Chapter-1

1.1.Crystal Structure

Cont.....

A *primitive cell* is constructed using three non-coplanar *primitive basis vectors* with lattice points located only at the vertices of the parallelepiped, so that the effective number of lattice points belonging to the primitive cell is always unity. Primitive cell is the smallest unit cell (in volume) in a Bravais lattice. Figure 1-3 shows (a) the rhombohedral primitive cell for a face-centered cubic (FCC) lattice and (b) the relation of the primitive cell in the hexagonal lattice (heavy lines) to a prism of hexagonal symmetry. The rhombohedral primitive cell of the FCC lattice is formed by three primitive translation basis vectors '**a** ,'**b**and '**c** connecting the lattice point at the origin with lattice points at the three face-center lattice points. The volume of the primitive cell is only one-fourth of the volume of the conventional parallelepiped unit cell for the FCC lattice.

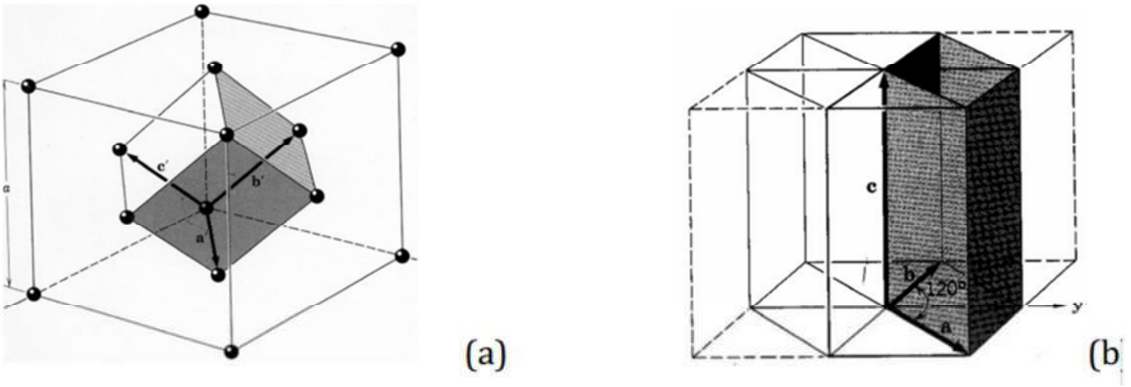


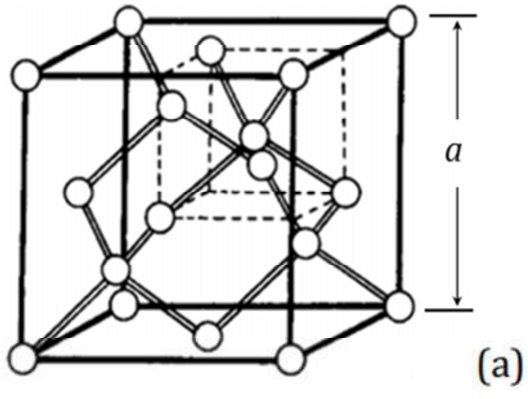
Figure 1-3: The (a) rhombohedral primitive cell for a face-centered cubic (FCC) lattice and (b) relation of the primitive cell in the hexagonal lattice (heavy lines) to a prism of hexagonal symmetry.

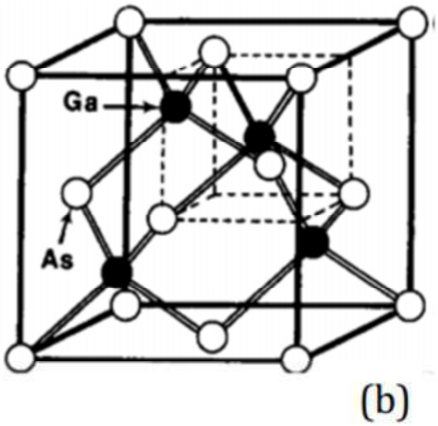
Symmetry is a very important consideration in crystalline solids because many of the physical, electrical, magnetic, elastic, and thermal properties of the solids are strongly dependent on the symmetry properties of their crystal lattice. For example, the electrical conductivity of a cubic crystal is isotropic and independent of its crystalline orientations, while the electrical conductivity of a trigonal crystal can be highly anisotropic along different

crystalline axes. The symmetry of a real crystal is determined by the symmetry of its basis and of the Bravais lattice to which the crystal belongs. Each Bravais lattice have different degrees of *translational*, *rotational*, *reflectional*, and *inversional* symmetry. The *rotational* symmetry of a crystal lattice is obtained when rotation about a certain crystal axis through an angle of $2\pi/n$ radians leaves the lattice invariant. The lattice is said to have an *n*-fold rotational axis. Due to the requirements of translational symmetry, the possible values of n are limited to 1, 2, 3, 4, and 6. There are no five- and seven-fold rotational symmetries in a Bravais lattice. A cubic crystal has four-fold rotational symmetry about the (100) axes, threefold rotational symmetry about the diagonal (111) axes.

The crystal structures

The Bravais lattice is a mathematical abstraction that describes the periodic arrangement of lattice points in space. A real crystal is not a perfect replica of a Bravais lattice, with identical atoms at every lattice point. There is generally a set of atoms, whose internal symmetry is restricted only by the requirement of translational periodicity that must be associated with each lattice point of the corresponding Bravais lattice. This set of atoms at each lattice point in an arrangement is known as the *basis*. Each basis of a particular crystal is identical in composition, arrangement, and orientation. The same spatial arrangement of





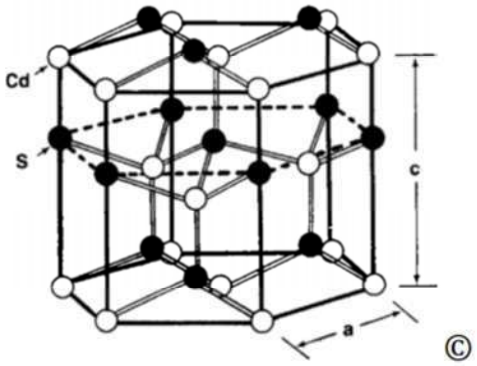


Figure 1-4: Four important crystal structures in semiconductors: (a) diamond structure, (b) zinc-blende structure, (c) wurtzite structure.

basis or when basis is attached to each lattice point, a *crystalline structure* is formed in the Bravais lattice. Many metals and semiconductors have a simple crystal structure with high degrees of symmetry. For example, alkali metals such as lithium, sodium, and potassium form the face-centered cubic (FCC) structure, while elemental and compound semiconductors form either the *Diamond*, *Zinc-blende*, or *Wurtzite structure*. Figure 1-4 shows (a) the diamond (b) the zinc-blende and (c) the wurtzite crystal structures.

The Diamond structure

The diamond structure is actually formed by two interpenetrating face-centered cubic lattices with the vertex atom of one FCC sub-lattice located at (0, 0, 0) and the vertex atom of another nearest FCC sub lattice located at (ć/4, ć/4, ć/4), where ć is the lattice constant as shown in Figure 1-4 (a). In the diamond lattice structure, the primitive basis of two identical atoms located at (0, 0, 0) and (ć/4,ć/4, ć/4) is associated with each lattice point of the FCC lattice. Elemental semiconductors such as silicon (Si) and germanium (Ge) belong to the diamond crystal structure.

The zinc-blende structure

The zinc-blende structure is similar to the diamond structure except that the two FCC sub-lattices are occupied alternately by two different kinds of atoms (*e.g.*, Ga and As in a GaAs crystal) as illustrated in Figure 1-4 (b). III-V compound semiconductors such as Gas, In, and Ins form the zinc-blende structure. Both the diamond and zinc-blende structures belong to the tetrahedral phase, with each atom surrounded by four equidistant nearest-neighbor atoms at the vertices of a tetrahedron.

The Wurtzite structure

The wurtzite structure is formed by two interpenetrating hexagonal close-packed structures occupied alternately by two different kinds of atoms. Figure 1-4 © shows the wurtzite crystal structure. II-VI compound semiconductors such as CdS, CdTe, ZnS, and ZnSe have this type of crystal structure. Some of the III-V and II-VI compound semiconductors including GaP, ZnS, and CdSe may be crystallized either in a zinc-blende or a wurtzite structure. Table 1-4 lists the crystal structures and the lattice constants for elemental and compound semiconductors.

Atomic packing factor

In crystallography, **atomic packing factor** (APF), **packing efficiency** or **packing fraction** is the fraction of volume in a crystal structure that is occupied by constituent particles. It is dimensionless and always less than unity. It indicates that how closely the atoms are packed together. In atomic systems, by convention, the APF is determined by assuming that atoms are rigid spheres. The radius of the spheres is taken to be the maximal value such that the atoms do not overlap. For one-component crystals (those that contain only one type of particle), the packing fraction is represented mathematically by

$$\boldsymbol{APF = \frac{Volume\ of\ atoms\ in\ unit\ c}{volume\ of\ unit\ cell} = \frac{number\ of\ atoms\ x\ volume\ of\ each\ atoms}{volume\ of\ uni}} \qquad 1$$

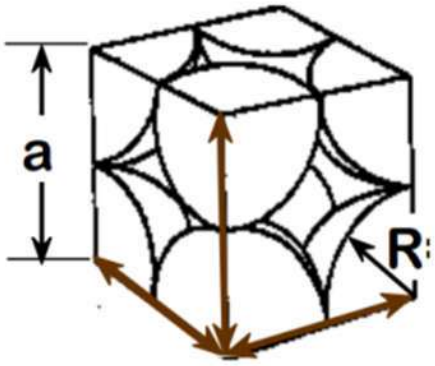
The percentage of the total space filled by the atoms (particles) is called packing efficiency.

To calculate Atomic Packing Factor first we have to know the ***atomic radius versus lattice parameter (the close packed directions in the unit cell) and the co-ordination numbers.***

Co-ordination number: it is the number of atoms that surround a central atom in a solid or the number of nearest neighbours that an atom has in crystals.
Close packed direction: Directions in the unit cell in which atoms are in continuous contact.

I) for simple(primitive)unit cell (sc)

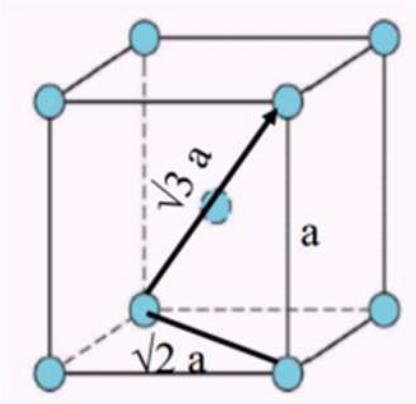
Close packed direction is any edge of the cube



$a = 2R$, $APF = \frac{1atom\, x\, \frac{4}{3}\pi(0.5a)^3}{a^3} =$ 0.52

II) For body centered cubic unit cell (BCC)

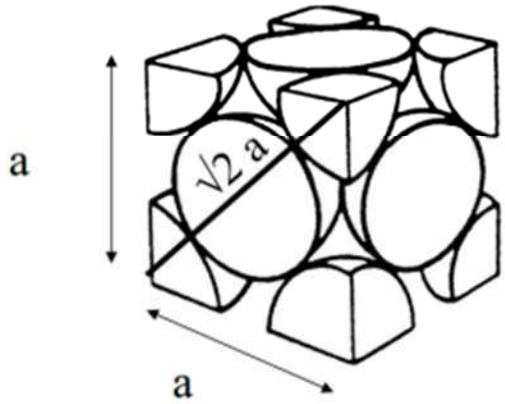
Close Packed Plane cuts the unit cube in half diagonally



$a = 4R/\sqrt{3}$, $APF = \frac{2atoms\, x\, \frac{4}{3}\pi\left(\frac{\sqrt{3}\,a}{4}\right)^3}{a^3} = 0.68$

III) For face centered cubic unit cell (FCC)

Close packed Plane: On each face of the cube



$a = 2\sqrt{2}R,\ APF = \frac{4atoms\ x\frac{4}{3}\pi(a/2\sqrt{2})^3}{a^3} = 0.74$

Index systems for crystal plane

Indexing is the process of determining the unit cell parameters from the peak positions. Miller indices are usually used to specify the crystal orientation of solids. It is shown above that a vector normal to a lattice plane may describe the orientation of this plane.

Miller Indices: Reciprocals of the (three) axial intercepts for a plane, cleared of fractions and common multiples. Miller indices are a symbolic vector representation for the orientation of an atomic plane in a crystal lattice and are defined as the reciprocals of the fractional intercepts which the plane makes with the crystallographic axes. All parallel planes have same Miller indices. Miller indices are used to specify directions and planes. These directions and planes could be in lattices or in crystals. The number of indices will match with the dimension of the lattice or the crystal. E.g. in 1D there will be 1 index and 2D there will be two indices etc.

To determine miller indices of a plane, take the following steps:

- ✓ Read off intercepts of plane with axes in terms of a, b, c
- ✓ Take reciprocals of intercepts
- ✓ Reduce to smallest integer values. If fraction results, multiply each by the denominator of the smallest fraction.

- ✓ Enclose in parentheses, no commas i.e., miller index of the plane is (hkl).

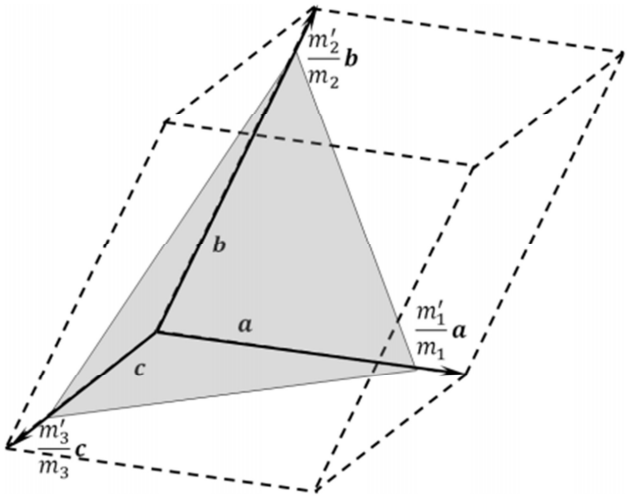


Fig. a: Intersection points of a plane on the three crystal vectors.

If a plane cuts an axis on the negative side of the origin, the corresponding index is negative, indicated by placing a minus sign above the index: (h$\bar{k}$l). The cube faces of a cubic crystal are (100), (010), (001), ($\bar{1}$00), (0$\bar{1}$0), and (00$\bar{1}$). Planes equivalent by symmetry may be denoted by braces around indices: {hkl}. The direction is indicated as [hkl].

Example-1:

Axis	X	Y	Z
Intercept points	1	1	∞
Reciprocals	1/1	1/1	$\frac{1}{\infty}$
Smallest ratio	1	1	0
Miller indices	(110)		