Basic Semiconductors  
(Properties & Growth)

- used for most solid state devices
- silicon (and others)

Solid state device - a component whose operation depends on the control of electrical or magnetic phenomena in solids, such as a transistor, diode, or ferrite.

- could include glass lasers

We will concentrate on semiconductor devices.

What distinguishes semiconductors?

- resistance/resistivity
- crystaline structure
The resistance of a bar of material with dimensions L, W, t and resistivity $\rho$ is:

$$R = \frac{\rho L}{W t}$$

**metals:** $\rho < 10^{-3}\,\Omega\cdot\text{cm}$
**insulators:** $\rho > 10^{2}\,\Omega\cdot\text{cm}$
**semiconductors:** $10^{-3}\,\Omega\cdot\text{cm} < \rho < 10^{2}\,\Omega\cdot\text{cm}$
Three types of solids, classified according to atomic arrangement: (a) crystalline and (b) amorphous materials are illustrated by microscopic views of the atoms, whereas (c) polycrystalline structure is illustrated by a more macroscopic view of adjacent single-crystalline regions, such as (a)

(a) Crystalline  (b) Amorphous  (c) Polycrystalline
Semiconductors are found in columns II-VI of the periodic table. Why is silicon so popular if there are so many to choose from?
elemental semiconductors: Si, Ge
compound semiconductors: GaAs, InP
ternary semiconductors: AlGaAs, HgCdTe
quaternary semiconductors: InGaAsP, InGaAlP

Common semiconductor materials: (a) the portion of the periodic table where semiconductors occur; (b) elemental and compound semiconductors.

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Some characteristics of semiconductors

1) melting temperature
2) relative abundance/cost
3) band gap (light generation/absorption)
4) ease of doping
5) ease of growth
6) ease of processing
7) performance

Crystal Lattices

- An ideal crystalline solid is periodic and is referred to as “single crystal”
- The periodic arrangement is called the lattice.
• A **unit cell** is a volume that is repeated throughout the crystal.
A two-dimensional lattice showing translation of a unit cell by \( r + 3a + 2b \).
A unit cell need not be “primitive” (the smallest possible unit cell).

In Fig. 1.2 (p.6), \( \vec{a} \) and \( \vec{b} \) are called basis vectors (defined by the sides of the unit cell).

Points within the lattice are indistinguishable if the vector \( \vec{r} \) between the points is given by

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

\( p, q, s \) integers

(• future: we will find that the lattice dimensions are involved in the allowed energies of the electrons in the crystal.)
Fig 1.3 Unit cells for three types of cubic lattice structures.
Fig 1-4 Packing of hard spheres in an fcc lattice.
• The dimensions $|\vec{a}|$, $|\vec{b}|$, and $|\vec{c}|$ are called lattice constants.

**Packing factor (fcc) (Example 1-1)**

• Assume nearest neighbors touch (maximum packing)
\[
\left(\frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2 = c^2 = 2 \frac{a^2}{4} \Rightarrow c = \frac{1}{2} \sqrt{2}a
\]

The radius of the spheres = \( \frac{\sqrt{2}}{4} a \)

atoms/cell:
- each corner contributes 1/8
- (8 corners) \( \Rightarrow \) 1 sphere
- each face contributes 1/2
- (6 faces) \( \Rightarrow \) 3 spheres
Packing factor = \( \frac{\text{(# of spheres/cell) } V_{\text{sphere}}}{V_{\text{unit cell}}} \)

\[
4 \left( \frac{4}{3} \pi \left( \frac{\sqrt{2}}{4} a \right)^3 \right) = \frac{4}{3} \pi a^3 = \frac{42}{3} \pi \left( \frac{\sqrt{2}}{4} a \right)^3 = \frac{\pi \sqrt{2}^3}{3 \cdot 4}
\]

\[
= \frac{\pi \sqrt{2}}{6} = 0.7404\ldots = 74\%
\]
Planes and Directions

- We can define a plane in the crystal lattice with 3 integers:

1. find the intercepts of the plane in terms of integral multiples of the basis vectors

\[(\text{Fig 1-5} \Rightarrow 2\vec{a}, \, 4\vec{b}, \, 1\vec{c})\]
2. take the reciprocal of the integers and reduce to smallest set of integers $h, k, l$

$$\left[\left(\frac{1}{2}, \frac{1}{4}, 1\right)\right] \rightarrow [(2,1,4)]$$

3. label the plane $(h k l) \left[\begin{array}{c}(214)\end{array}\right]$

- $h, k, l$ are known as **Miller Indices**
• if the intercept is negative, the minus sign is written above the indice:

\[
(h\bar{k}l)
\] [pronounced “h, k-bar, l”]

Fig 1.5 A (214) crystal plane.
Fig. 1-6  Equivalence of the cubic faces (100 planes) by rotation of the unit cell within the cubic lattice.
Directions in a crystal
• direction is expressed as a set of 3 integers
• the 3 integers represent the vector components of the direction along the crystalographic axis $a, b, c$
The diagrams illustrate the crystallographic orientations of n-type and p-type semiconductor surfaces.

- **{111} n-TYPE**
  - Primary flat with a secondary flat at 45°.

- **{111} p-TYPE**
  - Primary flat only.

- **{100} n-TYPE**
  - Primary flat with a secondary flat at 180°.

- **{100} p-TYPE**
  - Primary flat with a secondary flat at 90°.
Fig. 1-7 Crystal directions in the cubic lattice
Fig. 1-8 Diamond lattice structure: (a) a unit cell of the diamond lattice constructed by placing atoms $1/4$, $1/4$, $1/4$ from each atom in an fcc; (b) top view (along) of an extended diamond lattice. The colored circles indicate one fcc sublattice and the black circles indicate the interpenetrating fcc.
(special facts, cont’d)

A group of equivalent planes is referred to by braces:

\[(010),(001),(\bar{1}00),(0\bar{1}0),(00\bar{1}) \equiv \{100\}\]

### Miller Notation Summary

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<th>convention</th>
<th>meaning</th>
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<td>equivalent directions</td>
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The Diamond Lattice

- basic lattice for many elements (Si, Ge)
- basic lattice for many compound semiconductors (GaAs, InP...)

In compound semiconductors that have the “diamond lattice”, one element (Ga or Zn) is placed on one fcc lattice and the other element (As or S) is placed on the other fcc lattice.
Fig. 1

As or S

Ga or Zn
Fig. 1  Atomic positions in the unit cell of the diamond structure projected on a cube face. Fractions denote height. The points at 0 & 1/2 are on one set of fcc lattices (As or Zn), while the points 1/4 and 3/4 are on another set of fcc lattices (Ga or Zn) [known as zinc blende structure]

Example: Find the number of Si atoms/cm² on the (100) surface of a Si wafer.

a=5.43 Å
(room temperature)
For an area of $a^2$, there are:

4 corner atoms which each contribute $1/4$
1 center atom which is not shared

$1+1=2$ atoms/cell

$$\Rightarrow \frac{2}{(5.43 \text{ A}^\circ)^2} = \frac{2}{(5.43 \times 10^{-8} \text{ cm})^2} = 6.783... \times 10^{14} \text{ atoms/cm}^2$$

on (100) plane
Another Example: Find the number of silicon atoms on the (110) plane:
Figure 21  Miller indices of some important planes in a cubic crystal. The plane (200) is parallel to (100), but it divides the unit cube in two equal parts.
(edge view of (110) plane)
(side view of (110) plane)
Fig 1.9  Diamond lattice unit cell, showing the four nearest neighbor structure.
In, Al, Ga and column III elements and all go on the same sublattice.

As and P are column V elements and all go on the other sublattice.

\[ \text{In Al}_x \text{Ga}_{1-x} \text{As}, \text{ with } x=0.3, \]
\[ \Rightarrow 30\% \text{ of the column III sites are Al,} \]
\[ 70\% \text{ are Ga.} \]

\[ \text{In In}_x \text{Ga}_{1-x} \text{As}_y \text{P}_{1-y}, \text{ with } x=0.47, y=0.25 \]
\[ \Rightarrow 47\% \text{ of the column III sites are In} \]
\[ 53\% \text{ are Ga} \]
\[ \Rightarrow 25\% \text{ of the column V sites are As} \]
\[ 75\% \text{ are P} \]
### Properties of Semiconductor Materials

<table>
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<th>$E_g$ (eV)</th>
<th>$\mu$ (cm$^2$/V-s)</th>
<th>$p_0$ (cm$^3$/cm$^3$)</th>
<th>$\sigma_0$ (O-m$^{-1}$ cm$^{-1}$)</th>
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<th>Density</th>
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Example 1.3  Calculate the density of Si from the lattice constant, atomic weight, and Avogadro’s number. Recall: Avogadro’s number (6.02 X 10$^{23}$) is the number of molecules/atoms in a gram molecular weight of a substance.

lattice constant = a = 5.43 X 10$^{-8}$cm

how many Si atoms in the diamond cell?

8 corner atoms X (1/8) = 1
6 face atoms X (1/2) = 3
+ 4 interior atoms = 4  8 atoms/unit cell
(see Fig. 1-8 p. 25)

\[
\frac{\text{# of atoms}}{\text{cm}^3} = \frac{8}{a^3} = \frac{8}{(5.43 \times 10^{-8} \text{ cm})^3} = \\
= \frac{8}{1.60 \times 10^{-22}} = 4.996... \times 10^{22} \text{ atoms/cm}^3
\]

\[
\text{density} = \left(\frac{\text{# of atoms}}{\text{cm}^2}\right) \left(\frac{\text{# of grams}}{\text{mole}}\right) = \\
\left(\frac{\text{# of atoms}}{\text{mole}}\right)
\]
\[
\frac{\#\text{grams}}{cm^3} = \left(\frac{4.996 \times 10^{22} \text{ atoms} / cm^3}{6.02 \times 10^{23}}\right) 28.1 \text{ g / mole} = \\
= 2.332 \text{ g / cm}^3
\]
Comments on crystal planes

- mechanical, electrical, chemical and optical properties depend on crystal orientation.

- crystals can be cleaved along atomic planes ⇒ very flat, smooth surfaces

- mirror facets for semiconductor lasers
- wet chemical etchants etch along crystal planes
Electronic Grade Silicon:

1. 

| sand (SiO$_2$) | SiC(solid) + SiO$_2$(solid) |
| coal, wood    | → Si(liquid) + SiO(gas) + CO(gas) |
| chips, ...    | heat |

The liquid Si solidifies (~98% pure) (called metalurgical grade silicon -- impurities of ~few thousand ppm

2. The solid silicon is pulverized and subjected to HCl gas:

   \[
   \text{Si(solid) + 3HCl(gas) } \rightarrow \text{ SiHCl}_3(\text{gas}) + \text{ H}_2(\text{gas})
   \]

   SiHCl\(_3\) is called \textit{trichlorsilane}.

3. EGS is prepared from SiHCl3:
\[ 2\text{SiHCl}_3(\text{gas}) + 2\text{H}_2(\text{gas}) \rightarrow 2\text{Si}(\text{solid}) + 6\text{HCl}(\text{gas}) \]

result: high purity (a few ppm) EGS

(In 1998, \(~95\%\) of all semiconductor devices produced were silicon devices)

**Methods to produce Single Crystals**

- Horizontal Bridgeman
- Czochralski
• Floating Zone

Fig 1-11 Crystal growing from the melt in a crucible: (a) solidification from one end of the melt (horizontal Bridgman method); (b) melting and solidification in a moving zone.
Fig. 1-2 Pulling of a Si crystal from the melt (Czochralski method): (a) schematic diagram of the crystal growth process.
Fig. 1-14  Floating-zone crystal growth: (a) schematic diagram of the growth process.
The Distribution Coefficient
For any material, there is a different affinity for impurities for the liquid phase and the solid phase. This characteristic is described by the distribution coefficient $k_d$.

$$k_d = \frac{c_s}{c_L}$$

$c_s = \text{impurity concentration in the solid}$
$c_L = \text{impurity concentration in the liquid}$

$k_d = f(\text{material, impurity, temperature})$

Example: if $k_d=1/2$, there are twice the impurities in the liquid as in the solid.
Example 1-4  Find the concentration of phosphorous (P) atoms in the melt to obtain Si doped with 1016 atoms/cm³ (Czochralski growth)

\[ kd = 0.35 \text{ for P in S} \]

\[ k_d = \frac{c_S}{c_L} = \frac{10^{16} \text{ atoms} / \text{cm}^3}{0.35} = 2.86 \times 10^{16} \text{ atoms} / \text{cm}^3 \]

b) how many grams of P should be added if the initial load in the crucible is 5 kg of Si?
density of Si = 2.33g/cm$^3$

the volume of Si in the melt is

$$\frac{5000g}{2.3g/cm^3} = 2145.9cm^3$$

In the total melt volume, we want $2.86 \times 10^{16}$ atoms/cm$^3$.

The number of atoms is

$$2.86 \times 10^{16} \text{ atoms/cm}^3 \left[ V_{Si} + V_P \right]$$

but $V_P \ll V_{Si}$, so $V_C \approx V_{si}$
\[ \text{P atoms} = 2.86 \times 10^{16} \text{ atoms / cm}^3 \left( 2145.0 \text{ cm}^3 \right) = 6.137 \times 10^{19} \]

\[ \frac{637 \times 10^{19} \text{ atoms} \times 31 \text{ g / mole}}{6.023 \times 10^{23} \text{ atoms / mole}} = 3.159 \times 10^{-3} \text{ g} = 3.16 \text{ mg} \]