreases, and conductivity decreases

General Interpretation of τ

- Metals and majority carriers in semiconductors
  - τ is the scattering length
  - Phonons (lattice vibrations), impurities, dislocations, and grain boundaries can decrease τ

$$\frac{1}{\tau} = \frac{1}{\tau_{phonon}} + \frac{1}{\tau_{impur}} + \frac{1}{\tau_{disl}} + \frac{1}{\tau_{gb}} + \ldots$$

$$\tau_i = \frac{l_i}{v_{th}} = \frac{1}{v_{th}\sigma_i N_i}$$

$$l_i \sigma_i N_i = 1$$

where σ is the cross-section of the scatterer, N is the number of scatterers per volume, and l is the average distance before collisions

The mechanism that will tend to dominate the scattering will be the mechanism with the shortest l (most numerous), unless there is a large difference in the cross-sections

Example: Si transistor, τ_{phonon} dominates even though τ_{impur} gets worse with scaling.

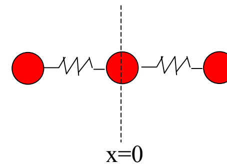
Estimate of T dependence of conductivity

- τ~l for metals
- τ~l/v_{th} for semiconductors
- First need to estimate l=1/Nσ

$$l_{ph} = \frac{1}{N_{ion}\sigma_{ion}}$$

$$\sigma_{ion} \propto \pi \langle x^2 \rangle$$

$$\langle x^2 \rangle = \frac{\int_{-\infty}^{+\infty} \Psi^* x^2 \Psi dx}{\int_{-\infty}^{+\infty} \Psi^* \Psi dx}$$



Use Ψ for harmonic oscillator, get:

$$k\langle x^2 \rangle = \langle E \rangle = \frac{\hbar\omega}{e^{\frac{\hbar\omega}{kT}} - 1}$$

Average energy of harmonic oscillator

Estimate of T dependence of conductivity

$$k\langle x^2\rangle = \langle E\rangle = \frac{\hbar\omega}{e^{\frac{\hbar\omega}{kT}}-1}$$

$$\hbar\omega = k\theta$$

$$\langle E\rangle = \frac{k\theta}{e^{\frac{\theta}{T}}-1}$$

Therefore, <x^2> is proportional to T if T large compared to θ:

$$e^{\frac{\theta}{T}} \approx 1+\frac{\theta}{T}$$

$$\langle x^2\rangle \propto T$$

$$l \propto \frac{1}{\sigma} \propto \frac{1}{\langle x^2\rangle} \propto \frac{1}{T}$$

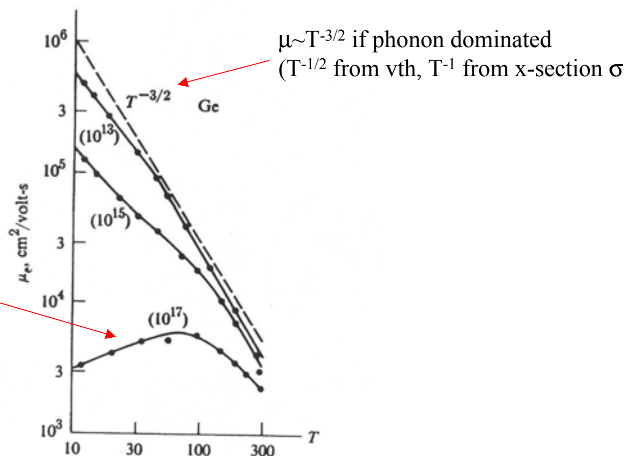
For a metal: $\sigma_{cond} \propto \mu \propto \tau \approx \frac{l}{v_F} = \frac{1}{v_F N_{ion}\pi\langle x^2\rangle} = \frac{1}{v_F N_{ion}\pi T}$

For a semiconductor, remember that the carriers at the band edges are classical-like:

$$\tau = \frac{l}{v_{th}} = \frac{l}{\sqrt{\frac{3kT}{m^*}}} \propto \frac{\frac{1}{T}}{T^{\frac{1}{2}}} \propto T^{-\frac{3}{2}}$$

$$\mu = \frac{e\tau}{m^*} \propto T^{-\frac{3}{2}}$$

Example: Electron Mobility in Ge



μ~$T^{-3/2}$ if phonon dominated ($T^{-1/2}$ from vth, T^{-1} from x-section σ

At higher doping, the ionized donors are the dominate scattering mechanism