Lecture 17

Applications of Free Energy Minimum

Semiconductors, intrinsic and doped

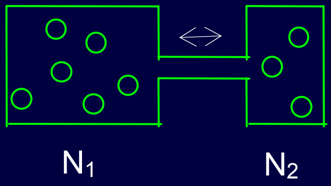
Reference for this Lecture:
Elements Ch 12

Reference for Lecture 19:
Elements Ch 13

Last Time

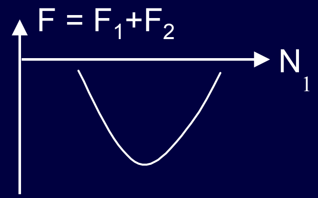
Thumbnail review of free energy:
Equilibrium corresponds to maximum $S_{tot} = S_{reservoir} + S_{small\ system}$.
When we calculate ΔS, we only need to know the temperature of the reservoir. In minimizing F (equivalent to maximizing S_{tot}) we don't have to deal explicitly with $S_{reservoir}$.

Consider exchange of material (particles) between two containers.
These are two small systems in equilibrium with a reservoir (not shown) at temperature T. In equilibrium, $dF/dN_1 = 0$:



$$\frac{dF}{dN_1} = \frac{dF_1}{dN_1} + \frac{dF_2}{dN_1} = \frac{dF_1}{dN_1} - \frac{dF_2}{dN_2} = 0$$

$$\frac{dF_1}{dN_1} = \frac{dF_2}{dN_2}$$



The derivative of free energy with respect to particle number is so important that we define a special name and symbol for it:

$$\boxed{\mu_i \equiv \frac{dF_i}{dN_i}}$$

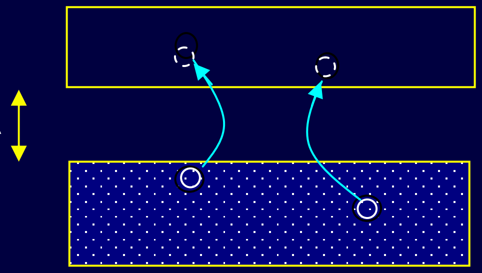
The chemical potential of subsystem "i"

For two subsystems exchanging particles, the equilibrium condition is:

$$\boxed{\mu_1 = \mu_2}$$

Maximum Total Entropy ⟶ Minimum Free Energy ⟶ Equal chemical potentials

Electrons in Semiconductors



Energy gap, Δ

At T = 0:
Conduction band has no electrons

Valence band totally filled with electrons

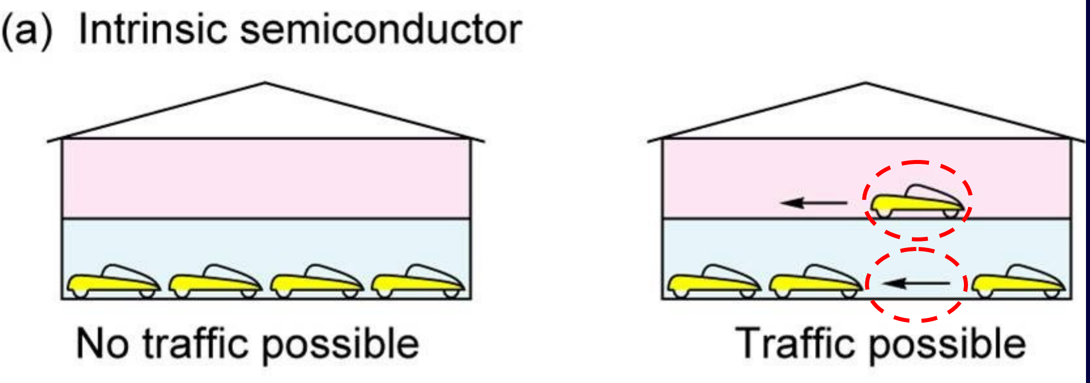
In many materials, electrons cannot have every conceivable energy. There is a low energy range (the “valence band”) and a high energy range (the “conduction band”). A “gap” of disallowed energies separates them. (The reason for the gap is a Physics 214 topic.)

At T = 0, every valence band state is occupied. At T ≠ 0, electrons are thermally excited from the valence band to the conduction band. How many determines the electrical conductivity.

The activated free electrons and the “holes” (unfilled states) left behind act as two ideal gases. We can compute the density of thermally excited electrons (and holes) by minimizing $F_{\text{electron}} + F_{\text{hole}}$.

Here, to simplify the problem we assume that excitation from valence to conduction band always requires the same energy, *i.e.*, every conduction state has energy Δ more than every valence state. This avoids having to do integrals.

Electrons in Semiconductors (2)



Conduction electron

Hole

This is Shockley's* cartoon of an intrinsic semiconductor. At T = 0, the cars (electrons) can't move. If some are raised to the upper level (the conduction band) then motion becomes possible.

The vacant spaces on the lower level are "holes". Motion of the cars on the lower level is more simply described by pretending that the holes are the objects that move.

An intrinsic semiconductor is one in which the number of electrons equals the number of valence band states, so that at T = 0 every state is filled, and no electrons are left over.

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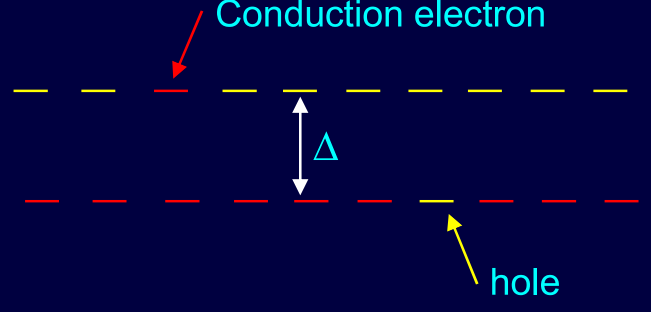
*John Bardeen, Walter Brattain, and William Shockley invented the transistor in 1947.

Intrinsic Semiconductors

We have
- N electrons
- N valence states (call their energy zero)
- N conduction states (energy Δ)



We want to know
- N_e and N_h,
- the numbers of conduction electrons and holes at temperature T

Our analysis will be similar to the “Defects in a Lattice” problem.

Conduction electrons and holes are created in pairs, so: $N_e = N_h$ (and $dN_e = dN_h$)

Method: Minimize $F = F_e + F_h$:

$$\frac{dF}{dN_e} = \frac{dF_e}{dN_e} + \frac{dF_h}{dN_e} \xrightarrow{dN_e = dN_h} \frac{dF_e}{dN_e} + \frac{dF_h}{dN_h} = 0 \qquad \boxed{\mu_h + \mu_e = 0}$$

One big difference: electrons and holes actually behave like ideal gases --they are free to rapidly move around in the crystal, with an “effective mass” m_e, m_h.

So, what are S, F, and μ for an Ideal Gas of Particles?

How Do S, F, μ Depend on N/V?

In general, this is a complicated function of particle properties and the environment. To keep things simple, we'll only work with ideal gases.

For an ideal gas the internal energy per particle, u ≡ U/N, depends on T, but not on N. For many problems we can set this to 0.

How does S depend on N? Let's count microstates and see.

$$\Omega = \frac{M^N}{N!} \quad \text{so } S = k\ln\left(\frac{M^N}{N!}\right) = k\left(N\ln M - \ln N!\right)$$

The number of "bins", M, is proportional to V. It also depends on T (see next slide).

Thus, $$\left.\frac{\partial S}{\partial N}\right|_M = k\ln\left(\frac{M}{N}\right) \quad \text{since} \quad \frac{d(\ln N!)}{dN} = \ln N$$

and the chemical potential for an ideal (monatomic) gas is:

$$\mu \equiv \left.\frac{\partial F}{\partial N}\right|_{V,T} = u - T\left.\frac{\partial S}{\partial N}\right|_M = u - kT\ln\left(\frac{M}{N}\right) = u + kT\ln\left(\frac{N}{Vn_Q}\right) = \boxed{u + kT\ln\left(\frac{n}{n_Q}\right)}$$

n ≡ N/V = particle density, n_Q ≡ M/V = number of states per unit volume. n_Q can only be calculated using quantum mechanics, so we will treat it as an empirical quantity (*i.e.*, we'll tell you the numerical value when necessary). n_Q is a function of T, but not of the particle density, n.

For ideal gases, μ ~ logarithm of particle density.

What is n_Q?

n_Q = total no. states (per unit volume) available to a particle at temp. T

$$\frac{n_Q}{n} = \frac{n_Q V}{N} = \frac{\text{number of states in volume V}}{\text{number of particles}}$$

Considering both position and momentum.

QM: particle with momentum p has wavelength $\lambda = h/p$. (h = Plank's constant)

Taking λ as a characteristic length, the effective cell volume is $\sim\Delta V \approx \lambda^3 = (h/p)^3$.

Using $p^2/2m = (3/2)kT$, the quantum-mechanical 'cell density' has a T-dependence:

$$n_Q \approx 1/\lambda^3 = (3mkT/h^2)^{3/2}$$

If we do the problem more carefully (see *Elements* for details) we find*

$$\boxed{n_Q = (2\pi mkT/h^2)^{3/2} \quad = \quad (10^{30}\,meter^{-3})(m/m_p)^{3/2}(T/300K)^{3/2}}$$

Examples: $n_Q(\text{H @ 300K}) = (10^{30}\,\text{meter}^{-3})(m/m_p)^{3/2}(T/300K)^{3/2} = 10^{30}\,\text{meter}^{-3}$

$$n_Q(\text{He @ 300K}) = (10^{30}\,\text{meter}^{-3})(4m_p/m_p)^{3/2}(300/300K)^{3/2} = 8\times10^{30}\,\text{meter}^{-3}$$

$$n_Q(He\ @\ 3\text{K}) = (10^{30}\,\text{meter}^{-3})(4m_p/m_p)^{3/2}(3/300K)^{3/2} = 8\times10^{27}\,\text{meter}^{-3}$$

*For a monatomic gas, the $n_T(T)$ we had before <u>is</u> n_Q; otherwise there are modifications.

Act 1

We just saw that the quantum density for an ideal monatomic gas of particles of mass m, at temperature T, is given by

$$\boxed{n_Q = (2\pi mkT/h^2)^{3/2} \quad = \quad (10^{30}\,meter^{-3})(m/m_p)^{3/2}(T/300K)^{3/2}}$$

What is the quantum density $n_{Q,e}$ for a 'gas' of electrons at T = 300K, taking into account their spin? (m_p = 1837 m_e)

a) $1.27 \times 10^{25}/m^3$

b) $2.54 \times 10^{25}/m^3$

c) $5.45 \times 10^{26}/m^3$

d) $1.84 \times 10^{33}/m^3$

e) $7.87 \times 10^{34}/m^3$

Solution

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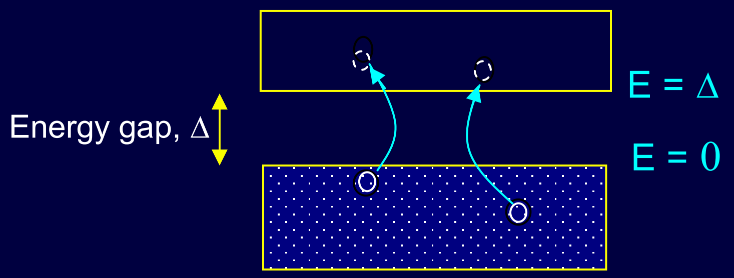
A direct calculation using the above formula would give choice a). But we also need to take into account that every electron spin could be either up or down, i.e., increasing the number of states by a factor of 2.

If we have more complicated particles (e.g., diatomic molecules that can rotate), this will also increase the quantum density.

See Textbook for more details.

Electrons and holes in Semiconductors



At T = 0:
Conduction band has no electrons

Valence band totally filled with electrons

We now have the tools to solve for the equilibrium **density of e-h pairs**:

1. Since they act like ideal gases, the chemical potentials are

$$\mu_h = kT\ln\left(\frac{n_h}{n_{Qh}}\right) \qquad \mu_e = \Delta + kT\ln\left(\frac{n_e}{n_{Qe}}\right)$$

2. Electrons and holes are created in pairs→ total free energy is minimized when

$$\mu_h + \mu_e = 0 = kT\ln\left(\frac{n_h}{n_{Qh}}\right) + \Delta + kT\ln\left(\frac{n_e}{n_{Qe}}\right) = \Delta + kT\ln\left(\frac{n_h n_e}{n_{Qh} n_{Qe}}\right)$$

3. For a pure semiconductor, $n_e = n_h = n_i$ ("intrinsic pair density")

$$\ln\left(\frac{n_h n_e}{n_{Qh} n_{Qe}}\right) = \frac{-\Delta}{kT} \quad\Rightarrow\quad \frac{n_h n_e}{n_{Qh} n_{Qe}} = \frac{n_i^{\,2}}{n_{Qh} n_{Qe}} = e^{\frac{-\Delta}{kT}} \quad\Rightarrow\quad \boxed{\frac{n_i}{n_Q} = e^{\frac{-\Delta}{2kT}}}$$

Compare to I-V result (p. 11).

n_Q = (geometric mean of $n_{Qe}n_{Qh}$) ≡ $(n_{Qe}n_{Qh})^{1/2}$.

E-h pair density vs. T

In a pure semiconductor, there are equal numbers of conduction-band electrons and valence-band holes:

$$n_e = n_h \equiv n_i = n_Q e^{-\Delta/2kT}$$

This “intrinsic density” n_i clearly varies strongly with energy gap.

Some numerical values (at T = 300 K):

material	Δ(eV)	n_Q (meter^{-3})	n_i (meter^{-3})
Si	1.14	1.72×10^{25}	5.2×10^{15}
Ge	0.67	7.21×10^{24}	-
GaAs	1.43	2.63×10^{24}	-

Question:

Why aren’t the n_Q all equal? In particular, if you set $m = m_e$ in the formula, $n_Q = 1.27\times10^{25}$. The answer is that the effective mass of a hole is not equal to the effective mass of an electron (and even $m_{e,\text{effective}} \neq m_e$ 9.11×10^{-31}kg!), due to interactions with the lattice. Therefore, we will treat n_Q as an empirical quantity.

Exercise: Intrinsic Silicon

At 300 K the intrinsic carrier density in Si is $n_i = 5.2 \times 10^{15}/\mathrm{m}^3$, with a bandgap of $\Delta = 1.14$ eV, and quantum density $n_Q = 1.72 \times 10^{25}/\mathrm{m}^3$.

What is the carrier density at 150 K?

a. $4.3 \times 10^5/\mathrm{m}^3$ b. $3.4 \times 10^{10}/\mathrm{m}^3$ c. $2.6 \times 10^{15}/\mathrm{m}^3$

Solution

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$$n_e = n_i = n_Q\, e^{-\Delta/2kT}$$

$$\Rightarrow n_e\left(\tfrac{T}{2}\right) = n_Q\left(\tfrac{T}{2}\right) e^{-\Delta/2k(T/2)}$$

$$n_Q\left(\tfrac{T}{2}\right) = n_Q(T)\times\left(\tfrac{1}{2}\right)^{3/2} = 0.35\, n_Q(T)$$

→Change to $n_Q(T)$ relatively minor

$$e^{-\Delta/2k(T/2)} = e^{-1.14/2k(150)} = e^{-44.1} = 7\times10^{-20}$$

$$\Rightarrow n_e = 0.35(1.72\times10^{25})(7\times10^{-20}) = 4.3\times10^{5}\,/\text{m}^3$$

Exponential sensitivity to temperature!

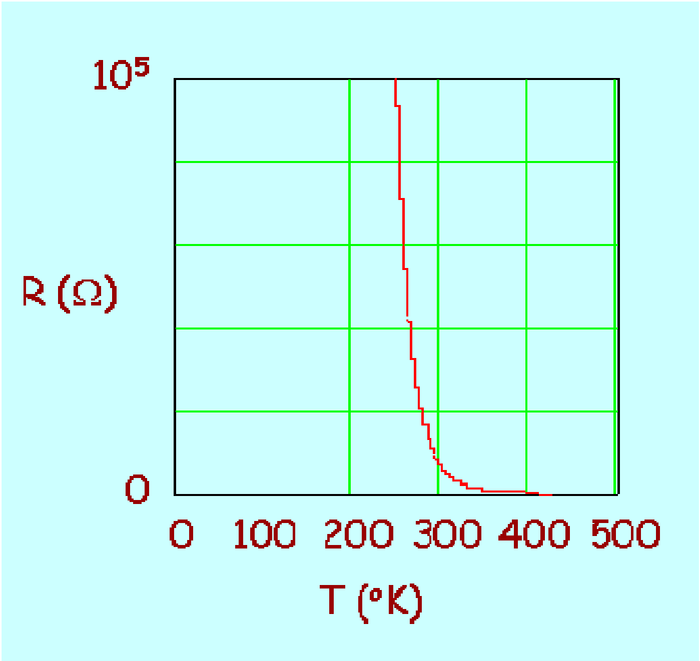
This is very rapid variation. To get a feeling for it, consider T → 301 K (an 0.3% change). Then 5.2 → 5.6 (a 7.6% change!)

For comparison, there are 5×10^{28} Si atoms/m^3

→ even at 300K only 10^{-13} electrons are excited.

Digital Thermometers

The rapid (exponential) variation of resistance with temperature is used to measure temperature. Many modern digital thermometers use a “thermistor”, a semiconductor device whose resistance depends on temperature.



Exercise: Other Semiconductors

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Ge: $n_i = n_Q e^{-0.67eV/2\times 0.026eV} = 1.8\times 10^{19}\,/\text{m}^3$

using $n_Q = 7.2\times 10^{24}\,/\text{m}^3$

GaAs: $n_i = n_Q e^{-1.43eV/2\times 0.026eV} = 3.0\times 10^{12}\,/\text{m}^3$

using $n_Q = 2.6\times 10^{24}\,/\text{m}^3$

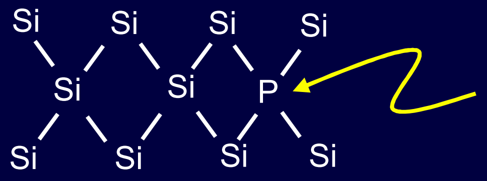
The difference is almost entirely due to the band gap.

Doping of Semiconductors

At T = 0, in a pure semiconductor the valence band is completely filled with electrons, and there are none in the conduction band. Suppose we replace one Si atom with a P atom. Phosphorous has one more electron, which is very weakly bound (its Δ is very small), and will almost certainly end up in the conduction band. Think of Shockley's garage. If we add one car, it will have to go into the upper level, and there are still no vacancies (holes) in the lower level. Phosphorus is called a "donor atom".

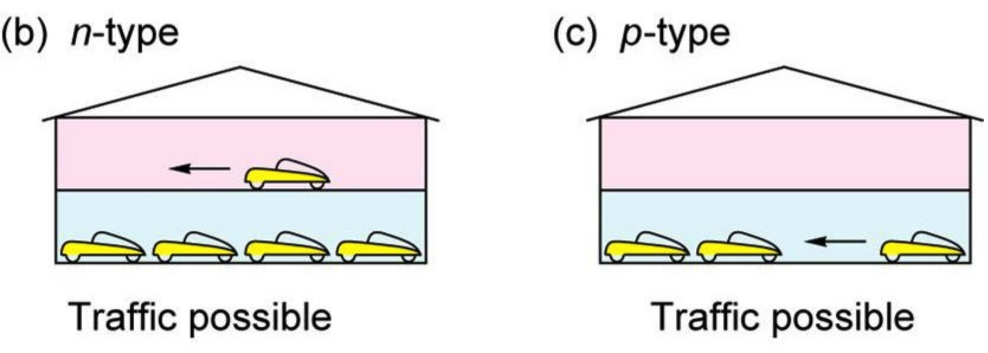
Silicon (Group IV)

Phosphorous (Group V)



An extra (free) electron.
No extra hole.

The addition of impurities that have a different number (more or fewer) of valence electrons is called doping. It can have a dramatic effect on the material's electrical properties.



More of Shockley's cartoon

With doping, we no longer have $N_e = N_h$.
Instead, $N_e = N_h + N_d$, where N_d is the number of donor atoms.

Act 2

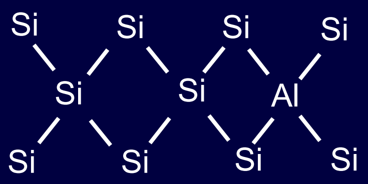
1. There are 5×10^{28} Si atoms/m^3. At 300 K, $n_{i,Si} = 5.2 \times 10^{15}/m^3$. If we replace one out of every million Si atoms with P, how much will the conductivity increase?

a) 10^4 b) 10^6 c) 10^7

2. We can also replace Si atoms with Al. Aluminum has one fewer electron than silicon. What is the relation between N_e and N_h in this case?

Silicon (Group IV)

Aluminum (Group III)



a) $N_e = N_h - N_{Al}$ b) $N_e = N_h$ c) $N_e = N_h + N_{Al}$

Solution

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a) 10^4 b) 10^6 [✓ c) 10^7]

$n_e = n_i + n_d = n_i + 10^{-6}\, n_{Si} \approx 10^{-6}\, n_{Si} = 5 \times 10^{22}/m^3$, 7 orders of magnitude more than with no doping.

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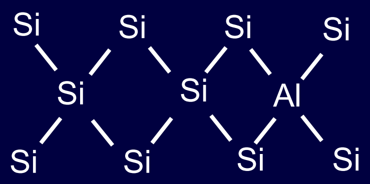

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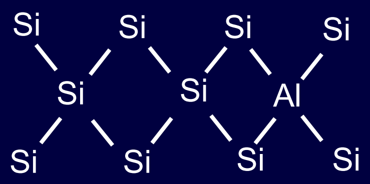

$\boxed{\text{a) } N_e = N_h - N_{Al}}$ b) $N_e = N_h$ c) $N_e = N_h + N_{Al}$

We are missing some valence electrons, so even when N_e (electrons in the conduction band) is zero, we have one hole per Aluminum atom.

Look at the “p-type” part of Shockley’s cartoon.

Aluminum is called an “acceptor atom”. In the equations, acceptors act like negative N_d.

Doping of Semiconductors (2)

We can follow the same procedure to minimize the free energy.
Assume $n_d \ll n_Q$. (This is called "light doping".) $\Delta F = 0$ implies that $\mu_e + \mu_h = 0$.
This is again like the vacancy-interstitial problem.

$$\mu_e + \mu_h = \Delta + kT\ln\left(\frac{n_e}{n_{Qe}}\right) + kT\ln\left(\frac{n_h}{n_{Qh}}\right) = 0$$

$n_e = n_h + n_d$
Assume: n_e and $n_h \ll n_Q$.

Solution: $\boxed{\frac{n_e n_h}{n_Q^2} = e^{-\Delta/kT}}$ or $\boxed{n_e n_h = n_i^2}$ ← This is an example of "the law of mass action".

"intrinsic pair density" $n_i = n_e = n_h$

$n_Q = (n_{Qe} n_{Qh})^{1/2}$

Typically, $n_d \gg n_i$. Therefore $n_e = n_i + n_d \approx n_d$.
Almost all of the "free" (conduction) electrons come from the dopant atoms.

For Si at T = 300 K:

$$\frac{n_e n_h}{n_Q^2} \approx 10^{-19}$$

If there were no doping, both n_e/n_Q and n_h/n_Q would be $\sim 3\times10^{-9}$.
Even a small amount of doping: $n_d/n_Q = 10^{-7}$, increases n_e dramatically and suppresses n_h. $n_e/n_Q \sim 10^{-7}$, $n_h/n_Q \sim 10^{-12}$.

In the I-V problem, adding interstitial atoms to a crystal reduces the number of vacancies.

Summary:

Particle equilibrium in Semiconductors

$$\Delta F = 0 \quad \rightarrow \quad \mu_e + \mu_h = 0 \quad \rightarrow \quad n_e n_h = n_Q^2 e^{-\Delta / kT}$$

if n_e and $n_h << n_Q$.

Pure (intrinsic) semiconductor

$n_e = n_h = n_i = n_Q\, e^{-\Delta/2kT}$ n_i is called the “intrinsic carrier concentration”

= intrinsic e-h pair concentration

Doped semiconductor

$n_e = n_h + n_d$

$n_e n_h = n_i^2$ The law of mass action.

This is valid for intrinsic and doped semiconductors.

Example: Law of Mass Action

The addition of impurities increases the crystal’s conductivity. Let’s add $n_d = 10^{24}/m^3$ phosphorous atoms to Si. Using the intrinsic carrier density, n_I, that we calculated for silicon, compute the density of holes, n_h , in this “doped” crystal.

Solution

The addition of impurities increases the crystal’s conductivity. Let’s add $n_d = 10^{24}/\text{m}^3$ phosphorous atoms to Si produces. Using the intrinsic carrier density, n_I, that we calculated for silicon, compute the density of holes, n_h , in this “doped” crystal.

$n_I = 5.2\times10^{15} << n_d$, so $n_e \approx n_d$.
This doping overwhelms the intrinsic carrier density.

$n_e \neq n_h$, but $\underbrace{n_e n_h = n_i^2}_{\text{Law of Mass Action}}$ still holds.

$$\Rightarrow \quad n_h = \frac{n_i^2}{n_e} = \frac{\left(5.2\times10^{15}\right)^2}{1\times10^{24}} = 2.7\times10^{7}\,/\text{m}^3$$

The addition of electrons has depressed the density of holes by over 8 orders of magnitude!

Question: Is 10^{24} atoms/m^3 a lot or a little?
Hint: There are 5×10^{28} Si atoms/m^3.

Act 3

Suppose you have a piece of “dirty” silicon, with lots of unwanted phosphorous impurities (making the conductivity too high because there are too many free electrons). What might you do to fix this?

a) dope with more phosphorous

b) dope with a different type of donor

c) dope with an acceptor atom, like boron

Solution

Suppose you have a piece of “dirty” silicon, with lots of unwanted phosphorous impurities (making the conductivity too high because there are too many free electrons). What might you do to fix this?

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Adding more donors will only make the problem worse. Adding more acceptor atoms, we increase the number of holes. Since $n_e n_h$ = constant, increasing the number of holes decreases the number of free electrons.

This technique is called “compensation”.

Next Monday

- Chemical equilibria - Law of mass action again
- Surface chemistry
- Phase equilibria and chemical potentials