The University Of Sheffield.

EEE 6212
Semiconductor Materials

Lecture 3: Semiconductor crystals

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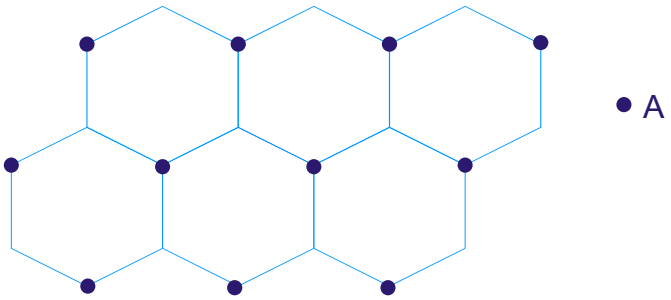
- relationship between cubic & hexagonal close-packing (partial repeat)
- coordination numbers of fcc & hcp lattices
- bond lengths and lattice spacings in fcc & hcp
- filling of interstices in close-packed arrays and atomic positions
- semiconductor crystals as examples of structures based on filling of interstices
- polymorphism and stacking faults

relation between cubic & hexagonal close-packing

consider filling of successive planes in top view
but mark only atom positions rather than spheres



relation between cubic & hexagonal close-packing

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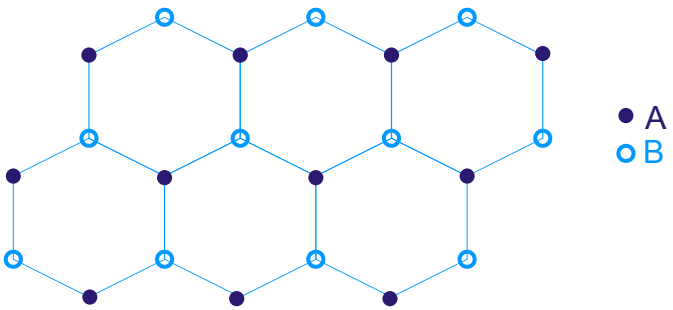
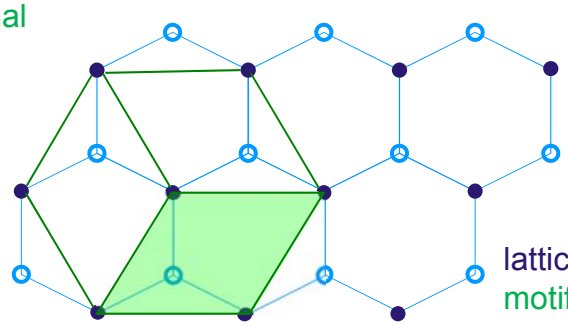


relation between cubic & hexagonal close-packing

consider filling of successive planes in top view
but mark only atom positions rather than spheres

hexagonal
unit cell



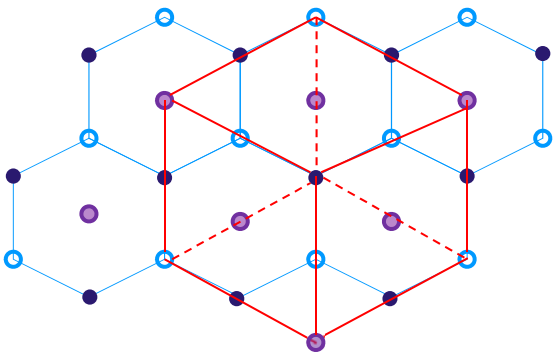
A
B

lattice: dark points
motif:

N=2 atoms per cell

relation between cubic & hexagonal close-packing

consider filling of successive planes in top view
but mark only atom positions rather than spheres

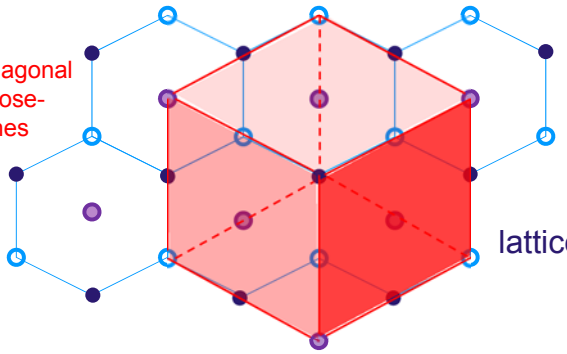


A
B
C

relation between cubic & hexagonal close-packing

consider filling of successive planes in top view
but mark only atom positions rather than spheres

cubic
unit cell
with body diagonal
normal to close-
packed planes



● A
○ B
● C

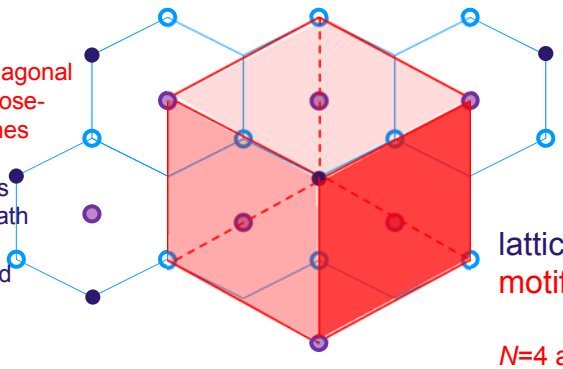
lattice: dark points

relation between cubic & hexagonal close-packing

consider filling of successive planes in top view
but mark only atom positions rather than spheres

cubic
unit cell
with body diagonal
normal to close-
packed planes

with A atoms
on underneath
faces of the
cube omitted



● A
○ B
● C

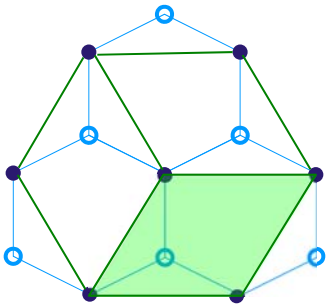
lattice: dark points
motif: fcc

N=4 atoms per cell

comparison of hcp & fcc: coordination numbers

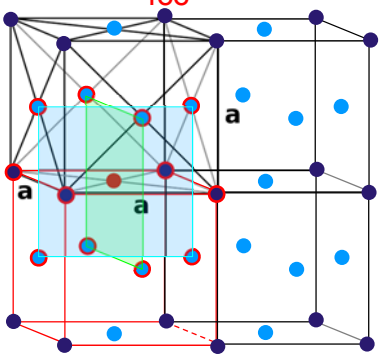
consider # of nearest-neighbour atoms in adjacent unit cells

hcp



3 underneath (layer A)
+ 6 in layer (layer B)
+ 3 on top (layer A) =12

fcc

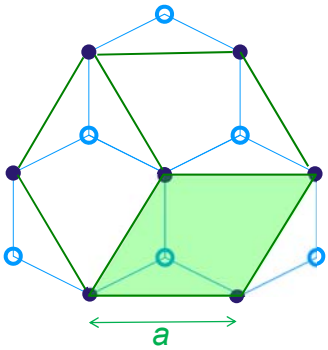


all 4x3 =12 atoms with a red circle are equally far away from central red atom

comparison of hcp & fcc: bond lengths

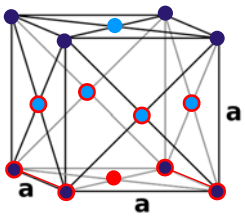
consider distance between nearest-neighbour atoms

hcp



atoms touch along [100]
-> $d=a$

fcc

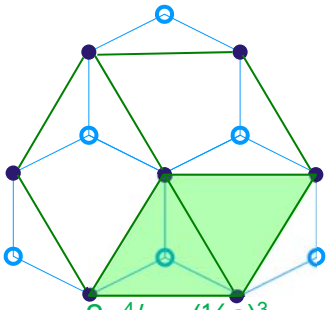


atoms touch along [110], where
2 bond lengths = 4x atomic radius
= face diagonal = $a\sqrt{2}$ -> $d=a/\sqrt{2}$

comparison of hcp & fcc: space filling

consider fractional ratio of atomic volume to unit cell volume

hcp

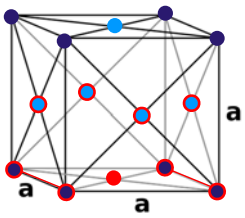


$V_{atoms} = 2 \cdot {}^4/_3 \, \pi \, (½a)^3$

$V_{unit\ cell} = 2c \, ¼ \, a^2\sqrt{3}$ with $c/a = 2\sqrt{⅔}$

ratio= $\pi/(3\sqrt{2}) = 74\%$

fcc



V

$V_{atoms} = 4 \cdot {}^4/_3 \, \pi \, (¼ \, a\sqrt{2})^3$

$V_{unit\ cell} = a^3$

ratio= ${}^1/_6 \, \pi \sqrt{2} = 74\%$

relation between cubic & hexagonal close-packing

AB(ABAB): hexagonal close-packed (hcp) along *c*-axis

and

ABC(ABC): cubic close-packed or face-centred cubic (fcc) along <111> direction

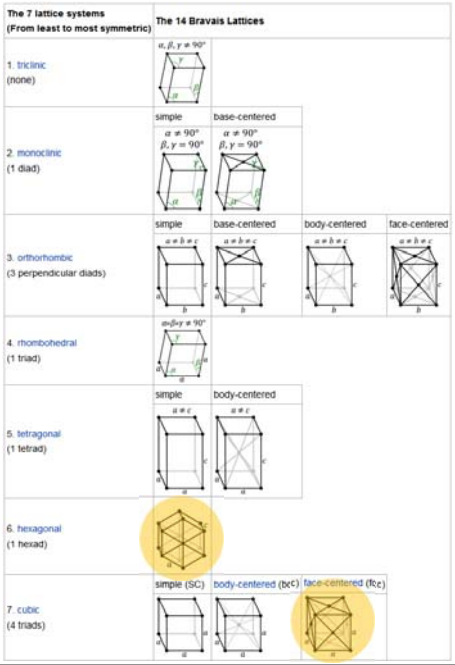
only differ in their stacking sequence!

The 14 Bravais Lattices

The 14 Bravais lattices come about due to combinations of point symmetry (7 lattice systems) with 4 space centerings:

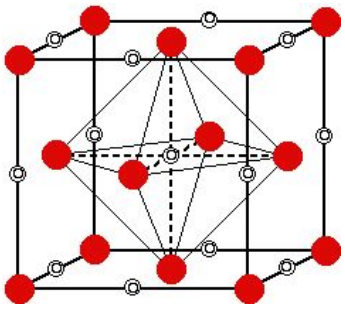
notation:	lattice points at 0,0,0 and
P: primitive	-
C: base centred	½, ½,0
I: body centred	½, ½, ½
F: face centred	½,½,0; ½,0,½; 0,½,½
R:	$^2/_3,^1/_3,^1/_3$; $^1/_3,^2/_3,^2/_3$

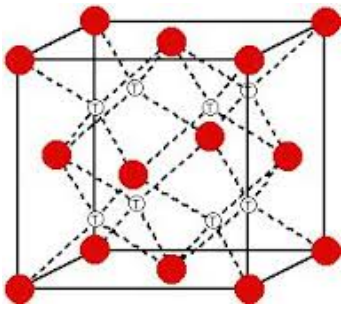
Note: trigonal R can be hexagonal P or rhombohedral.



filing of interstices in close-packed arrays like fcc

4x octahedral type (O) 8x tetrahedral type (T)



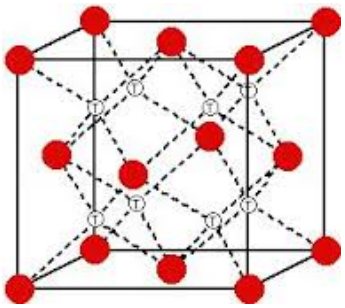


at half height at ¼ and ¾ heights

semiconductor crystals: examples of structures based on filling of interstices

8x tetrahedral type (T)

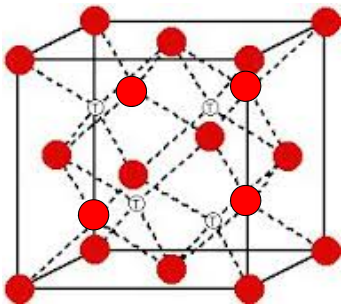
diamond structure:
fill 4/8 T sites with
same atoms, i.e.
atoms also at
(¼, ¼, ¼),
(¾ , ¾ ,¼),
(¼, ¾, ¾),
(¾, ¼, ¾)



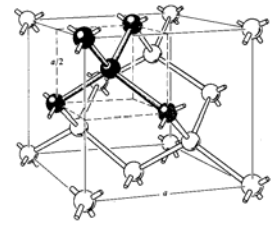
semiconductor crystals: examples of structures based on filling of interstices

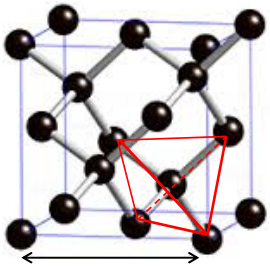
8x tetrahedral type (T)

diamond structure:
fill 4/8 T sites with
same atoms, i.e.
atoms also at
(¼, ¼, ¼),
(¾ , ¾ ,¼),
(¼, ¾, ¾),
(¾, ¼, ¾)



Semiconductor crystals





1. diamond (C, Si, Ge, α-Sn)

consists of two face-centred cubic crystals shifted by ¼ of the body diagonal; all 8 atoms are identical and connected via 4 neighbours via bonds forming tetrahedra.

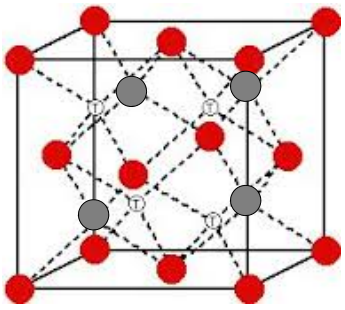
space group 227: $Fd\bar{3}m$
1 atom at corners: 8 x $^1/_8$
3 atoms at centre of faces: 6 x ½
4 atoms at tetrahedral sites: 4 x 1

a=0.381nm (C), 0.543nm (Si), 0.566nm (Ge)

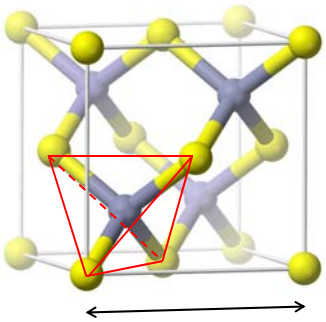
semiconductor crystals: examples of structures based on filling of interstices

8x tetrahedral type (T)

sphalerite structure:
fill 4/8 T sites with
different atoms, i.e.
different atoms at
(¼, ¼, ¼),
(¾ , ¾ ,¼),
(¼, ¾, ¾),
(¾, ¼, ¾)



Semiconductor crystals

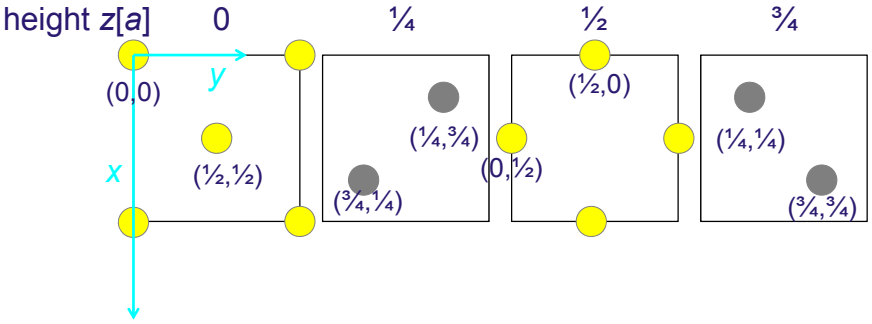


a=0.542nm (c-ZnS)
0.565nm (GaAs),
0.587nm (InP),
0.648nm (InSb),
0.450nm (c-GaN),

2. sphalerite or zinc blende (ZnS, GaP, InP, GaAs, AlAs, InAs, GaSb, InSb, ZnSe, HgTe,…)
consists of two face-centred cubic crystals shifted by ¼ of the body diagonal; both sub-lattices are occupied by different atoms which again are tetrahedrally connected to their 4 neighbours. All tetrahedra are in the same orientation.
space group 216: F$\bar{4}$3m
1 atom at corners: 8 x $^1/_8$
3 atoms at centre of faces: 6 x ½
4 atoms at tetrahedral sites: 4 x 1

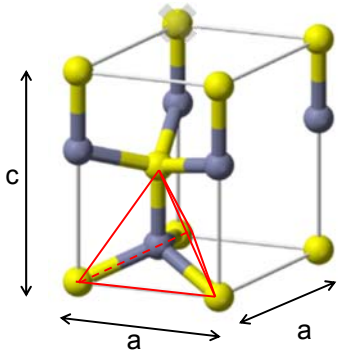
Semiconductor crystals

2. sphalerite or zinc blende



space group 216: F$\bar{4}$3m
1 atom at corners: 8 x $^1/_8$
3 atoms at centre of faces: 6 x ½
4 atoms at tetrahedral sites: 4 x 1

Semiconductor crystals



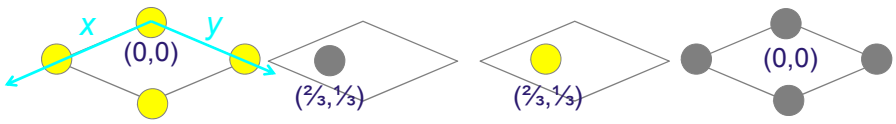
a=0.381nm, c=0.623nm (h-ZnS),
a=0.319nm, c=0.519nm (h-GaN),

3. wurtzite (ZnS, GaN, ZnO, BeO,…) consists of two hexagonal crystals (dihexagonal pyramidal) shifted by u*c* (u≈$^3/_8$+δ) along ***c***-axis; both sub-lattices are occupied by different atoms which again are tetrahedrally connected to 4 neighbours. Tetrahedra in adjacent (001) planes are rotated by 180° about [001].
space group 186: $P6_3mc$
1 atom at corners (0, 0,0)
1 atom at position ($^1/_3$,$^2/_3$,$^1/_2$)
1 atom at position (0,0,$^3/_8$)
1 atom at position ($^1/_3$,$^2/_3$,$^7/_8$)

Semiconductor crystals

3. wurtzite

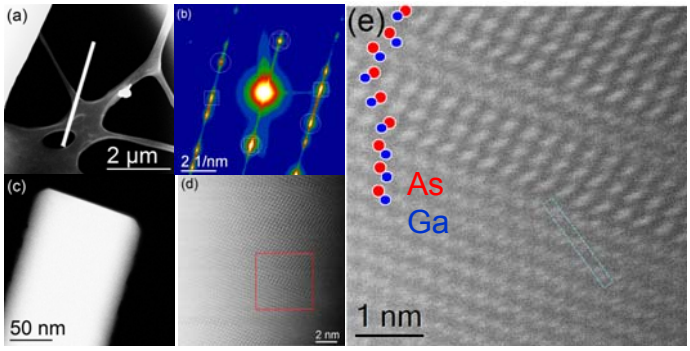
height *z*[*c*] 0 *u*≈⅛ ½ ½+*u*



space group 186: $P6_3mc$
1 atom at corners (0, 0,0)
1 atom at position ($^1/_3$,$^2/_3$,$^1/_2$)
1 atom at position (0,0,$^3/_8$)
1 atom at position ($^1/_3$,$^2/_3$,$^7/_8$)

polymorphism and stacking faults

As hcp and fcc structures are so similar, many materials can adopt both, and their energetics are rather similar, as shown here for a GaAs nanowire imaged along <110> zone axis. Changing from hcp to fcc (or back) produces stacking faults.



T. Walther & A.B. Krysa, Cryst. Res. Technol. (2014) DOI: 10.1002/crat.201400166

Summary

- hcp and fcc differ in their **stacking** sequence (ABAB… vs. ABCABC…) but have the same coordination numbers and space filling efficiency (which is why they are both called '**close-packed**').
- Semiconductor crystals exist in 3 modifications:

(i) The **diamond** structure is based on two identical fcc lattices shifted by ¼ of the body diagonal, which fills 4/8 of the tetrahedral interstices.

(ii) The **sphalerite** structure is an ordered version of the diamond structure.

(iii) The **wurtzite** structure is based on two hcp lattices shifted by u**c** (with $u \approx {}^{3}/_{8} + \delta$) along the **c**-axis.

- Changing from fcc to hcp stacking, or vice versa, produces **stacking faults**. Crystals that exist in both modifications are called **polymorphs**.