TODAY’S LECTURES

Energy Band Structure in Semiconductors
- Electrons in Periodic Potential
- Band Structure of Selected Semiconductors
- Band Gaps in Alloy Semiconductors
- Systematics of Semiconductor Band Caps
- Electron Dispersion
- Holes
- Density of States

Electrical Defect States in Semiconductors
- Dopants
- Fermi Distribution
- Charge Carrier Concentration
- Donors and Acceptors
ENERGY BAND STRUCTURE
REVOLUTION: BONDS

- Wave functions $\psi$ of valence electrons overlap as atoms in semiconductor crystal come closer to each other.

- In other words:
  - Atoms, electrons have quantized energy values;
  - Solids, electrons have a range of available energies because of the overlapping of wave functions.
REVISION: CRYSTALS / DIRECT LATTICE

- **Diamond** crystal structure (a) is typical to many elemental semiconductors, e.g. C, Si, Ge.
- **Zincblende** structure (b) is typical to many compound semiconductors, e.g. GaAs (III-V), CdTe (II-VI).

  - Both are as two interpenetrating fcc (face-centered-cubic) lattices.
  - The primitive cell, or **direct lattice**, has lattice constant $a$.
  - Each atom has tetrahedral configuration (c).
  - One primitive cell has totally eight atoms.
In the reciprocal, or k-space, or momentum space, the Wigner-Seitz cell, or the [first] Brillouin zone, presents the wave function of the original lattice.

The Brillouin zone of fcc lattice is truncated octahedron.

Special k points:
- \( \mathbf{k} = 0 \) @ \( \Gamma \);
- \( \mathbf{X} \) in [001] direction; \( \mathbf{K} \) for [110]; \( \mathbf{L} \) for [111];
- Paths: \( \Delta \): \( \Gamma - \mathbf{X} \) (2\( \pi \)/\( a \)); \( \Sigma \): \( \Gamma - \mathbf{K} \) (\( \sqrt{2} \pi \)/\( a \)); \( \Lambda \): \( \Gamma - \mathbf{L} \) (\( \sqrt{3} \pi \)/\( a \)).
- \( a \) is the lattice constant of the direct lattice.

http://www.iue.tuwien.ac.at/phd/dhar/node18.html
ELECTRONS IN PERIODIC POTENTIAL

- Valence electrons moving in periodic crystals (e.g. semiconductors) feel periodic potential $U(r)$ for all vectors $R$ of the direct lattice:

$$U(r) = U(r + R)$$

- $R = ma_1 + na_2 + oa_3$, where $m$, $n$, $o$ are integers

- The potential $U(r)$ is due to the effect of [positive] ion cores and other [negative] electrons.

- The wave function $\Psi(r,k)$ of an electron in periodic potential can be solved from Schrödinger equation:

$$H\Psi(r) = \left[-\frac{\hbar^2}{2m} \nabla^2 + U(r)\right]\Psi(r) = E\Psi(r)$$
ELECTRONS IN PERIODIC POTENTIAL

According to Bloch’s theorem, the solutions (i.e. eigenstates) $\Psi(r,k)$ / $\Psi_{nk}(r)$ can be written as the product of plane waves $Ae^{ikr}$ and a lattice-periodic function $u(r,k)$ / $u_{nk}(r)$:

$$\Psi_{nk}(r) = Ae^{ikr}u_{nk}(r)$$

Here, the normalization constant $A$ is often omitted.

Here, $n$ is quantum number and $k$ is wave vector.

Here, the Bloch’s function $u_{nk}$ is periodic with the lattice:

$$u_{nk}(r) = u_{nk}(r + R)$$

For all vectors $R$ in direct lattice.
ELECTRONS IN PERIODIC POTENTIAL

- If $E_{nk}$ is an energy eigenvalue, then $E_{nk+G}$ is also an eigenvalue for all vectors $G$ in reciprocal lattice:

$$E_n(k) = E_n(k + G)$$

- $G = pb_1 + qb_2 + rb_3$ & $G \cdot R = 2\pi s$, where $p$, $q$, $r$, $s$ are integers.
- Thus, the energy band structure is periodic in reciprocal space.
- Energy eigenvalues can be solved numerically [for one k-direction]:

Note the energy gaps.

http://www.damtp.cam.ac.uk/user/tong/aqm/aqmtwo.pdf

Figure 19: The extended zone scheme.

Figure 20: The reduced zone scheme.
Thus, as the result of the periodicity of crystals, many levels of energy are possible for a given wave number \( k \) and some energies are not possible for any \( k \).

The collection of all possible energies as the function of \( k \) is the energy band structure of a material.

In three dimensions, the band structure is typically shown along particular paths in the Brillouin zone.
PERIODIC POTENTIAL: KRONIG-PENNEY MODEL

- Kronig-Penney model is simplified and easily solvable quantum mechanical model for studying electrons in crystals.
- Periodic potential function is approximated by an infinite array of one-dimensional hard-wall potential barriers of finite height.

https://www.slideshare.net/KMMonir52/chapter3-introduction-to-the-quantum-theory-of-solids
PERIODIC POTENTIAL: KRONIG-PENNEY MODEL

- Solutions to the Schrödinger equation are well known:

\[
-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x)}{\partial x^2} + U(x)\Psi(x) = E\Psi(x)
\]

\[
0 < x < a : \quad \Psi(x) = A e^{iKx} + B e^{-iKx} \\
a < x < a + b : \quad \Psi(x) = C e^{\kappa x} + D e^{-\kappa x}
\]

\[
K^2 = \frac{2mE}{\hbar^2} > 0; \quad \kappa^2 = \frac{2m(U_0 - E)}{\hbar^2} > 0
\]

- Boundary conditions:
\(\psi\) & \(\psi'\) continuous
@ \(x=0\) & \(x=a\)
\(\rightarrow\) A, B, C, D.

- Then, after some tedious algebra, incl. simplifications \(\rightarrow E(k)\).
ENERGY BANDS OF SEMICONDUCTORS

- The band below the band gap is called valence band. The band above the band gap is conduction band.
- No energy states exist in the band gap $E_g$. It is one of the most important parameters in semiconductor physics.
- Valence band maximum for most semiconductors is at the $\Gamma$ point. Minimum of the conduction band may vary.
- Typically in semiconductors the band gap $E_g \sim 0.2 – 2$ eV.
BAND STRUCTURE / SILICON

- In silicon (Si), the minimum of the conduction band is close to the X point at \(0.85\pi/a\) in the <100> direction.
- Thus, not in the same point in \(k\) space as the top of the valence band.
- Thus, silicon has indirect band structure.
- \(E_g = 1.12\) eV (300K)
Germanium has indirect band structure.

The conduction band minima are at the L point in the <111> direction.

\[ E_g = 0.66 \text{ eV (300K)} \]
BAND STRUCTURE / GALLIUM ARSENIDE

- Gallium Arsenide (GaAs) has direct band gap.
- The top of the valence band and the bottom of the conduction band are at the same position in k space at Γ point.
- \( E_g = 1.43 \text{ eV (300K)} \)
SEMICONDUCTOR
BAND GAPS

Semiconductor Band Gaps

<table>
<thead>
<tr>
<th>Material</th>
<th>Energy gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0K</td>
</tr>
<tr>
<td>Si</td>
<td>1.17</td>
</tr>
<tr>
<td>Ge</td>
<td>0.74</td>
</tr>
<tr>
<td>InSb</td>
<td>0.23</td>
</tr>
<tr>
<td>InAs</td>
<td>0.43</td>
</tr>
<tr>
<td>InP</td>
<td>1.42</td>
</tr>
<tr>
<td>GaP</td>
<td>2.32</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.52</td>
</tr>
<tr>
<td>GaSb</td>
<td>0.81</td>
</tr>
<tr>
<td>CdSe</td>
<td>1.84</td>
</tr>
<tr>
<td>CdTe</td>
<td>1.61</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.44</td>
</tr>
<tr>
<td>ZnS</td>
<td>3.91</td>
</tr>
</tbody>
</table>

http://hyperphysics.phy-astr.gsu.edu/hbase/tables/semgap.html
ENERGY BANDS OF ALLOY SEMICONDUCTORS

- Alloy semiconductor is a mixture of several compounds.
- Band gap $E_g$ and lattice constant $a_0$ depend on the composition.
- In alloy semiconductors, the band gap can be tuned i.e. for applications in optoelectronics.
Systematics of Band Gaps

- The trend of semiconductor band gaps $E_g$ is explained by bond strength and ionicity.

- $E_g$ decreases with decreasing bond strength, i.e. increasing lattice constant, e.g. $E_g$(C) > $E_g$(Si) > $E_g$(Ge).

- For the same lattice constant, $E_g$ increases with increasing ionicity, i.e. $E_g$(IV-IV) < $E_g$(III-V) < $E_g$(II-VI).
BAND GAP VS. TEMPERATURE

- Band gap $E_g$ typically decreases with increasing temperature $T$.
- The reasons are the change of electron-phonon interaction and the expansion of the lattice.

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{T + \beta}$$

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_g(0)$ (eV)</th>
<th>$\alpha$ (meV/K)</th>
<th>$\beta$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Germanium</td>
<td>0.7437</td>
<td>0.477</td>
<td>235</td>
</tr>
<tr>
<td>Silicon</td>
<td>1.166</td>
<td>0.473</td>
<td>636</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.519</td>
<td>0.541</td>
<td>204</td>
</tr>
</tbody>
</table>

Electron dispersion occurs when in a wave packet there are different wavelengths with different propagation velocities.

The dispersion relation yields how the energy of a [quasi-]particle depends on the wave vector \( \mathbf{k} \), i.e. \( E = E(\mathbf{k}) \).

The group velocity of quantum-mechanical electron wave packets in the energy band structure:

\[
v = \frac{1}{\hbar} \nabla_{\mathbf{k}} E(\mathbf{k})
\]

Here \( \nabla_{\mathbf{k}} \) is the gradient with respect to \( \mathbf{k} \).

Electric field acts on the electron in the band structure. Crystal momentum \( \mathbf{p} = \hbar \mathbf{k} \), electric field \( \mathbf{E} \) and external force \( \mathbf{F} \) are related:

\[
\hbar \frac{d\mathbf{k}}{dt} = -e \mathbf{E} = \mathbf{F}
\]
ELECTRON DISPERSION

- In one dimension:

\[ \nu = \frac{1}{\hbar} \frac{dE}{dk} \quad \text{and} \quad F = \hbar \frac{dk}{dt} \]

\[ \Rightarrow m^* = F / a = \frac{F}{dv/dt} = \frac{\hbar^2}{d^2E/dk^2} \]

- Effective mass of electron \( m^* \), is the mass that the electron seems to have when responding to forces.

- Effective masses for different semiconductors can be found in the literature.
Schematics:
1. Energy dispersion $E(k)$ of the lowest conduction band in a typical semiconductor (blue),

2. Related electron velocity (red)
   \[ v \propto \frac{\partial E}{\partial k} \]

3. Related effective mass (green)
   \[ m^* \propto \frac{1}{\partial^2 E / \partial k^2} \]
HOLEs

- Holes are **missing electrons** in otherwise filled valence band.
- Holes are **quasi-particles**.
- The wave vector of hole is related to that of missing electron by \( k_h = -k_e \).
- Valence band at \( \Gamma \) point is a 3-fold degenerate with **heavy holes, light holes and split-off holes**.
Density of states $D(E)$ indicates the number of states at energy $E$.

$$D(E) = \frac{\text{number of states in } \Delta E}{\Delta E \cdot \text{volume}} \left( \frac{1}{\text{eV} \cdot \text{cm}^3} \right)$$

Number of states between $E$ and $E + \delta E$ is $D(E) \delta E$.

If several bands overlap, the $D(E)$s of all bands need to be summed up. For the energy $\tilde{E}$ for the given band:

$$D\left(\tilde{E}\right) dE = 2 \int \frac{d^3k}{(2\pi/L)^3} \delta(\tilde{E} - E(k))$$

- Here, $(2\pi/L)^3$ is the $k$-space volume for one state.
- Here, factor 2 is for spin degeneracy. The integral runs over the entire $k$-space and selects only those states that are at $\tilde{E}$.
n-doped silicon

ELECTRICAL DEFECT STATES
DOPANTS IN SEMICONDUCTORS

- Important characteristics of semiconductors: their properties can be varied by doping with different types and concentrations of impurities.

- In n-doped semiconductor, impurity atoms with five valence electrons (donor, e.g. phosphorous) donate extra negative-charged electron ($e^-$) to the lattice in the conduction band.

- In p-doped semiconductor, impurity atoms with three valence electrons (acceptor, e.g. boron) create positive-charged hole ($h^+$) in the valence band.

http://as.in.net/asdn/physics/semiconductor.php
The number of electrons $n$ in conduction band, i.e. occupied conduction band energy levels, is given by:

$$n = \int_{E_C}^{\infty} N(E)F(E)\,dE.$$  

Here, $E$ is energy, $N(E)$ is the total number of states, $F(E)$ is occupancy, and $E_C$ is the energy at the lowest edge of the conduction band.

The occupancy $F(E)$ is represented by Fermi-Dirac distribution function:

$$F(E) = \frac{1}{1 + \exp\left[\frac{(E - E_F)}{kT}\right]}.$$  

$k = \text{Boltzmann constant, } 8.6174\times10^{-5} \text{ eV/K}$

Here, $E_F$ is Fermi energy level that describes the top of the collection of electron energy levels at absolute zero temperature.
In other words, the Fermi [-Dirac] function $F(E)$ gives the probability that a state at energy $E$ is populated at thermodynamic equilibrium (i.e. no electrical or optical excitation).

$F(E)$ is a strong function of temperature $T$ and energy $E$. 

**Intrinsic**

\[ f(E) = \frac{1}{e^{(E - E_F)/kT} + 1} \]
In intrinsic semiconductors thermal agitation excites electrons from valence band to conduction band, leaving equal number of holes in the valence band.

This process is balanced with recombination of electrons (in the conduction band) with holes (in the valence band).

At steady state, the carrier concentration of electrons \( n \) and holes \( p \):

\[
n = p = n_i \quad [\text{cm}^{-3}]\]

Here, \( n_i \) is carrier concentration in intrinsic semiconductor, or intrinsic carrier concentration.
In nondegenerate semiconductors, the donor / acceptor doping concentrations \( N_D / N_A \) are smaller than the effective density of states in the conduction / valence band, i.e. and \( E - E_F >> kT \) (i.e. Boltzmann statistics apply).

Then, the number of electrons \( n \) in conduction band:

\[
n = N_C e^{-(E_c - E_F)/kT}
\]

Similarly, the number of holes \( p \) in valence band:

\[
p = N_V e^{(E_V - E_F)/kT}
\]

Here, \( N_C \) and \( N_V \) are the density of states in conduction and valence bands, respectively.

The product of majority and minority charge carriers is fixed:

\[
 pn = n_i^2
\]

This is know as the mass action law.
In degenerate semiconductors, doping concentrations are high, Boltzmann statistics does NOT apply, and Fermi levels are outside the energy gap.

Then, an estimation:

\[
E_F - E_C \approx kT \left[ \ln \left( \frac{n}{N_C} \right) + 2^{-3/2} \left( \frac{n}{N_C} \right) \right],
\]

\[
E_V - E_F \approx kT \left[ \ln \left( \frac{p}{N_p} \right) + 2^{-3/2} \left( \frac{p}{N_p} \right) \right].
\]
DONORS AND ACCEPTORS

- When semiconductor is doped with donor or acceptor impurity atoms, impurity energy levels are introduced to energy gap.

- Ionized donor atoms leave behind positive ions, i.e. positive space charge; ionized acceptor atoms leave behind negative space charge.

Donors and Acceptors / Energy Levels

- Ionization / binding energy for donors can be estimated (especially for shallow impurities):

\[
E_D^b = \frac{m_e^*}{m_0} \frac{1}{\varepsilon_r^2} \frac{m_0 e^4}{2(4\pi\varepsilon_0 h)^2}
\]

- For very shallow levels, the ionization energies for the impurities ~ thermal energy kT → ionization is usually complete in the room temperature (300K).
- Impurities can be intentionally or unintentionally introduced.
- Many unintentional deep level impurities (e.g. Fe, Cu) are very harmful to semiconductor properties.

- Effective mass of electrons in semiconductor 
- Dielectric constant of semiconductor 
- Electron rest mass 9,11*10^{-31} kg 
- Elementary charge 1,60*10^{-19} C 
- Permittivity in vacuum 8,85*10^{-12} F/m = 1,05*10^{-34} Js 
- Reduced Planck constant 1,05458*10^{-34} Js
DONORS AND ACCEPTORS
/ ENERGY LEVELS

Measured ionization energies

[Image of a diagram showing measured ionization energies for various elements, including Li, Sb, P, As, S, Se, Te, Ge, Si, and GaAs, with energy levels marked in eV.]
DONORS AND ACCEPTORS / SCHEMATICS

From left right:
1. band diagram,
2. density of states,
3. Fermi distribution,
4. carrier concentrations

From up down
1. intrinsic,
2. n-type,
3. p-type

semiconductor at thermal equilibrium.
The Fermi level $E_F$ depends on temperature and impurity concentration.

The higher the doping and the lower the temperature, the further $E_F$ is from the intrinsic Fermi level $E_i$.

Note: The band gap $E_g$ depends on temperature, too.
DONORS AND ACCEPTORS / CHARGE NEUTRALITY

- Charge neutrality applies in doping: the amount of negative charges (electrons and ionized acceptors) must be equal to the amount of positive charges (holes and ionized donors):
  \[ n + N_A^- = p + N_D^+ \]

- At relatively high temperatures, most impurities are ionized:
  \[ n + N_A = p + N_D \]
  \( N_A = \text{acceptor doping [cm}^{-3}\text{]} \)
  \( N_D = \text{donor doping [cm}^{-3}\text{]} \)

- In n-type: \( N_D > N_A \):
  \( n_{n0} \sim N_D \)
  And if \( N_D >> N_A \)
  \( p_{p0} = n_i^2 / n_{n0} \sim n_i^2 / N_D \)

- In p-type \( N_A > N_D \):
  \( p_{p0} \sim N_A \)
  And if \( N_A >> N_D \)
  \( n_{p0} = n_i^2 / p_{p0} \sim n_i^2 / N_A \)

- Note: The subscripts \( n \) and \( p \) refer to the type of semiconductors, and the subscript \( 0 \) refer to the thermal equilibrium condition.
SUMMARY

- Energy bands and electrical defect states explain many semiconductor properties and form the foundation of the understanding of semiconductor devices.

- Band structure of a semiconductor describes those ranges of energy that an electron in the semiconductor may have (energy bands), and ranges of energy that it may not have (band caps).

- In n-doped semiconductor, impurity atoms with five valence electrons (donor, e.g. phosphorous) donate extra negative-charged electron ($e^-$) to the lattice in the conduction band.

- In p-doped semiconductor, impurity atoms with three valence electrons (acceptor, e.g. boron) create positive-charged hole ($h^+$) in the valence band.