2015, Spring Semester

Energy Engineering (Class 458.624)

- Professor
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  - ☐ Classroom : 302-720
  - ☐ Class time : Monday, Wednesday 11:00 ~ 12:15

- Textbook

(1) Introduction to Solid State Physics (Charles Kittel)

(2) Solid State Electronic Devices (Ben G. Streetman, Sanjay Kumar Benerjee)

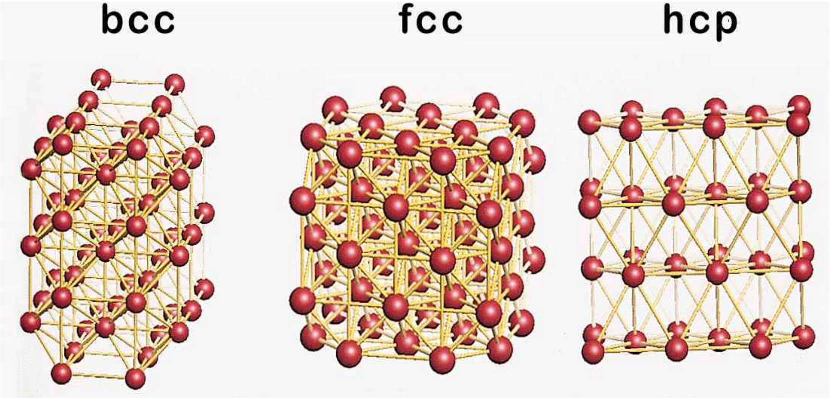
Crystal Structure and Bonding

In this chapter, our interest is in

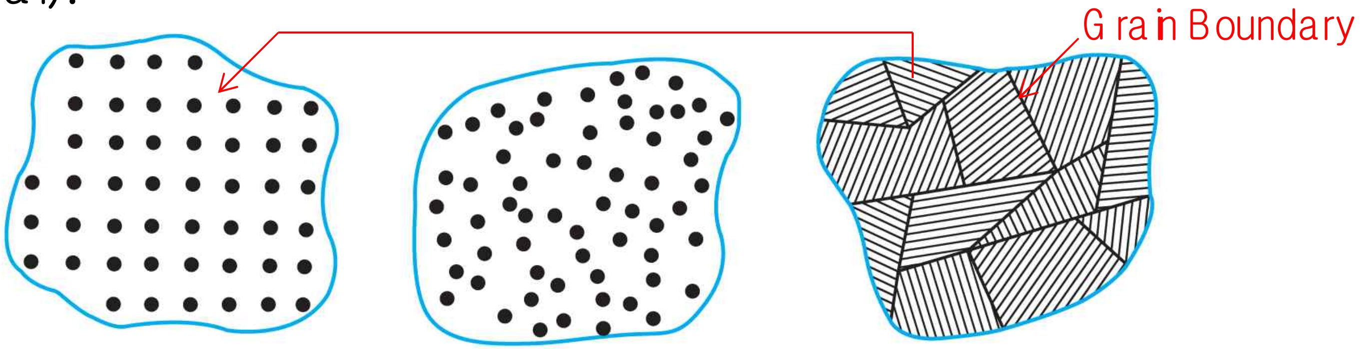
(1) Crystal Structures and Properties
(2) Grain Boundaries
(3) Lattice Classification
(4) Close Packing and Packing Efficiency
(5) Typical Crystal Structures
(6) Planes and Directions
(7) Epitaxial Growth
(8) Types of Bonding in Crystals

Crystal Structures

- Crystal structure tells how atoms are arranged in the solid.
- Many properties of materials are affected by their crystal structure.
- Typical method to check the crystal structure : X-ray scattering



- However, not all solids are crystal: some have no periodic structure at all (amorphous), and others have many small regions of single crystal materials (polycrystal).



(a) Crystalline
Microprocessor, DRAM

(b) Amorphous
Thin film PV, LCD

(c) Polycrystalline
Si bulk PV, OLED

Grain boundaries

Grain boundaries

~ interfaces where crystals of different orientations meet

~ crystals on each side of the boundary being identical except in orientation ~ grain boundary areas contain defects, dislocations, and impurities

-Since grain boundaries are defects in the crystal structure they tend to decrease the electrical and thermal conductivity of the material.

-The high interfacial energy and relatively weak bonding in most grain boundaries often makes them preferred sites for the onset of corrosion.

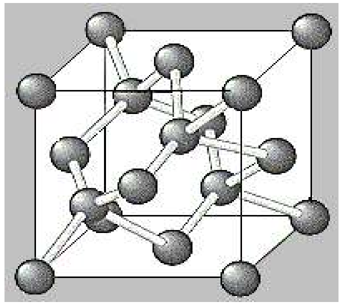
-Grain boundaries are in general only a few nanometers wide. In common materials, crystallites are large enough that grain boundaries account for a small fraction of the material.

- In nanocrystalline solids, however, grain boundaries become a significant volume fraction of the material, with profound effects on material properties. In the limit of small crystallites, the material ceases to have any crystalline character, and thus becomes an amorphous solid.

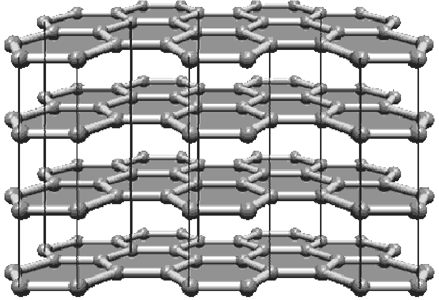
Diamond vs Graphite

Why is the crystal structure important? Let's see examples..

FCC structure

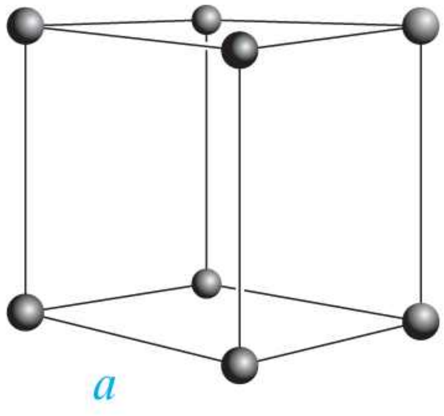


Planar, layered structure

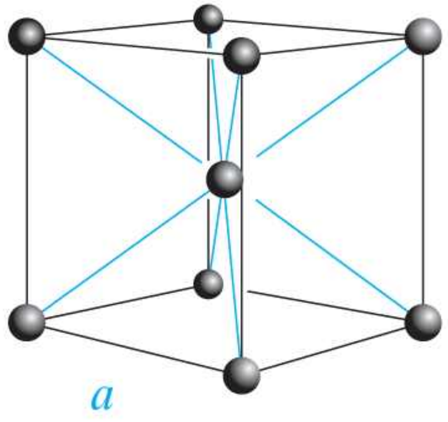


- Both diamond and graphite consist of only 1 kind of atom, carbon.
- The difference is in how those atoms are arranged: diamond has FCC structure and graphite has planar, layered structure of hexagonal honeycomb layer (graphene).
- Diamond is transparent and very hard. And diamond is chemically inert.
- Graphite is black and soft, and easy to be exfoliated into graphene layers. Graphite is very useful for catalyzing reactions (electrochemical electrodes).
- The carbon atoms in diamond are each bound to 4 others in a 3-dimensional network (FCC). To change the shape of a diamond or break it requires many of these strong bonds be broken, which explains its superb strength. Since there is little room for other molecules to get into the structure, diamond is not very reactive.
- Graphite consists of hexagonal sheets. Each sheet is weakly bound and spaces between the layers allow other molecules to enter, explaining catalytic properties.

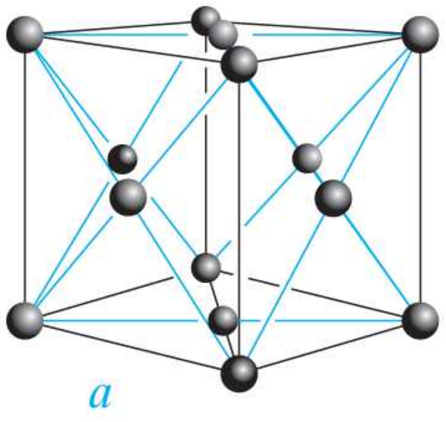
Cubic Lattice



Simple cubic



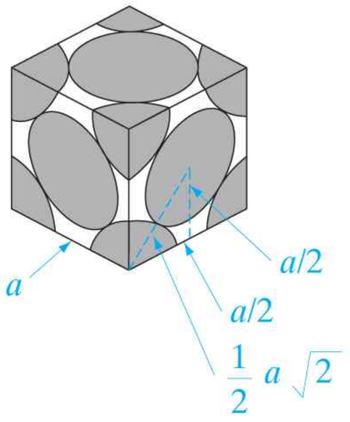
Body-centered cubic



Face-centered cubic

- Cubic Lattices: above figures are unit cells for three types of cubic lattice structures.
- SC (simple cubic), BCC (body-centered cubic), FCC (face-centered cubic)

- We can calculate the max fraction of the lattice volume filled with atoms by assuming atoms as hard spheres (Let's see FCC case).
- FCC (right figure): a“” is the lattice constant. The distance between atoms is $\sqrt{2}a/2$. The radius of atom is $\sqrt{2}a/4$.
- Since there are 4 atoms per cube, the packing fraction is as follows: volume of atom × 4 / volume of cube × 100 = 74%

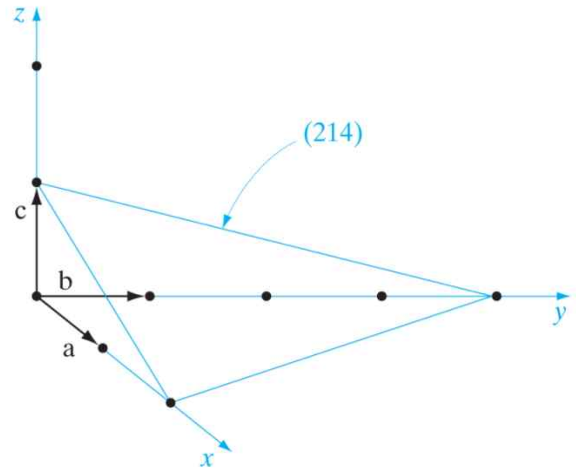


Planes and Directions

- When we discuss about single crystal materials, it is very useful to use planes and directions of the lattice, such as [hkl], where h, k, l are integers.
- For example, [100] surface or [111] surface of single crystal silicon wafer have different electrical and chemical properties. [100] surface has higher electron mobility and higher etching rate than [111] surface.
- The three integers describing a particular plane are found in the following way:
  - (1) Find the intercepts of the plane with the crystal axes. Then express these intercepts by using basis vectors multiplied with integers.
  - (2) Take the reciprocal of these integers. Then reduce these to the smallest set of integers h, k, and l.
  - (3) Label the plane as [hkl].

Example)

- The plane on the right figure has intercepts at 2a, 4b, and 1c.
- The reciprocals are $\frac{1}{2}$, $\frac{1}{4}$, and 1.
- These are reduced to 2, 1, and 4.
- Therefore the plane has the label of [214].



Planes and Directions

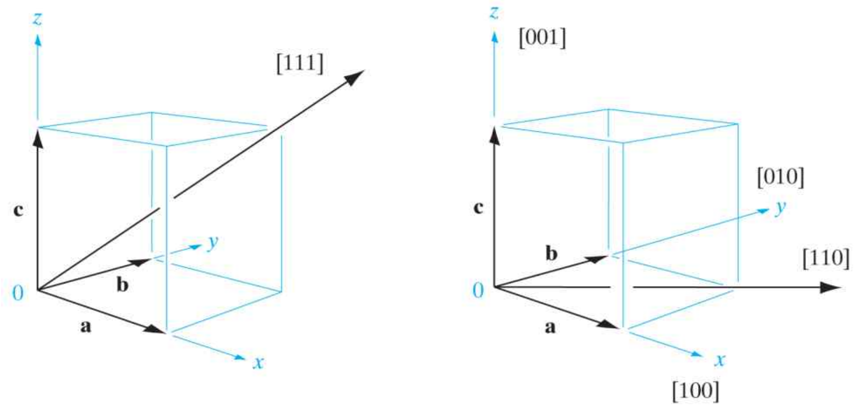


Figure.
Crystal directions
in the cubic lattice

- Crystal directions have the same relationship with the labeling of the plane. In other words, [214] plane has the crystal direction of [214].
- The body diagonal of cubic lattice (above, left frame) has [111] direction.
- Many directions of the lattice are equivalent. The crystal axes in the cubic lattice [100], [010], and [001] are all equivalent and are called <100> directions. (See above figure, on the right frame)

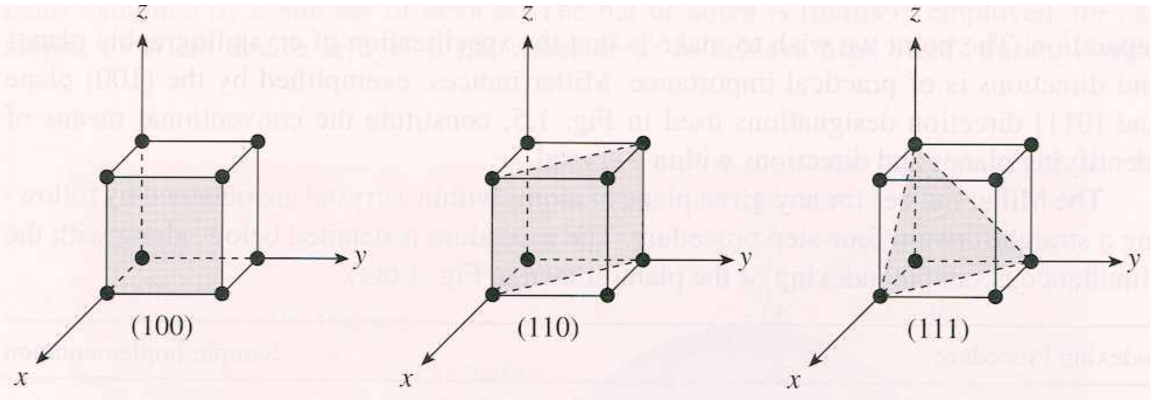
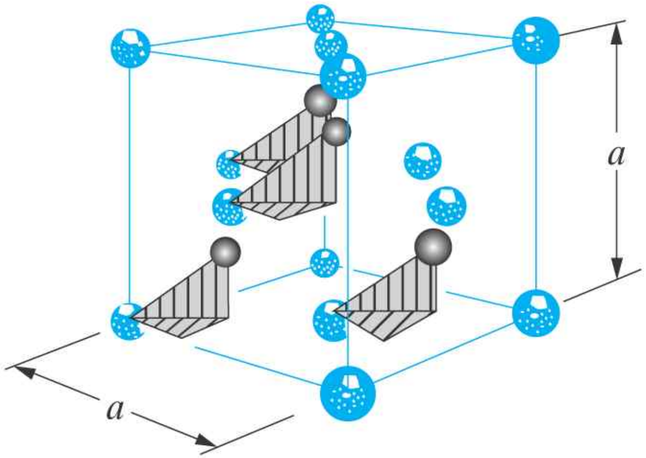
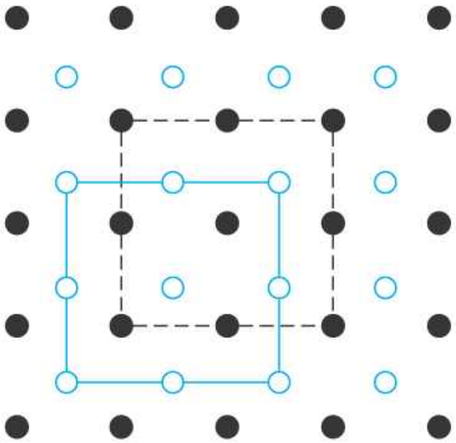
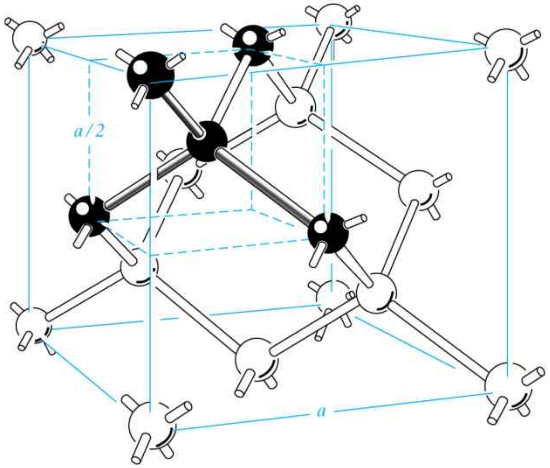


Figure.
[100], [010], and
[001] crystal planes

Diamond Lattice



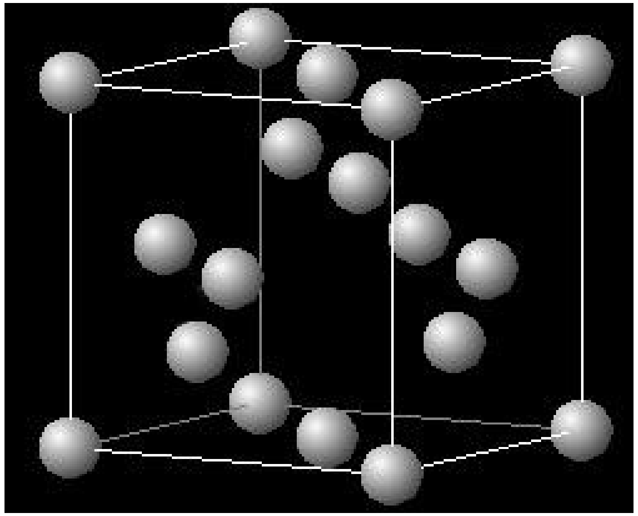




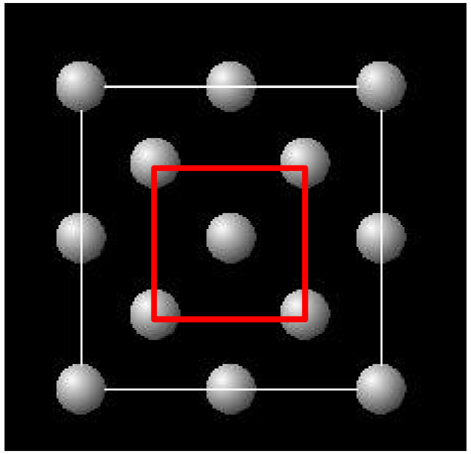
- Many important semiconductor crystals (Si,Ge,C) have diamond lattice structure, which is composed of fcc lattices.
- The diamond structure can be thought of as an fcc lattice with an extra atom placed at a/4+b/4+c/4 from each of the fcc atoms.
- Above figures show diamond lattice structure: a unit cell of two fcc structures (left), its top view (center) and 3D view (right).

Crystal Planes of Si

Unit cell:

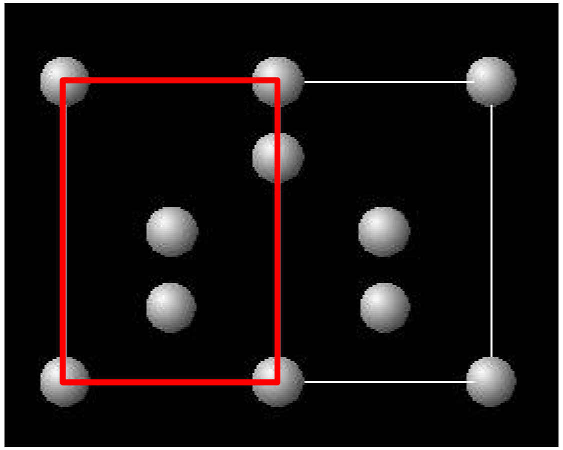


View in <100> direction



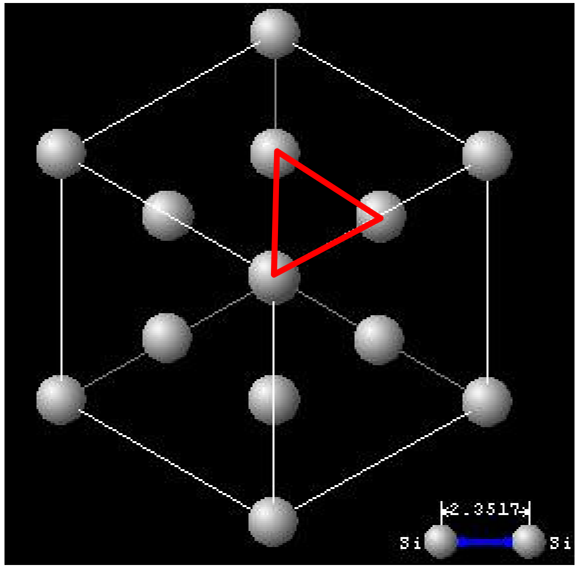
Areal density: $2.0/a^2$

View in <110> direction



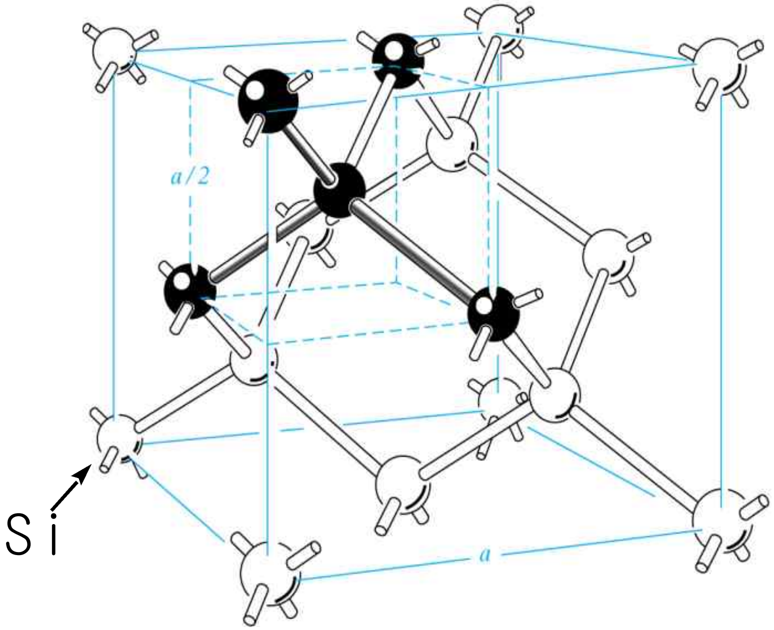
Areal density: $2.82/a^2$

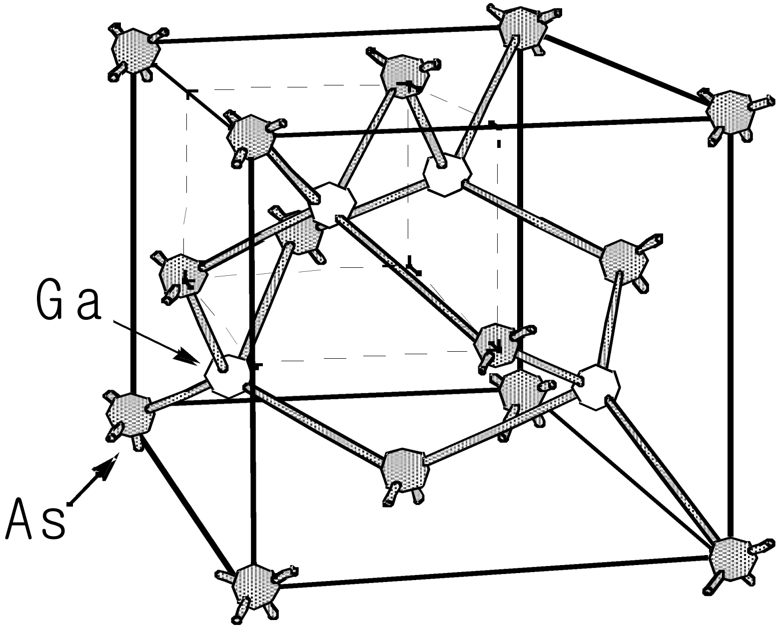
View in <111> direction



Areal density: $2.31/a^2$

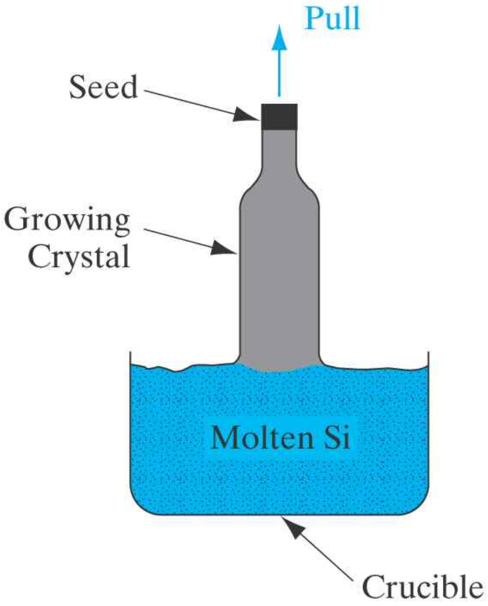
Zinc Blend Lattice

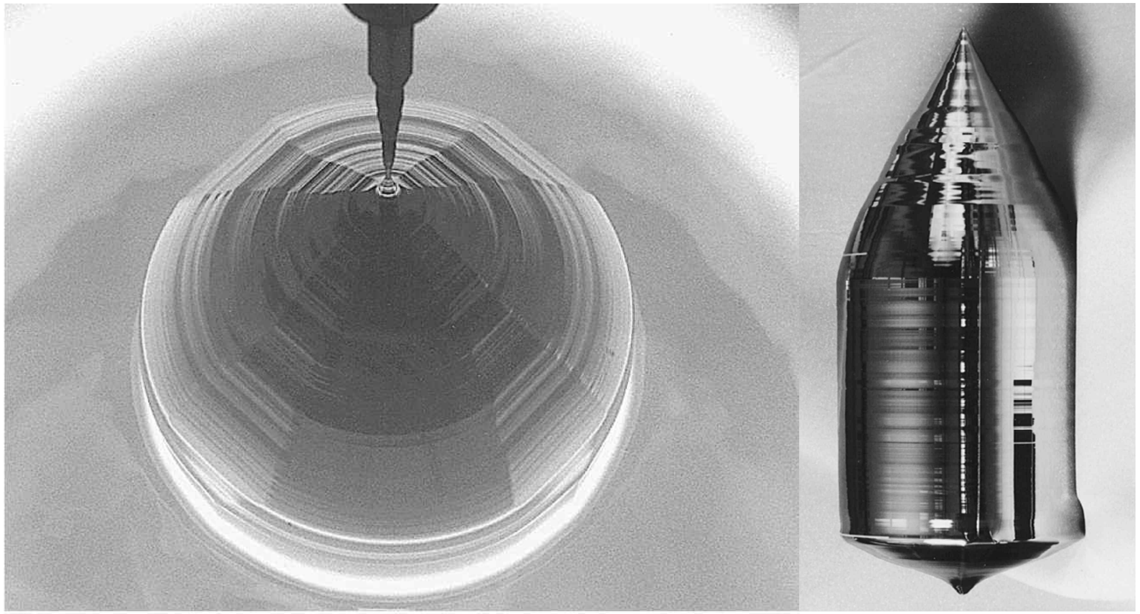




- Many important III-V compound semiconductor crystals (GaAs, GaN, InP) have zinc blend lattice structure, which is similar with diamond structure.
- The basic structure (two misaligned fcc structures) is same. But if the atoms of two fcc structures are same, then it is diamond structure, while if two are different, then it is zinc blend structure.
- Compound semiconductors are important for optoelectronic devices, such as light emitting diodes or photodetectors, and high speed devices (MESFET).

Bulk Crystal Growth





- Bulk single crystal silicon is made through Czochralski method.
- Si is melted in qualtz-lined graphite crucible, whose temperature is >1400°C.
- Single crystal seed is dipped into the molten Si and pulled to make Si ingot.
- Cutting and polishing finishes the fabrication of silicon wafers.
- Most silicon wafers have [100] surface due to its high mobility.

Bondings between Atoms

Types of Bonding in Crystals

Between atoms
(1) Metallic Bonding
(2) Ionic Bonding
(3) Covalent Bonding

Between molecules
(1) Hydrogen Bonding
(2) Van der Waals Force

Metallic Bonding

- Definition

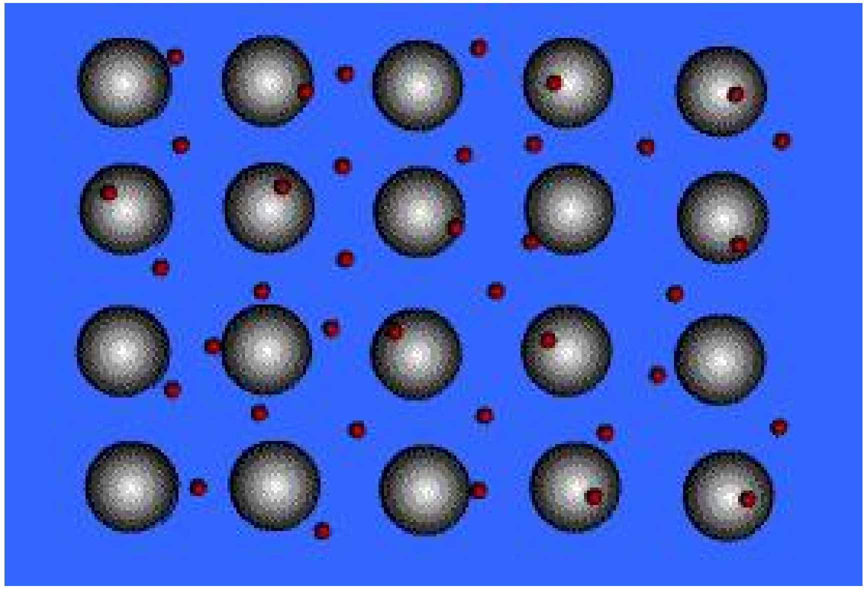
  -a bond formed by the attraction between positively charged metal ion (cation) and the shared electrons that surround it (sea of electrons;electron clouds)

  ex.Cu

- Properties

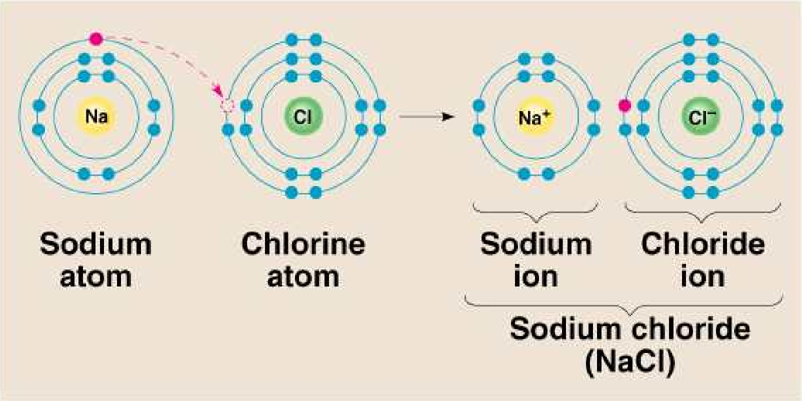
  -Conductivity:Good;electrons can move freely

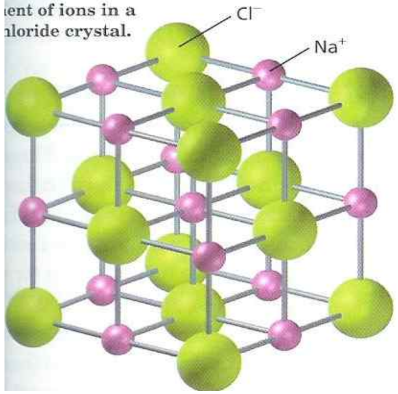
  -Mechanical property:malleable;lattice structure is flexible

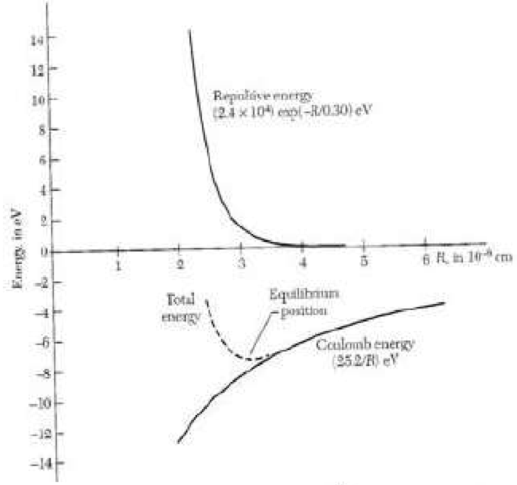


← Sea of electrons

Ionic Bonding







$$U(R) = \underbrace{-N\frac{\alpha e^2}{4\pi\varepsilon_0 R}}_{\text{attractive (Coulomb)}} + \underbrace{N\frac{A}{R^n}}_{\text{repulsive}}$$

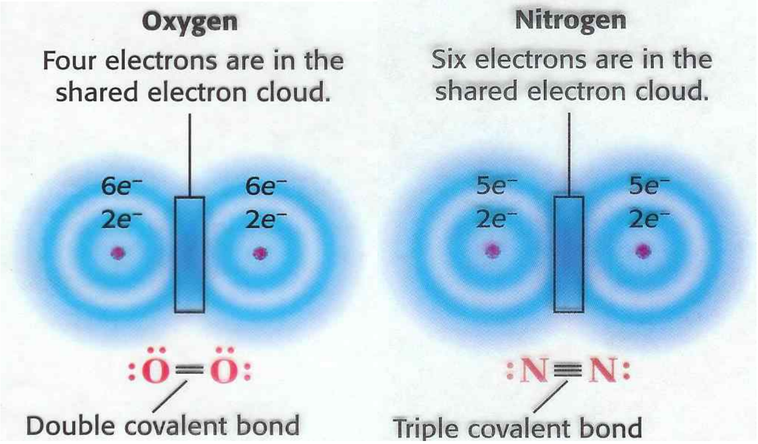
- Usually involve atoms of strongly different electro-negativity
- Bond formed by transfer of electrons
- Examples; NaCl, $CaCl_2$, K_2O
- Strong electrical attractions between oppositely charged ions : strong bonds
  - -high melting/boiling point
  - -conductivity
    - solid : ions are so close together, fixed positions, (can't move)
      NO conductivity
    - liquid : ions are freely moving due to a broken lattice structure
      Good conductivity

Covalent Bonding

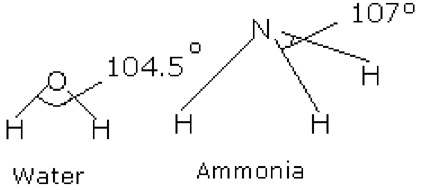
- Definition
  - Chemical bond in which two atoms share a pair of valence electrons
  - Between non-metallic elements of similar electronegativity
  - Stable non-ionizing particles: they are not conductors at any state
  - Can be a single, double, or triple bond

    single, 2e^-s (−); double, 4e^-s (=); triple, 6e^-s (≡)
  - Mostly low melting/boiling points
- 2 types of bonds
  - Non Polar
    - bonded atoms that share e^-s equally
    - same atoms bonded

      ex. Cl - Cl: Cl_2
  - Polar
    - bonded atoms that do not share e^-s equally
    - different atoms bonded



ex.



Hydrogen Bonding

A special case of permanent dipole-dipole interactions

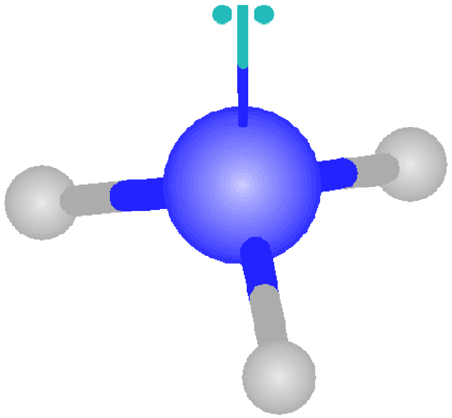
Properties

- They are stronger than Van der Waals forces (next slide)
- Molecules with hydrogen bonds have higher BPs than molecules that don't

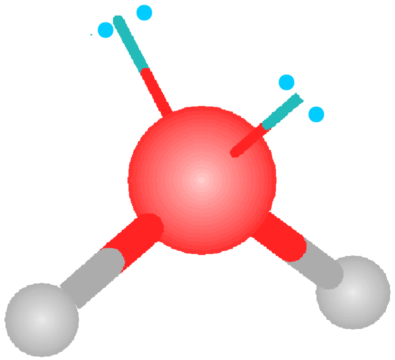
What we need…

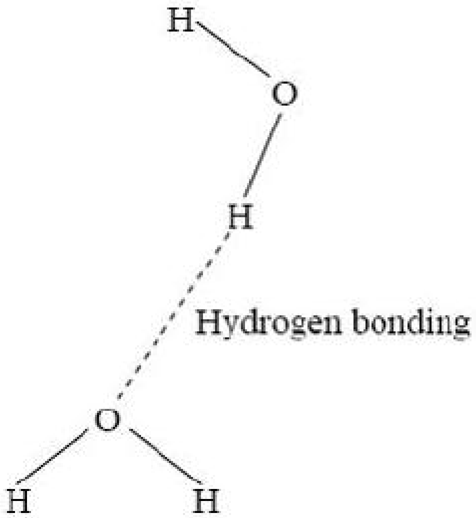
- A hydrogen atom covalently bonded to an electronegative atom … N, O or F.
- A lone pair of electrons on the electronegative atom.

ammonia, NH_3 …



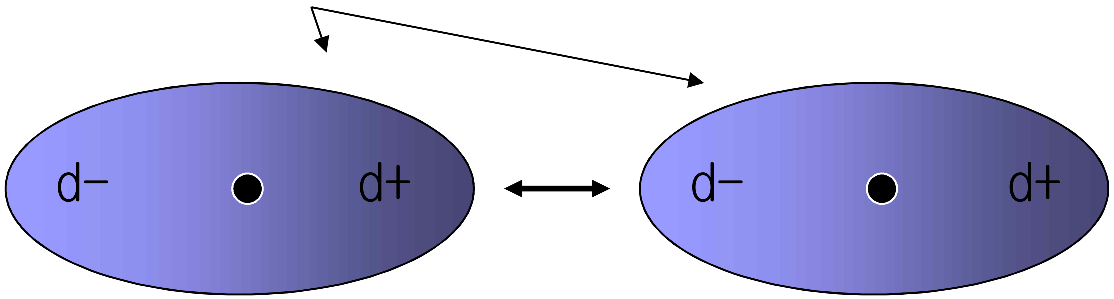
water, H_2O …





van der Waals Force

Two electrically neutral, closed-shell atoms



i) Temporary dipole resulting from quantum fluctuation

Gives net attraction

ii) Induced dipole, due to presence of other dipole

- Weak interaction forces due to the quantum fluctuation of charge, which causes arising of temporary dipole moments and weak attractive force
- Although Van der Waals forces are weak, they are often the only attractive force between molecules.