Chapter 2. Atomic Packing

Contents

2-1. Packing of directional bonding atoms

- 1장에서는 원자와 원자와의 결합.
- 2장에서는 원자들의 충전(packing)을 통해

전체 결정(crystal)이 어떻게 형성되는지.

- 결정은 이온이나 원자 또는 분자들로 구성된 3차원적인 집합체.
- 원자, 분자, 이온에서 시작하여 모든 방향으로 계속 추가로 결합이 일어나서 결정을 형성함.

- 원자들의 배열과 충전은 결합이 방향성인지 비방향성인지에 따라 달라진다.

- **Directional bond** : covalent bond, hydrogen bond, van der Waals bond
- **Indirectional bond** : ionic bond, metallic bond

- For the directional bond, atoms are packed by satisfying the bonding angle. This bonding angle determines the **bonding polyhedron(결합다면체)**.

- For the indirectional bond, bondings are like spherical symmetry and there is no restriction on the bonding angle. Generally, the method to pack the spheres in the box can be thought.
- 이 경우에는 원자 배열은 중심 원자나 이온을 접하는 모든 이웃하는 원자나 이온의 중심을 연결해서 만들어지는 배위다면체(coordination polyhedron)로 이루어진다고 설명할 수 있음.

2-1 Atomic packing for directional bond

- Directional bonds are asymmetric and the number of bonds and bonding angle for one atom are determined. Therefore, the atomic array are determined by the the number of bonds and bonding angle.
- The direction of bonding is determined by the quantum mechanical state of the electron that contributes to the bonding.

(ex) s-orbital : no preferred direction

p, d-orbital : preferred direction.

- For the covalent bond, half-filled orbital will contribute to the bonding, so the number of half-filled orbitals same as that of bondings.
- For example, for the atom P(phosphorous), there are 3-half-filled orbitals. So, each P atom has 3-bondings to the other P atoms to make net structure by satisfying the octet rule.

For IVA family like Si(규소), Ge(게르마늄), Sn(주석), as discussed in C(탄소), there are 4-mixed bondings like 3sp3, 4sp3, 5sp3 to make a regular tetrahedron as shown in Fig. 2-1(a). Figure 2-(b) shows the 2-dimensional plane figure of carbonic bond and electron arrays.

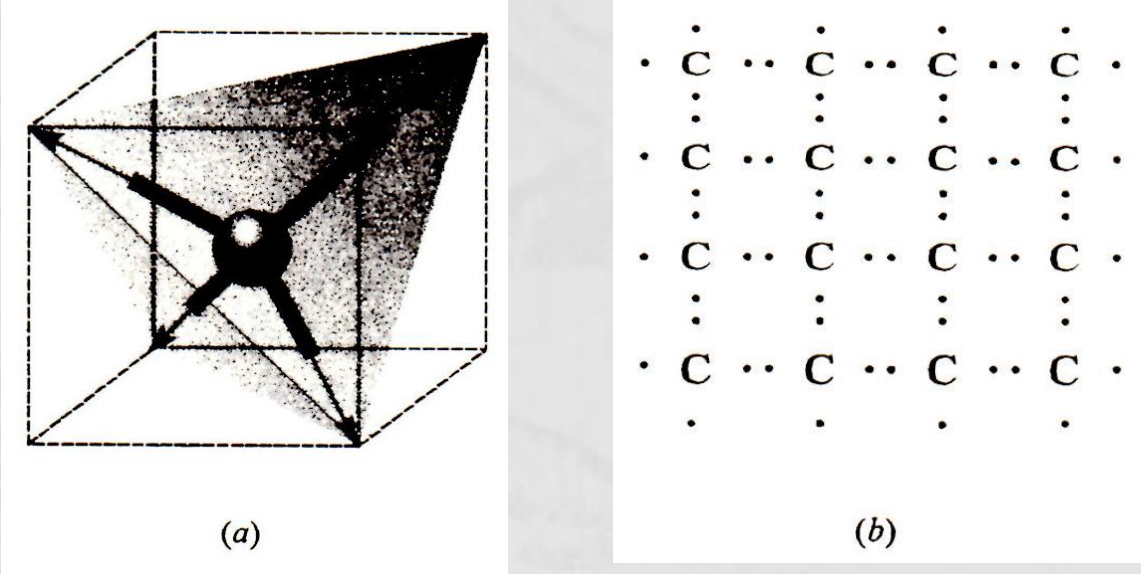


Fig. 2.1 (a) geometrical array of sp3 mixed bond on the surround of C(carbon). (b)2-dimensional plane figure of carbonic bond and electron arrays.

실제 결정은 3 차원에서의 원자 배열이므로, 3 차원에서의 충전을 살펴보자. 하나의 탄소 주위에 탄소의 꼭지점을 갖는 정사면체가 만들어지도록 하면서 그림 2-1과 같이 탄소를 계속해서 결합시켜 3 차원적인 망목(network)을 만들 수 있다. 이렇게 만들어진 탄소의 원자 배열이 바로 그림 2-2에 나타낸 **다이아몬드 구조**이다.

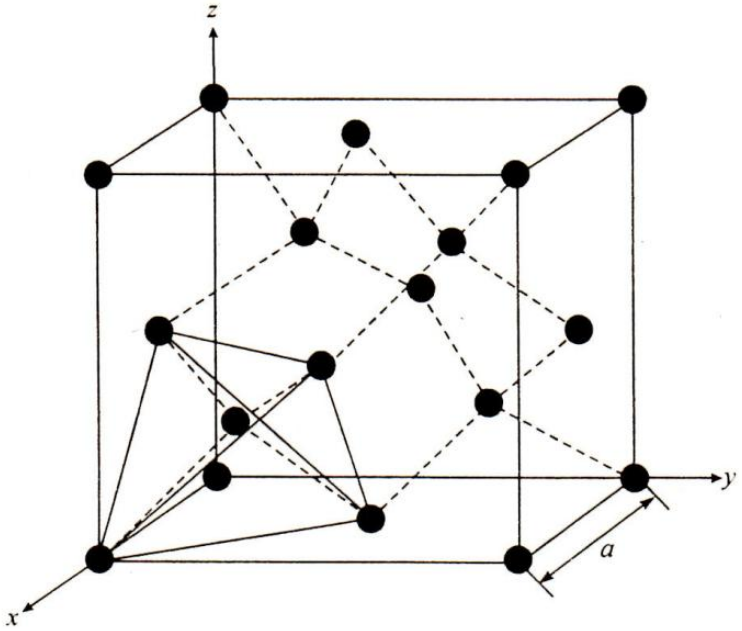


그림 2-2 다이아몬드 구조.

Body-centered cubic, bcc

- For indirectional bonds of atoms, about 2/3 of metal atoms, they have hcp or fcc structure to get the minimized binding energy system.
- Otherwise, 1/3 of metal atoms, they have **body-centered cubic (bcc) structure** as shown in Fig. 2-6.
- They are the alkali elements including **Li, Na, K** and transition metal elements including **Fe, Cr, W**.

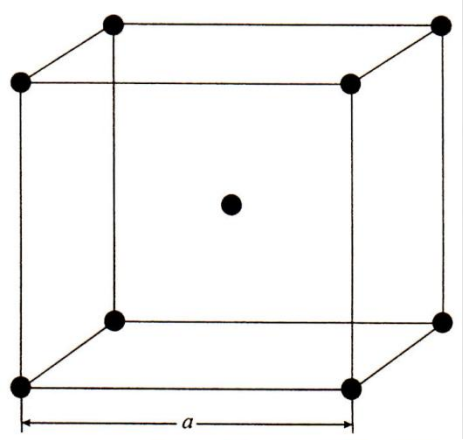


그림 2-6 체심 입방 구조.

2-2 Atomic packing for indirectional bond with same size atoms

- For indirectional bond, there are ionic, metallic and van der Waals bond.
- Matallic bond is for the atoms with same size and ionic bond is for the atoms with different size.

- Generally speaking, bonding is made by following the method to minimize the binding energy per unit volume.
- For the metallic bonding, all the atoms are same kind and same size, so there is no directional dependency.
- As discussed in chap. 1 about the metallic bonds, the binding energy for 1 bonding is 'negative', therefore, as the number of bondings increase, the total binding energy will be lower.

- 금속결합에서 결합에너지를 최소화하는 방법은 결합 수를 최대로 하는 것이다. 이는 **단위 체적당 원자수가 최대로 되게 충전하는 것을 의미**한다.
- We can suppose that the metal atom is like a hard sphere. As shown in Fig. 2-3(a), around one sphere, there can be six spheres for maximum. If we extend to the 3-dimension, 12 spheres will surround the sphere for maximum as shown in Fig. 2-3(b).
- 12개의 원자가 접하도록 충전되어 최대한의 충전 밀도를 갖는 충전을 조밀 충전(close-packing)이라 한다.

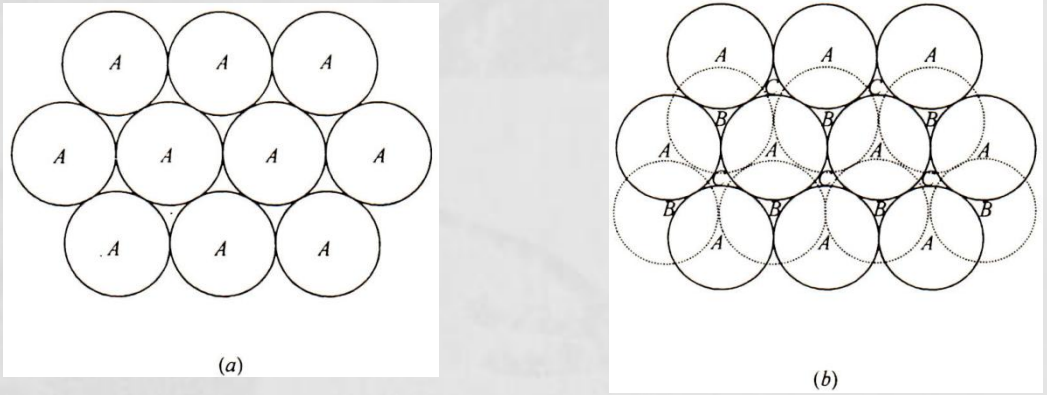


그림 2-3 (a) 2 차원에서 구를 조밀 충전하는 방법, (b) 3 차원에서 구를 조밀 적층하는 방법.

Hexagonal close-packing structure

- Characteristics shared by HCP
- Every atom has ***twelve nearest neighbors***
- Stacking sequence: ABABAB…
- Stacking direction: c-axis of the hexagonal unit cell
- Close-packed planes º *basal planes of the unit cell* 6 in same layer, forming a hexagon
- Atomic packing factor(APF) = 74% - maximum packing efficiency for equal-sized spheres

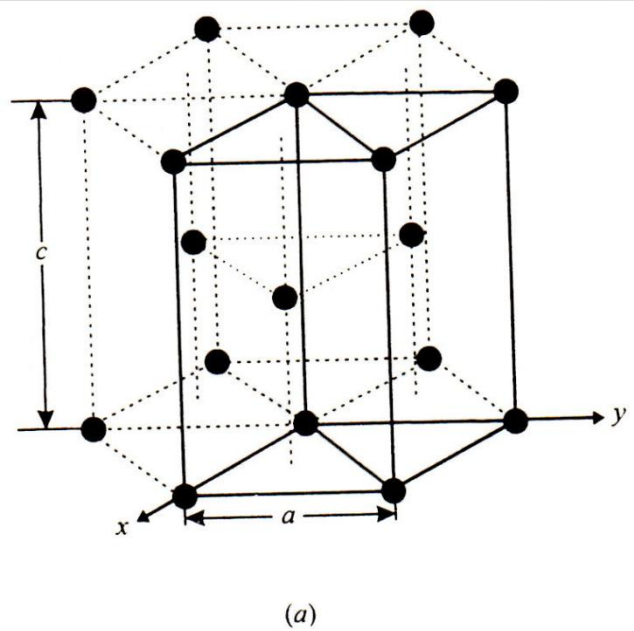
• Interstices (per cell)

4 trahedral : (0, 0, 3/8), (0 ,0, 5/8), (2/3, 1/3, 1/8), (2/3 ,1/3, 7/8)

2 octahedral : (1/3, 2/3, ¼), (1/3, 2/3, ¾)

- In ideal HCP, with atomic radius r, $a = 2r$, $c = 4\sqrt{2/3}\, r$
- Examples: ***Mg, Ti, Zn, Be, Co, Zr, Cd***

Hexagonal close-packing structure



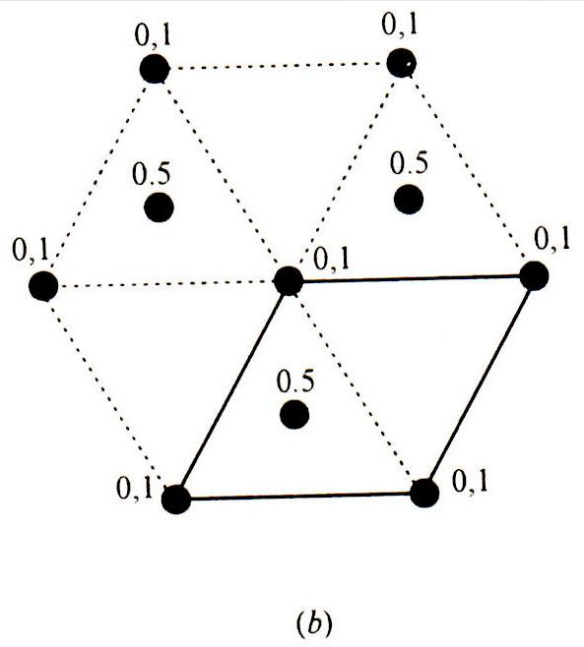


그림 2-4 (*a*) 육방 조밀 충전, (*b*) 육방 조밀 충전을 *c* 축 방향에서 본 그림.

For HCP structure, APF(atomic packing factor) can be calculated as following ;

$$\text{채움율} = \frac{2(\frac{4}{3}\pi r^3)}{(2r)(2r)\sin 120^\circ (4\sqrt{2/3}\, r)} = \frac{\pi}{3\sqrt{2}} = 0.74 \qquad (2\text{-}1)$$

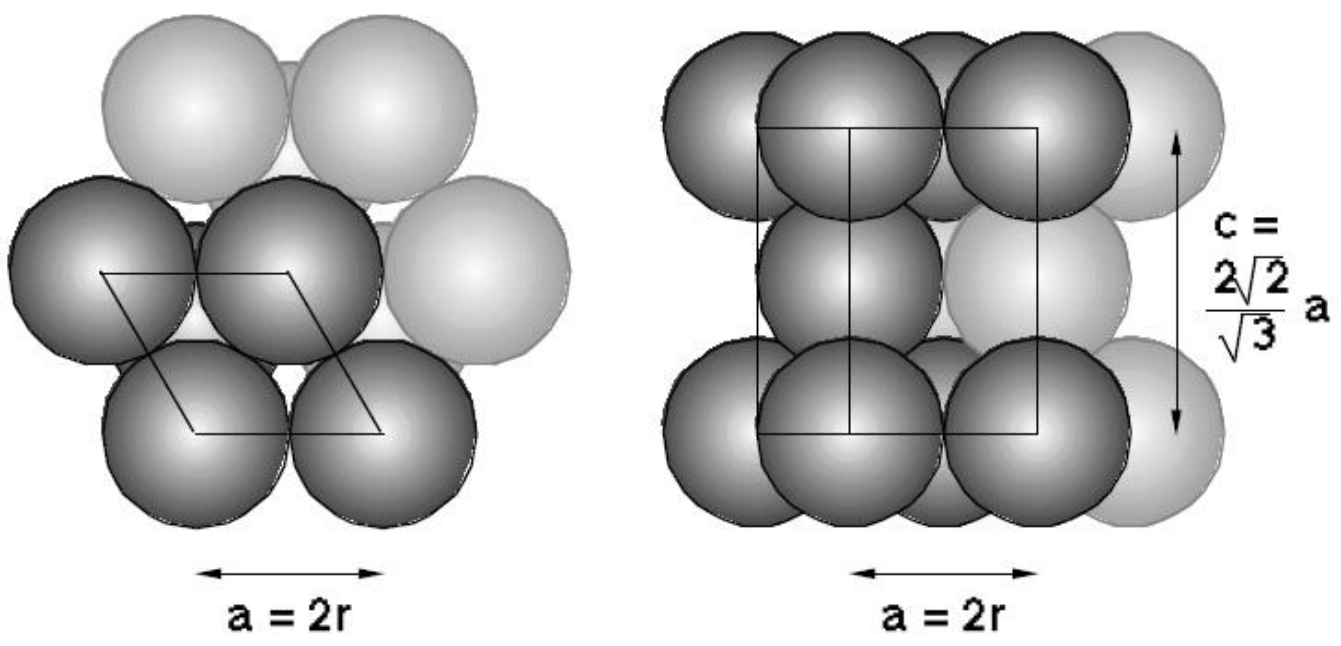


그림 2-4-1 (a) Second "A" layer (0001). (b) Front view of HCP structure

Cubic close-packing (CCP)

- For another method, if the stacking order is ABCABCABC……, then this close-packing is called **'cubic close-packing'**.
- As shown in figure 2-5(a), if the close-packing stacking direction is the diagonal of a cube, then the structure will be **face-centered cubic(fcc)** structure as shown in Fig. 2-5(b).

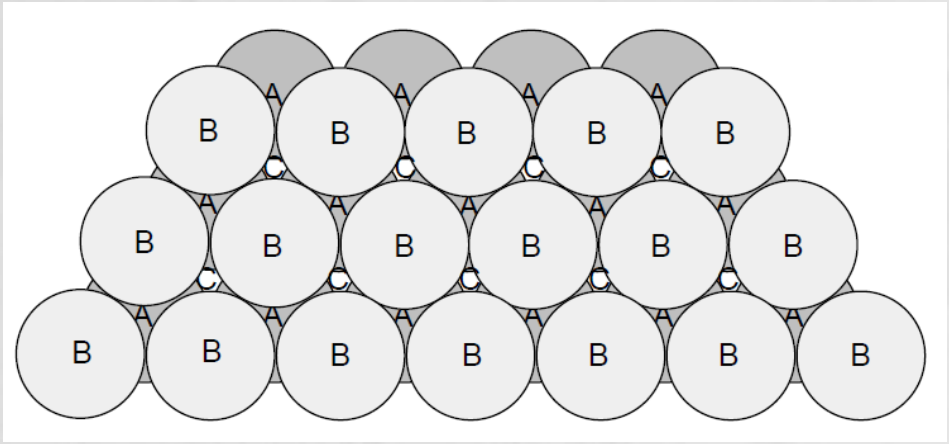
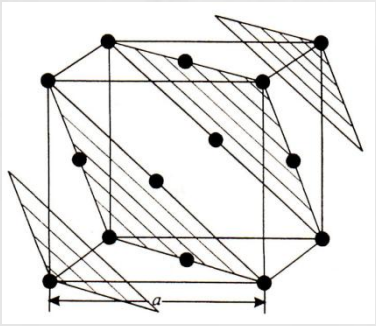


그림 2-3(b) 3 차원에서 구를 조밀 충전하는 방법, Cubic close-packing(CCP).

(a)



(b)

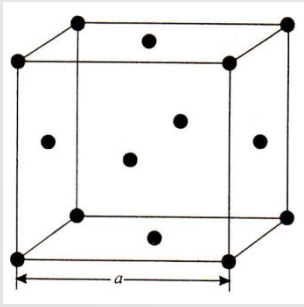


그림 2-5(b) 면심입방구조.
(a)의 빗금진 면이 조밀 충전 면임.

Cubic close-packed (CCP)

- Stacking sequence: ABCABC…
- Stacking direction: [111] in FCC lattice
- Close-packed planes: {111}
- 4 atoms per unit cell: (0, 0, 0), (1/2,1/2,0), (1/2,0,1/2), (0,1/2,1/2)
- Interstices (per CCP cell):

  - 8 tetrahedral : (1/4,1/4,1/4), (3/4,1/4,1/4), (1/4,3/4,1/4), (3/4,3/4,1/4), (1/4,1/4,3/4), (3/4,1/4,3/4), (1/4,3/4,3/4), (3/4,3/4,3/4)

  - 4 octahedral : (1/2,1/2,1/2), (1/2,0,0),(0,1/2,0),(0,0,1/2)

- Examples:

  γ-Fe (high-T form), Al, Ni, Cu, Ag, Pt, Au, Pb