CHAPTER 1

The Crystal Structure of Solids
Semiconductor Materials

- possible elements for making semiconductor materials
  - Si most well known semiconductor. C and Ge can also be semiconductors.
  - Other possibilities combinations of III and V group. Eg. GaAs

<table>
<thead>
<tr>
<th>Group III</th>
<th>Group IV</th>
<th>Group V</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>C</td>
<td>P</td>
</tr>
<tr>
<td>Ga</td>
<td>Si</td>
<td>As</td>
</tr>
<tr>
<td>In</td>
<td>Ge</td>
<td>Sb</td>
</tr>
</tbody>
</table>

A portion of the periodic table
Elemental and Compound Semiconductors

### Elemental Semiconductors

<table>
<thead>
<tr>
<th>Element</th>
<th>Semiconductor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>Silicon</td>
</tr>
<tr>
<td>Ge</td>
<td>Germanium</td>
</tr>
</tbody>
</table>

### Compound Semiconductors

<table>
<thead>
<tr>
<th>Compound</th>
<th>Semiconductor</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlP</td>
<td>Aluminium Phosphide</td>
</tr>
<tr>
<td>AlAs</td>
<td>Aluminium Arsenide</td>
</tr>
<tr>
<td>GaP</td>
<td>Gallium Phosphide</td>
</tr>
<tr>
<td>GaAs</td>
<td>Gallium Arsenide</td>
</tr>
<tr>
<td>InP</td>
<td>Indium Phosphide</td>
</tr>
</tbody>
</table>

**Binary Semiconductor (2 elements):**

\[ \text{Si}_{1-x}\text{Ge}_x, \text{SiC} \]

**Ternary Semiconductor (3 elements):**

\[ \text{Al}_x\text{Ga}_{1-x}\text{P} \]

**Quaternary Semiconductor (4 elements):**

\[ \text{AlGaAsP} \]

- Single element → elemental semiconductor
- More than one element → compound semiconductor

Properties of comp semi can be controlled by changing the concn of the elements.
GaN and ZnO are recently discovered semiconductor materials which are promising materials for laser diodes (blue light).

These laser diodes are used in blue-ray DVD recorders. Blue light having smaller wavelength helps in lowering the resolution and increasing the packing density of bits.
Types of Solids

Three general types of solids: (a) amorphous, (b) polycrystalline and (c) crystalline
Amorphous Si

Advantages
• Low temperature deposition (~ 250°C)
• Large Area deposition possible at low cost

Disadvantages
• Low conductivity
• Cannot be used for High speed circuits
Uses of amorphous-Si

Solar cells

Efficiency: 6-10%

Thin Film Transistors for LCDs

Mobility: 1cm²/Vs
Gate for MOSFETs

Semiconductor layer for TFTs (recent development)

Polycrystalline silicon has higher conductivity as compared to amorphous silicon.
Crystal

In a very broad sense crystal means something that repeats

So even a wall paper with a repeating pattern is a crystal !!
Lattice and unit cell

Lattice: A regular periodic arrangement of points in space as in the arrangement of atoms or molecules in a crystal.

Each point in the lattice is a lattice point. It can be an atom, a group of atoms, an ion or a molecule.

Unit cell: A small volume of a crystal that can be used to reproduce the entire crystal.

Two dimensional representation of a single crystal lattice

Two dimensional representation of a single crystal lattice with various possible unit cells
The relationship between the cell and the lattice is characterized by three vectors $\vec{a}$, $\vec{b}$ and $\vec{c}$. These vectors need not to be perpendicular to each other and need not to be of the same length. Every equivalent lattice point in the crystal can be found using the equation –

$$\vec{r} = p\vec{a} + q\vec{b} + s\vec{c}$$  \hspace{1cm} (1.1)

A generalized primitive unit cell

A **PRIMITIVE CELL** is the *Smallest* unit cell!
Basic Crystal Structures

The easiest 3-D lattice to work with is the simple cubic lattice (SCC) which has lattice points on all the corners of a cube. The Cubic (Isometric) crystal system is characterized by its total symmetry. It has three crystallographic axes that are all perpendicular to each other and equal in length. The cubic system has one lattice point on each of the cube's four corners.

Different possible cubic lattices
Lattice constant
Other crystal structures

Crystal structures which are combinations of these are also possible.
FCC lattice structure has high packing density

See Video and Quiz question on packing density.

Al, Cu, Ni, Pd, Ag, Ce, Pt, Au, Pb...
Also Na, K, V, Cr, Fe, Rb, Nb, Mo, Cs, Ba, Eu, Ta etc. have BCC lattice structure.

SCC is the most spacious crystal structure with least packing density. So nature does not prefer it!!
Almost no naturally occurring crystal has SCC structure.
Atomium in Brussels has BCC structure!!
Hexagonal structure

The Hexagonal crystal system has four crystallographic axes consisting of three equal horizontal or equatorial (a, b, and d) axes at 120°, and one vertical (c) axis that is perpendicular to the other three. Hexagonal structure is characterized by close packing density.

Quartz

Snow flake
Diamond structure
The tetrahedral structure is basically a body-centered cubic with four of the corner atoms missing. Every atom in the tetrahedral structure has four nearest neighbors with equal distance. This is the basic building block of the diamond lattice.
The diamond structure

Bottom half (a) and top half (b) portions of diamond lattice.
The diamond structure can also be interpreted as two Interpenetrating FCCs.

See video in course material.
Zincblend structure in GaAs

Covalent + Ionic bonding

Zincblend structure is similar to diamond structure, but atoms in penetrating FCC are different.
Crystal plane and Miller Indices

Surface or plane through the crystal can be described by the intercepts of the plane along the $a$, $b$ and $c$ axes used for the lattice. Reciprocal of these intercepts are called the miller indices.

Three lattice planes – (a) (100) plane, (b) (110) plane and (c) (111) plane
The plane (a) is parallel to the \( \vec{b} \) and \( \vec{c} \) axes so the intercepts are given as 1, infinite and infinite. Taking reciprocal, we obtain Miller indices as (1,0,0), so the plane is referred to as (100) plane. Any plane parallel to this is equivalent and is referred to as the (100) plane.
For an example on how to find the Miller indices of a plane, refer to example 1.2 in the reference book.

For an example on how to find the surface density of atoms on a particular crystal plane, refer to example 1.3 in the reference book.
Atomic Bonding

Covalent bonding

Ionic bonding

Metallic bonding

Van der Waals bonding

Strong

Weak
Covalent bonding

(a) hydrogen valence electrons and (b) covalent bonding in hydrogen molecule

Representation of (a) silicon valence electrons and (b) covalent bonding in the silicon crystal
Atomic structure for C, Si and Ge

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>K</th>
<th>L</th>
<th>M</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>C</td>
<td>1s²</td>
<td>2s²2p²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Si</td>
<td>1s²</td>
<td>2s²2p⁶</td>
<td>3s²3p²</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>Ge</td>
<td>1s²</td>
<td>2s²2p⁶</td>
<td>3s²3p⁶3d¹⁰</td>
<td>4s²4p²</td>
</tr>
</tbody>
</table>

Silicon has only 2 unpaired electrons. Then why does Si form 4 covalent bonds?
Promotion of one electron from s-orbital to p-orbital to form four orbitals of equal energy is hybridisation. This happens so that all available energy states in the outermost shell are occupied. Else it will lead to instability.

With electrons in two different kinds of orbitals, we cannot get four identical covalent bonds. Hybridisation results in four similar electronis and hence identical bonds.
Shape of s & p orbitals in n=3 shell before hybridisation.
Valence electron cloud

Orbitals in n=3 shell after hybridisation

The silicon atom in its crystalline surroundings has a similarly shaped electron cloud
Similar hybridisation phenomenon happens in carbon. Above figure is after bonding with Hydrogen in CH$_4$. 
Metallic bonding

Sodium has the electronic structure $1s^22s^22p^63s^1$. When sodium atoms come together, the electron in the 3s atomic orbital of one sodium atom shares space with the corresponding electron on a neighbouring atom to form a molecular orbital - in much the same sort of way that a covalent bond is formed.

The difference, however, is that each sodium atom is being touched by eight other sodium atoms (BCC structure) and the sharing occurs between the central atom and the 3s orbitals on all of the eight other atoms. And each of these eight is in turn being touched by eight other sodium atoms and so on. So electrons are shared over a large distance and this makes flow of electrons easy.

This same reason also makes metals malleable!!
Van der Waals bond

Effective center of the positive charge is not the same as the negative one, e.g., HF molecule.

The electric dipole interacts with the other dipole.

Inert Gas Elements – He, Ne, Ar, Kr, Xe

FCC
Hydrogen bonding

Van der Waal’s bonds in water
Diamond is one of the hardest material in nature because covalent bonding is very strong. In graphite, bonding between 2 graphene layers is weak Van der Waals bonding. This makes graphite very soft and graphene layers can be easily separated.

Recently a single layer of graphene has been found to be a promising semiconductor material.
Carbon nanotube (1D crystal)

Carbon nano-tubes are formed by rolling a single layer of graphene. These are used to make quantum devices!!
Ionic Bond

- Bond between two oppositely charged ions.
Imperfections in solids

Lattice imperfection is any deviation from perfect periodic arrangement of lattice points. Point defects can be in the form of vacancy (missing atom), substitutional impurity (atom replaced by another atom) or interstitial impurity (additional impurity not at lattice point).
Line Defects

Edge dislocation is a type of line defect.
Grain boundaries are a type of plane defect.

Precipitates are a type of volume defect.
Crystalline defects in semiconductors.

<table>
<thead>
<tr>
<th>Defect Type</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point</td>
<td>Vacancies, interstitials, impurity atoms</td>
</tr>
<tr>
<td>Line</td>
<td>Dislocations</td>
</tr>
<tr>
<td>Plane</td>
<td>Stacking faults, twins and grain boundaries</td>
</tr>
<tr>
<td>Volume</td>
<td>Precipitates and voids</td>
</tr>
</tbody>
</table>
Growth of Semiconductor Materials

• Growth from Melt

• Epitaxial growth
Czochralski method

Growth from melt

Silicon ingot from czochralski process

Larger diameter, impurity from crucible
μ-Czochralski (Grain-Filter) Process with Excimer-Laser

Initially holes which act as seeds are formed by photolithography. Then excimer laser is used to melt silicon. Square shaped grains are formed at the seed locations.
Epitaxial growth

Single-crystalline layer growth on a single-crystalline substrate with the same crystal structure

Homo-epitaxy  Hetero-epitaxy

Si on Si          Si on SiGe, AlGaAs on GaAs

by means of

Chemical vapor deposition (CVD)
Liquid Phase Epitaxy (LPE)
Molecular Beam Epitaxy (MBE)
Chemical Vapour Deposition (CVD)

Used mainly for silicon but also for SiGe, GaN

Good for production, safety consideration

\[
\begin{align*}
\text{SiCl}_4 + H_2 & \leftrightarrow \text{SiHCl}_3 + \text{HCl} \\
\text{SiHCl}_3 & \leftrightarrow \text{SiCl}_2 + \text{HCl} \\
\text{SiCl}_2 + H_2 & \leftrightarrow \text{Si(solid)} + 2\text{HCl}
\end{align*}
\]
Liquid Phase Epitaxy (LPE)

Used for GaAs, InP, HgCdTe

High quality compound semiconductors, difficult to monitor
Molecular Beam Epitaxy (MBE)

Physical process

Used for GaAs, GaN

Precise growth monitor, high quality (compound) semiconductor layers, slow growth rate
Floating zone method (for purifying silicon ingot)

Floating zone method relies on the segregation co-efficient. For this process to be used for purification this co-efficient should be less than 1.
Segregation coefficient ($k_0$)

Impurity concentration ratio between the solid and liquid

$$k_0 = \frac{C_{Solid}}{C_{Liquid}}$$
<table>
<thead>
<tr>
<th>Element</th>
<th>$K_o$</th>
<th>$D \times 10^{-4}$ cm$^2$/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>0.8</td>
<td>2.4</td>
</tr>
<tr>
<td>Al</td>
<td>0.002</td>
<td>7.0</td>
</tr>
<tr>
<td>Ga</td>
<td>0.008</td>
<td>4.8</td>
</tr>
<tr>
<td>In</td>
<td>0.0004</td>
<td>6.9</td>
</tr>
<tr>
<td>C</td>
<td>0.07</td>
<td>2</td>
</tr>
<tr>
<td>P</td>
<td>0.35</td>
<td>2.3</td>
</tr>
<tr>
<td>As</td>
<td>0.3</td>
<td>3.3</td>
</tr>
<tr>
<td>Sb</td>
<td>0.023</td>
<td>1.5</td>
</tr>
<tr>
<td>O</td>
<td>1.40</td>
<td>3.3</td>
</tr>
</tbody>
</table>

Oxygen cannot be removed by floating zone method because its segregation coefficient is more than 1. The diffusion co-efficient ($D$) determines the speed of purification.
Si wafer fabrication

**SiO₂**

→

**Metallic Si**

→

**Pure trichlorosilane**

\[ Si + 3SiCl₄ + 2H₂ \rightarrow 4SiHCl₃ \]

→

**Pure poly-Si**

99.999999999%  

→

**Single-crystalline Si**

→

**Si wafer**