PY2N20
Material Properties and Phase Diagrams
Lecture 10

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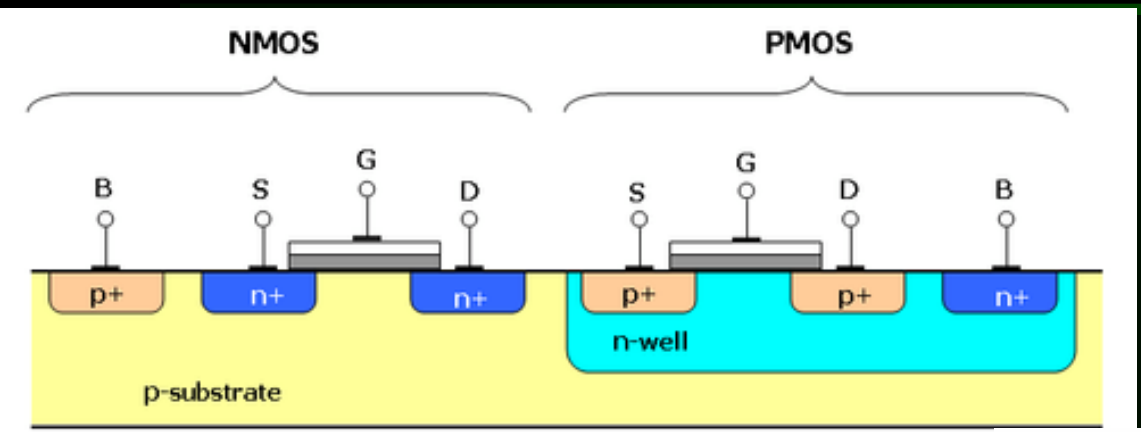
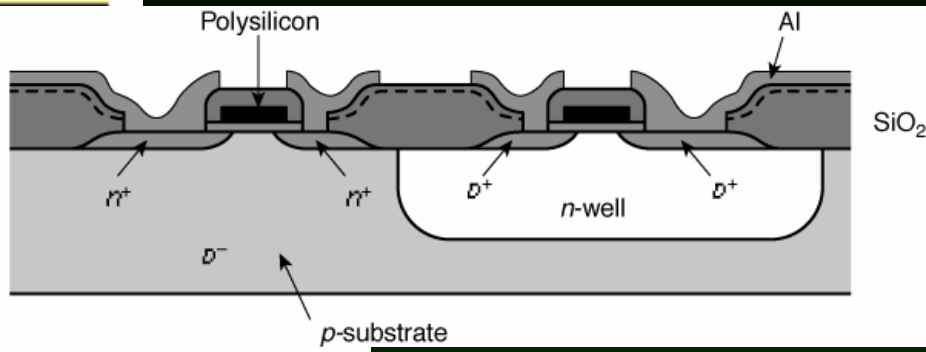
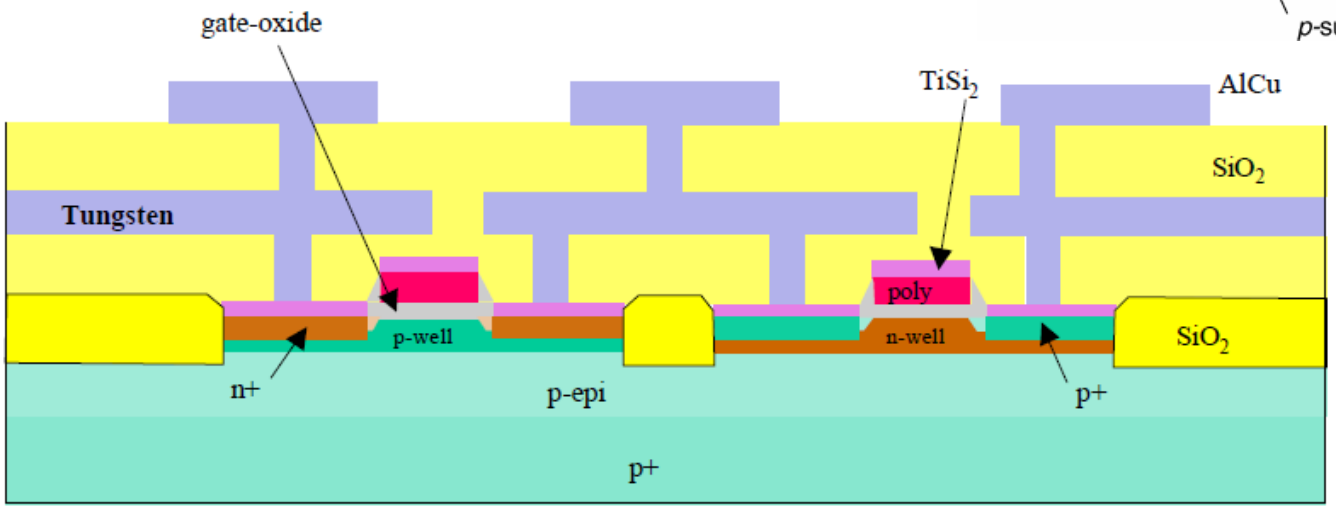
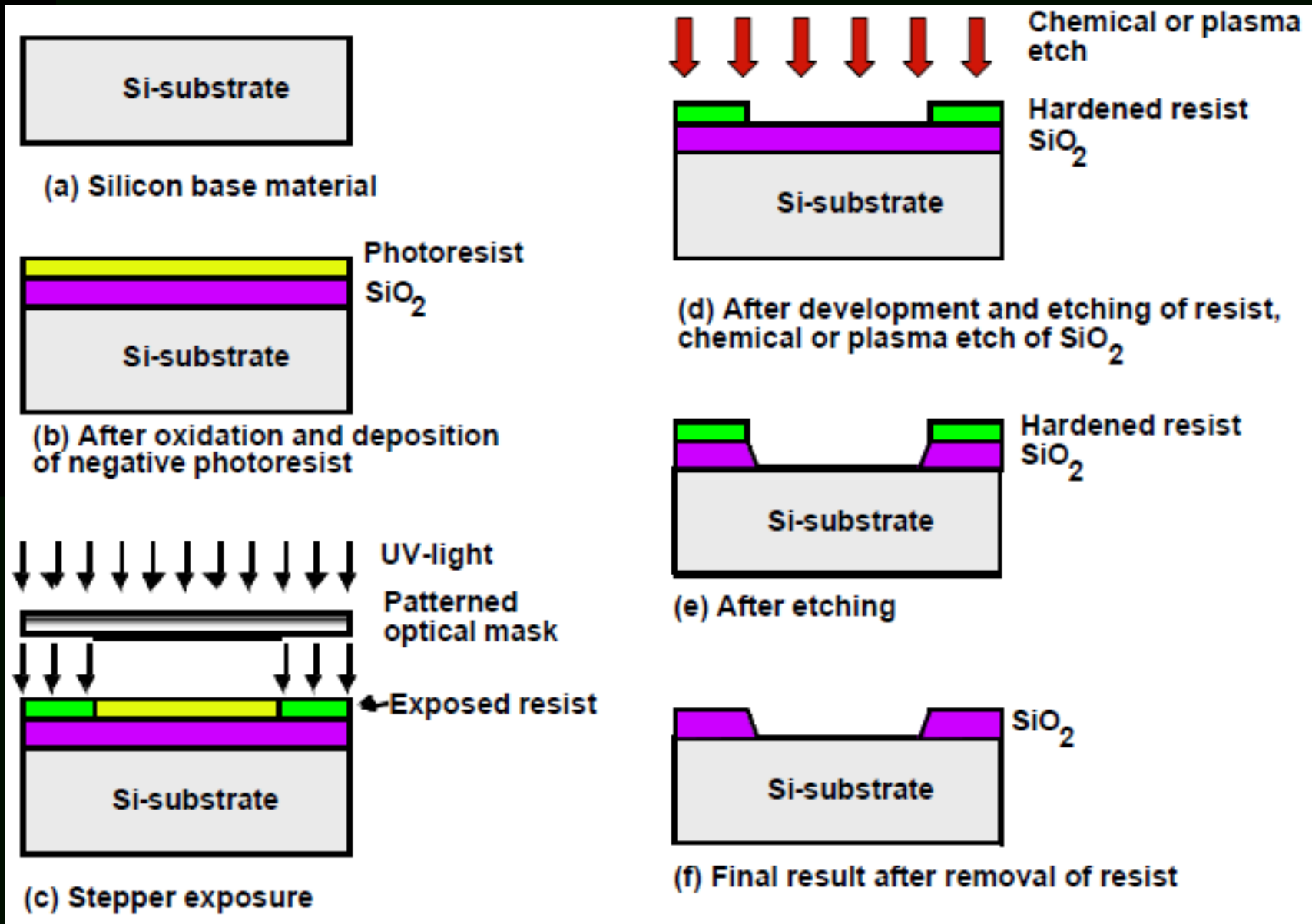
Modern CMOS pair structure



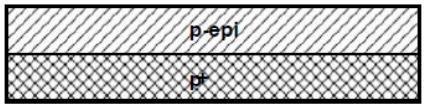




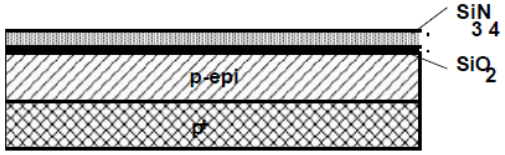
Photolithographic Process



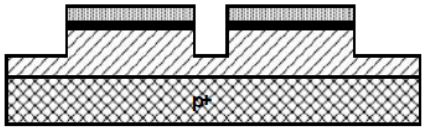
CMOS Processing Steps



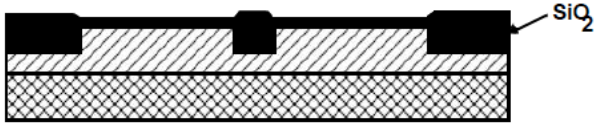
(a) Base material: p+ substrate with p-epi layer



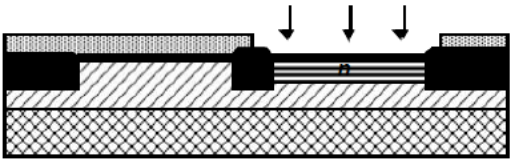
(b) After deposition of gate-oxide and sacrificial nitride (acts as a buffer layer)



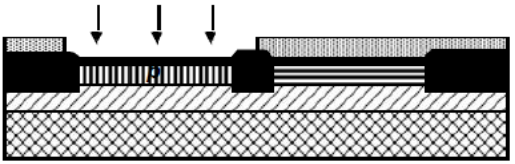
(c) After plasma etch of insulating trenches using the inverse of the active area mask



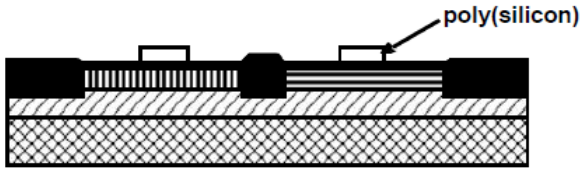
(d) After trench filling, CMP planarization, and removal of sacrificial nitride



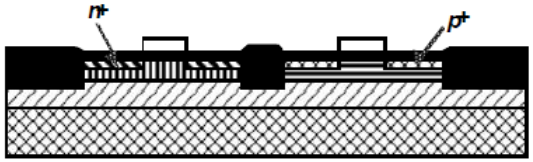
(e) After n-well and V_{Tp} adjust implants



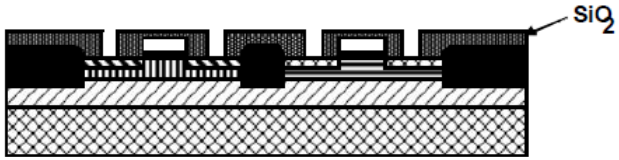
(f) After p-well and V_{Tn} adjust implants



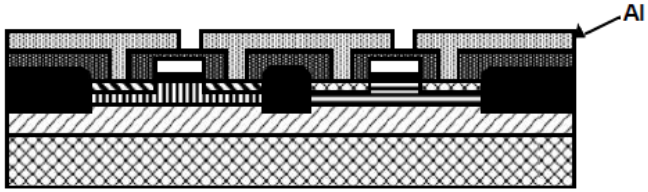
(g) After polysilicon deposition and etch



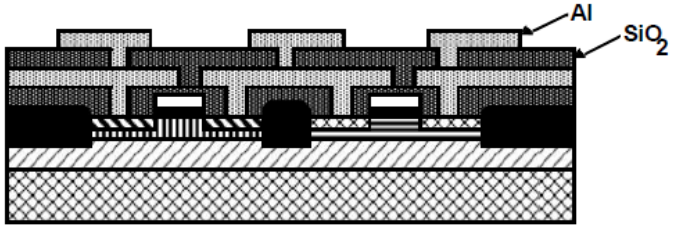
(h) After *n*+ source/drain and *p*+ source/drain implants. These steps also dope the polysilicon.



(i) After deposition of SiO_2 insulator and contact hole etch.

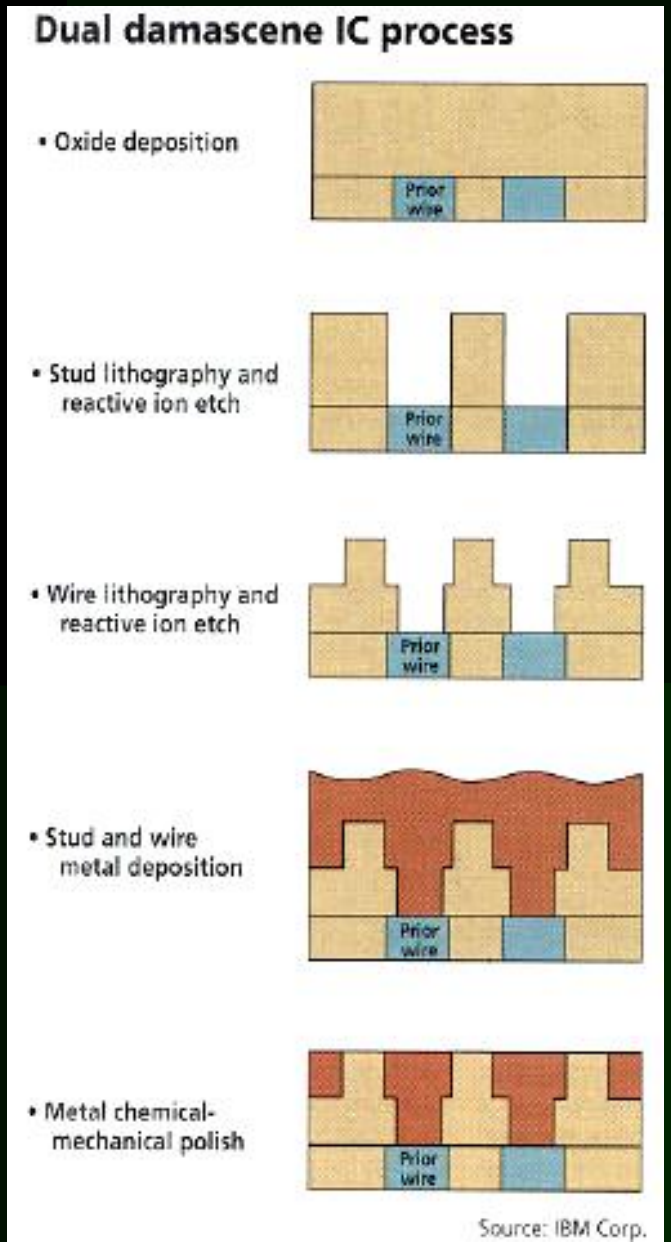


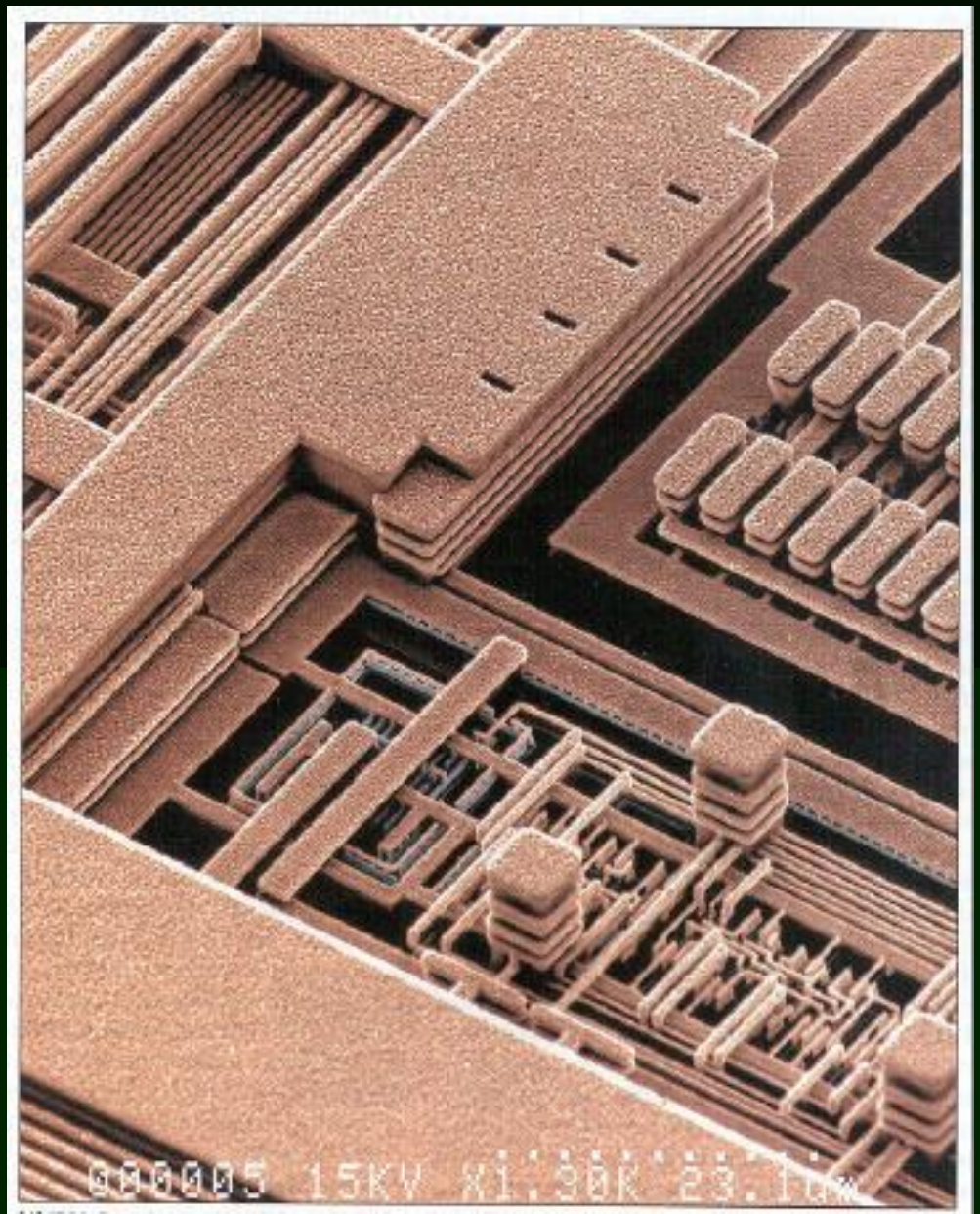
(j) After deposition and patterning of first Al layer.



(k) After deposition of SiO_2 insulator, etching of via's, deposition and patterning of second layer of Al.

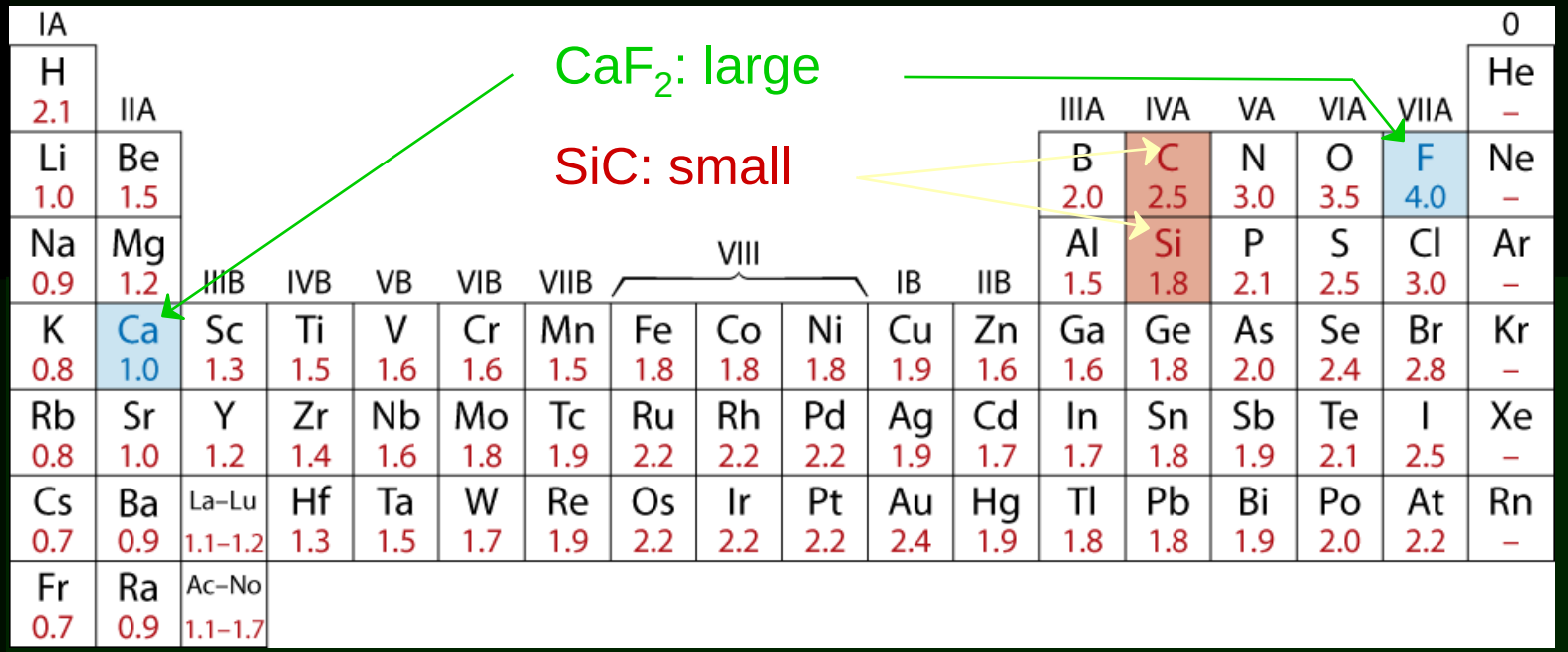
Cu Damascene Process





Ceramic Bonding

- Bonding:
  - Mostly ionic, some covalent.
  - % ionic character increases with difference in electronegativity.
- Large vs small ionic bond character:



IA												IIIA	IVA	VA	VIA	VIIA	0
H 2.1	IIA																He –
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne –
Na 0.9	Mg 1.2	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar –
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr –
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe –
Cs 0.7	Ba 0.9	La–Lu 1.1–1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn –
Fr 0.7	Ra 0.9	Ac–No 1.1–1.7															

Adapted from Fig. 2.7, *Callister 7e.* (Fig. 2.7 is adapted from Linus Pauling, *The Nature of the Chemical Bond*, 3rd edition, Copyright 1939 and 1940, 3rd edition. Copyright 1960 by Cornell University.

Ceramic Crystal Structures

Oxide structures

- oxygen anions much larger than metal cations
- close packed oxygen in a lattice (usually FCC)
- cations in the holes of the oxygen lattice
- often with direct relation between coordination numbers and type of local environment
- structures are often represented by mixed polyhedral/atomic models
- partial substitutions often lead to distortions of the ideal structure
- a few different elements can do similar tricks (Se, Te, …)

Site Selection

Which sites will cations occupy?

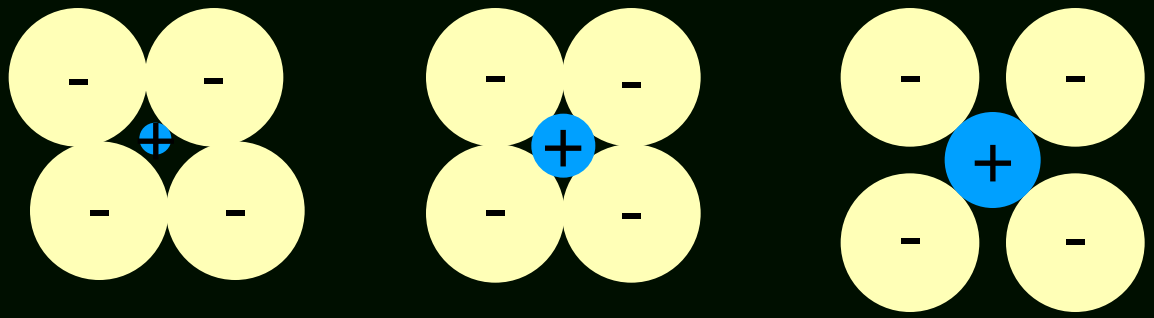
1. Size of sites
   - does the cation fit in the site

2. Stoichiometry
   - if all of one type of site is full the remainder have to go into other types of sites.

3. Bond Hybridization

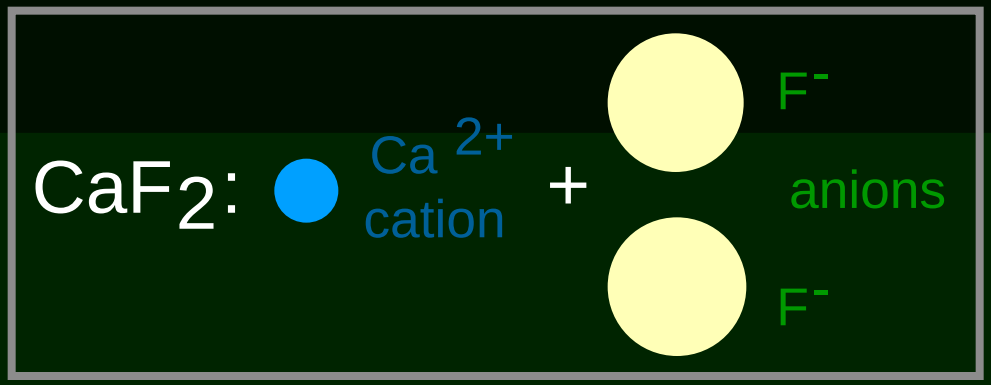
Ionic Bonding & Structure

1. Size - Stable structures:
   -maximize the # of nearest oppositely charged neighbors.



Adapted from Fig. 12.1, *Callister 7e.*

- Charge Neutrality:
  - Net charge in the structure should be zero.



- General form: A_mX_p

m, p determined by charge neutrality

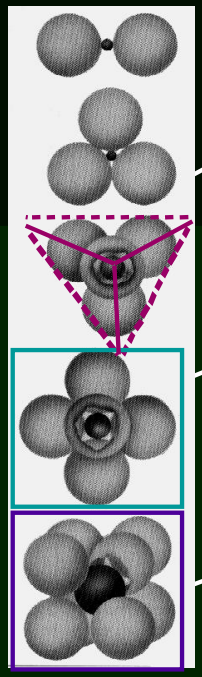
Coordination # and Ionic Radii

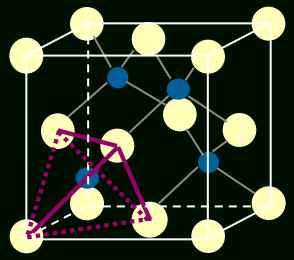
- Coordination # increases with $\frac{r_{cation}}{r_{anion}}$

Issue: How many anions can you arrange around a cation?

$\frac{r_{cation}}{r_{anion}}$	Coord #	
< 0.155	2	linear
0.155 - 0.225	3	triangular
0.225 - 0.414	4	T_D
0.414 - 0.732	6	O_H
0.732 - 1.0	8	cubic

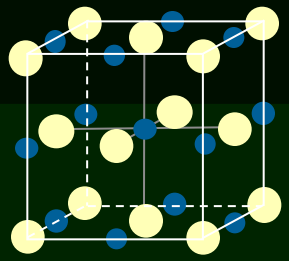
Adapted from Table 12.2, *Callister 7e.*





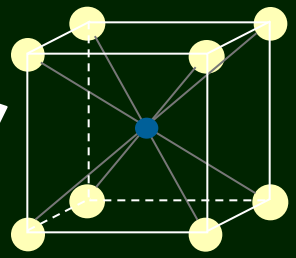
ZnS (zincblende)

Adapted from Fig. 12.4, *Callister 7e.*



NaCl (sodium chloride)

Adapted from Fig. 12.2, *Callister 7e.*

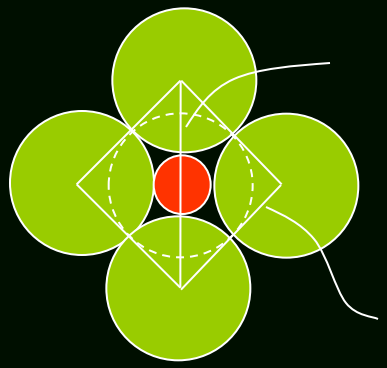


CsCl (cesium chloride)

Adapted from Fig. 12.3, *Callister 7e.*

Cation Site Size

- Determine minimum r_{cation}/r_{anion} for O_H site (C.N. = 6)



$$2r_{anion} + 2r_{cation} = \sqrt{2}a$$

$$a = 2r_{anion}$$

$$2r_{anion} + 2r_{cation} = 2\sqrt{2}r_{anion}$$

$$r_{anion} + r_{cation} = \sqrt{2}r_{anion}$$

$$r_{cation} = (\sqrt{2} - 1)r_{anion}$$

$$\frac{r_{cation}}{r_{anion}} = 0.414$$

Site Selection II

2. Stoichiometry
   - If all of one type of site is full the remainder have to go into other types of sites.

Ex: FCC unit cell has 4 O_H and 8 T_D sites.

If for a specific ceramic each unit cell has 6 cations and the cations prefer O_H sites

4 in O_H

2 in T_D

Site Selection III

3. Bond Hybridization – significant covalent bonding
   - the hybrid orbitals can have impact if significant covalent bond character present
   - For example in SiC
     - X_{Si} = 1.8 and X_C = 2.5

$$\%\ ionic\ \text{character} = 100\ \{1\text{-exp}[-0.25(X_{Si} - X_C)^2]\} = 11.5\%$$

- ca. 89% covalent bonding
- both Si and C prefer sp^3 hybridization
- Therefore in SiC get T_D sites

Example: Predicting Structure of FeO

- On the basis of ionic radii, what crystal structure would you predict for FeO?

Cation	Ionic radius (nm)
Al^{3+}	0.053
Fe^{2+}	0.077
Fe^{3+}	0.069
Ca^{2+}	0.100

Anion	
O^{2-}	0.140
Cl^{-}	0.181
F^{-}	0.133

- Answer:

$$\frac{r_{\text{cation}}}{r_{\text{anion}}} = \frac{0.077}{0.140} = 0.550$$

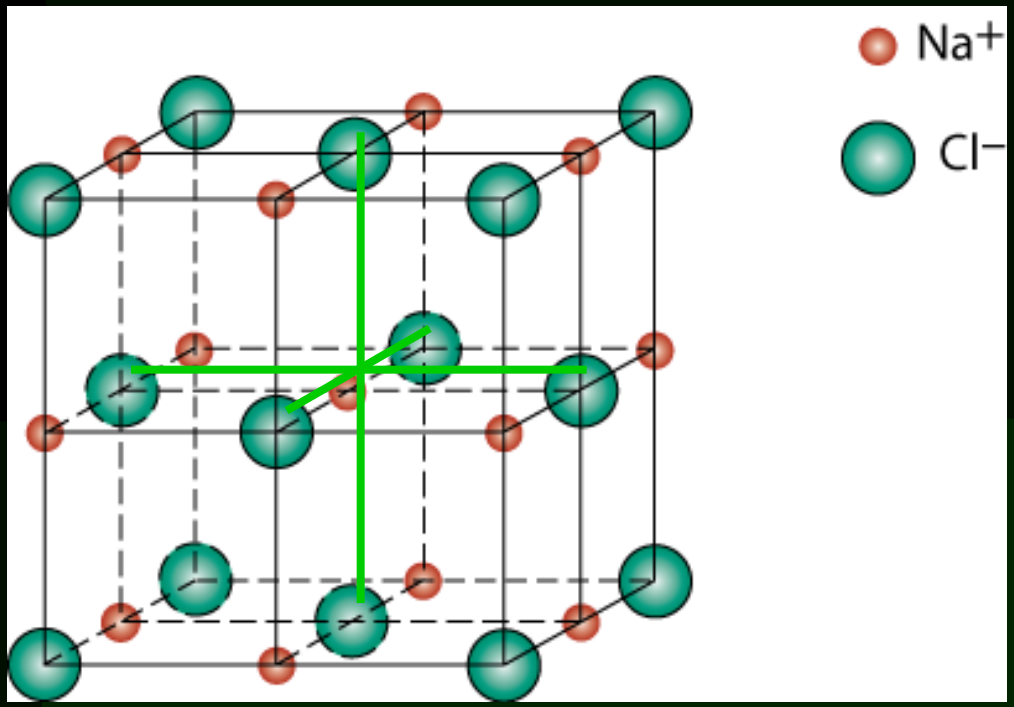
based on this ratio,
- coord # = 6
- structure = NaCl

Data from Table 12.3, *Callister 7e.*

Rock Salt Structure

Same concepts can be applied to ionic solids in general.

Example: NaCl (rock salt) structure



Adapted from Fig. 12.2, *Callister 7e.*

r_{Na} = 0.102 nm

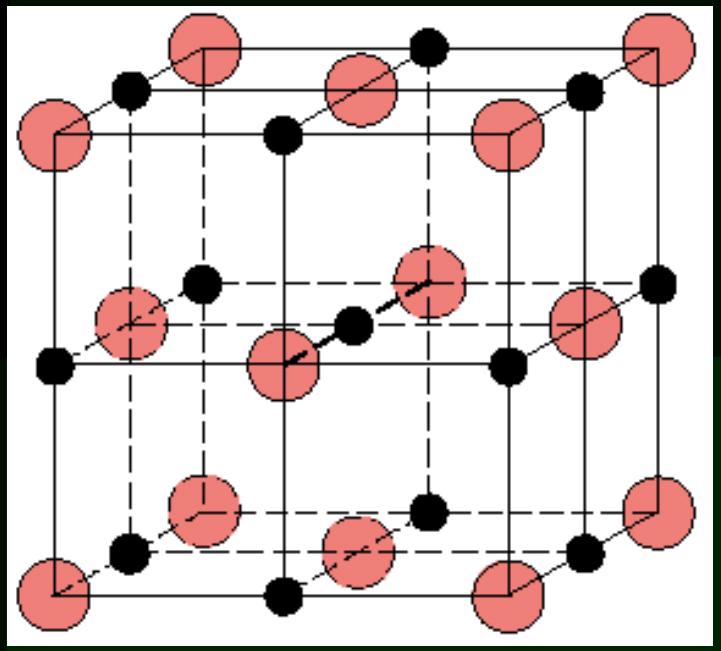
r_{Cl} = 0.181 nm

r_{Na}/r_{Cl} = 0.564

$\therefore$ cations prefer O_H sites

MgO and FeO

MgO and FeO also have the NaCl structure



Adapted from Fig. 12.2, *Callister 7e.*

O^{2-} $r_O = 0.140$ nm

Mg^{2+} $r_{Mg} = 0.072$ nm

$r_{Mg}/r_O = 0.514$

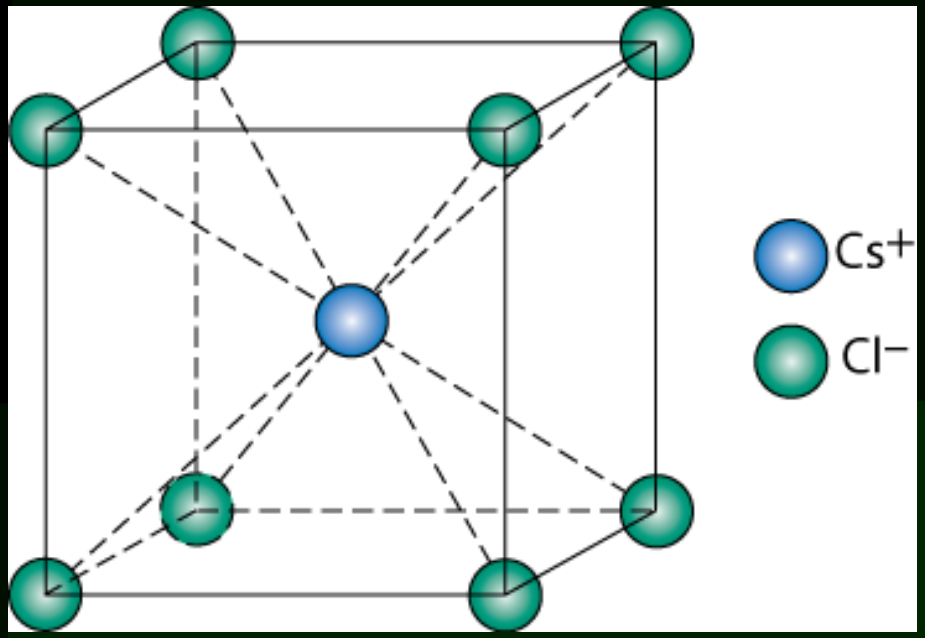
$\therefore$ cations prefer O_H sites

So each oxygen has 6 neighboring Mg^{2+}

AX Crystal Structures

AX–Type Crystal Structures include NaCl, CsCl, and zinc blende

Cesium Chloride structure:



Adapted from Fig. 12.3, *Callister 7e.*

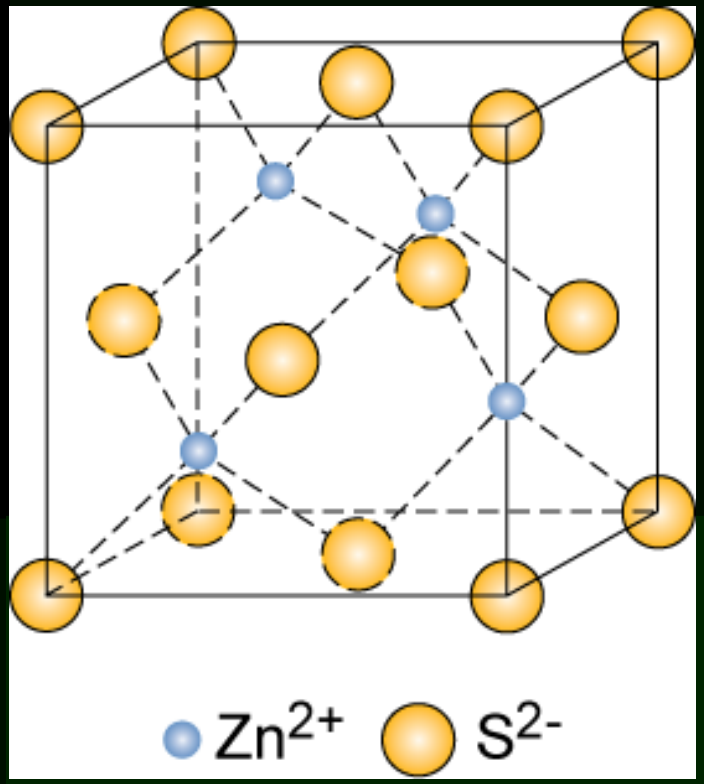
$$\frac{r_{Cs^+}}{r_{Cl^-}} = \frac{0.170}{0.181} = 0.939$$

$\therefore$ cubic sites preferred

So each Cs^+ has 8 neighboring Cl^-

AX Crystal Structures

Zinc Blende structure



Adapted from Fig. 12.4, *Callister 7e.*

Ex: ZnO, ZnS, SiC

$$\frac{r_{Zn^{2+}}}{r_{O^{2-}}} = \frac{0.074}{0.140} = 0.529 \Rightarrow O_H??$$

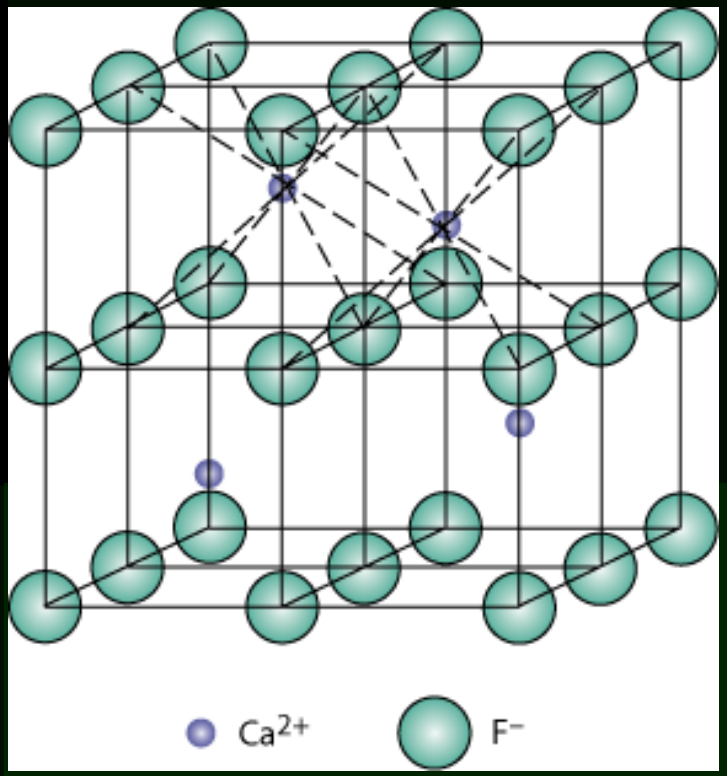
- Size arguments predict Zn^{2+} in O_H sites,
- In observed structure Zn^{2+} in T_D sites

- Why is Zn^{2+} in T_D sites?
  - bonding hybridization of zinc favors T_D sites

So each Zn^{2+} has 4 neighboring O^{2-}

AX_2 Crystal Structures

Fluorite structure



Adapted from Fig. 12.5, *Callister 7e.*

- Calcium Fluorite (CaF_2)
- cations in cubic sites

- UO_2, ThO_2, ZrO_2, CeO_2

- antifluorite structure – cations and anions reversed

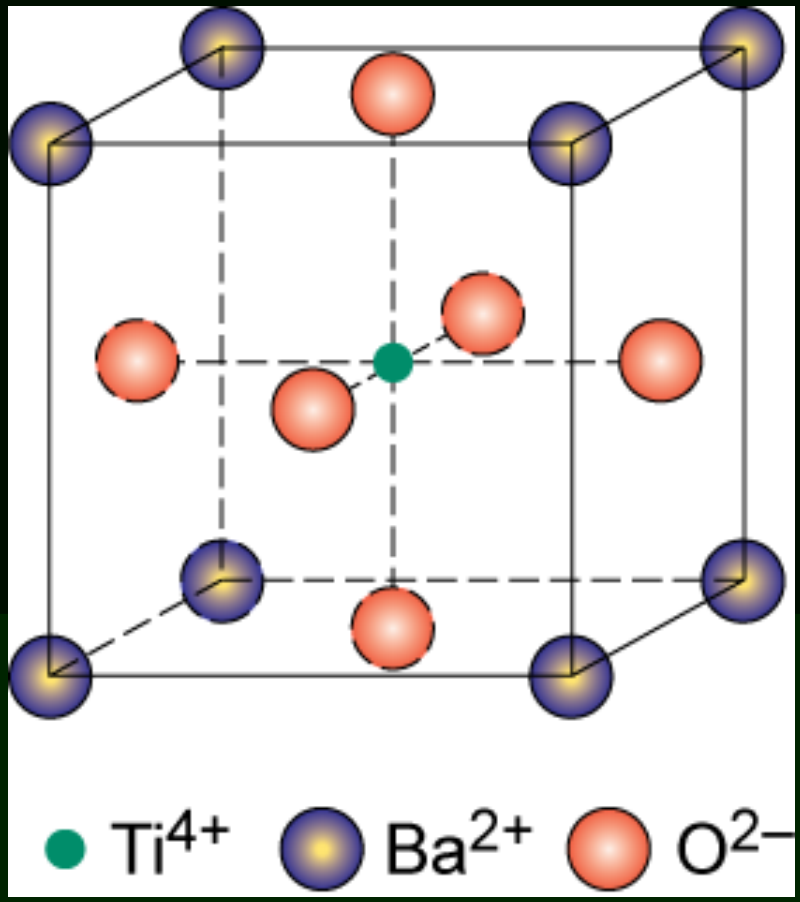
ABX_3 Crystal Structures

- Perovskite

Example:

complex oxide

$BaTiO_3$



Adapted from Fig. 12.6, *Callister 7e.*

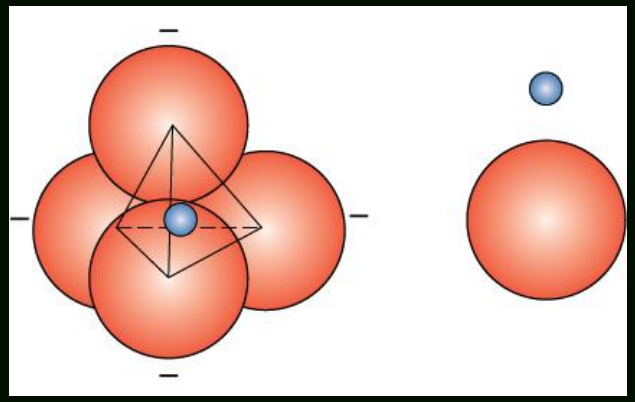
Mechanical Properties

We know that ceramics are more brittle than metals. Why?

- Consider method of deformation
  - slippage along slip planes
    - in ionic solids this slippage is very difficult
    - too much energy needed to move one anion past another anion

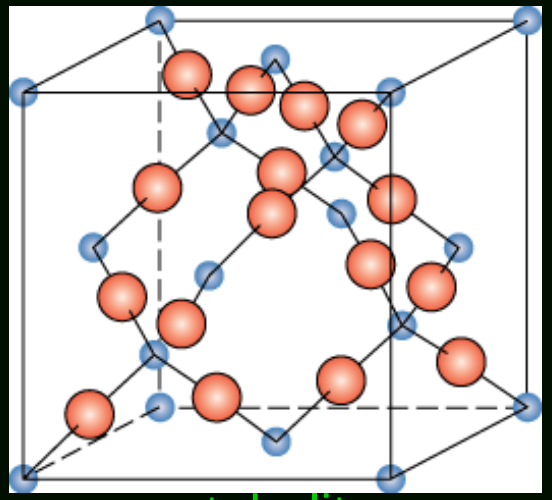
Silicate Ceramics

Most common elements on earth are Si & O



Si^{4+}

O^{2-}



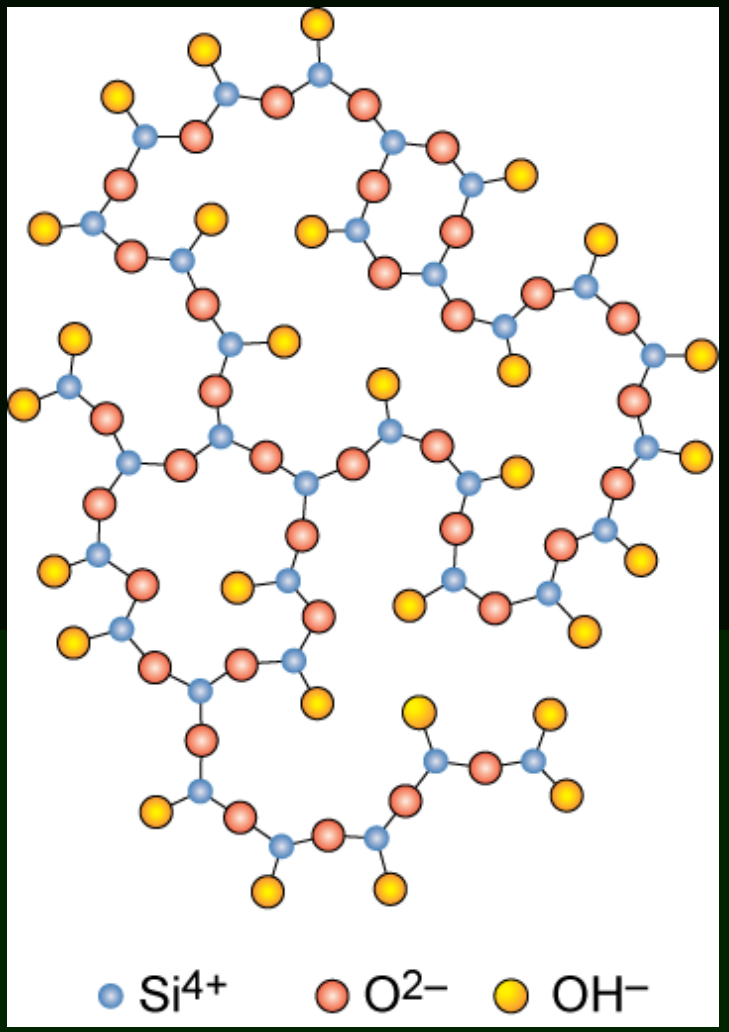
crystobalite

Adapted from Figs. 12.9-10, *Callister 7e.*

- SiO_2 (silica) structures are quartz (trigonal), crystobalite (tetragonal), & tridymite (hexagonal, orthorhombic and monoclinic) – coesite, stishovite and siefertite at high pressure and temperature
- The strong Si-O bond leads to a strong, high melting material (1710ºC)

Amorphous Silica

- Silica gels - amorphous SiO_2
  - Si^{4+} and O^{2-} not in well-ordered lattice
  - Charge balanced by H^+ (to form OH^-) at "dangling" bonds
    - very high surface area > 200 m^2/g
  - SiO_2 is quite stable, therefore unreactive
    - makes good catalyst support



Adapted from Fig. 12.11, *Callister 7e.*

Silica Glass

- Dense form of amorphous silica
  - Charge imbalance corrected with “counter cations” such as Na^+
  - Borosilicate glass is the pyrex glass used in labs
    - better temperature stability & less brittle than sodium glass

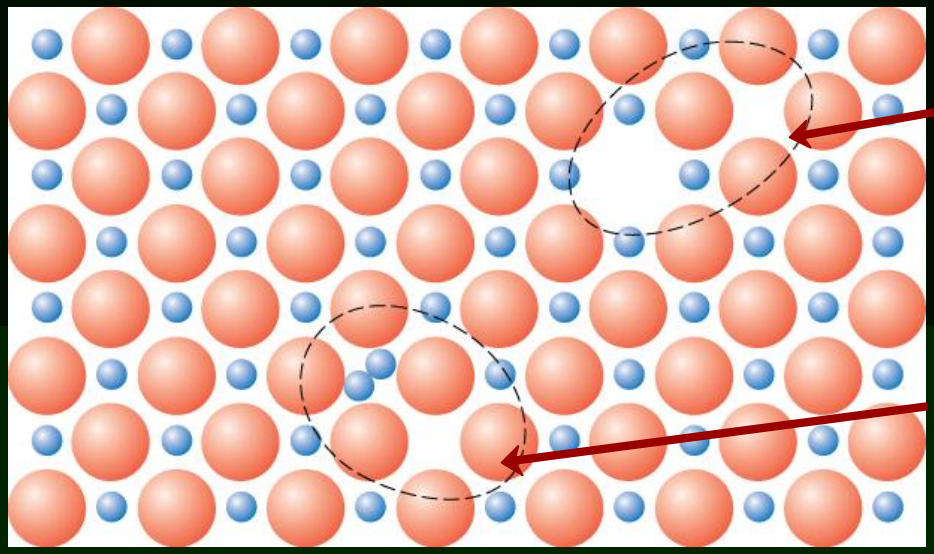
Defects in Ceramic Structures

Frenkel Defect

- a cation is out of place.

Shottky Defect

- a paired set of cation and anion vacancies.



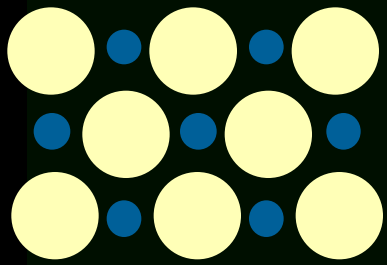
Adapted from Fig. 12.21, *Callister 7e.* (Fig. 12.21 is from W.G. Moffatt, G.W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. 1, *Structure*, John Wiley and Sons, Inc., p. 78.)

- Equilibrium concentration of defects $\sim e^{-Q_D/kT}$

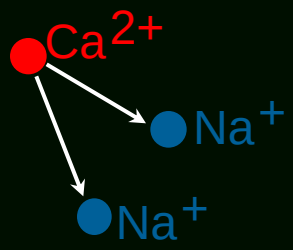
Impurities

- Impurities must also satisfy charge balance = Electroneutrality
- Ex: NaCl

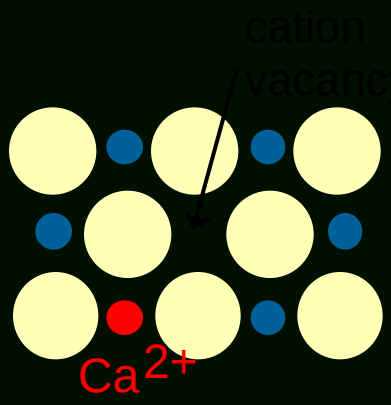
- Substitutional cation impurity



initial geometry

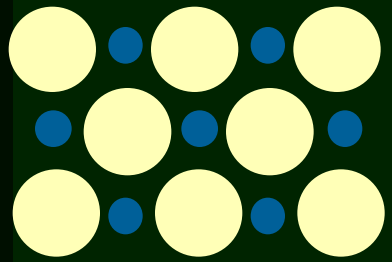


Ca^{2+} impurity

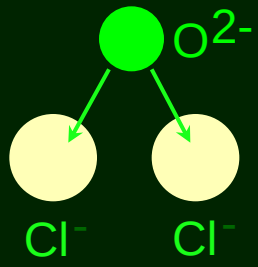


resulting geometry

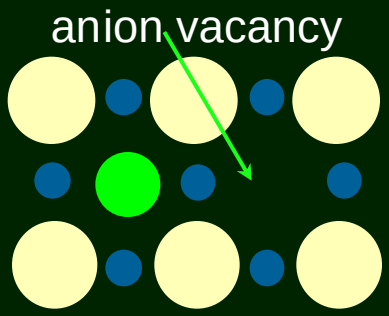
- Substitutional anion impurity



initial geometry



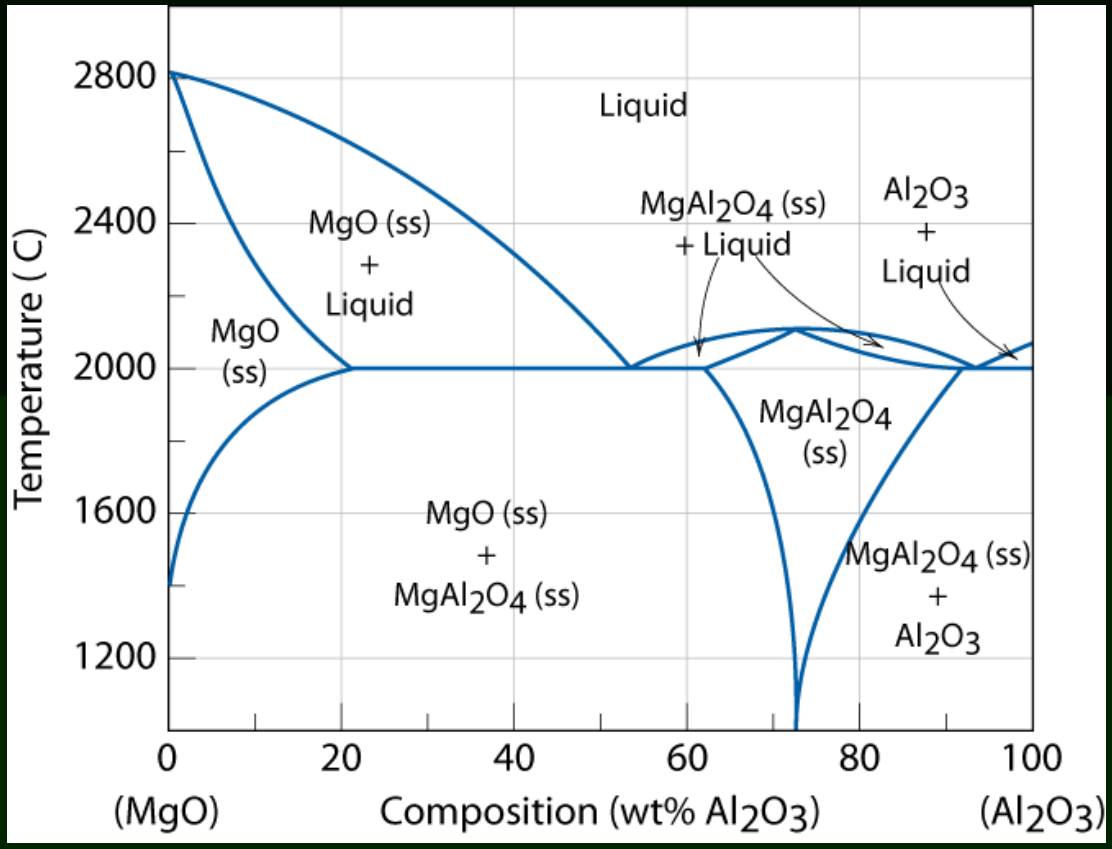
O^{2-} impurity



resulting geometry

Ceramic Phase Diagrams

MgO-Al_2O_3 diagram:



Adapted from Fig. 12.25, *Callister 7e.*