Lecture 13

Doped Semiconductors

Suggested reading: 5.2-5.4
Why doping is good for semiconductor devices

Planar transistor

Intel’s new 3D transistor (May 2011)
Semiconductor conductivity

\[ \sigma = e n \mu_e + e p \mu_h \]

\( \sigma \) = conductivity, \( e \) = electronic charge, \( n \) = electron concentration in the CB

\( \mu_e \) = electron drift mobility, \( p \) = hole concentration in the VB, \( \mu_h \) = hole drift mobility
Semiconductor conductivity

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Intrinsic Semiconductor \( n \) in the CB & VB

\[
 n = N_c \exp\left[-\frac{(E_c - E_F)}{kT}\right] \\
p = N_v \exp\left[-\frac{(E_F - E_v)}{kT}\right]
\]

\( N_c \& N_v \) = effective electron/hole density of states at the band edge,  
\( E_c \) = conduction band edge, \( E_v \) = valence band edge, \( E_F \) = Fermi energy, \( k \) = Boltzmann constant, \( T \) = temperature

The product of \( n \) and \( p \) is a temperature-dependent constant:

\[
np = N_c N_v \exp\left(-\frac{E_g}{kT}\right) = n_i^2
\]

\( n_i \) = intrinsic carrier concentration
Fermi energy of intrinsic semiconductors

Recall for a metal that all levels up to the Fermi energy are filled with electrons. For an intrinsic semiconductor:

\[ n = p \quad \text{and} \quad n_i^2 = N_c N_v \exp\left(-\frac{E_g}{kT}\right) \]

Substitute \( p \) in for \( n_i \):

\[ p = N_v \exp\left[-\left(\frac{E_F - E_v}{kT}\right)\right] \]

\[ n_i = p = N_v \exp\left[-\left(\frac{E_{Fi} - E_v}{kT}\right)\right] = \sqrt{N_c N_v} \exp\left(-\frac{E_g}{2kT}\right) \]

We can rearrange this expression to find the Fermi level for an intrinsic semiconductor, \( E_{Fi} \)
Fermi energy of intrinsic semiconductors

\[ E_{Fi} = E_v + \frac{1}{2} E_g - \frac{1}{2} kT \ln \left( \frac{N_c}{N_v} \right) \]

\( E_{Fi} \) = Fermi energy in the intrinsic semiconductor, \( E_v \) = valence band edge, \( E_g = E_c - E_v \) is the bandgap energy, \( k \) = Boltzmann constant, \( T \) = temperature, \( N_c \) = effective density of states at the CB edge, \( N_v \) = effective density of states at the VB edge

Substituting our expressions for \( N_c \) and \( N_v \):

\[ E_{Fi} = E_v + \frac{1}{2} E_g - \frac{3}{4} kT \ln \left( \frac{m_e^*}{m_h^*} \right) \]

\( m_e^* \) = electron effective mass (CB), \( m_h^* \) = hole effective mass (VB)
Fermi energies: intrinsic & doped semiconductors

What happens to the hole concentration if I double the concentration of electrons (i.e., n-doping)?
Fermi energies: intrinsic & doped semiconductors

In all cases, $np = n_i^2$
Fermi energies: intrinsic & doped semiconductors

Intrinsic
\( (n=p) \)

\( p \)-type

\( n \)-type

In all cases, \( np = n_i^2 \)
Work function $\phi$ (for intrinsic & doped)

Work function: energy difference between vacuum and the Fermi energy.

**The energy required to remove an electron, even though there are no electrons at EF in a semiconductor. **
Average electron energy in the CB (intrinsic)

\[ \overline{E}_{\text{CB}} = E_c + \frac{3}{2} kT \]

Recall: \((3/2)kT\) is also the average kinetic energy per atom in a monatomic gas (kinetic molecular theory) in which the gas atoms move around freely and randomly inside a container.

The electron in the CB behaves as if it were “free” with a mean kinetic energy that is \((3/2)kT\) and an effective mass \(m_e^*\).

Very different from a metal, where the average energy is \(3/5 \ E_F\) and is practically temperature independent.
Doped (extrinsic) semiconductors

Modifying the carrier concentration (electrons or holes) with impurities

1. By adding impurities to Si that had a valency of more than 4 (i.e., the pentavalent elements of group V on the periodic table, such as As), we can obtain a semiconductor with $n \gg p$.

   $\rightarrow$ n-type doping

2. By adding trivalent impurities (like B), with a valency of less than 4, we can find an excess of holes

   $\rightarrow$ p-type doping
Doped (extrinsic) semiconductors

Arsenic-doped Si crystal. The four valence electrons of As allow it to bond just like Si, but the fifth electron is left orbiting the As site. The energy required to release the free fifth electron into the CB is very small.
n-type Doping (i.e., adding As, P, or Sb to Si)

For As: $\epsilon = 11.9$, $m_e^* \approx \frac{1}{3} m_e$  
$\Rightarrow E_D = 0.032$ eV  

Room temp vibrations ~ 0.07 eV

Add a small amount of impurity atoms (1 impurity atoms for every million host atoms) $\Rightarrow$ want to maintain diamond crystal structure

To ionize the impurity (i.e., release the electron into CB, free from it’s As host), we require energy:

$$E_D = 13.6 eV \left(\frac{m_e^*}{m_e}\right)\left(\frac{1}{\epsilon_r}\right)$$
Energy band diagram for an n-type Si doped with 1 ppm As. There are donor energy levels just below $E_c$ around As$^+$ sites.

At room temperature, $n \sim N_D$ (the donor atom concentration)
n-type Conductivity at room temperature

\[ np = n_i^2 \quad \rightarrow \quad n \sim N_D \quad \rightarrow \quad p = \frac{n_i^2}{N_d} \]

\[ \sigma = e n \mu_e + e p \mu_h \]

\[ \sigma = e N_D \mu_e + e \left( \frac{n_i^2}{N_D} \right) \mu_h \approx e N_D \mu_e \]
n-type Conductivity at LOW temperature

At low temperatures, not all the donors will be ionized $\rightarrow$ fewer electrons in CB than at room temperature.

$N_D^T =$ ionized donor concentration at temperature $T$

$N_D^T = N_D \times$ probability of not finding an electron at $E_D$

$$N_D^T = N_D \times [1 - f_D(E_D)]$$

$$f_D(E_d) = \frac{1}{1 + \frac{1}{2} \exp \left( \frac{(E_D - E_F)}{kT} \right)}$$

Can only take one electron (spin up or spin down, not both)
p-type Doping (i.e., adding B, Al, Ga, In to Si)

B has only three valence electrons. When B substitutes for a Si atom, one of its bonds has an electron missing and therefore a hole. The hole orbits around the B\(^+\) site by the tunneling of electrons from neighboring bonds. Eventually, thermally vibrating Si atoms provide enough energy to free the hole from the B\(^+\) site into the VB.
Energy band diagram for a $p$-type Si doped with 1 ppm B. There are acceptor energy levels $E_A$ just above $E_v$ around B$^-$ sites. These acceptor levels accept electrons from the VB and therefore create holes in the VB.
p-type Conductivity at room temperature

\[ np = n_i^2 \quad \rightarrow \quad p \sim N_A \quad \rightarrow \quad n = \frac{n_i^2}{N_A} \]

\[ \sigma = e n \mu_e + e p \mu_h \]

\[ \sigma = e \left( \frac{n_i^2}{N_A} \right) \mu_e + e N_A \mu_h \approx e N_A \mu_h \]
Example: Resistance of a doped Si crystal

Let’s calculate the resistance of a 1 cm³ pure Si crystal given:

Atomic concentration = $5 \times 10^{22}$ cm⁻³

$n_i = 1 \times 10^{10}$ cm⁻³

$\mu_e = 1350$ cm²/(Vs)

$\mu_h = 450$ cm²/(Vs)

$R = 347$ kΩ

Now, let’s dope this crystal with As, such that one atom in every billion is As. What is the resistivity at room temperature?

$R = 92.6$ Ω
Compensation Doping (at room temperature)

To precisely control a semiconductor’s properties, we can dope with both donors (contribute electrons) and acceptors (contribute holes).

More donors than acceptors \( N_d - N_a \gg n_i \)

\[
n = N_d - N_a \quad \quad \quad \quad \quad \quad p = \frac{n_i^2}{n} = \frac{n_i^2}{N_d - N_a}
\]

More acceptors than donors \( N_a - N_d \gg n_i \)

\[
p = N_a - N_d \quad \quad \quad \quad \quad \quad n = \frac{n_i^2}{p} = \frac{n_i^2}{N_a - N_d}
\]
Temperature Dependence of Conductivity

- Main application: Thermoelectric coolers (move heat away from a source) & thermoelectric switches/modulators
Temperature Dependence of Conductivity

Depends on two properties:
1. The temperature dependence of the carrier concentration
2. The temperature dependence of the mobility
Carrier concentration versus $T$

Low temperature: some donors are being ionized. Ionization continues with increasing temperature until all donors have been ionized.
Intermediate temperature: nearly all donors have been ionized. At a temperature $T_i$, $n_i$ becomes equal to $N_D$. 

$T < T_s$  $T_s < T < T_i$
Carrier concentration versus $T$

High temperature: The concentration of electrons generated by thermal excitation of electrons across $E_g$ exceeds $N_D$. The semiconductor behaves as if it were intrinsic.

$\Rightarrow n = n_i(T)$ and $p = n$ (“intrinsic range”)
Carrier concentration versus T: Low temperature

Combine:

1. Charge carrier statistics: \( n = N_C \exp\left[-(E_C - E_F)/kT\right] \)

2. Mass action law: \( np = n_i^2 \)

3. Electric neutrality of the crystal: \( p + N_{D^+} = n \)

4. Statistics of ionization of dopants: \( N_D^T = N_D \times [1 - f_D(E_D)] \)

\[
n = \left( \frac{1}{2} N_C N_D \right)^{1/2} e^{-\Delta E/(2kT)} \quad \Delta E = E_C - E_D
\]
Carrier concentration versus T: Medium and high temperature

Medium temperature: \[ n \sim N_D \]

High Temperature: \[ n = n_i(T) \]
\[ n \sim T^{3/2} e^{-E_g/(2kT)} \]

Low Temperature:
\[ n = \left( \frac{1}{2} N_C N_D \right)^{1/2} e^{-\Delta E/(2kT)} \]
The temperature dependence of the electron concentration in an $n$-type semiconductor.
Temperature Dependence of Conductivity

Depends on two properties:
1. The temperature dependence of the carrier concentration
2. The temperature dependence of **mobility**
Mobility

Two temperature ranges:

1. High temperatures: limited by scattering from lattice vibrations

2. Low temperatures: limited by Coulombic attraction between carriers and ionized impurities
High temperature Mobility

Electron drift mobility depends on mean time between scattering events:

\[ \mu_d = \frac{e \tau}{m_e} \]

\[ \tau = \frac{1}{S \nu_{th} N_s} \]

Cross-sectional area of the scatterer

Mean speed of electrons (thermal velocity)

# scatterers per unit volume
High temperature Mobility

\[
\tau = \frac{1}{S \nu_{th} N_s}
\]

\[
S = \pi a^2 \propto T
\]

Also, since an electron in the conduction band is free:

\[
\frac{1}{2} m^* \nu_{th}^2 = \frac{3}{2} kT
\]

\[
\nu_{th} \propto T^{1/2}
\]

\[
\mu \propto \tau \propto \frac{1}{T \sqrt{T}} \propto T^{-3/2}
\]
Low temperature Mobility

Electron drift mobility limited not by scattering events, but by interactions with ionized impurities:

\[ KE = \frac{1}{2} m_e v^2 \quad KE > |PE| \]

\[ KE \approx |PE| \]

Scattering of electrons by an ionized impurity.
Low temperature Mobility

Scattering cross section:

\[ S = \pi r_c^2 \]

Critical radius for scattering given by \( KE = |PE(r_c)| \)

\[ \frac{3}{2} kT = \frac{e^2}{4\pi \varepsilon_0 \varepsilon_r r_c} \]

\[ S \propto \frac{1}{T^2} \]

\[ \mu = \tau = \frac{1}{S v_{th} N_I} \propto \frac{1}{T^{-2} T^{1/2} N_I} \propto \frac{T^{3/2}}{N_I} \]

\# ionized impurities
Lattice-Scattering-Limited Mobility (High Temp)

\[ \mu_L \propto T^{-3/2} \]

\( \mu_L \) = lattice vibration scattering limited mobility, \( T \) = temperature

Ionized Impurity Scattering Limited Mobility (Low Temp)

\[ \mu_I \propto \frac{T^{3/2}}{N_I} \]

\( \mu_I \) = ionized impurity scattering limited mobility, \( N_I \) = concentration of the ionized impurities (all ionized impurities including donors and acceptors)
Overall Mobility

\[
\frac{1}{\mu_e} = \frac{1}{\mu_I} + \frac{1}{\mu_L}
\]

\(\mu_e = \) effective drift mobility

\(\mu_I = \) ionized impurity scattering limited mobility (low temperature)

\(\mu_L = \) lattice vibration scattering limited mobility (high temperature)

The scattering process having the lowest mobility determined the overall effective mobility.
Log-log plot of drift mobility versus temperature for $n$-type Ge and $n$-type Si samples. Various donor concentrations for Si are shown. $N_d$ are in cm$^{-3}$.

The upper right inset is the simple theory for lattice limited mobility, whereas the lower left inset is the simple theory for impurity scattering limited mobility.
The variation of the drift mobility with dopant concentration in Si for electrons and holes at 300 K.
Temperature Dependence of Conductivity

Depends on two properties:
1. The temperature dependence of the carrier concentration
2. The temperature dependence of the mobility