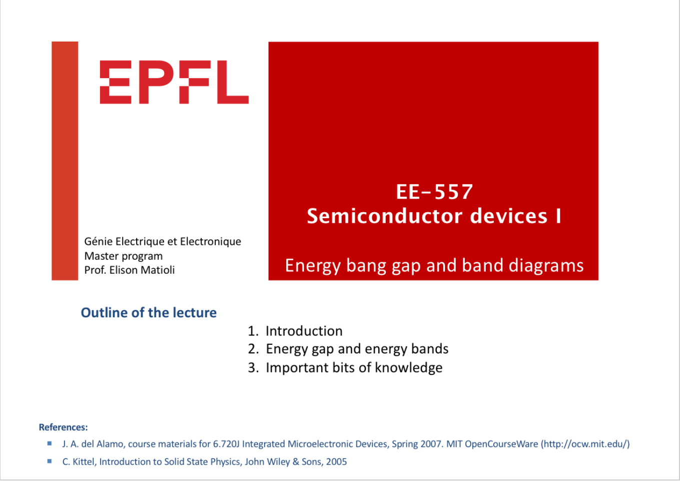
Course 2

Wednesday, 11 September 2024 09:58

EE557Cours
2 -...

EPFL
Equal opportunity makes us brighter
Diversity is our strength
Listen and dare to speak up
?!
@ :)
Look out for each other
Kindness brings serenity
Together we go further
RESPECT
EPFL



EPFL

Génie Electrique et Electronique
Master program
Prof. Elison Matioli

EE-557
Semiconductor devices I

Energy bang gap and band diagrams

Outline of the lecture

1. Introduction
2. Energy gap and energy bands
3. Important bits of knowledge

References:

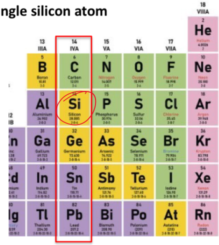
- J. A. del Alamo, course materials for 6.720J Integrated Microelectronic Devices, Spring 2007. MIT OpenCourseWare (http://ocw.mit.edu/)
- C. Kittel, Introduction to Solid State Physics, John Wiley & Sons, 2005

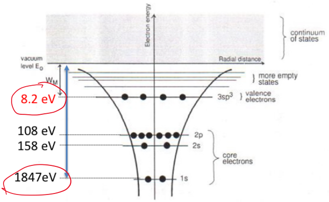
Key questions

- What is a semiconductor?
- What is an energy band gap?
- How do we treat electrons in a solid?
- How do atoms arrange themselves? And the consequences…
- How do electrons arrange themselves (in energy) in an electronic system?

Energy band-gap

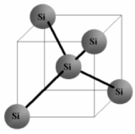
Single silicon atom

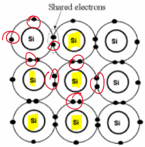

13 IIIA
14 IVA
15 VA
16 VIA
17 VIIA
18 VIIIA
He
B
C
N
O
F
Ne
Al
Si
P
S
Cl
Ar
Ga
Ge
As
Se
Br
Kr
In
Sn
Sb
Te
I
Xe
Tl
Pb
Bi
Po
At
Rn


Electron energy
continuum of states
Radial distance
vacuum level E_0
W_M
more empty states
$3sp^3$
valence electrons
8.2 eV
108 eV
158 eV
2p
2s
core electrons
1847eV
1s

14e

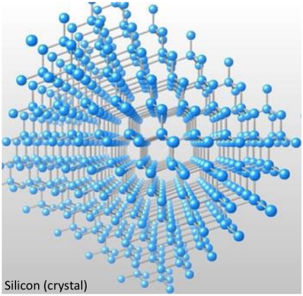
$$1s^2\,2s^2\,2p^6\ \underbrace{3s^2\,3p^2}_{3sp^3}$$


Si
Si
Si
Si
Si


Shared electrons
Si

Covalent bonds

From atoms to semiconductors

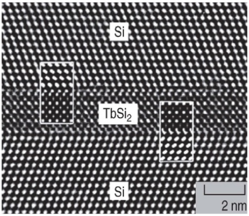


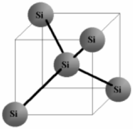
Silicon (crystal)

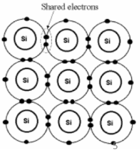
Take a look at this link to ”play” its crystal structure:
https://sketchfab.com/3d-models/silicon-crystal-lattice-73e292f32ffe4ca490e166faeba317e7

Silicon intrinsic: $\rho = 3.2\text{x}10^5\ \Omega\text{cm} = 3.2\text{x}10^3\ \Omega\text{m}$

Transmission electron microscope (TEM)

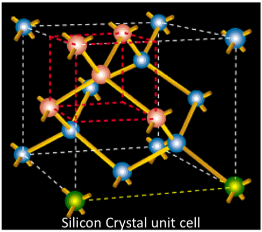

Si
TbSi$_2$
Si
2 nm


Si
Si
Si
Si
Si


Shared electrons
Si
Si
Si
Si
Si
Si
Si
Si
Si

Semiconductors are solids

- Semiconductors are **crystalline solids**
- Crystalline solid = elemental atomic arrangement, or unit cell, repeated “ad infinitum” in space in three dimensions.
  Si lattice constant: 0.54 nm
  Si atomic spacing: 0.24 nm
- Solid is an electronic system with **periodic potential**



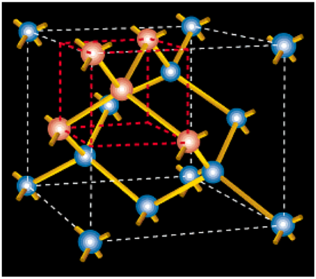
Silicon Crystal unit cell

Structure is held together by covalent bonding 4 valence electrons shared with 4 neighbors: lowest energy situation (stable configuration)

See: http://www.science.oregonstate.edu/~gablek/CH231H/Silicon.htm
https://sketchfab.com/3d-models/silicon-crystal-lattice-73e292f32ffe4ca490e166faeba317e7

Crystal structure

Silicon Crystal unit cell



“diamond cubic” lattice

- **Each Si atom has 4 nearest neighbors**
- **lattice constant = 5.431 Å**

How Many Silicon Atoms per cm^3?

atoms:

corners : $8 \times 1/8 = 1$

faces : $6 \times 1/2 = 3$

inside : 4

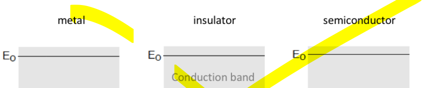
8 atoms

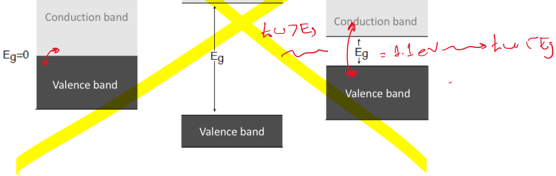
Volume : $V = (5.431 \times 10^{-10} m)^3 = (5.431 \times 10^{-8} cm)^3 = 1.6 \times 10^{-22} cm^3$

$\Rightarrow \dfrac{8}{1.6 \times 10^{22} cm^3} = 5 \times 10^{22} \, \# / cm^3$

Energy band-gap

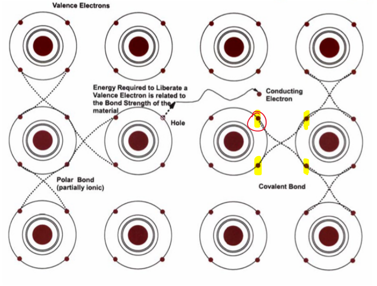
What is an energy bang gap Eg?


metal
insulator
semiconductor
E$_0$
E$_0$
E$_0$
Conduction band


Conduction band
Eg=0
Valence band
Eg
Valence band
Conduction band
Eg
Valence band
$\hbar\omega > E_g$
= 1.1 eV
$\hbar\omega < E_g$

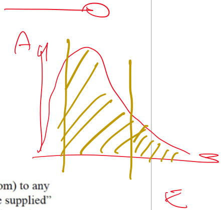
Energy band-gap

What is a Semiconductor Energy Bandgap?


Valence Electrons
Energy Required to Liberate a Valence Electron is related to the Bond Strength of the material
Conducting Electron
Hole
Polar Bond (partially ionic)
Covalent Bond

$E = q \cdot V$

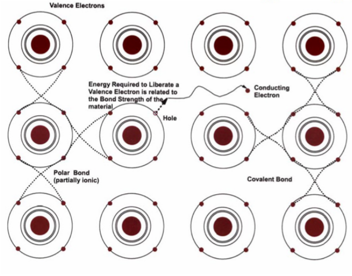
$+ \quad V$



- For metals, the electrons can jump from the valence orbits (outermost core energy levels of the atom) to any position within the crystal (free to move throughout the crystal) with no "extra energy needed to be supplied"
- For insulators, it is VERY DIFFICULT for the electrons to jump from the valence orbits and requires a huge amount of energy to "free the electron" from the atomic core.
- For semiconductors, the electrons can jump from the valence orbits but does require a small amount of energy to "free the electron" from the atomic core.

Energy band-gap

What is a Semiconductor Energy Bandgap?


Valence Electrons
Energy Required to Liberate a Valence Electron is related to the Bond Strength of the material
Conducting Electron
Hole
Polar Bond (partially ionic)
Covalent Bond

- Semiconductor materials are a sub-class of materials distinguished by the existence of a range of disallowed energies between the energies of the valence electrons (outermost core electrons) and the energies of electrons free to move throughout the material.
- The energy difference (**energy gap or bandgap**) between the states in which the electron is bound to the atom and when it is free to conduct throughout the crystal is related to the bonding strength of the material, it's density, the degree of ionicity of the bond, and the chemistry related to the valence of bonding.
- High bond strength materials (diamond, SiC, AlN, GaN etc...) tend to have large energy bandgaps.
- Lower bond strength materials (Si, Ge, etc...) tend to have smaller energy bandgaps.

Energy band-gap

How do energy bands and band gaps form?

Energy band-gap

Simple case: Hydrogen atom

Electron experiences an electrostatic Coulomb attraction to the nucleus $V = -\frac{e^2}{4\pi\epsilon_0 r}$

Hamiltonian for this problem (time-independent Schroedinger's equation):

$$\underbrace{-\frac{\hbar^2}{2m}\nabla^2\psi}_{\text{Kinetic energy}} + \underbrace{V\psi}_{\text{Potential energy}} = \underbrace{E\psi}_{\text{total energy}}$$

Energies electrons are allowed to have

Wavefunction of an electron

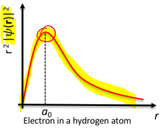
After writing the Laplacian ∇^2 in spherical coordinates:

$$H = -\frac{\hbar^2}{2m_e r^2}\left\{\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\} - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$$

$$E_n = -\frac{\hbar^2}{2m_e a_0^2}\frac{1}{n^2} \qquad n = 1, 2, 3, \ldots \qquad a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \approx 0.529\,177\,210\,7\ 10^{-10}\ \mathrm{m}$$

The wave nature of electrons results in only a few allowed energies (like a guitar string)

$|\psi(\mathbf{r})|^2$ gives the probability of finding an electron in a given position **r**



Electron in a hydrogen atom

Energy band-gap

Simple case: Hydrogen atom

Electron experiences an electrostatic Coulomb attraction to the nucleus $V = -\frac{e^2}{4\pi\epsilon_0 r}$

Hamiltonian for this problem (time-independent Schroedinger's equation):

$$\boxed{\hat{H}\psi} = \underbrace{-\frac{\hbar^2}{2m}\overset{=\hat{p}}{\nabla^2}\psi}_{\text{Kinetic energy}} + \underbrace{V\psi}_{\text{Potential energy}} = \underbrace{E\psi}_{\text{total energy}}$$

Energies electrons are allowed to have

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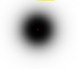
$$E_n = -\frac{\hbar^2}{2m_e a_0^2}\frac{1}{n^2} \qquad n = 1, 2, 3, \ldots$$

Ground state:

$$E_1 = -13.6\ \text{eV}$$

$$\psi_{100}(r) = \frac{1}{\sqrt{\pi a_0^3}}e^{-r/a_0}$$

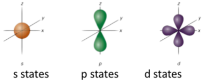
1s orbital

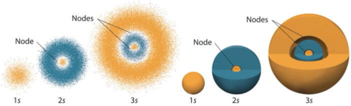


Energy band-gap

The dual nature of the electron

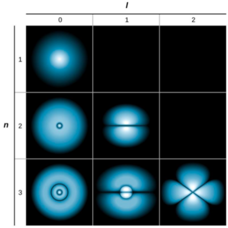
This results in different levels with principal quantum number **n**, and with sub-levels **s,p,d**... defined by the angular momentum number **l**,...

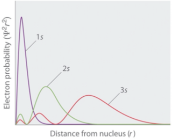

z
y
x
s
p
d
s states
p states
d states


Node
Nodes
1s
2s
3s
Node
Nodes
1s
2s
3s

(a) Electron probability

(b) Contour probability





(c) Radial probability

Figure from: https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/06._Electronic_Structure_of_Atoms/6.6%3A_3D_Representation_of_Orbitals

Energy band-gap

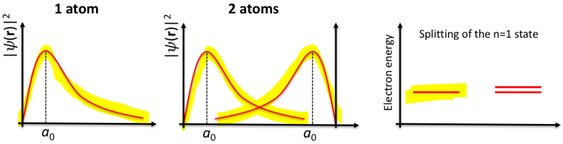
What happens when atoms come together?

Pauli exclusion principle: no two electrons occupying the same space, can have the same energy.

Thus, as **atoms are brought closer** towards one another and begin to bond together, their **energy levels must split** into bands of discrete levels so closely spaced in energy that they can be considered a continuum of allowed energy.

The wavefunction of the electrons overlap: two electrons will interact

This perturbation results in discrete quantized energy levels **splitting into two discrete energy levels**



Strongly bonded materials tend to have small interatomic distances between atoms. Thus, the strongly bonded materials can have larger energy bandgaps than weakly bonded materials.

Energy band-gap

What happens when atoms come together?

$\hat{H}\cdot\underline{\Psi} = E\Psi$

$$H_1\varphi_1 = E_{01}\varphi_1$$

$$H_2\varphi_2 = E_{02}\varphi_2$$

When atoms come close to each other, the electron wavefunction is delocalized on atoms 1 and 2 :

$$\boxed{\psi} = \underbrace{(c_1\varphi_1 + c_2\varphi_2)}$$

Linear combination of atomic orbitals

$$\frac{\hbar^2}{2m}\nabla^2$$

$$\boxed{\frac{p^2}{2m}}\psi + (V_1 + V_2)\psi = E\psi$$

Courtesy of J-Y Duboz

Energy band-gap

What happens when atoms come together?

Develop and project on φ_1 and φ_2

$$c_1 E_{01} + c_2 E_{02}\langle\varphi_1|\varphi_2\rangle + c_2\langle\varphi_1|V_1|\varphi_2\rangle + c_1\langle\varphi_1|V_2|\varphi_1\rangle = Ec_1 + c_2 E\langle\varphi_1|\varphi_2\rangle$$

$$c_1 E_{01}\langle\varphi_2|\varphi_1\rangle + c_2 E_{02} + c_2\langle\varphi_2|V_1|\varphi_2\rangle + c_1\langle\varphi_2|V_2|\varphi_1\rangle = Ec_2 + c_1 E\langle\varphi_2|\varphi_1\rangle$$

$$\begin{vmatrix} (E_{01}-E)+\langle\varphi_1|V_2|\varphi_1\rangle & (E_{02}-E)\langle\varphi_1|\varphi_2\rangle+\langle\varphi_1|V_1|\varphi_2\rangle \\ (E_{01}-E)\langle\varphi_2|\varphi_1\rangle+\langle\varphi_2|V_2|\varphi_1\rangle & (E_{02}-E)+\langle\varphi_2|V_1|\varphi_2\rangle \end{vmatrix} = 0$$

- Can be solved as it is ☺
- But it can be simplified by introducing assumptions which are done in the real semiconductor band structure calculations based on this approach (Tight Binding) ☺ ☺

Courtesy of J-Y Duboz

Energy band-gap

What happens when atoms come together?

$$\begin{vmatrix} (E_{01}-E)+\langle\varphi_1|V_2|\varphi_1\rangle & (E_{02}-E)\langle\varphi_1|\varphi_2\rangle+\langle\varphi_1|V_1|\varphi_2\rangle \\ (E_{01}-E)\langle\varphi_2|\varphi_1\rangle+\langle\varphi_2|V_2|\varphi_1\rangle & (E_{02}-E)+\langle\varphi_2|V_1|\varphi_2\rangle \end{vmatrix} = 0$$

$\langle\varphi_1|\varphi_2\rangle = 0$ Not strictly true. In addition E_{02}-E is expected to be small

$\langle\varphi_1|V_2|\varphi_1\rangle = \langle\varphi_2|V_1|\varphi_2\rangle$ by symmetry

Describes the effect of the potential of atom 2 on the energy in atom 1, and vice versa. It is a shift of the energy, with no important effect.

(when atoms are different or with less trivial symmetries, it has an effect).

Let us renormalize the energies :

$$E_1 = E_{01} + \langle\varphi_1|V_2|\varphi_1\rangle$$
$$E_2 = E_{02} + \langle\varphi_2|V_1|\varphi_2\rangle$$

Courtesy of J-Y Duboz

Energy band-gap

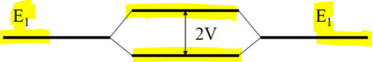
What happens when atoms come together?

$$\begin{vmatrix} (E_1 - E) & \langle \varphi_1 | V_1 | \varphi_2 \rangle \\ \langle \varphi_2 | V_2 | \varphi_1 \rangle & (E_2 - E) \end{vmatrix} = 0$$

We introduce : $\langle \varphi_1 | V_1 | \varphi_2 \rangle \times \langle \varphi_2 | V_2 | \varphi_1 \rangle = V^2$

$$E = \frac{(E_1 + E_2)}{2} \pm \sqrt{\left(\frac{E_1 - E_2}{2}\right)^2 + V^2}$$

If atoms are identical: $E_1 = E_2$ $\quad E = E_1 \pm |V|$



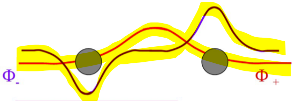
2 new energy eigenvalues

Courtesy of J-Y Duboz

Energy band-gap

What happens when atoms come together?

2 new eigen states



$$\boxed{\Phi_+ = \frac{1}{\sqrt{2}}(\varphi_1 + \varphi_2)}$$

Lowest energy: bonding state

$$\boxed{\Phi_- = \frac{1}{\sqrt{2}}(\varphi_1 - \varphi_2)}$$

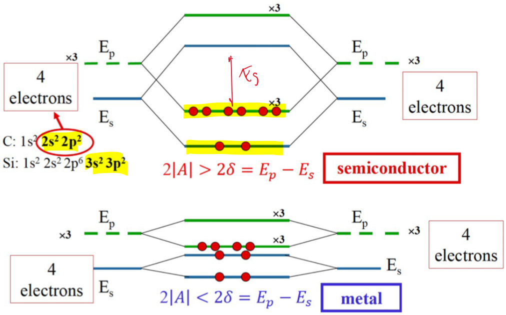
Highest energy: anti-bonding state

Courtesy of J-Y Duboz

Energy band-gap

What happens when atoms come together?

Metals versus semiconductors


×3
E_p
E_s
4 electrons
×3
E_p
E_s
4 electrons
Xs
×3
C: 1s² 2s² 2p²
Si: 1s² 2s² 2p⁶ 3s² 3p²
×3
E_p
E_s
4 electrons
×3
E_p
E_s
4 electrons

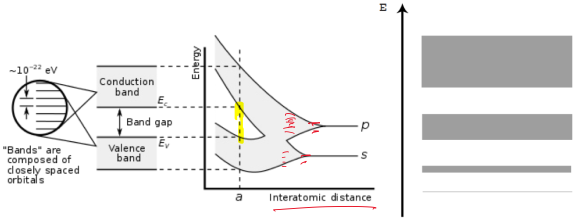
$2|A| > 2\delta = E_p - E_s$ **semiconductor**

$2|A| < 2\delta = E_p - E_s$ **metal**

Courtesy of J-Y Duboz

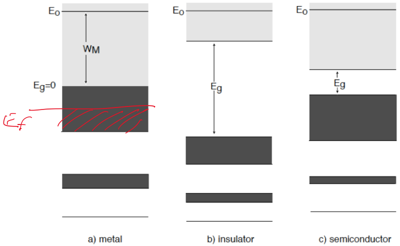
Energy band-gap

Quantum states cluster in bands leaving bandgaps (regions without allowed states) in between.


~10⁻²² eV
"Bands" are composed of closely spaced orbitals
Conduction band
E_c
Band gap
E_v
Valence band
Energy
p
s
a
Interatomic distance
E

Electronic structure of semiconductors

Quantum states filled with one electron per state starting from lowest energy state (Pauli exclusion principle)


Eo
WM
Eg=0
Ef
Eo
Eg
Eo
Eg

a) metal b) insulator c) semiconductor

At 0 K: the energy of the top-most energy state filled is called the **Fermi level**

No conduction is possible in a full band insulators: semiconductors do not conduct at 0 K.

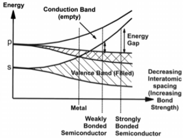
Conduction requires a partially filled band: metals conduct at 0 K.

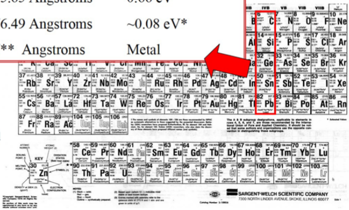
But in semiconductors at finite temperatures, some electrons populate next band above bandgap conduction becomes possible.

Energy band-gap

Consider the case of the group 4 elements, all covalently bonded

Element	Atomic Radius/Lattice Constant (How closely spaced are the atoms?)	Bandgap
C	0.91/3.56 Angstroms	5.47 eV
Si	1.46/5.43 Angstroms	1.12 eV
Ge	1.52/5.65 Angstroms	0.66 eV
α-Sn	1.72/6.49 Angstroms	~0.08 eV*
Pb	1.81/** Angstroms	Metal


Energy
Conduction Band (empty)
Energy Gap
p
s
Valence Band (Filled)
Decreasing Interatomic spacing (Increasing Bond Strength)
Metal
Weakly Bonded Semiconductor
Strongly Bonded Semiconductor


SARGENT-WELCH SCIENTIFIC COMPANY

*Only has a measurable bandgap near 0K

**Different bonding/Crystal Structure due to unfilled higher orbital states

How Energy Bands and Energy Gap are calculated?

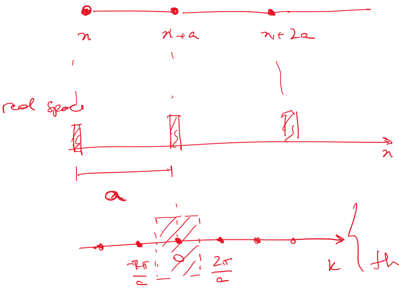
The dual nature of the electron

If it is a wave, we can define a wavevector: $\psi(x,t) = A\cos(kx - wt + \varphi)$

where:

$$\omega = \frac{2\pi}{T} \text{ and } k = \frac{2\pi}{\lambda}$$

periodic arrangement



x
x+a
x+2a
real space
x
a
$-\frac{2\pi}{a}$
$\frac{2\pi}{a}$
k

$n(x) = \sum n_p \exp\left(i \frac{2\pi}{a} p \cdot x\right)$

$\vec{k}$: is also periodic

if a-periodic in real space

then $\frac{2\pi}{a}$-periodic in $\vec{k}$ space

How Energy Bands and Energy Gap are calculated?

Energy-momentum relationship: characterizes the band structure

- Important for the interactions with photons and phonons

Schrödinger's equation: $\left[-\frac{\hbar^2}{2m^*}\nabla^2 + V(\boldsymbol{r})\right]\psi(\boldsymbol{r},\boldsymbol{k}) = E(\boldsymbol{k})\psi(\boldsymbol{r},\boldsymbol{k})$

Bloch function $\psi(\boldsymbol{r},\boldsymbol{k}) = \exp(j\boldsymbol{k}\cdot\boldsymbol{r})U_b(\boldsymbol{r},\boldsymbol{k})$

$\psi(\boldsymbol{r},\boldsymbol{k})$ and $U_b(\boldsymbol{r},\boldsymbol{k})$ are periodic in R in real space

Thus:

$$\begin{aligned}\psi(\boldsymbol{r}+\boldsymbol{R},\boldsymbol{k}) &= \exp[j\boldsymbol{k}\cdot(\boldsymbol{r}+\boldsymbol{R})]U_b(\boldsymbol{r}+\boldsymbol{R},\boldsymbol{k}) \\ &= \exp(j\boldsymbol{k}\cdot\boldsymbol{r})\exp(j\boldsymbol{k}\cdot\boldsymbol{R})U_b(\boldsymbol{r},\boldsymbol{k})\end{aligned}$$

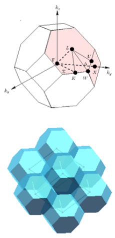
$\boldsymbol{k}\cdot\boldsymbol{R}$ is a multiple of 2π.

Consequences:

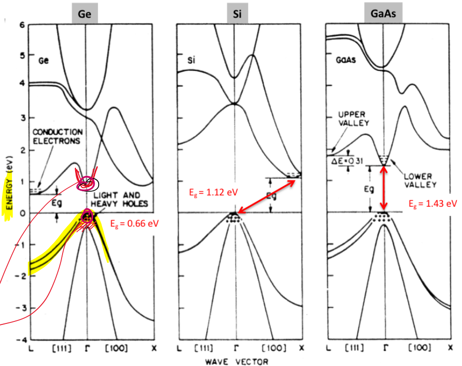
- In 1D: only *k* = 2**π**/*a* are allowed (where *a* is the real space period)
- E(*k*) is periodic in k-space: E(*k*) = E(*k*+G)
- It is sufficient to define *k* in a primitive cell, which is defined by the Brillouin zone
- Entire band structures need only to be calculated within the brillouin zone.

Energy band-gap

Reciprocal space directions:



k_z
L
U
Γ
Σ
Δ
X
K
W
k_y
k_x



$E_g = 0.66$ eV

$E_g = 1.12$ eV

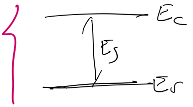
$E_g = 1.43$ eV

Conduction

valence

Indirect band gap

direct band gap

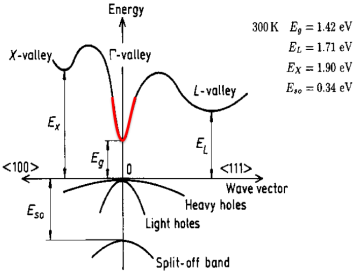


A few important concepts

Effective mass

Band diagram: We focus on minimum of the bands (quadratic region)

GaAs


Energy
X-valley
Γ-valley
L-valley
E_X
E_g
E_L
<100>
0
<111>
Wave vector
E_{so}
Heavy holes
Light holes
Split-off band
300 K $E_g = 1.42$ eV
$E_L = 1.71$ eV
$E_X = 1.90$ eV
$E_{so} = 0.34$ eV

Energy-momentum relationship near band edges

$$E(k) = \frac{p^2}{2m^*} = \frac{\hbar^2 k^2}{2m^*}$$

Effective mass in 1D

$$m_j^* = \hbar^2 \left(\frac{\partial^2 E_j}{\partial k_y^2} \right)^{-1}$$

Momentum

$$p = \hbar k$$

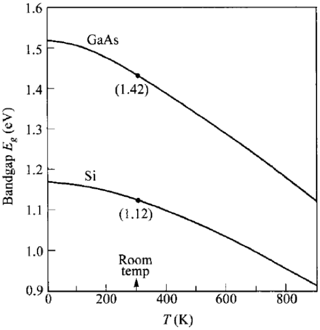
$\hbar = h/2\pi$: planck's constant = 6.58 eV.s

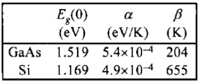
For example:

Si: $m^* = 1.09\ m_0$
GaN: $m^* = 0.2\ m_0$
GaAs: $m^* = 0.06\ m_0$

A few important concepts

Temperature dependence of the band gap





	$E_g(0)$ (eV)	α (eV/K)	β (K)
GaAs	1.519	5.4×10^{-4}	204
Si	1.169	4.9×10^{-4}	655

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

Appendix – Supplementary Material

Crystal structure: Definitions

Unit cell: Defines the symmetry and structure of the entire lattice

Bravais lattices: describe the geometric arrangement of the lattice points

Crystal structure and symmetry play a critical role in determining many physical properties, such as:

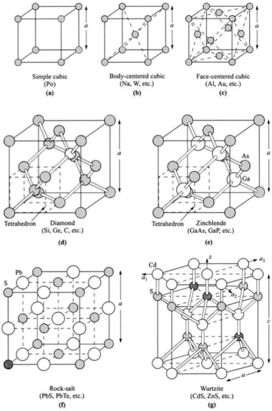
- Cleavage
- Mechanical properties (elastic compliance, stiffness)
- Electronic band structure: Band gap
- Optical transparency
- Thermal properties
- Polarization fields

a is the lattice constant.

GaN: most common in wurtzite structure

Zincblende structure: III-V compound semiconductors: GaAs, GaP, *etc*

- Important for optoelectronics and high-speed Ics


a
As
Ga
Pb
S
Cd
S
z
a_1
a_2
a_3
c
Tetrahedron
Tetrahedron

Simple cubic (Po) (a)

Body-centered cubic (Na, W, etc.) (b)

Face-centered cubic (Al, Au, etc.) (c)

Diamond (Si, Ge, C, etc.) (d)

Zincblende (GaAs, GaP, etc.) (e)

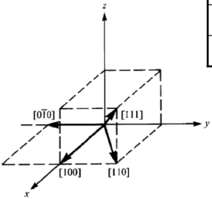
Rock-salt (PbS, PbTe, etc.) (f)

Wurtzite (CdS, ZnS, etc.) (g)

Crystallographic Notation

Miller Indices:

Notation	Interpretation
$(h\ k\ l)$	crystal plane
$\{ h\ k\ l \}$	equivalent planes
$[h\ k\ l]$	crystal direction
$< h\ k\ l >$	equivalent directions


z
y
x
[0$\bar{1}$0]
[111]
[100]
[110]

Sample direction vectors and their corresponding Miller indices.

***h*: inverse *x*-intercept of plane**
***k*: inverse *y*-intercept of plane**
***l*: inverse *z*-intercept of plane**

(Intercept values are in multiples of the lattice constant;
***h*, *k* and *l* are reduced to 3 integers having the same ratio.)**

** Wurtzite materials have an hexagonal crystal structure:
4 Miller indices are used to represent it more easily (see appendix for more information)

Crystal structure

How Many Silicon Atoms per cm^3?

- **Number of atoms in a unit cell:**
  - 4 atoms completely inside cell
  - Each of the 8 atoms on corners are shared among cells → count as 1 atom inside cell
  - Each of the 6 atoms on the faces are shared among 2 cells → count as 3 atoms inside cell

  ⇒ Total number inside the cell = 4 + 1 + 3 = **8**
- **Cell volume:**

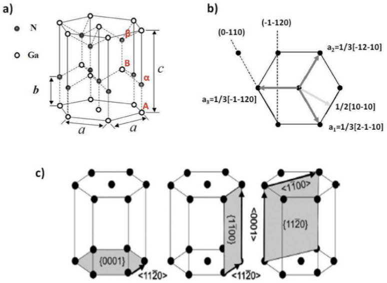
  $(.543\ \text{nm})^3 = 1.6 \times 10^{-22}\ \text{cm}^3$
- **Density of silicon atoms**

  = (8 atoms) / (cell volume) = $\mathbf{5 \times 10^{22}}$ **atoms/cm^3**

Crystallographic Notation (Appendix)

Wurtzite materials have an hexagonal crystal structure

4 Miller indices are used to represent it more easily


a)
N
Ga
β
B
α
A
c
b
a
a
b)
(-1-120)
(0-110)
a₂=1/3[-12-10]
a₃=1/3[-1-120]
1/2[10-10]
a₁=1/3[2-1-10]
c)
{0001}
<1120>
{1100}
<1120>
<0001>
<1100>
{1120}

$$[u'v'w'] \rightarrow [uvtw]$$

$$u = \frac{1}{3}(2u'-v')$$

$$v = \frac{1}{3}(2v'-u')$$

$$t = -(u+v)$$

$$w = w'$$

Coulon, Pierre-Marie. (2014). Growth and characterization of GaN nanowires/microwires

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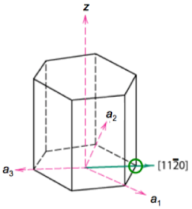
Crystallographic Notation (Appendix)

Wurtzite materials have an hexagonal crystal structure

HCP Crystallographic Directions

1. Vector repositioned (if necessary) to pass through origin.
2. Read off projections in terms of unit cell dimensions a1, a2, a3, or c 3.
3. Adjust to smallest integer values
4. 4. Enclose in square brackets,


z
a_2
a_3
$[11\bar{2}0]$
a_1

Adapted from Fig. 3.8(a), *Callister 7e.*

ex: ½, ½, -1, 0

$$[u'v'w'] \rightarrow [uvtw]$$

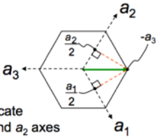
$$u = \frac{1}{3}(2u'-v')$$

$$v = \frac{1}{3}(2v'-u')$$

$$t = -(u+v)$$

$$w = w'$$

=> $[11\bar{2}0]$


a_2
$\frac{a_2}{2}$
$-a_3$
a_3
$\frac{a_1}{2}$
a_1

dashed red lines indicate projections onto a_1 and a_2 axes

http://courses.washington.edu/mse170/lecture_notes/RinaldiF09/Lecture5-MR2009.pdf

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Interesting links and videos

Crystallography and reciprocal space

https://www.youtube.com/watch?v=DFFU39A3fPY

Quantum mechanics through walkers

https://www.youtube.com/watch?v=WIyTZDHuarQ

Slides on semiconductor physics

https://slideplayer.com/slide/6940114/