Semiconductors – Band Formation & direct and indirect gaps -II

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http://folk.uio.no/ravi/semi2013
Energy Levels

An Atom

E = 0

Energy

Empty States

Filled States

A Small Molecule

LUMO

HOMO

A Large Molecule

Vacuum Level

Fermi Level

Bulk Material

Chemistry is controlled by the states around the filled/empty transition.
Our focus in this course is on semiconductors.
Allowed energy levels of an electron acted on by the Coulomb potential of an atomic nucleus.

Splitting of energy states into allowed bands separated by a forbidden energy gap as the atomic spacing decreases; the electrical properties of a crystalline material correspond to specific allowed and forbidden energies associated with an atomic separation related to the lattice constant of the crystal.
Energy Band Formation

Energy Bandgap
where ‘no’ states exist

- Strongly bonded materials: small interatomic distances.
- Thus, the strongly bonded materials can have broader energy band than do weakly bonded materials.

Pauli Exclusion Principle

Only 2 electrons, of spin+/−1/2, can occupy the same energy state at the same point in space.

As atoms are brought closer towards one another and begin to bond together, their energy levels overlap into bands of discrete levels so closely spaced in energy, they can be considered a continuum of allowed energy.
Energy Band Formation

- Broadening of allowed energy levels into allowed energy bands separated by forbidden-energy gaps as more atoms influence each electron in a solid.

One-dimensional representation

Two-dimensional diagram in which energy is plotted versus distance.
When 2 Si atoms are brought together:

- Linear combinations of atomic orbitals (LCAO) for two-electron wave functions ($\psi_1$, $\psi_2$) of atoms leads to 2 distinct “normal” modes: a higher energy anti-bonding (anti-symmetric) orbital, and a lower energy bonding (symmetric) orbital (Pauli’s exclusion principle).

- For bonding state: an electron in the region between the two nuclei is attracted by two nuclei $\Rightarrow$ $V(r)$ is lowered in this region $\Rightarrow$ electron probability density is higher in this region than for anti-bonding state $\Rightarrow$ It is the lowering of $E$ of bonding state that causes cohesion of crystal.

Bonding Forces & Energy Bands in Solids

Energy Band

- Antionbonding orbital
- Bonding orbital
- Antibonding energy level
- Bonding energy level
When N Si atoms (1s:2N, 2s:2N, 2p:6N, 3s:2N, 3p:2N electrons) are brought together to form a solid:

- As interatomic spacing decreases, the energy levels split into bands, beginning with valence (n=3) shell (sp$^3$ hybridization) → 3s & 3p bands grow and merge into a single band (8N states) → As distance between atoms approaches the equilibrium interatomic spacing, this band splits into 2 bands separated by energy gap ($E_g$): upper band [conduction band; 4N states are empty(0K)], lower band [valence band; 4N states are completely filled with electrons (0K)].
The permitted energies that an electron can occupy in the isolated atoms are split into energy bands as the atoms get closer to each other. This can also be visualized in terms of an overlap of the electron wave functions.

Since the solid is made of a very large number of atoms (N), these bands are actually constituted by N levels of energies (almost a continuum!). The position of upper and lower extreme of each band is however independent of N (depends only on the materials).
Mathematically, it means solving the time-independent Schrödinger’s equation:

$$-rac{\eta^2}{2m} \nabla^2 + U(r) \psi(r) = E \psi(r)$$

where $U(r)$ is the periodic effective potential energy that describes the arrangement of atoms in the crystal.

e.g. a 1-D crystal could for instance be represented in the following manner:

Adapted from: R. Eisberg, R. Resnick, Quantum physics of atoms, molecules, solids, nuclei, and particles (2nd ed.), Wiley, 1985
Review of Energy Bands (4)

Usually given form of a “band diagram” $E$ vs $k$.

For device description a much more simple and practical representation is typically used:

- $E_g \approx 1.4$ eV

**Actual band diagram**


Direct band gap semiconductors (e.g. GaAs, InP, InAs, GaSb)

\[ \text{Eg} \approx 1.4 \text{ eV} \]

The minimum of the conduction band occurs at the same \( k \) value as the valence band maximum.

Review of Energy Bands (6)

Indirect band gap semiconductors (e.g. Si, Ge, AlAs, GaP, AlSb)

The minimum of the conduction band does not occur at the same k value as the valence band maximum.

An electron promoted to the conduction band requires a change of its momentum to make the transition to the valence band (typ. occurs via lattice vibrations).

Eg ~ 2.3 eV

4) Direct/Indirect Semiconductors

- **E (energy) - k (propagation constant; wave vector) relationship:**
  - Free electron satisfies \( k = \frac{\langle p \rangle}{\hbar} \)
  
  \[
  E = \frac{1}{2} mv^2 = \frac{\langle p \rangle^2}{2m} = \frac{\eta^2 k^2}{2m} \quad \text{(free electron)}
  \]

- For e- within a periodic lattice (has a periodic potential function): energy gap \( E_g \) appears in E-k characteristics

• **Direct Semiconductors:**
  - It has a min. in CB & a max. in VB for the same k value (k=0).
  - An electron in the CB min. can fall to an empty state in the VB max., giving off energy difference \( E_g \) as a photon of light without a change in k (or p) value. \( \rightarrow \) used for semiconductor LED, laser
  - ex) GaAs, Al\(_x\)Ga\(_{1-x}\)As (\( x<0.38 \)), GaAs\(_{1-x}\)P\(_x\) (\( x<0.45 \))

• **Indirect Semiconductors:**
  - It has its VB max. at a different k value than its CB min.
  - When an electron in the CB min. falls to an empty state in the VB max., \( \rightarrow \) 1) it falls first to defect state (Et) within the band gap, giving off energy difference as heat with a change in k (or p) value. 2) it falls then to the VB max., giving off energy difference Et as a photon of light without a change in k (or p) value.
  - ex) Si, Al\(_x\)Ga\(_{1-x}\)As (1\( \geq x > 0.38 \)), GaAs\(_{1-x}\)P\(_x\) (1\( \geq x > 0.45 \))
Direct & Indirect band gaps

- Two semiconductors types: direct and indirect gap;

- On direct gap semiconductor, such as GaAs, an electron at the minimal CB (Conduction Band) can deexcite to an unoccupied state in the VB (Valence Band) through the emission of a photon with energy equaling $E_g$.

Indirect transition via phonon.
Recombination in direct and indirect bandgap materials

• Let us consider recombination of an electron and a hole, accompanied by the emission of a photon.

• The simplified and most probable recombination process will be that where the electron and hole have the same momentum value. This is a direct-band-gap material.

• For indirect-band-gap materials, the conduction –band minimum and the valence band maximum energy levels occur at different values of momentum.

• Here band-to-band recombination must involve a third particle to conserve momentum, since the photon momentum is very small. Phonons (i.e. Crystal lattice vibrations) serve this purpose.
Direct & Indirect band gaps

- An electron at the indirect minimum of the Si CB doesn’t unexcite directly to the maximum of the VB e suffers a momentum and energy change. For example, it can be captured by a gap flaw state.

- On an indirect transition that involves a $k$ variation, the energy is usually freed to the lattice (phonons) instead of emitting photons.

- These differences between direct and indirect band structures, are particularly important on deciding which semiconductors should be used in light emitting devices;

- LED’s and lasers should be based on direct gap semiconductors.
A simplified energy band diagram with the highest almost-filled band and the lowest almost-empty band.
Metals vs. Semiconductors

- Pertinent energy levels

\[ qF_M (4.75 \text{ eV}) \]

\[ q\Phi_s \]

\[ q\chi_s \]

\[ qX (4.05 \text{ eV}) \]

- Metal

\[ E_f \]

\[ E_0 \]

- Semiconductor

\[ E_f \]

\[ E_c \]

\[ E_v \]

- Only the work function is given for the metal.

- Semiconductor is described by the work function \( q\Phi_s \), the electron affinity \( q\chi_s \), and the band gap \( (E_c - E_v) \).

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The Fermi-level in semiconductors

- Formal definition of the Fermi-level: the energy level where the probability of occupancy is 0.5:
  \[ f(W) = \frac{1}{1 + \exp\left(\frac{W - W_F}{kT}\right)} = 0.5 \]

- In case of intrinsic semiconductor this is in the middle of the band gap. This is the intrinsic Fermi-level \( W_i \)

\[ W_F = \frac{W_c + W_v}{2} \]
Fermi Level in metals

- In metals the Fermi level is defined as the top most occupied energy level. Also defined as the energy level from where one can remove an electron to vacuum with minimum Energy.

Focus on the electrons near the filled/empty boundary (i.e. top most occupied band. Each material’s energy state distribution is unique; different EF.

Minimum energy to remove electron from sample

\[ E = 0 \text{ (vacuum level)} \]

\[ E_F \text{ (Fermi level)} \]

Metal 1

Metal 2

The closer an electron is to the vacuum level, the weaker it is bound to the solid or the more energetic is the electron.

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<table>
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<th>Cristal</th>
<th>Banda</th>
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<td>TiO$_2$</td>
<td></td>
<td>3.03</td>
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</tbody>
</table>

$^a$ El HgTe es un semimetal; las bandas se solapan.
For GaAs, calculate a typical (band gap) photon energy and momentum, and compare this with a typical phonon energy and momentum that might be expected with this material.

**Photon**

\[
E(\text{photon}) = E_g(\text{GaAs}) = 1.43 \text{ ev}
\]

\[
E(\text{photon}) = h\nu = hc / \lambda
\]

\[c = 3 \times 10^8 \text{ m/sec}\]

\[
P = h / \lambda = 6.63 \times 10^{-34} \text{ J-sec}
\]

\[\lambda (\text{photon}) = 1.24 / 1.43 = 0.88 \mu\text{m}\]

\[
P(\text{photon}) = h / \lambda = 7.53 \times 10^{-28} \text{ kg-m/sec}
\]

**Phonon**

\[
E(\text{phonon}) = h\nu = hv_s / \lambda
\]

\[
\lambda (\text{phonon}) \approx a_0 = \text{lattice constant} = 5.65 \times 10^{-10} \text{ m}
\]

\[V_s = 5 \times 10^3 \text{ m/sec (velocity of sound)}\]

\[
E(\text{phonon}) = hv_s / a_0 = 0.037 \text{ eV}
\]

\[
P(\text{phonon}) = h / \lambda = h / a_0 = 1.17 \times 10^{-24} \text{ kg-m/sec}
\]
- Photon energy = 1.43 eV
- Phonon energy = 37 meV
- Photon momentum = $7.53 \times 10^{-28}$ kg-m/sec
- Phonon momentum = $1.17 \times 10^{-24}$ kg-m/sec

Photons carry large energies but negligible amount of momentum.

On the other hand, phonons carry very little energy but significant amount of momentum.
Absorption Coefficient

- Absorbed Photon create Electron-Hole Pair.

\[ \lambda_g [\mu m] = \frac{1.24}{E_g [eV]} \quad \text{Cut-off wavelength vs. Energy bandgap} \]

- Incident photons become absorbed as they travel in the semiconductor and light intensity decays exponentially with distance into the semiconductor.

\[ I(x) = I_0 \cdot e^{-\alpha x} \quad \text{Absorption coefficient} \]
Absorption Coefficient

- Absorption coefficient $\alpha$ is a material property.
- Most of the photon absorption (63%) occurs over a distance $1/\alpha$ (it is called penetration depth $\delta$)
Absorption Coefficient

Absorption

The indirect-gap materials are shown with a broken line.

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The indirect transition involve both photons and phonons ($h\omega, h\Omega$):

\[ E_f = E_i + \eta \omega \pm \eta \Omega, \]
\[ \eta k_f = \eta k_i \pm \eta \eta. \]

This is a second-order process, the transition rate is much smaller than for direct absorption.

Absorption coefficient of indirect band gap:

\[ \text{For indirect, } \alpha^i (\eta \omega) \propto (\eta \omega - E_g \mu \eta \Omega)^2. \]
\[ \text{For direct, } \alpha^d (\eta \omega) \propto (\eta \omega - E_g)^2. \]

The differences:

1. Threshold;
2. Frequency dependence.

The differences provide a way to determine whether the band gap is direct or not.

As $T$ decrease, phonons decrease gradually. At very low $T$, no phonons excited with enough energy. Thus at the lowest $T$, the indirect absorption edge is determined by phonon emission rather than phonon absorption;

5. The direct absorption dominates over the indirect processes once $h\omega > 0.8$ eV,

\[ \alpha^2 \propto (\eta \omega - E_{g\text{dir}}), \text{ where } E_{g\text{dir}} = 0.8 \text{eV} \]

Comparison of the absorption coefficient of GaAs and Silicon near their band edges. GaAs has a direct band gap at 1.42 eV, while silicon has an indirect gap at 1.12 eV. The absorption rises much faster with frequency in a direct gap material, and exceeds the indirect material.

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1. The lowest conduction band minimum occurs at the L point \( k = \pi/a(1,1,1) \), not at \( \Gamma \) \((k=0)\);
2. Indirect gap = 0.66 eV, direct gap \((\Gamma) = 0.8 \) eV;

### Table 3.1 Phonon energies for germanium at the L point where \( q = \frac{\pi}{a}(1,1,1) \), \( a \) being the unit cell size. After [6].

<table>
<thead>
<tr>
<th>Mode</th>
<th>( \hbar\omega ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Longitudinal acoustic (LA)</td>
<td>0.027</td>
</tr>
<tr>
<td>Transverse acoustic (TA)</td>
<td>0.008</td>
</tr>
<tr>
<td>Longitudinal optic (LO)</td>
<td>0.030</td>
</tr>
<tr>
<td>Transverse optic (TO)</td>
<td>0.035</td>
</tr>
</tbody>
</table>

1. \( \sqrt{\alpha} \) vs \( h\omega \) close to the band gap at 0.66 eV;
2. The straight line extrapolates back to 0.65 eV, which indicates that a phonon (TA) of energy \(~0.01\) eV has been absorbed and \( q \) (phonon) = \( k \) (electron) at L-point of the Brillouin zone;
3. A tail down to 0.6 eV, this is caused by absorption of the higher frequency and also multi-phonons absorption;
4. The temperature dependence of the absorption edge:

\[
\beta_{BE}(E) = \frac{1}{\exp(E/k_B T) - 1}
\]
The interband absorption spectrum of silicon

The band structure of silicon

The interband absorption spectrum of silicon

$E_g$ is indirect and occurs at 1.1 eV;

$E_1$ and $E_2$ are the separation of the bands at the L and X points, where the conduction and valence are approximately parallel along the (111) and (100).

$E_1 = 3.5$ eV is the minimum direct separation, and corresponds to the sharp increase in absorption at $E_1$, and $E_2$ correspond to the absorption maximum at 4.3 eV. Absorption at these energies is very high due to the Van Hove singularities in the joint density of states (bands are parallel. $E$ for direct transition does not depend on $k$, $dE/dk = 0$, $g(E)$ diverges (critical point)

1. The optical properties at the band edge determine the emission spectra;

   For indirect, \( \alpha^i(\eta \omega) \propto (\eta \omega - E_g \mu \eta \Omega)^2 \).

   For direct, \( \alpha^d(\eta \omega) \propto (\eta \omega - E_g)^{1/2} \).

2. The spectrum can be worked out by $dE/dk$ from the full band structure.

   \[
   g(E) = \frac{2g(k)}{dE/dk}
   \]
Absorption Coefficient

Photon absorption in a direct bandgap semiconductor.

Photon absorption in an indirect bandgap semiconductor.

- Direct Bandgap
- Indirect Bandgap
- Photon
- Phonons
Absorption Coefficient

- Direct bandgap semiconductors (GaAs, InAs, InP, GaSb, InGaAs, GaAsSb), the photon absorption does not require assistant from lattice vibrations. The photon is absorbed and the electron is excited directly from the VB to CB without a change in its k-vector (crystal momentum $\hbar k$), since photon momentum is very small.

$$\eta k_{CB} - \eta k_{VB} = \text{photon momentum} \approx 0$$

- Absorption coefficient $\alpha$ for direct bandgap semiconductors rise sharply with decreasing wavelength from $\lambda g$ (GaAs and InP).
Absorption Coefficient

- Indirect bandgap semiconductors (Si and Ge), the photon absorption requires assistant from lattice vibrations (phonon). If $K$ is wave vector of lattice wave, then $\hbar K$ represents the momentum associated with lattice vibration $\rightarrow \hbar K$ is a phonon momentum.

- Thus the probability of photon absorption is not as high as in a direct transition and the $\lambda g$ is not as sharp as for direct bandgap semiconductors.

\[ \eta k_{CB} - \eta k_{VB} = \text{phonon momentum} = \eta K \]
Absorption coefficient, $\alpha$

- $\alpha$ of a material determines generation as a function of wavelength.
- $\alpha$ small for photons with energy below $E_G$ — no absorption below band gap.
- For photon energies above $E_g$, $\alpha$ will determine the critical thickness of absorption.
Absorption coefficient

Absorption coefficient strongly affected by type of band gap.

Direct band gap

Indirect band gap

Energy, $E$

Crystal momentum, $p$

Direct band gap graph:
- $E_C$
- $E_V$
- $h\nu_1$
- $h\nu_2$

Indirect band gap graph:
- $E_G + E_p$
- $E_G - E_p$
- Phonon emission
- Phonon absorption
Optical band gap

\[ \alpha(\lambda) = -\frac{\ln\frac{T}{1-R}}{d} \]

\[ \alpha = A^* \cdot (h\nu - E_g)^n \]

- direct \( n = \frac{1}{2} \)
- direct forbidden \( n = \frac{3}{2} \)
- indirect \( n = 2 \)
- indirect forbidden \( n = 3 \)

ZnO
(direct band gap)

\[ E_{\text{gap}} = 3.343 \text{ eV} \]