Lecture 6
Defects 1
Schroder: Chapter 5

Announcements
Homework 1/6:
• Is online now.
• Due Monday 23rd April at the start of the lecture (10:00am).
• I will return it one week later (30th April).
Homework 2/6:
• Will be posted online on Monday 23rd April.
• Due Monday 30th April at the start of the lecture (10:00am).
• I will return it one week later (7th May).
Lecture 6

• Shallow Doping.
• Deep Impurities (Traps).
• Deep Level Dynamics.

Shallow Doping
Doping

• Semiconductors are useful materials because we can intentionally and reproducibly modify their conductivity by doping with impurity atoms which have shallow ionization levels.

Interstitial

Substitutional

Doping

• Typically, we dope with a substitutional (versus interstitial) impurity atom which has either one more or one less valence electron than the atom which it replaces.
  • The atom is called a donor if it has an extra electron.
  • The atom is called an acceptor if it is electron deficit (hole).
Doping

- The idea is that the electrons associated with the substitutional impurity atom all go into forming chemical bonds with neighboring atoms.
- We are left with one extra (donor) or one less (acceptor) electron which is only weakly held to the impurity, so that it is easily ionized.

\[
\begin{array}{c}
\text{Si} \\
\text{Si} \\
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\text{Si} \\
\text{Si} \\
\text{Si} \\
\text{Si} \\
\text{Si} \\
\end{array}
\]

E\text{C}

\[e^-\]

\[E_D\]

\[E_A\]

\[h^+\]

\[E_V\]

Doping

- Many doping and defect trends can be rationalized, and to a certain extent predicted if you understand these simple doping trends.

<table>
<thead>
<tr>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>Al</td>
<td>Ag</td>
<td>In</td>
</tr>
<tr>
<td>Zn</td>
<td>Cd</td>
<td>Hg</td>
<td>Sn</td>
</tr>
<tr>
<td>B</td>
<td>Si</td>
<td>Ga</td>
<td>Sb</td>
</tr>
<tr>
<td>C</td>
<td>P</td>
<td>Ge</td>
<td>As</td>
</tr>
<tr>
<td>N</td>
<td>S</td>
<td>As</td>
<td>Se</td>
</tr>
<tr>
<td>O</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Note that these simple substitutional doping rules do not always work (especially in compound semiconductors – e.g. III-V’s).
Types of Dopants

- Use the following notation to denote more complicated donors and acceptors in an energy band diagram.

\[ \text{double donor} \]
\[ \text{double acceptor} \]
\[ \text{amphoteric} \]

Shallow Dopants

- Shallow levels may be understood within the framework of effective mass theory, which asserts (for a donor) that the electron is only weakly bound to the impurity atom by a spherically symmetric Coulombic potential.

- Thus, we have a Schrödinger equation for a shallow impurity which looks like:

\[ E\psi = -\frac{\hbar^2}{2m^*}\psi - \frac{e^2}{4\pi\varepsilon_0\varepsilon_r}\psi \]

- This is simply the Schrödinger equation for the hydrogen atom, except that the effective mass replaces the rest mass, and the dielectric constant of the semiconductor replaces the dielectric constant of free space.
Shallow Dopants

\[ E\psi = -\frac{\hbar}{2m^*}\psi - \frac{q^2}{4\pi\varepsilon_0\varepsilon_r}\psi \]

- \( E \): Particle energy.
- \( \psi \): Particle wavefunction.
- \( m^* \): Particle effective mass.
- \( \hbar \): Reduced Planck Constant (\( h \)-bar).
- \( q \): Fundamental unit of charge.
- \( \varepsilon_0 \): Permittivity of free space.
- \( \varepsilon_r \): Relative permittivity.

Binding Energy

- The hydrogen atom problem is well known, so we can just give the result:
  \[ E_1 = \frac{m^*}{m_e} \left( \frac{\varepsilon_0}{\varepsilon_r} \right)^2 \times 13.5 \text{ eV} \]
- \( E_1 \): Binding energy.
- \( m^* \): Effective mass of particle.
- \( m_e \): Rest mass of electron.
- \( \varepsilon_0 \): Permittivity of free space.
- \( \varepsilon_r \): Relative permittivity.
Effective Orbital Radius

- The hydrogen atom problem is well known, so we can just give the result:
  \[ a_1 = \frac{\varepsilon_r m_e}{\varepsilon_0 m^*} \times 0.053 \text{nm} \]

- \( a_1 \): Effective orbital radius.
- \( m^* \): Effective mass of particle.
- \( m_e \): Rest mass of electron.
- \( \varepsilon_0 \): Permittivity of free space.
- \( \varepsilon_r \): Relative permittivity.

Example Values

<table>
<thead>
<tr>
<th>Semiconductor</th>
<th>Level Type</th>
<th>( E_1 ) (meV)</th>
<th>( a_1 ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>Donor</td>
<td>25</td>
<td>2.4</td>
</tr>
<tr>
<td>Si</td>
<td>Acceptor</td>
<td>35</td>
<td>1.7</td>
</tr>
<tr>
<td>GaAs</td>
<td>Donor</td>
<td>5</td>
<td>10.4</td>
</tr>
<tr>
<td>GaAs</td>
<td>Acceptor</td>
<td>27</td>
<td>2.0</td>
</tr>
</tbody>
</table>

- The orbital radius of the loosely bound electron or hole is substantially greater than the atomic size, i.e., ~0.1 nm.
- I.e. it is free to move throughout the crystal.
Notes

• Note that according to effective mass theory, the ionization energy depends only on the effective mass and the dielectric constant, but is independent of the impurity atom.
• Effective mass theory usually yields surprisingly good results for simple substitutional impurities with one extra or missing electron.
• For more precision, however, simple theory has to be refined to account for the chemical shift, i.e., the discrepancy between theory and experiment.

Notes

• Actual binding energies are usually larger than that obtained from effective mass theory due to a stronger Coulombic attraction when the electron is near the nucleus.
• Basically, the concept of bulk dielectric screening breaks down, as implicit by the use of the dielectric constant, when the electron orbits near to the nucleus.
Deep Impurities (Traps)

Deep-Level Impurities

- Deep levels are likely to form when a substitutional impurity has an electronic structure much different than the atom which it replaces.
- Transition metal impurities (e.g. Fe, Ni, Cu, Au) in covalent semiconductors are obvious examples.
- Impurities occupying interstitial sites are likely candidates, as are native point defects such as vacancies, self-interstitials, and antisite defects.
Deep-Level Impurities

Vacancies

\[
\begin{array}{c}
\text{Si} \\
\text{Si} \\
\text{Si} \\
\text{Si} \\
\text{Si}
\end{array}
\]

Interstitials

\[
\begin{array}{c}
\text{Si} \\
\text{Si} \\
\text{Si} \\
\text{Si} \\
\text{Si}
\end{array}
\]

Self-Interstitials

\[
\begin{array}{c}
\text{Si} \\
\text{Si} \\
\text{Si} \\
\text{Si} \\
\text{Si}
\end{array}
\]

Antisite Defects

\[
\begin{array}{c}
\text{Ga} \\
\text{Ga} \\
\text{Ga} \\
\text{Ga} \\
\text{Ga}
\end{array}
\]

Definition 1

- There is no commonly accepted definition of exactly what determines a deep level.
- We will go through a few definitions.
- **Definition 1**: A level is deep if its binding energy is greater than 0.1 eV.
- The idea here is that if the trap energy is significantly greater than the thermal energy, the level is not readily thermally ionized at room temperature and, thus, acts like a trap.
Definition 2

- **Definition 2:** A level is deep if it is non-effective-mass-like.
- Theorists have shown that simple effective mass theory can break down even when the ionization energy is small or when the level is resonant with the conduction or valence band density of states.
- The issue is that the breakdown of effective mass theory is due to localization of the electron (hole) by a strong, atomic-like potential.

Definition 3

- **Definition 3:** A level is deep if it is important in non-radiative recombination, i.e., Shockley-Read-Hall recombination.
- The emphasis here is on how the level affects the concentration of free carriers.
- An intriguing aspect of deep levels is that a carrier trapped at a deep level is strongly localized in real space, which means that it must be strongly delocalized in k-space.
Definition 3

- An intriguing aspect of deep levels is that a carrier trapped at a deep level is strongly localized in real space, which means that it must be strongly delocalized in k-space.

Why are deep levels important?

- **1**: Deep levels can control the minority carrier lifetime, an important device parameter.
  - For an n-type semiconductor with one shallow level and one deep level separated by 0.4 eV, the lifetime is controlled by the deep level even if its concentration is 6 orders of magnitude smaller!
- **2**: Deep levels control the luminescent efficiency of LEDs and LASERs.
- **3**: Deep levels can control the carrier concentration and, thus, yield semi-insulating materials.
- **4**: Deep levels can cause device instabilities and reliability problems.
Band Diagram

- For a perfect single crystal semiconductor, we consider a valence band and conduction band separated by a forbidden energy region (band gap).
- When the periodicity of a single crystal is perturbed by foreign atoms or crystal defects, discreet states are introduced into the band gap ($E_T$):

\[ E_C \]

\[ E_V \]

Band Diagram

- There are four possible interactions between a deep level and delocalized electrons or holes.

(a) e\textsuperscript{-} capture
(b) e\textsuperscript{-} emission
(c) h\textsuperscript{+} capture
(d) h\textsuperscript{+} emission

Capture coefficient for electrons
Emission coefficient for electrons
Capture coefficient for holes
Emission coefficient for holes
Trap Occupancy

- Let’s consider thermal emission quantitatively.
- $N_T = \text{Number density of traps (e.g. cm}^{-3}\text{).}$
- $N_T f_T = \text{Number density of filled traps (e.g. cm}^{-3}\text{).}$
- $N_T (1 - f_T) = \text{Number density of empty traps (e.g. cm}^{-3}\text{).}$
- The trap occupancy ($f_T$) is defined in terms of Fermi-Dirac statistics:

$$f_T = \frac{1}{1 + \exp\left(\frac{E_T - E_F}{k_B T}\right)}$$

Capture Rate

- The rate of electron capture is proportional to the delocalized electron concentration in the conduction band times the number of empty traps.

$$r_a = \sigma_n n v_{th} n N_T (1 - f_T)$$

- $r_a = \text{Rate of electron capture.}$
- $\sigma_n = \text{Electron capture cross-section (e.g. cm}^2\text{).}$
- $n = \text{Effective area of defect.}$
- $v_{th} = \text{Electron thermal velocity.}$
- $n = \text{Delocalized electron density in conduction band.}$
- $N_T (1 - f_T) = \text{Number density of empty traps.}$
Thermal Velocity

- This is how fast electrons move.
- It may be found by setting the electron kinetic energy to its thermal energy, which leads to:

\[ v_{th} = \sqrt{\frac{3k_B T}{m^*}} \]

- Note that the thermal velocity depends on the (conductivity) effective mass of the carrier.
- Thus, in general, the thermal velocity of an electron is different than that of a hole.

Thermal Velocity

- It turns out that this leads to some additional complexity in analytical treatments.
- To circumvent this problem, we will assume that this effective mass contribution to the thermal velocity is included in the capture cross-section and that the thermal velocity is always determined by the electron rest mass.
- Most analytical treatments adopt this or a similar strategy.
Capture Cross Section

Classical coulombic trapping model

\[ \sigma_{\text{neutral}} \approx 10^{-15} \text{ cm}^2 \]
\[ \sigma_{\text{attractive}} \approx 10^{-12} \text{ cm}^2 \]
\[ \sigma_{\text{repulsive}} \approx 10^{-18} \text{ cm}^2 \]

Emission Rate

- The rate of electron emission is proportional to the number of filled traps, leading to
  \[ r_b = e_n N_T f_T \]
- \( r_b \) = Rate of electron emission.
- \( e_n \) = Proportionality constant equal to the rate at which a single electron in an occupied trap will jump into the conduction band.
- \( N_T f_T \) = Number density of filled traps.
Emission Rate

- We evaluate $e_n$ by considering equilibrium, in which case we apply the principle of detailed balance, i.e., the rate of a process and its inverse are equal for a system in equilibrium.

\[ r_a = r_b \]
\[ \sigma_n v_{th} n N_T (1 - f_T) = e_n N_T f_T \]

\[ e_n = \sigma_n v_{th} n \frac{1 - f_T}{f_T} \]  
(1)

Emission Rate

- Recall we describe occupancy by Fermi-Dirac statistics:

\[ f_T = \frac{1}{1 + \exp \left( \frac{E_T - E_F}{k_B T} \right)} \]

- We can re-arrange:

\[ 1 + \exp \left( \frac{E_T - E_F}{k_B T} \right) = \frac{1}{f_T} \quad \Rightarrow \quad \exp \left( \frac{E_T - E_F}{k_B T} \right) = \frac{1}{f_T} - 1 \]

\[ \frac{1 - f_T}{f_T} = \exp \left( \frac{E_T - E_F}{k_B T} \right) \]  
(2)
Emission Rate

• If we assume that we have nondegenerate conditions with respect to electrons in the conduction band, we have:

\[ n = N_c \exp\left( -\frac{E_C - E_F}{k_b T} \right) \]  

(3)

• Combining Equations (1), (2) and (3) gives us:

\[ e_n = \sigma_n v_{th} N_c \exp\left( -\frac{E_C - E_T}{k_b T} \right) \]

• This is a very important equation, the basis of DLTS (deep-level transient spectroscopy) – Next Lecture.

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Emission Rate

• We can (but won’t) derive a similar expression for holes:

\[ e_p = \sigma_p v_{th} N_V \exp\left( -\frac{E_T - E_V}{k_b T} \right) \]

• Note that the emission time, \( \tau_{i,em} \), which is the average time that a carrier spends in the trap before it is emitted into the conduction band, is given by:

\[ \tau_{n,em} = \frac{1}{e_n} \]  
\[ \tau_{p,em} = \frac{1}{e_p} \]
**Hole Traps**

- To complete our discussion of deep levels in a space charge region, note that the rate of capture of holes is proportional to the number of holes in the valence band times the number of deep levels which are filled with electrons, leading to:

\[ r_c = \sigma_p v_{th} p N_T f_T \]

- \( r_c \) = Rate of hole capture.
- \( \sigma_p \) = Hole capture cross-section (e.g. cm\(^2\)).
- \( v_{th} \) = Hole thermal velocity.
- \( p \) = Delocalized hole density in valence band.

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**Hole Traps**

- Also, the rate of hole emission is proportional to the number of empty traps, yielding:

\[ r_d = e_p N_T (1 - f_T) \]

- \( r_d \) = Rate of hole emission.
- \( e_p \) = Proportionality constant equal to the rate at which a single hole in an occupied trap will fall into the valence band.
- \( N_T (1 - f_T) \) = Number density of empty traps.
Deep Level Dynamics

The Continuity Equation

• When we quantitatively describe semiconductor materials or devices, we typically begin by employing the continuity equation.

• Our goal here is to initially develop a differential equation for deep level dynamics, and to then consider a few solutions to this differential equation.

\[
\frac{dn}{dt}_{GR} = r_b - r_a = e_n n_T - c_n n p_T
\]

Rate of electron emission
Rate of electron capture
Rate of change of carrier density
Denotes generation-recombination (we are not considering bimolecular or Auger)
Delocalized electron density in conduction band.
Electron Capture Coefficient

\[
\frac{dn}{dt}_{GR} = r_b - r_a = e_n n_T - c_n n p_T
\]  (4)

- \(c_n\) is the electron capture coefficient.
- \(c_n = \sigma_n v_{th}\)
- Has units of volume/time, e.g. \(\text{cm}^3\text{s}^{-1}\).
- \(\sigma_n\): Capture cross-section (e.g. \(\text{cm}^2\)).
- \(v_{th}\): Electron thermal velocity (e.g. \(\text{cm/s}\)).
- An equivalent expression exists for holes.
  \(c_p = \sigma_p v_{th}\)

Number density of traps

\[
\frac{dn}{dt}_{GR} = r_b - r_a = e_n n_T - c_n n p_T
\]

- Instead of explicitly showing the Fermi-Dirac occupancy function, recognize that the total trap concentration \(N_T\) is equal to a sum of the concentration of traps filled \(n_T\) and not filled with electrons \(p_T\).
  \[N_T = n_T + p_T\]
- This is just a notational difference.
Holes

- A similar continuity equation for the hole concentration in the case of generation-recombination via a deep level is given by:

\[
\frac{dp}{dt}_{GR} = r_d - r_c = e_p p_T - c_p p n_T
\]  

(5)

- \(p\) = Delocalized hole density in valence band.
- \(r_c\) = Rate of hole capture.
- \(r_d\) = Rate of hole emission.
- \(e_p\) = Proportionality constant.
- \(c_p\) = the hole capture coefficient.

The Continuity Equation

- From these continuity equations for delocalized electrons (Equation (4)) and holes (Equation (5)), a deep level continuity equation can be written as:

\[
\frac{dn_T}{dt}_{GR} = \frac{dp}{dt} - \frac{dn}{dt} = (c_n n + e_p)(N_T - n_T) - (c_p p + e_n)n_T
\]

- This is our differential equation describing deep level dynamics.
- In general, we cannot obtain an analytical solution to this differential equation, since it is nonlinear, i.e., both \(n\) and \(p\) are time-dependent.
The Continuity Equation

\[
\frac{dn_T}{dt} = \frac{dp}{dt} - \frac{dn}{dt} = (c_n n + e_p)(N_T - n_T) - (c_p p + e_n)n_T
\]

• However, this equation can be readily solved if it is linearized.
• Linearization is possible for the case of:
  1. A reverse-biased space charge region, in which case both \( n \) and \( p \) may be neglected \((n = p = 0)\).
  2. A quasi-neutral region, in which case \( n \) and \( p \) are time-independent.

The solution to the quasi-neutral region case is given by

\[
n_T(t) = n_T(0)e^{-t/\tau} \frac{(e_p + c_n n)N_T}{e_n + c_n n + e_p + c_p p} \left[ 1 - e^{-t/\tau} \right]
\]

\( n_T(0) \) is the density of occupied deep levels at \( t = 0 \).

\[
\tau = \frac{1}{e_n + c_n n + e_p + c_p p} \tag{6}
\]

• In steady-state, the solution simplifies to:

\[
n_T(t \to \infty) = \frac{(e_p + c_n n)N_T}{e_n + c_n n + e_p + c_p p} \tag{7}
\]
The Continuity Equation

• It is evident from this equation that the steady-state deep level occupancy depends on the electron and hole densities and on the emission and capture rates.

• These last two equations ((6) and (7)) underlie most deep level characterization measurements.
  • See next lecture.

Next Time...

• Defect Characterization
  • Classification of defects.

  $E_T \rightarrow E_C \rightarrow E_V$

  Electron trap

  $E_T \rightarrow E_C \rightarrow E_V$

  Recombination center

  $C(t, T)$

  Deep level transient spectroscopy (DLTS):