

Chapter 1

Crystal Properties and Growth of Semiconductors

- In studying solid state electronic devices we are interested primarily in the electrical and optical behaviors of the solids.
- The transport of charge through a metal or a semiconductor depends not only on the properties of the charge carriers but also on the arrangement of atoms in the solid.
- Discuss the atomic arrangements of various semiconductors, and some methods of crystal growth.

Objectives:

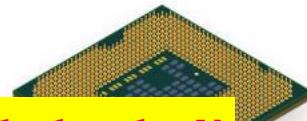
- Describe what a semiconductor is
- Perform simple calculations about crystals (e.g., number of atoms per unit cell, packing fraction (裝填分率), Miller indices, etc.)
- Understand what is involved in bulk (塊晶) Czochralski and thin-film epitaxial crystal (磊晶, 外延晶體) growth
- Learn about crystal defects

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改變世界的半導體

半導體的歷史、原理、及科技發展

課外指定閱讀 (列入考試範圍)



1. 半導體科技的發展簡史 (4) (1.1 - 1.4)
2. 物理學的革命及半導體物理理論的發展 (6)
3. 半導體元件: p-n 二極體 (摻雜與接合) (8)
4. 除了電子, 還有光子! 半導體光電元件的發展
5. 雙極式接合電晶體 (Bipolar Junction Transistors)
6. 場效應電晶體 (Field-Effect Transistors, FETs)

物理一乙 (PH148B) 半導體元件發展史

授課教師 : 邱寬城

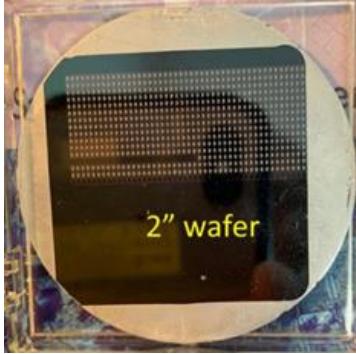
Contents

- **1.1 Semiconductor Materials**
**(inorganic) semiconductors; organic semiconductors;
novel semiconductors**
- **1.2 Crystal Lattices**
- **1.3 Bulk Crystal Growth**
- **1.4 Epitaxial Layer Growth**
- **1.5 Wave propagation in discrete, periodic structures**

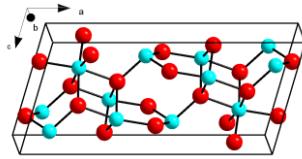
1.1 Semiconductor Materials (半導體材料)

- **Semiconductors** are a group of materials having electrical conductivities intermediate between metals and insulators (e.g., $\sigma_{\text{Au}} = 4 \times 10^5 \text{ S} \cdot \text{cm}^{-1}$ or $\text{S}/\text{cm} \Leftrightarrow \sigma_{\text{glass}} \approx 10^{-8} \sim 10^{-12} \text{ S} \cdot \text{cm}^{-1}$), where σ is called **electrical conductivity** (電導率), $\sigma = \rho^{-1}$ and ρ is called **electrical resistivity** (電阻率).
- **Band diagram** (band gap, doping \Rightarrow carrier concentration, $\sigma_n = q\mu_n n$)
- **G** (電導) & **R** (電阻) are properties of samples (devices or products). $R = 1/G = \rho L/A$. $\Leftrightarrow \sigma$ (電導率) and ρ (電阻率) are properties of materials with typical units of σ ($\text{S} \cdot \text{cm}^{-1}$) and ρ ($\Omega \cdot \text{cm}$).
- The siemens ($\text{S} = 1/\Omega$) is the SI derived unit of electric conductance **G** (= $1/R$, inverse of resistance) named after the German inventor and industrialist **Ernst Werner von Siemens** (1816–1892), founder of **Siemens AG** (西門子公司，其電子與電機產品是全球業界先驅，並活躍於能源、醫療、工業、基礎建設及城市業務等領域。)

半導體的種類



- 元素半導體 (Elemental): Si, Ge。
- 二元化合物半導體 (Binary): (1) III-V: GaAs, GaP, InP, GaN ... ;
(2) IV-IV: SiC((α)6H-, 4H-, (β)3C-SiC, ...), SiGe; (3) II-VI: CdS, CdTe, ZnS, ... ; (4) Other: HgI₂; Ga₂O₃; CuIn_xGa_{1-x}Se₂(CIGS, I-III-VI₂);。
- 元素半導體與二元化合物半導體有各自的能隙 (E_g), 與晶格常數 (a) ...。
- 三元化合物半導體 (Ternary): In_xGa_{1-x}As, GaAs_yP_{1-y}, ... ;
- 四元化合物半導體: (Quaternary): In_xGa_{1-x}As_yP_{1-y}, ...。



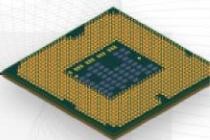
基於材料開發的成熟度與其在元件應用的拓展成效

- 第一類(代)半導體: Ge($E_g = 0.67$ eV), Si(1.11);
- 第二類(代)半導體: GaAs(1.43), InP(1.35), ...;
- 第三類(代)半導體: 4H-SiC(3.25), GaN(3.4), ...;
- 第四類(代)半導體 (?): Ultra-Wide BG (UWBG), Ga₂O₃(4.7-4.9), ...。



$\beta\text{-Ga}_2\text{O}_3$ crystal
 $E_g = 4.7 \sim 4.9$ eV

化學元素週期表



Group Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
	III	IV	V	VI															
1	1 H																	2 He	
2	3 Li	4 Be																	
3	11 Na	12 Mg																	
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	*	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
	*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb				
	*	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No				

		E_g (ev)	μ_n (cm ² /V-s)	μ_p (cm ² /V-s)	m_n^*/m_o (m _l , m _i)	m_p^*/m_o (m _{lh} , m _{hh})	a (Å)	ϵ_r	Density (g/cm ³)	Melting point (°C)
Si	(i/D)	1.11	1350	480	0.98, 0.19	0.16, 0.49	5.43	11.8	2.33	1415
Ge	(i/D)	0.67	3900	1900	1.64, 0.082	0.04, 0.28	5.65	16	5.32	936
SiC (α)	(i/W)	2.86	500	—	0.6	1.0	3.08	10.2	3.21	2830
AlP	(i/Z)	2.45	80	—	—	0.2, 0.63	5.46	9.8	2.40	2000
AlAs	(i/Z)	2.16	1200	420	2.0	0.15, 0.76	5.66	10.9	3.60	1740
AlSb	(i/Z)	1.6	200	300	0.12	0.98	6.14	11	4.26	1080
GaP	(i/Z)	2.26	300	150	1.12, 0.22	0.14, 0.79	5.45	11.1	4.13	1467
GaAs	(d/Z)	1.43	8500	400	0.067	0.074, 0.50	5.65	13.2	5.31	1238
GaN	(d/Z, W)	3.4	380	—	0.19	0.60	4.5	12.2	6.1	2530
GaSb	(d/Z)	0.7	5000	1000	0.042	0.06, 0.23	6.09	15.7	5.61	712
InP	(d/Z)	1.35	4000	100	0.077	0.089, 0.85	5.87	12.4	4.79	1070
InAs	(d/Z)	0.36	22600	200	0.023	0.025, 0.41	6.06	14.6	5.67	943
InSb	(d/Z)	0.18	10 ⁵	1700	0.014	0.015, 0.40	6.48	17.7	5.78	525
ZnS	(d/Z, W)	3.6	180	10	0.28	—	5.409	8.9	4.09	1650*
ZnSe	(d/Z)	2.7	600	28	0.14	0.60	5.671	9.2	5.65	1100*
ZnTe	(d/Z)	2.25	530	100	0.18	0.65	6.101	10.4	5.51	1238*
CdS	(d/W, Z)	2.42	250	15	0.21	0.80	4.137	8.9	4.82	1475
CdSe	(d/W)	1.73	800	—	0.13	0.45	4.30	10.2	5.81	1258
CdTe	(d/Z)	1.58	1050	100	0.10	0.37	6.482	10.2	6.20	1098
PbS	(i/H)	0.37	575	200	0.22	0.29	5.936	17.0	7.6	1119
PbSe	(i/H)	0.27	1500	1500	—	—	6.147	23.6	8.73	1081
PbTe	(i/H)	0.29	6000	4000	0.17	0.20	6.452	30	8.16	925

All values at 300 K.

*Vaporizes

Common semiconductor materials

(I, II, III, IV, V, VI, VII, VIII, IX, X ... are Roman numbers)

(a)	II	III	IV	V	VI
		B	C	N	
		Al	Si	P	S
Zn		Ga	Ge	As	Se
Cd		In	.	Sb	Te

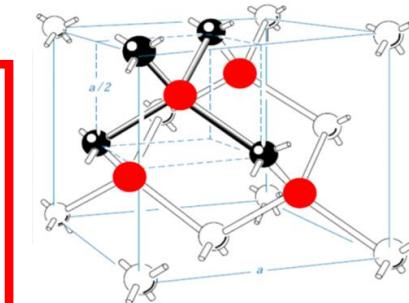
(b)	Elemental	silicon carbide IV compounds	Binary III-V compounds	Binary II-VI compounds
	Si Ge	SiC SiGe silicon-germanium	AlP AlAs AlSb GaN GaP GaAs GaSb InP InAs InSb	ZnS ZnSe ZnTe CdS CdSe CdTe HgI₂; Ga₂O₃; CuIn_xGa_{1-x}Se₂ (CIGS, I-III-VI₂);...
Stoichiometric ratio (化學組成比) for binary: III:V (or II:VI) ≈ 1.0000... : 1.0000...				
Ternary: In_xGa_{1-x}As; GaAs_yP_{1-y} Quaternary: In_xGa_{1-x}As_yP_{1-y}				

Variation on the magnitude of bandgap for III-V compound semiconductors (III-V 族化合物半導體)

III	IV	V
B	C	N
Al	Si	P
Ga	Ge	As
In		Sb

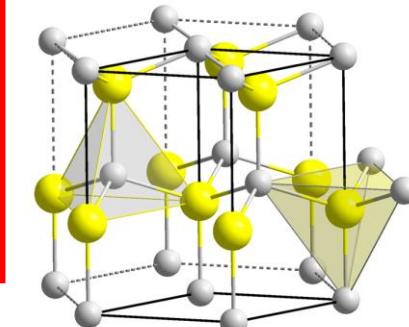
		E_g (eV)
Si	(i/D)	1.11
Ge	(i/D)	0.67

AlP	(i/Z)	2.45
AlAs	(i/Z)	2.16
AlSb	(i/Z)	1.6



		E_g (eV)	a (Å)
GaN	$(d/Z, W)$	3.4	4.50
GaP	(i/Z)	2.26	5.45
GaAs	(d/Z)	1.43	5.65
GaSb	(d/Z)	0.7	6.09

InP	(d/Z)	1.35
InAs	(d/Z)	0.36
InSb	(d/Z)	0.18

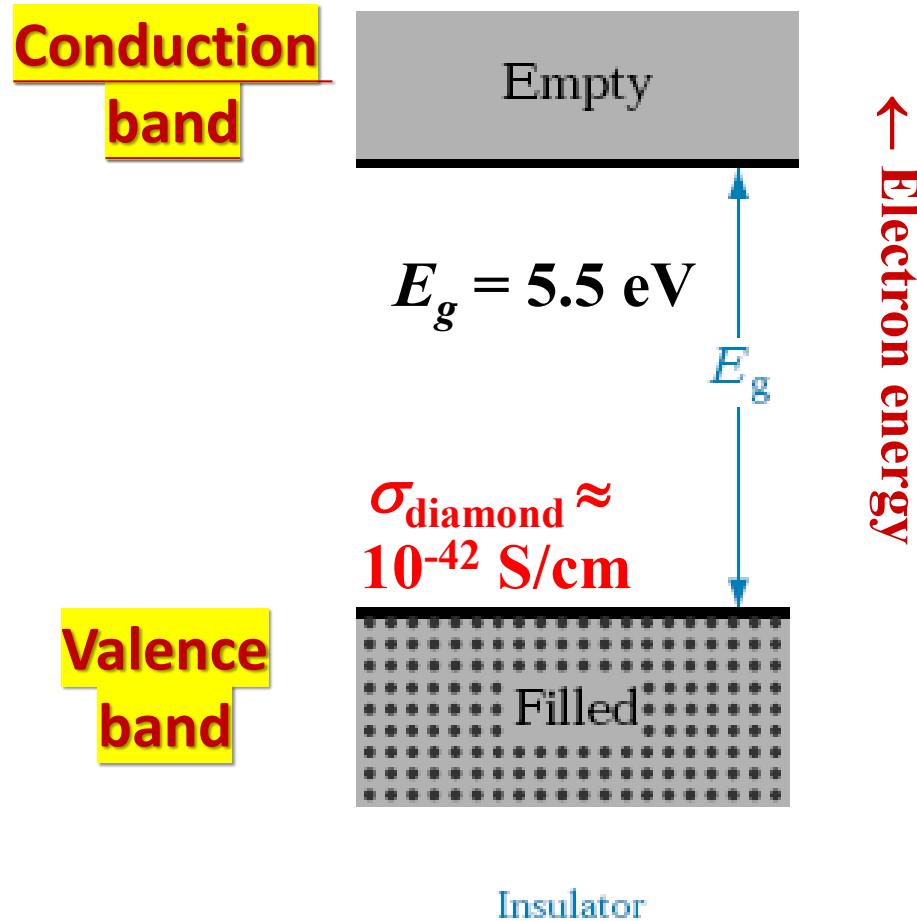


- What is the physics behind the trend of this variation? (**LCAO**)
- See Chap. 2 for linear combination of atomic orbitals (**LCAO**).

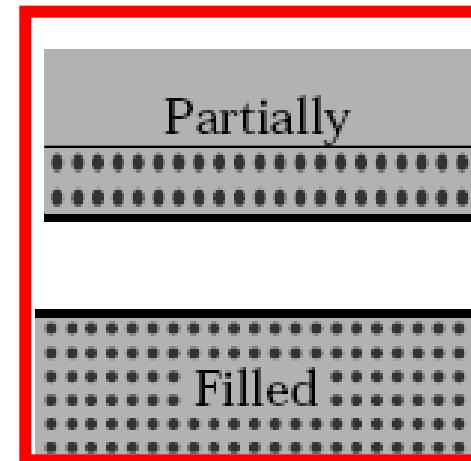
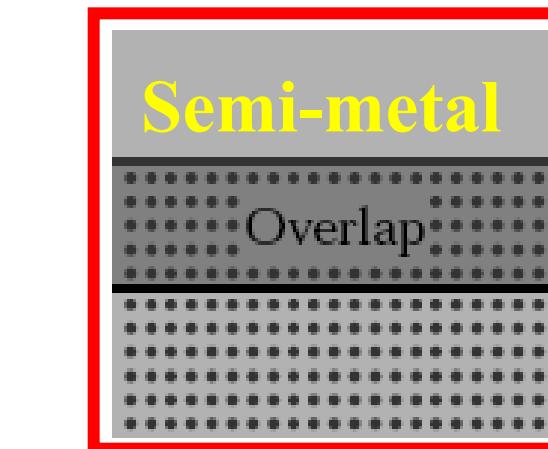
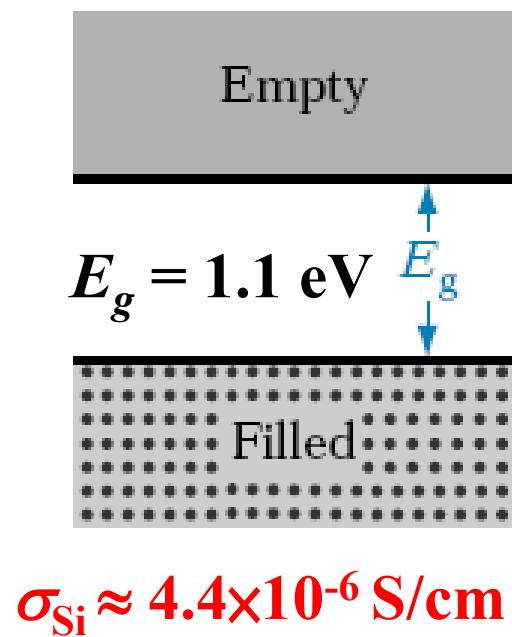
Typical band structures (E vs x), intrinsic charge carrier concentration, and intrinsic electrical conductivity at 300 K

For Cu, $n_0 = 8.5 \times 10^{22}/\text{cm}^3$

For intrinsic diamond,
 $n_i = p_i = 10^{-27}/\text{cm}^3$



For intrinsic Si,
 $n_i = p_i = 1.5 \times 10^{10}/\text{cm}^3$



$\sigma_{\text{Cu}} = 6 \times 10^5 \text{ S/cm}$

Metal

		E_g (ev)	μ_n (cm ² /V-s)	μ_p (cm ² /V-s)	m_n^*/m_o (m _l , m _i)	m_p^*/m_o (m _{lh} , m _{hh})	a (Å)	ϵ_r	Density (g/cm ³)	Melting point (°C)
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All values at 300 K.

*Vaporizes

III-V Compound semiconductors

III	IV	V
B	C	N
Al	Si	P
Ga	Ge	As
In		Sb

- III: boron, aluminum, gallium, indium;
- IV: carbon, silicon, germanium;
- V: nitrogen, phosphorus, arsenic, antimony (銻);
- Gallium **nitride (GaN; 氮化鎵)**, aluminum **phosphide (AlP; 磷化鋁)**, gallium **arsenide (GaAs; 砷化鎵)**, gallium **antimonide (GaSb; 銻化鎵)**;
- Gallium **arsenide phosphide (GaAs_{1-x}P_x; 磷砷化鎵)**
- Aluminium gallium **arsenide phosphide (Al_{1-y}Ga_yAs_{1-x}P_x; 磷砷化鋁鎵)**.

IV-IV compounds:

SiC: silicon carbide, 碳化矽

SiGe: silicon-germanium alloy

矽鍺合金, 可表成 $\text{Si}_x\text{Ge}_{1-x}$

Nitride: 氮化物

Phosphide: 磷化物

Arsenide: 砷化物

Antimonide: 銻化物

II-VI Compound semiconductors

II	III	IV	V	VI
	B	C	N	O
Zn	Al	Si	P	S
Cd	Ga	Ge	As	Se
Hg	In		Sb	Te

Oxide: 氧化物
Sulfide: 硫化物
Selenide: 硒化物
Telluride: 碲化物



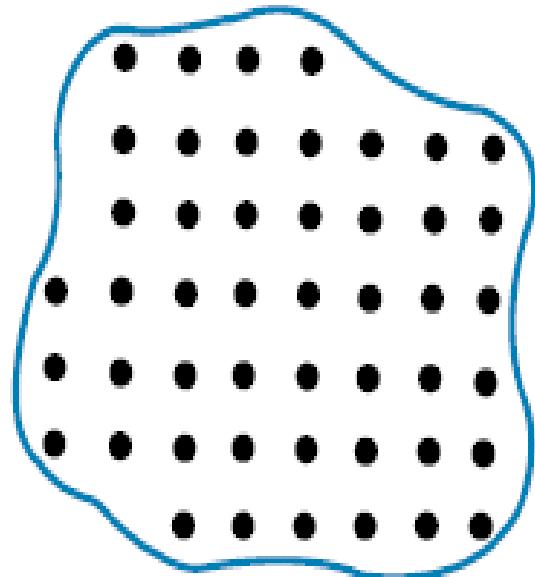
- II: zinc (鋅), cadmium (鎘), mercury (汞);
- VI: oxygen, sulfur (硫), selenium (硒), tellurium (碲);
- Zinc **oxide** (ZnO ; 氧化鋅), zinc **sulfide** (ZnS ; 硫化鋅), cadmium **sulfide** (CdS ; 硫化鎘), zinc **selenide** (ZnSe ; 硒化鋅), mercury **selenide** (HgSe ; 硒化汞), cadmium **telluride** (CdTe ; 碲化鎘).

Contents

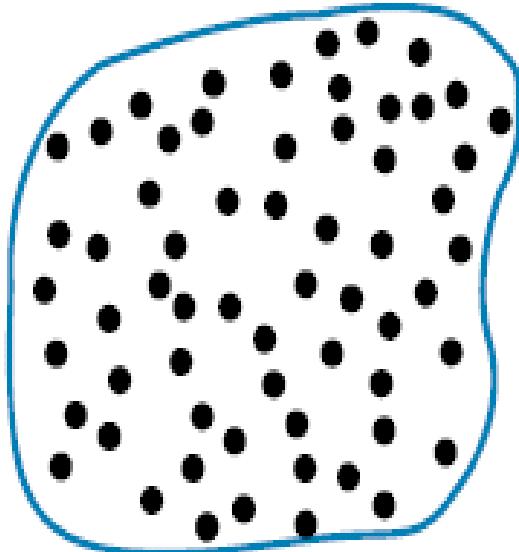
- 1.1 Semiconductor Materials
- 1.2 Crystal Lattices
 - sc, bcc, fcc, hcp, D, Z, W, etc; coordination number;
atoms/unit cell; packing density; Miller indices
- 1.3 Bulk Crystal Growth
- 1.4 Epitaxial Layer Growth
- 1.5 Wave propagation in discrete, periodic structures

1.2.1 Periodic structures

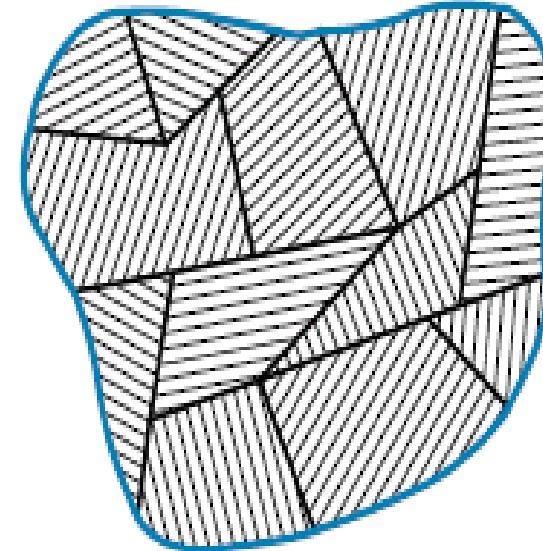
- **Three types** of **atomic arrangements** in the solid materials (Fig. 1.1).
- The periodic arrangement of atoms **in a crystal** is called lattice (晶格); the lattice contains a volume, called a unit cell (單位晶胞, 單元晶格), which is regularly repeated throughout the crystal (Fig. 1-2).
- Primitive cell (原始晶胞, 原始晶格): the smallest unit cell that can be repeated to form the lattice, *i.e.*, one lattice point (atom) per unit cell.



(a) Crystalline



(b) Amorphous



(c) Polycrystalline

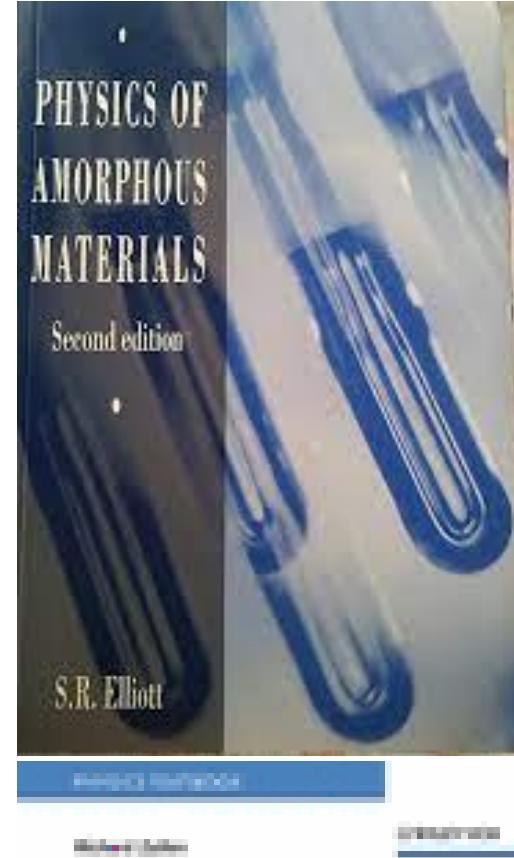
Three types of atomic arrangements in the solid materials

Figure 1–1

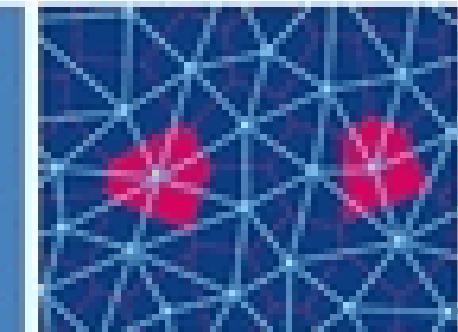
2D presentation

Three types of solids, classified according to atomic arrangement:

(a) crystalline and (b) amorphous materials are illustrated by microscopic views of the atoms, whereas (c) polycrystalline structure is illustrated by a more macroscopic view of adjacent single-crystalline regions, such as (a).



The Physics
of Amorphous Solids:



3D presentation

Crystalline



Amorphous

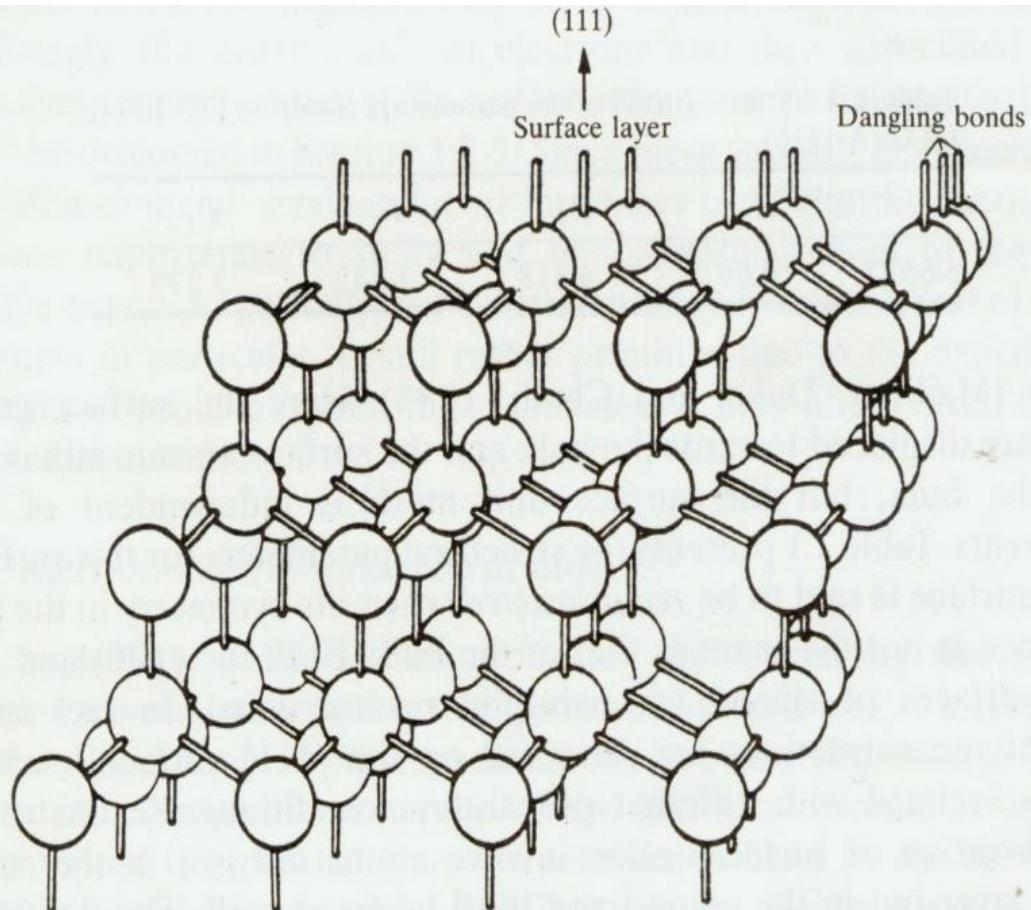


Fig. 1.1 The silicon structure, showing dangling bonds on the (111) face. (From Prutton, 1983. Copyright Oxford University Press.)

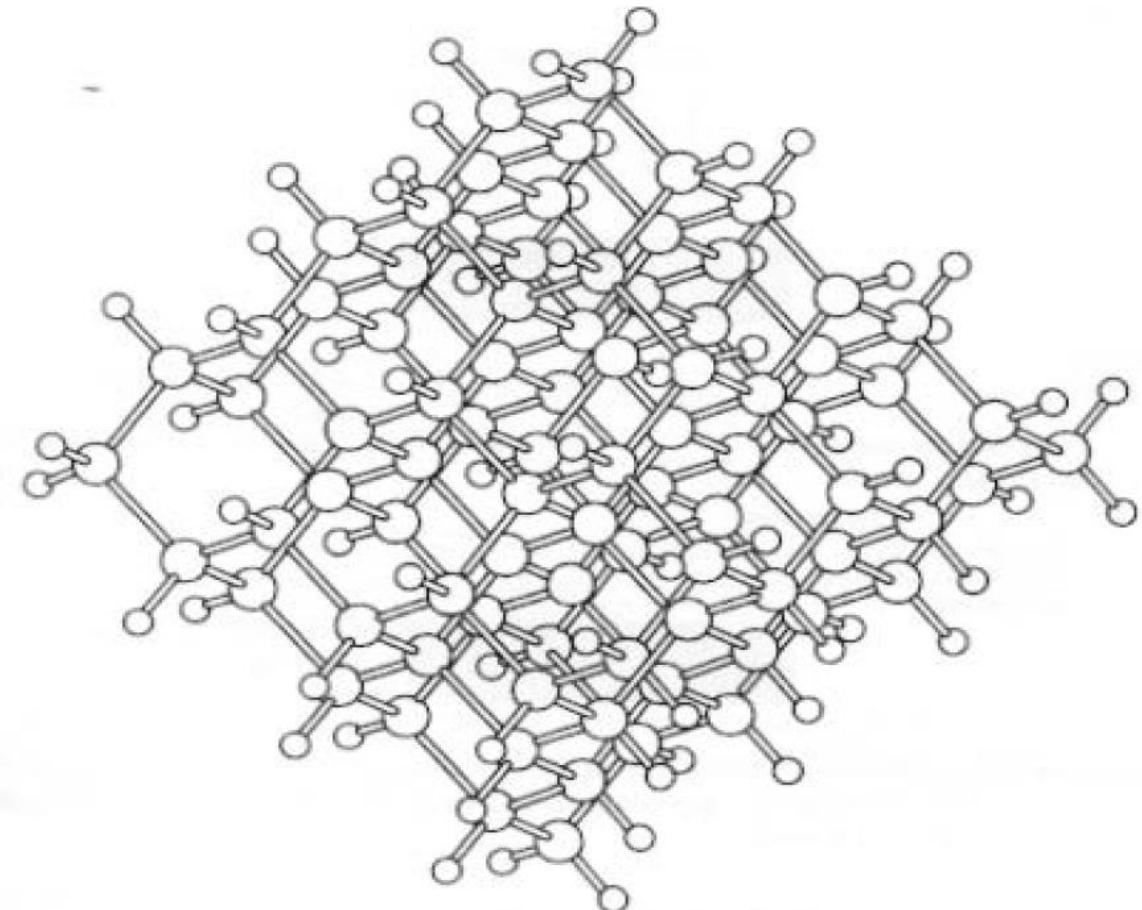


Figure 1.1 Structure of atomic network of a-Si showing dangling bonds.

2D presentation for a unit (單位) cell and a primitive (原始) unit cell or a primitive cell

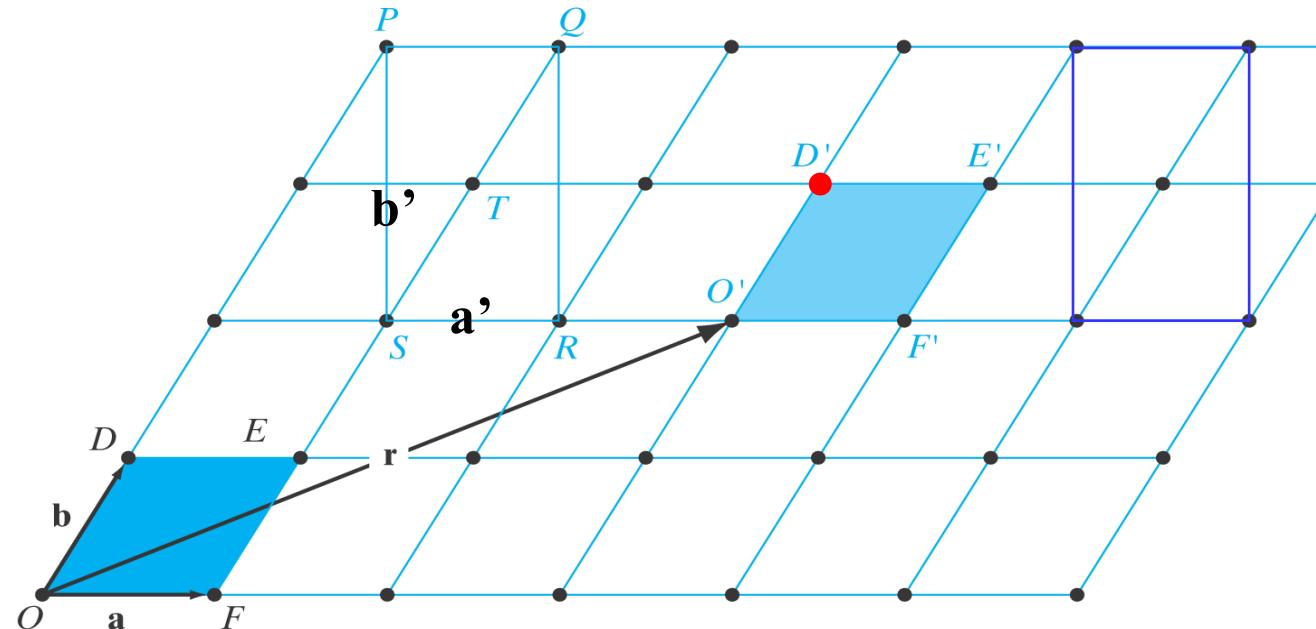


Figure 1.2

A two-dimensional lattice showing translation of a unit cell by $\mathbf{r} = 3\mathbf{a} + 2\mathbf{b}$.

$DEFO: 4 \times (1/4) = 1$ (primitive)
(lattice points only at its corners,
i.e. one lattice point per unit cell)

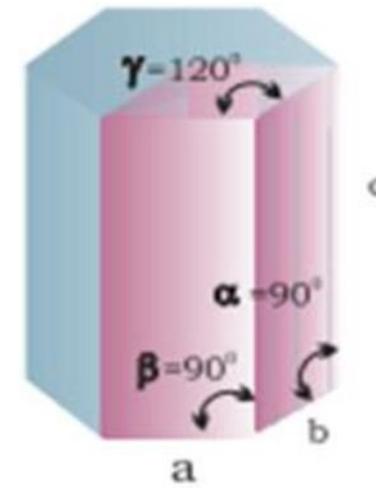
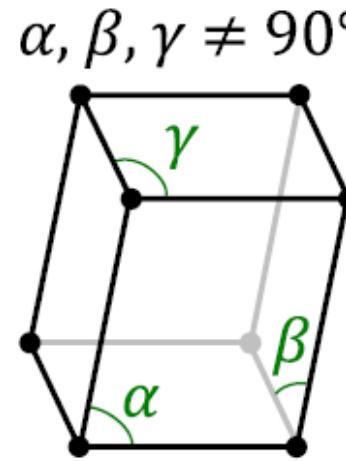
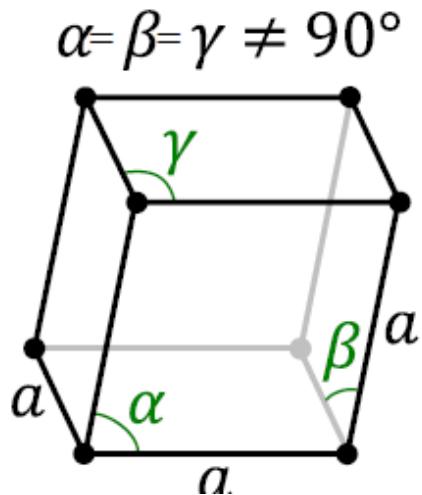
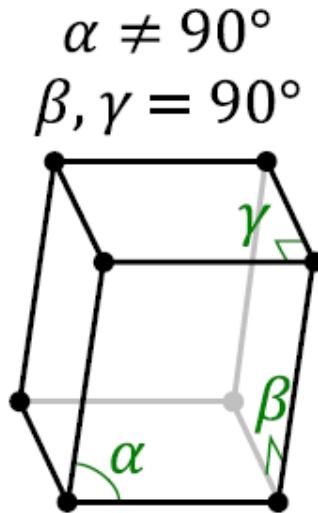
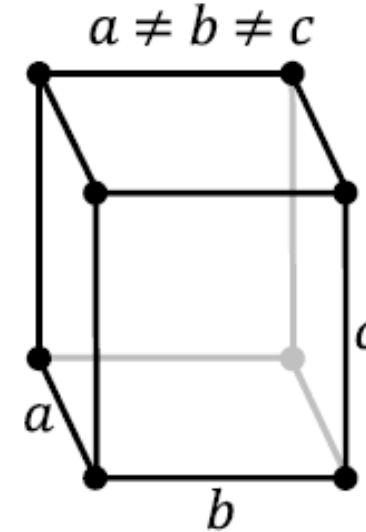
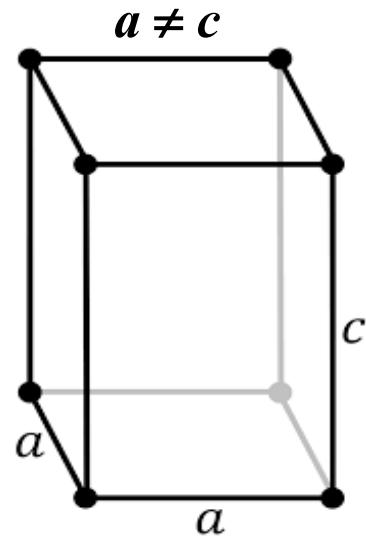
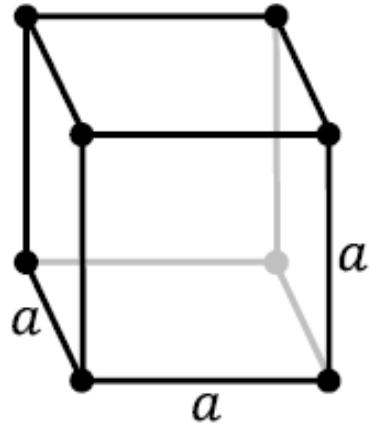
沿著晶格向量定向移動整數倍，
 $\mathbf{r} = 3\mathbf{a} + 2\mathbf{b}$ ，到另一個點時也能
找到同樣的基底，因此晶格在
任何一個晶格點上看起來都完
全一樣。

Fig. 1.2 While $PQRS$ and $DEFO$ (or $D'E'F'O'$) are unit cells,
but only $DEFO$ (or $D'E'F'O'$) is a primitive cell.

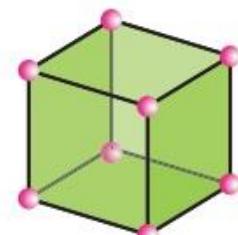
What is the difference between a unit (單位) cell and a primitive (原始) unit cell in a crystal?

- When **a unit in a crystal lattice** has **lattice points only at its corners**, it is called a **simple or primitive unit cell** (**one lattice point per unit cell**).
- There are **seven types of primitive unit cells** among crystal: 1. **Cubic unit cell** (立方晶胞); 2. **Tetragonal** (四方) unit cell; 3. **Orthorhombic** (正方) unit cell; 4. **Monoclinic** (單斜) unit cell; 5. **Rhombohedral** (菱形) unit cell; 6. **Triclinic** (三斜) unit cell; 7. **Hexagonal** (六方) unit cell.
- **A primitive cell** (**one lattice point per unit cell**) is **a minimum volume cell corresponding to a single lattice point** of a structure **with translational symmetry** in 2D, 3D, or other dimensions.

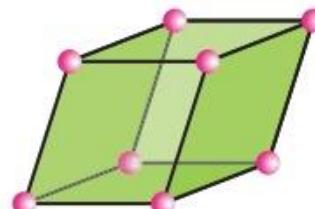
Seven primitive cells (七個原始晶胞):



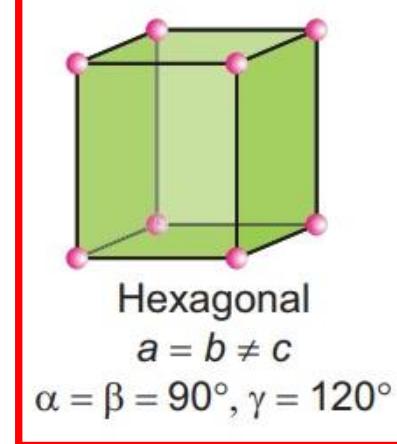
1. Cubic (立方); 2. Tetragonal (四方); 3. Orthorhombic (正方); 4. Monoclinic (單斜); 5. Rhombohedral (菱形); 6. Triclinic (三斜); 7. Hexagonal (六方, $a = b \neq c$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$).



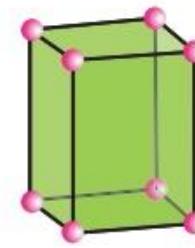
Cubic
 $a = b = c$
 $\alpha = \beta = \gamma = 90^\circ$



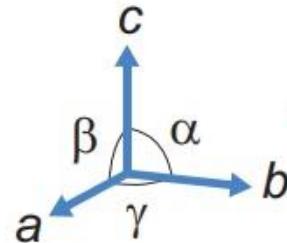
Rhombohedral
 $a = b = c$
 $\alpha = \beta = \gamma \neq 90^\circ$



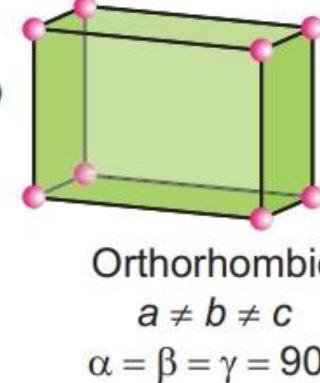
Hexagonal
 $a = b \neq c$
 $\alpha = \beta = 90^\circ, \gamma = 120^\circ$



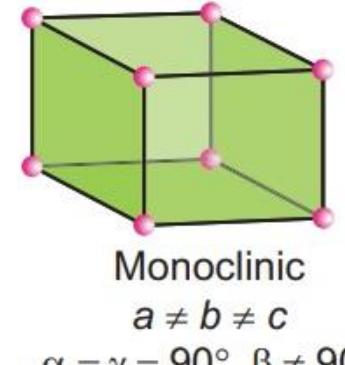
Tetragonal
 $a = b \neq c$
 $\alpha = \beta = \gamma = 90^\circ$



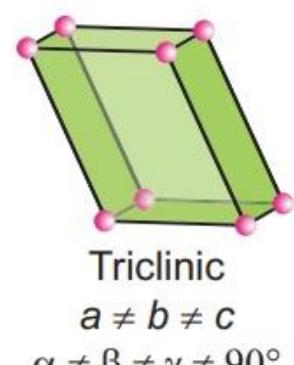
Seven primitive cells:



Orthorhombic
 $a \neq b \neq c$
 $\alpha = \beta = \gamma = 90^\circ$



Monoclinic
 $a \neq b \neq c$
 $\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$



Triclinic
 $a \neq b \neq c$
 $\alpha \neq \beta \neq \gamma \neq 90^\circ$

cubic			
tetragonal			
hexagonal			
orthorhombic			 basis face centered
monoclinic			
trigonal			
triclinic			

1. Cubic (立方); 2. Rhombohedral (菱形); 3. Hexagonal (六方, $a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$). 4. Tetragonal (四方); 5. Orthorhombic (正方); 6. Monoclinic (單斜); 7. Triclinic (三斜);

Bravais lattice (布拉菲晶格)

- 在幾何學以及晶體學中，Bravais lattices 是為了紀念法國物理學家 Auguste Bravais (1811 ~ 1863) 而命名的。
- Bravais lattice 是三維空間中由一個或多個原子所組成的基底所形成的無限點陣，每個晶格點上都能找到這樣同樣的基底，或者說沿著晶格向量定向移動整數倍到另一個點時也能找到同樣的基底，因此晶格在任何一個晶格點上看起來都完全一樣。
- 三維布拉菲晶格只有14種可能。
- 每一個單位晶格的體積可以由 $\vec{a} \cdot \vec{b} \times \vec{c}$ 計算得知，其中 $\vec{a}, \vec{b}, \vec{c}$ 是晶格向量。

晶系	布拉菲晶格			
	簡單 (P)	底心 (C)	體心 (I)	面心 (F)
三斜晶系				
單斜晶系				
斜方晶系 (正交晶系)				
四方晶系				
三方晶系 (棱方晶系)				
六方晶系				
等軸晶系 (立方晶系)				

1.2.2 Cubic lattices: sc, bcc, fcc

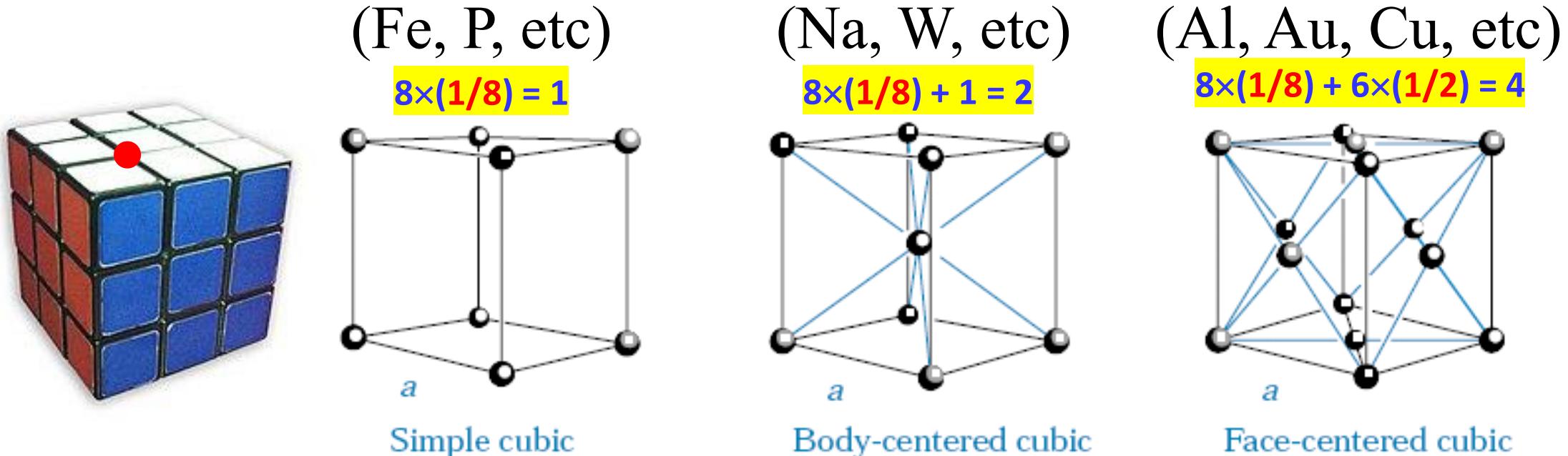
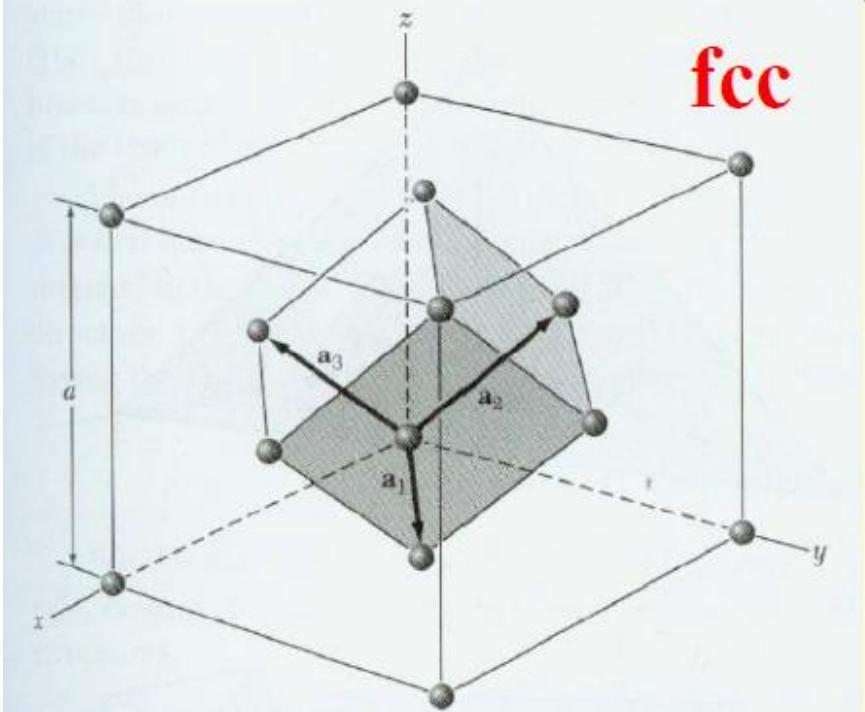
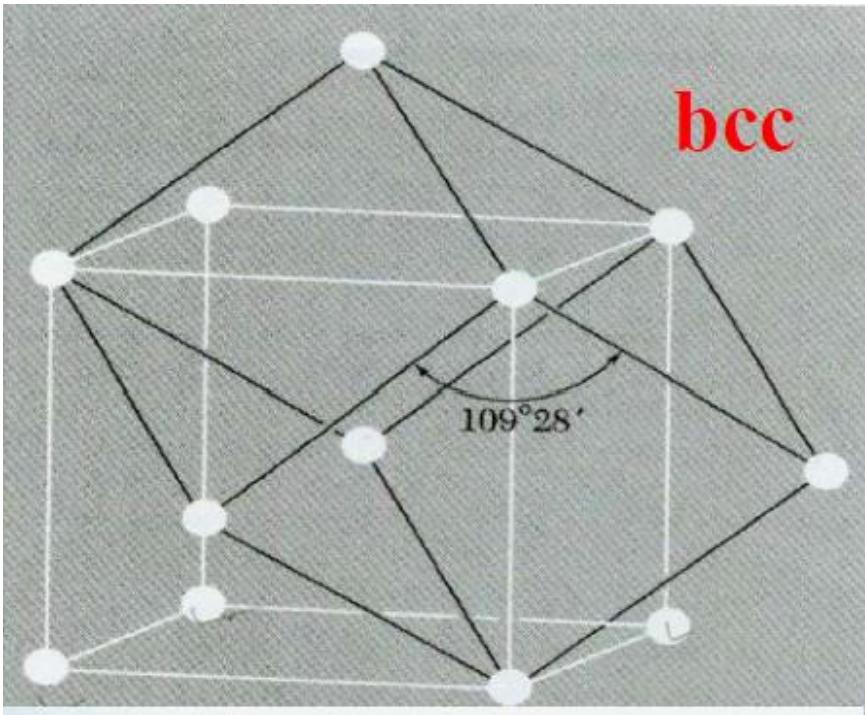


Figure 1-3

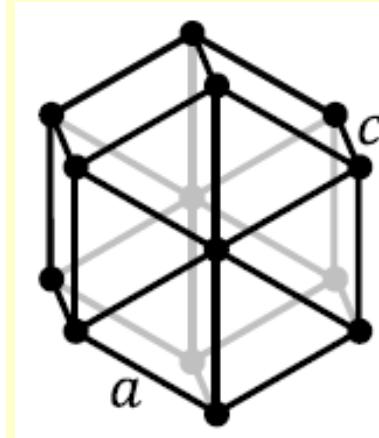
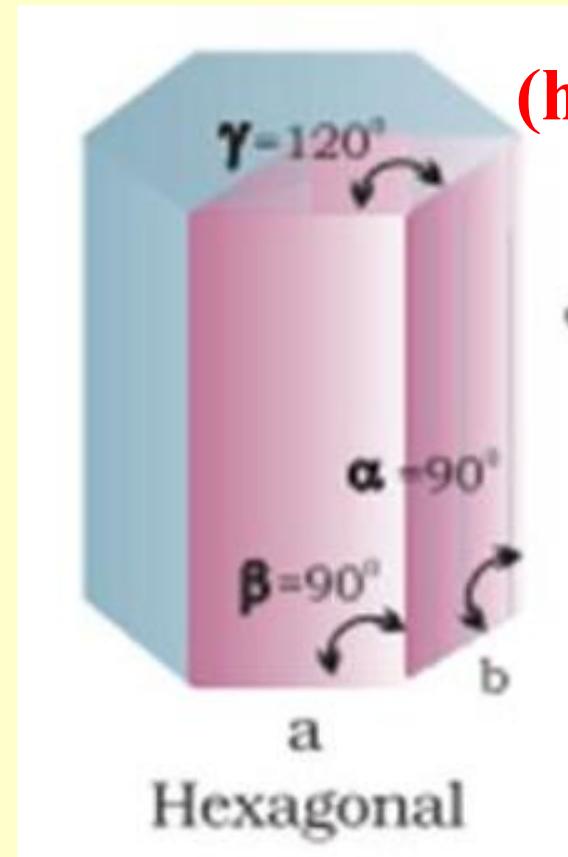
Unit cells for three types of cubic lattice structures.

Lattice constant: a

- (1) How many atoms per unit cell (單元晶格)? (1 for sc; 2 for bcc; and 4 for fcc)
- (2) See next page for primitive cells (原始晶格) to bcc, fcc, and hexagonal system.
Here, we work with unit cells only.



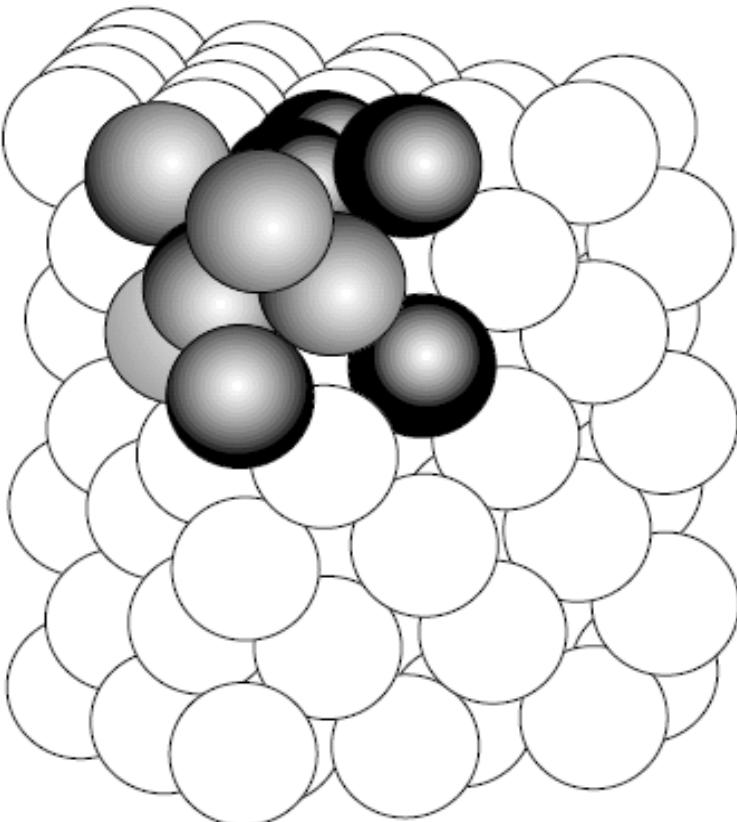
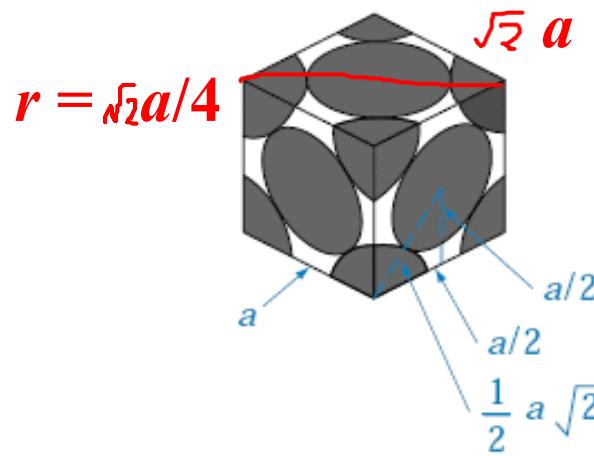
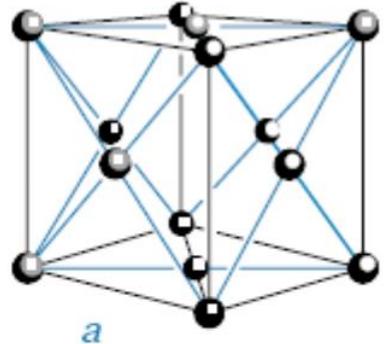
Primitive cell for bcc, fcc,
and hexagonal closed-
packed (hcp) systems



From Kittel's "Introduction to Solid State Physics".

Packing density (atomic packing factor, APF):

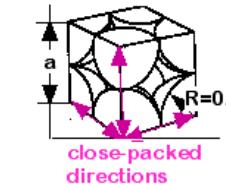
Find the fraction of the fcc unit cell volume filled with hard sphere as shown in Fig. 1-4.



Ans: 74 %

Figure 1-4
Packing of hard spheres in an fcc lattice.

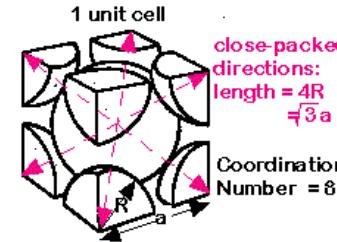
APF FOR SIMPLE CUBIC



$$APF = 0.52 \text{ for simple cubic}$$

$$\begin{aligned} \text{atom} &\rightarrow \frac{4}{3} \pi (0.5a)^3 \quad \text{volume atom} \\ \text{unit cell} &\rightarrow a^3 \quad \text{volume unit cell} \\ APF = & \frac{\text{volume atom}}{\text{volume unit cell}} \\ & \text{contains } 8 \times 1/8 = 1 \text{ atom/unit cell} \end{aligned}$$

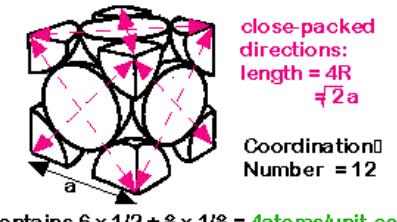
APF FOR BCC / BODY CENTERED CUBIC



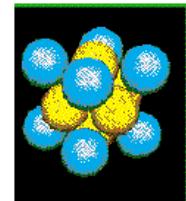
$$\text{contains } 1 + 8 \times 1/8 = 2 \text{ atoms/unit cell}$$

$$\begin{aligned} \text{atoms} &\rightarrow 2 \frac{4}{3} \pi (\sqrt{3}a/4)^3 \quad \text{volume atom} \\ \text{unit cell} &\rightarrow a^3 \quad \text{volume unit cell} \\ APF = & \frac{\text{volume atom}}{\text{volume unit cell}} \\ & \text{APF} = 0.68 \text{ for BCC} \end{aligned}$$

Face-Centred Cubic Structure (FCC)



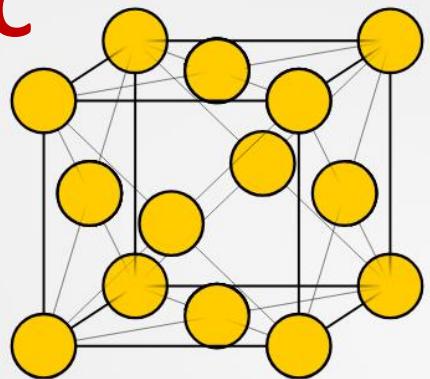
$$\begin{aligned} \text{close-packed directions:} & \text{length} = 4R = \sqrt{2}a \\ \text{Coordination Number} &= 12 \\ \text{contains} & 6 \times 1/2 + 8 \times 1/8 = 4 \text{ atoms/unit cell} \end{aligned}$$



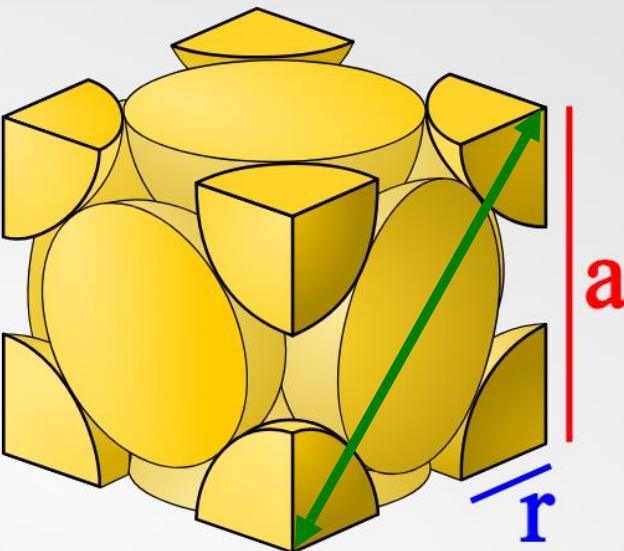
Courtesy of
Materials Science: A
Multimedia Approach,
by John C. Russ

$$\begin{aligned} \text{atoms} &\rightarrow 4 \frac{4}{3} \pi (\sqrt{2}a/4)^3 \quad \text{volume atom} \\ \text{unit cell} &\rightarrow a^3 \quad \text{volume unit cell} \\ APF = & \frac{\text{volume atom}}{\text{volume unit cell}} \\ & \text{APF} = 0.74 \text{ for FCC} \end{aligned}$$

FCC



Face-Centered Cubic
Open Visualization



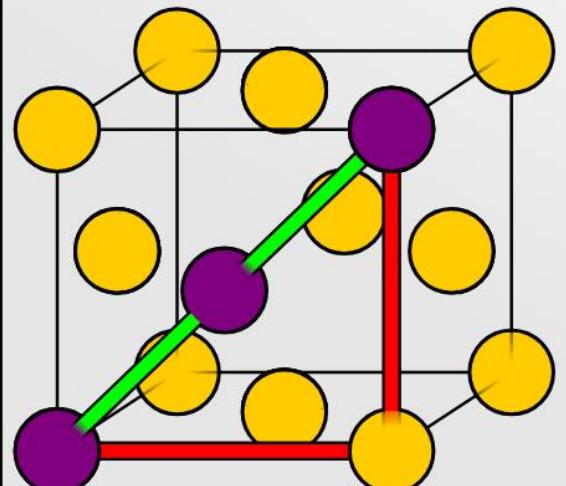
8 atoms on each corner, with $1/8$ of its volume inside the unit cell

(1)

+ 6 atoms on each face with $1/2$ of its volume inside the unit cell

(3)

= 4 atoms per unit cell



$$APF = \frac{\text{Volume of atoms}}{\text{Volume of unit cell}}$$

$$\begin{aligned} \text{Volume of atoms} &= 4 \cdot \frac{4}{3} \pi r^3 \\ \text{Volume of cube} &= (2\sqrt{2}r)^3 \end{aligned}$$

$$a^3 = 16\sqrt{2}r^3$$

$$\begin{aligned} 2a^2 &= (4r)^2 \\ a &= 2\sqrt{2}r \end{aligned}$$

For FCC

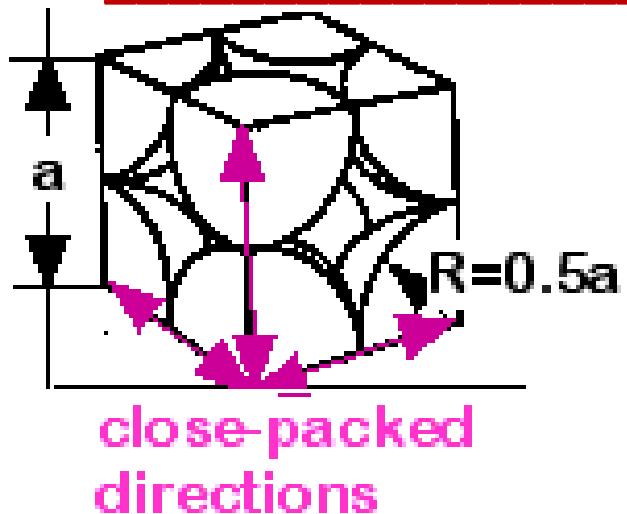
$$APF = \frac{\pi}{3\sqrt{2}} = 74\%$$

Atomic Packing Factor (APF) for SC

$$APF = \frac{\text{Volume of atoms in unit cell}^*}{\text{Volume of unit cell}}$$

*assume hard spheres

For simple cubic structure...



contains $8 \times 1/8 =$
1 atom/unit cell

APF = 0.52 for simple cubic

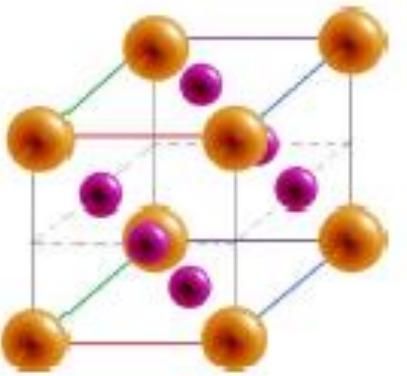
$$APF = \frac{\frac{1}{8} \cdot \frac{4}{3} \pi (0.5a)^3}{a^3}$$

atom
unit cell

volume
atom

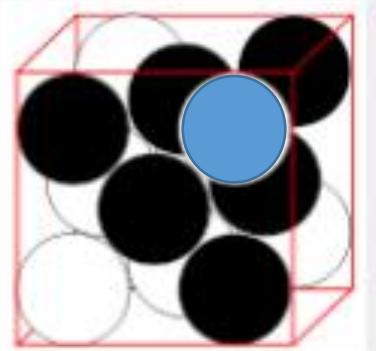
volume
unit cell

Face-centered Cubic



12

Cubic Closest Packed



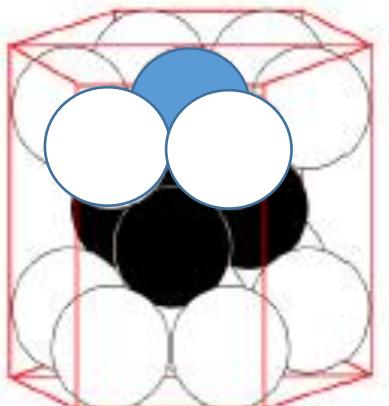
12



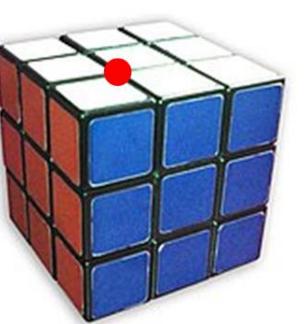
Coordination number (配位數) and closest packed structures

- In crystallography, the **coordination number** of a **central atom** in a crystal is the number of atoms bonded to it. (在晶體學中，晶體中某一中心原子的**配位數**是與其相距最近產生鍵結的原子個數 ⇒ **Nearest-neighbor interactions** are fundamental **forces** between two adjacent atoms where **their proximity** dictates the nature and strength of their mutual influence.)
- To maximize the efficiency of packing and minimize the volume of unfilled space, the spheres must be arranged as close as possible to each other. These arrangements are called **closest packed structures**.
- **FCC and HCP** have coordination number = 12 and packing density = 74.04%.
- https://chem.libretexts.org/Core/Physical_and_Theoretical_Chemistry/Physical_Properties_of_Matter/States_of_Matter/Properties_of_Solids/Crystal_Lattice/Closest_Pack_Structures

Hexagonal Closest Packed



12



1.2.3 Planes and directions:

- Solids: anisotropic (各向異性), facet (刻面)
- Miller indices (密勒指數) (hkl): Uses a set of three integers, h , k , and l , to describe the position of a plane or the direction of a vector within the lattice.

Miller indices in cubic (立方)
or orthorhombic (正方) lattice

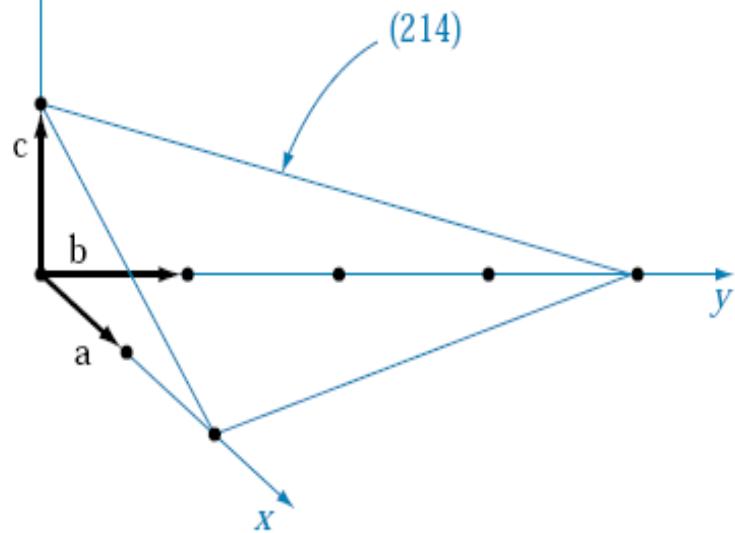
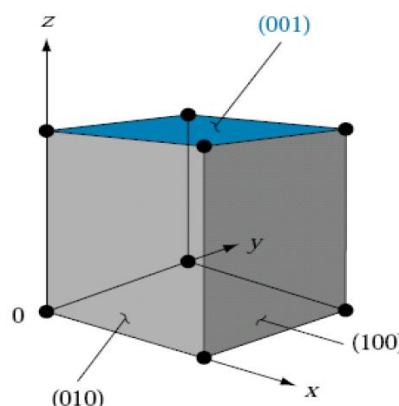


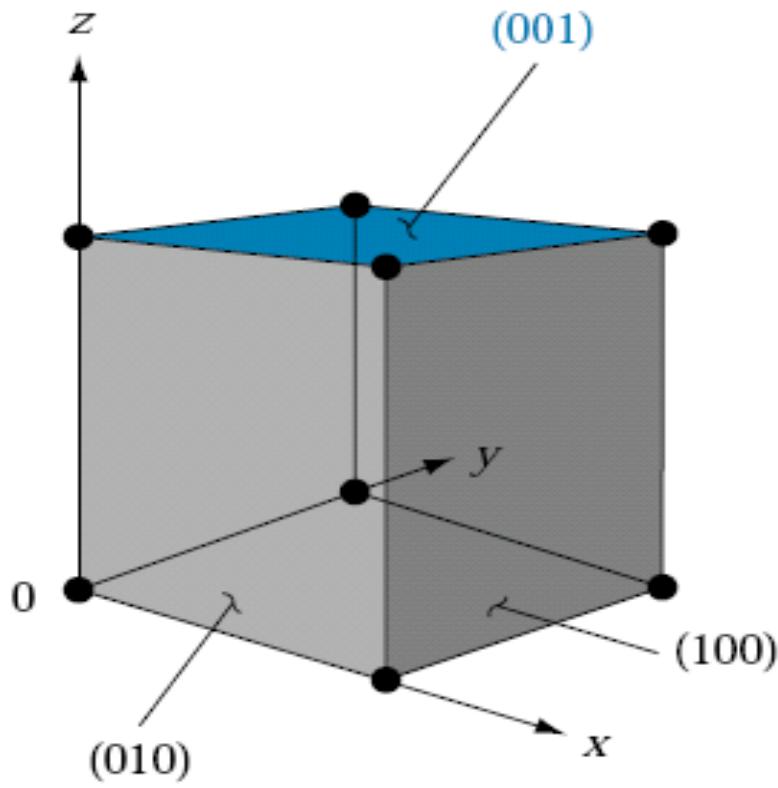
Figure 1-5
A (214) crystal plane.

Miller indices (hkl):

- (1) Find intercepts (截距): $2, 4, 1$ (not passing through the origin)
- (2) Take reciprocals (倒數): $\frac{1}{2}, \frac{1}{4}, 1$
- (3) Reduce (約化或簡化) to the smallest set of integers having the same ratio: $2, 1, 4$

密勒指數使用倒數之比
是為防止無窮大截距的出現。





Within the cubic lattice,
(100), (010), and (001) are all
equivalent planes {100}.

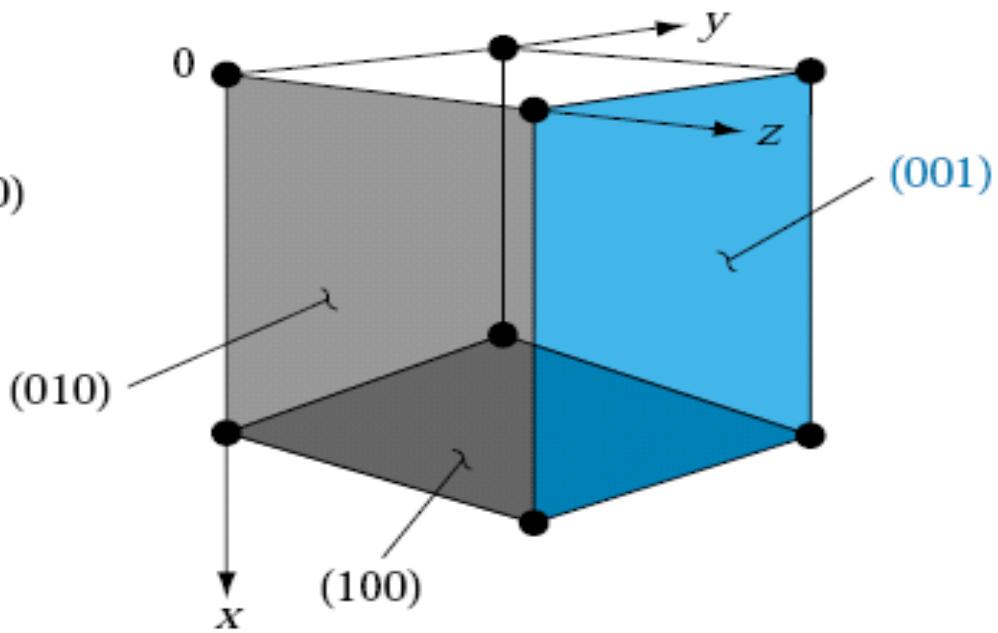
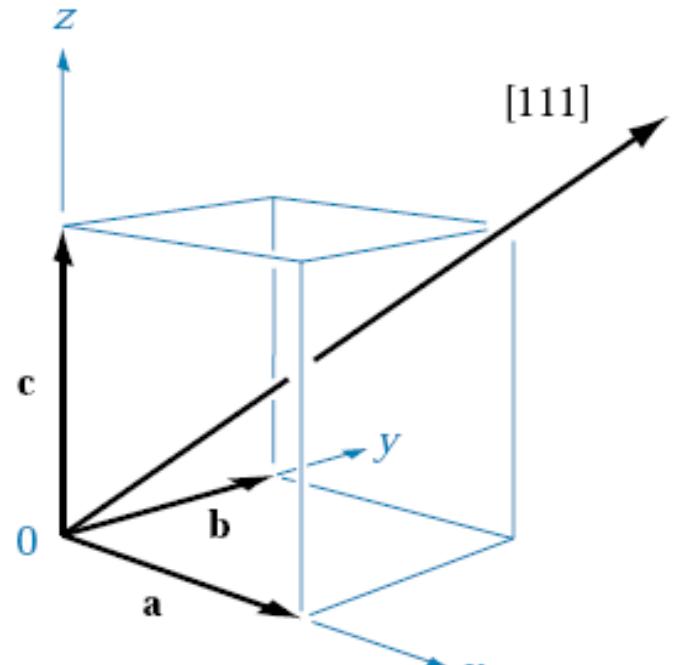


Figure 1–6

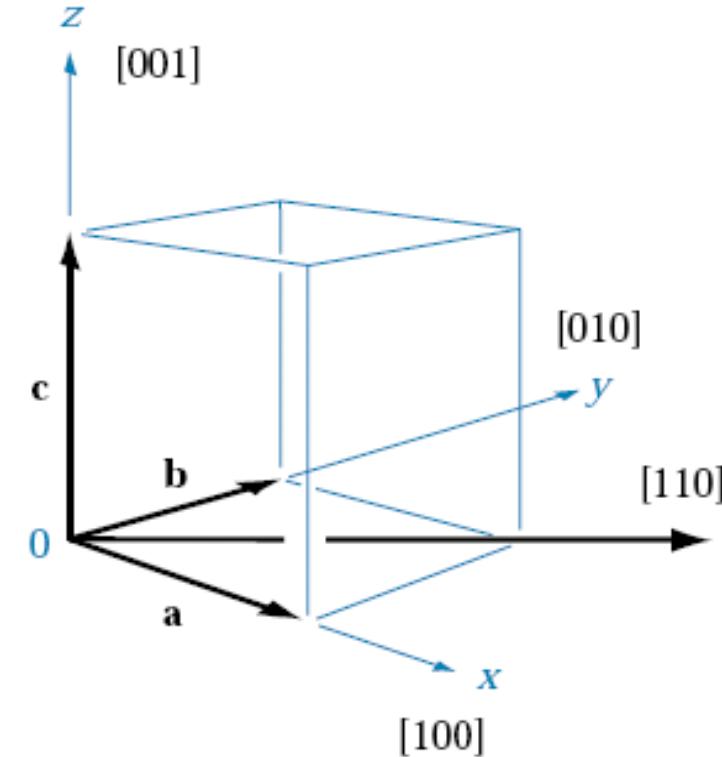
Equivalence of the cube faces ($\{100\}$ planes) by rotation of the unit cell within the cubic lattice.

Fig. 1-7 Crystal direction $[hkl]$

Only in **cubic lattice**, $[hkl]$ direction perpendicular to (hkl) plane



(a)



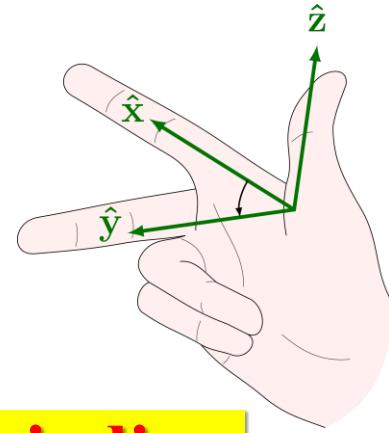
(b)

Figure 1-7

Crystal directions in the cubic lattice.

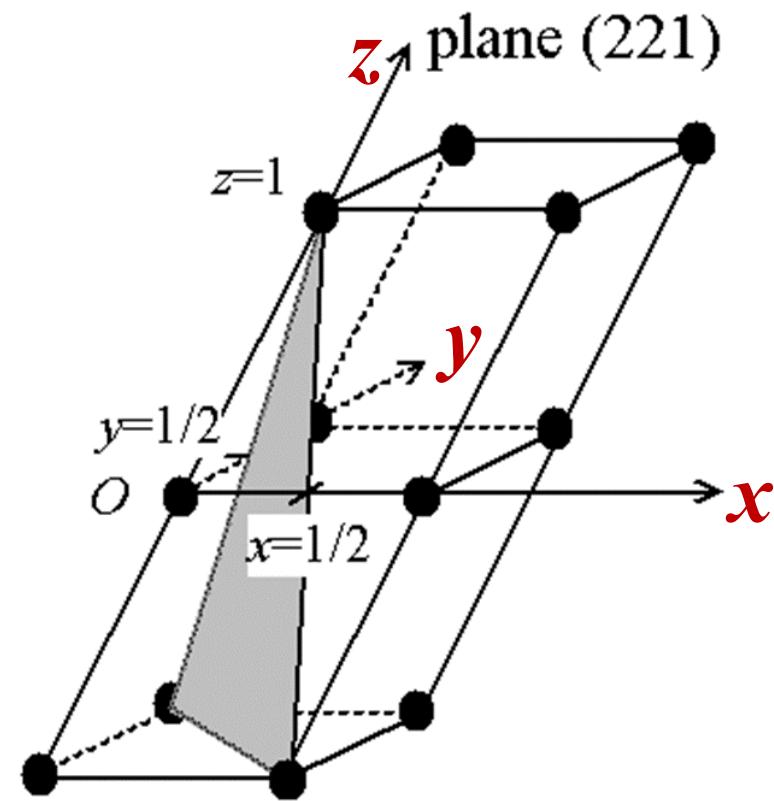
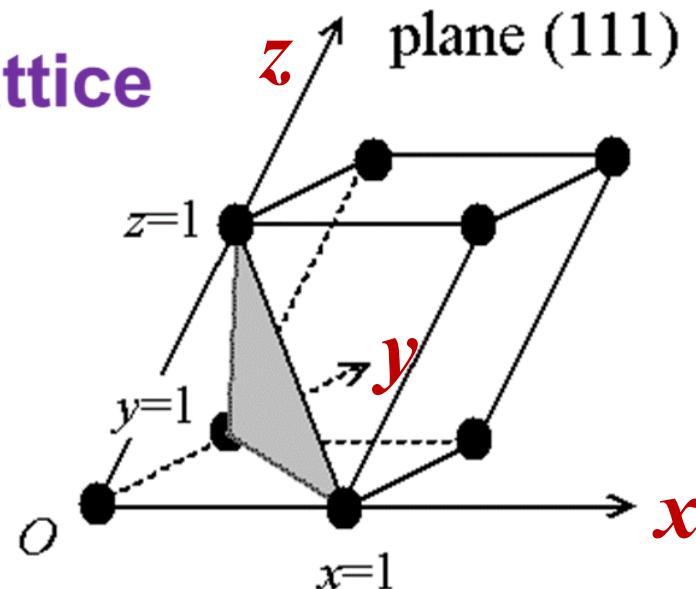
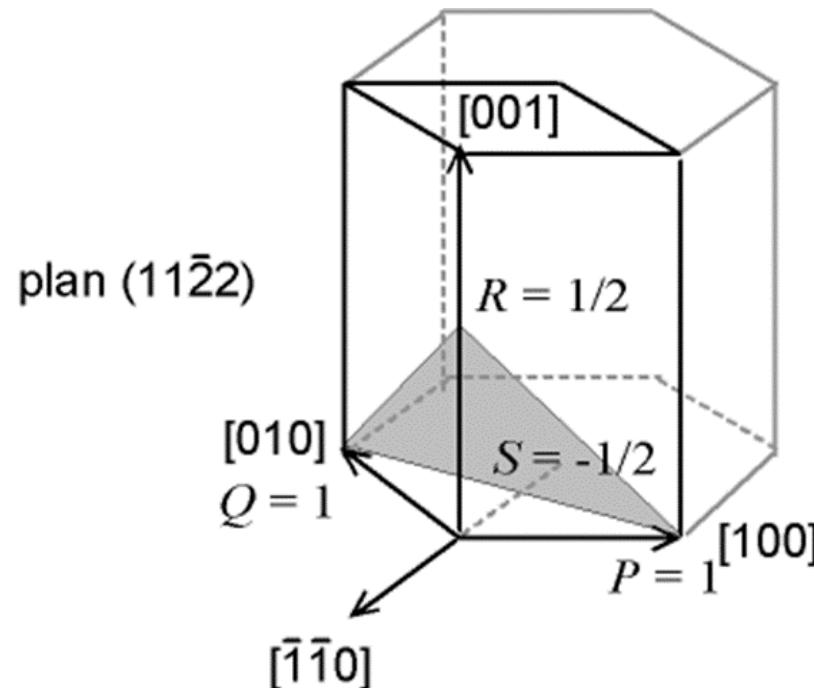
For monoclinic or triclinic lattice

Right-hand rule



Bravais-Miller indices

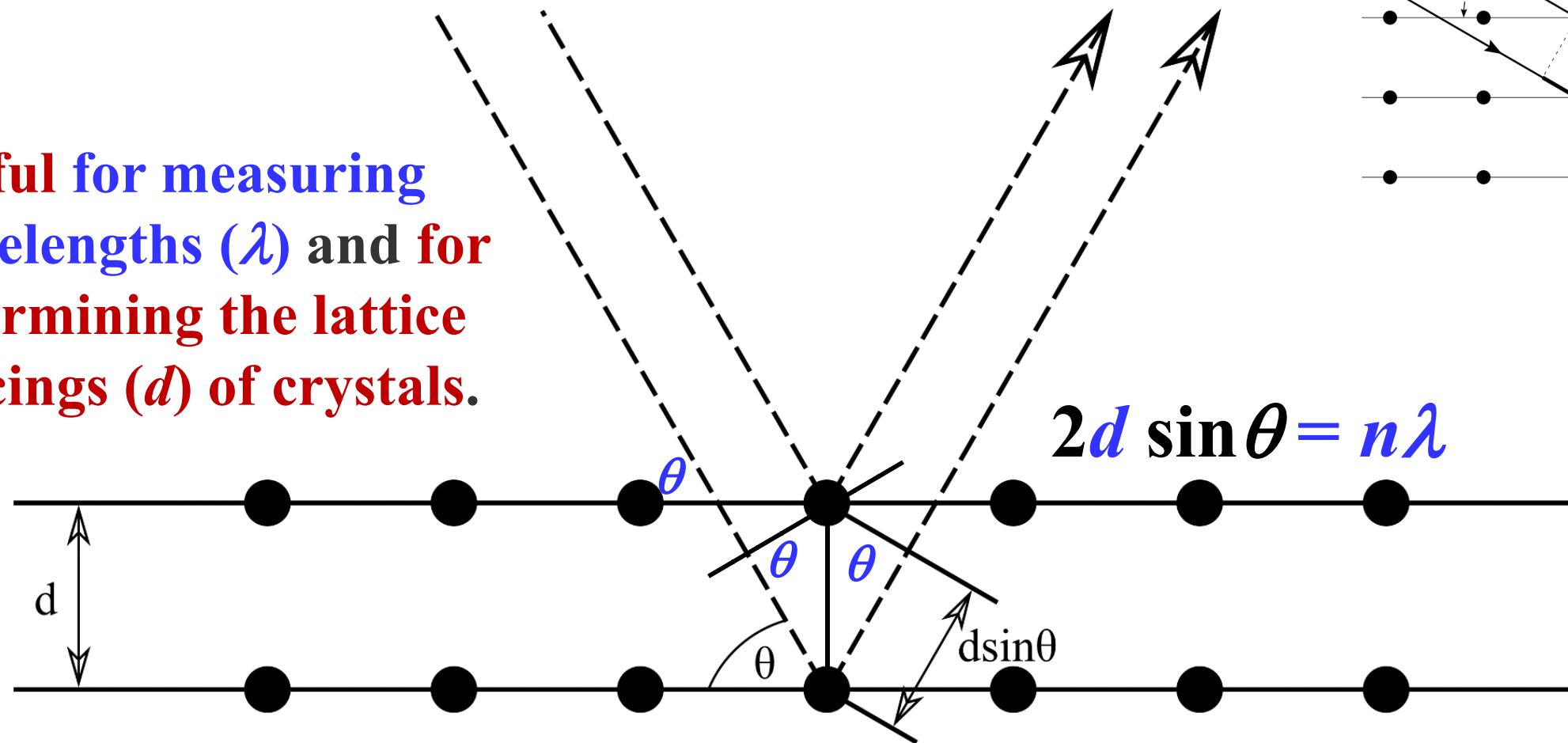
in hexagonal lattice



The Bravais-Miller system uses **four indices** $(h \ k \ i \ l) = (11\bar{2}2)$ that obey the constraint $h + k + i = 0$. Here h , k and l are identical to the corresponding Miller indices $(hkl) = (112)$, and i is a redundant (多餘) index.

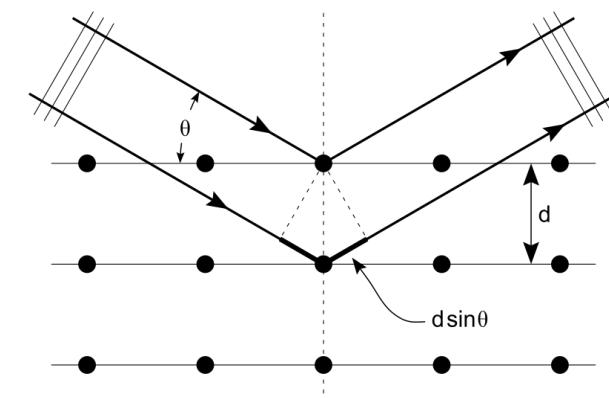
Bragg's Law: $2d \sin\theta = n\lambda$

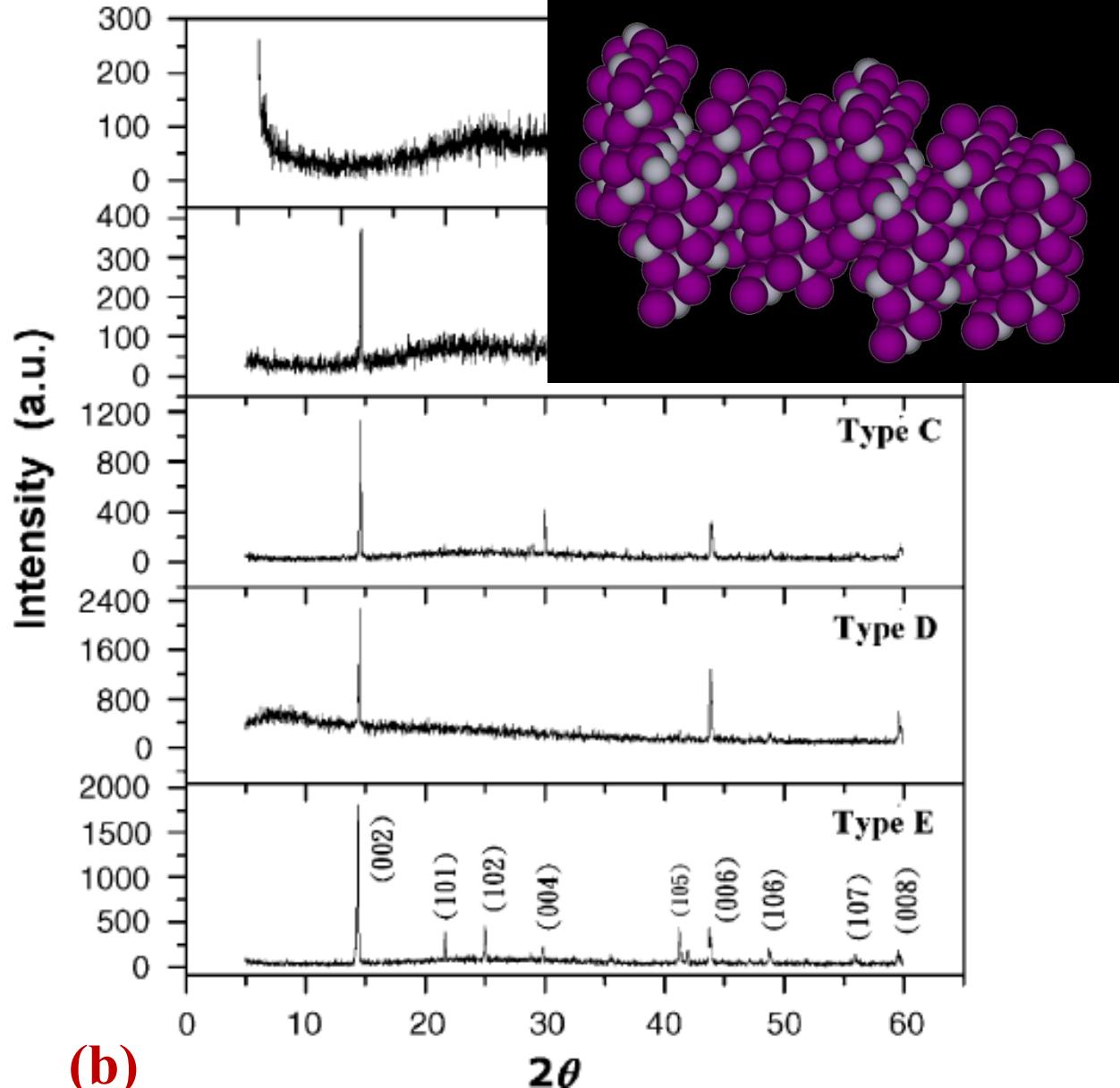
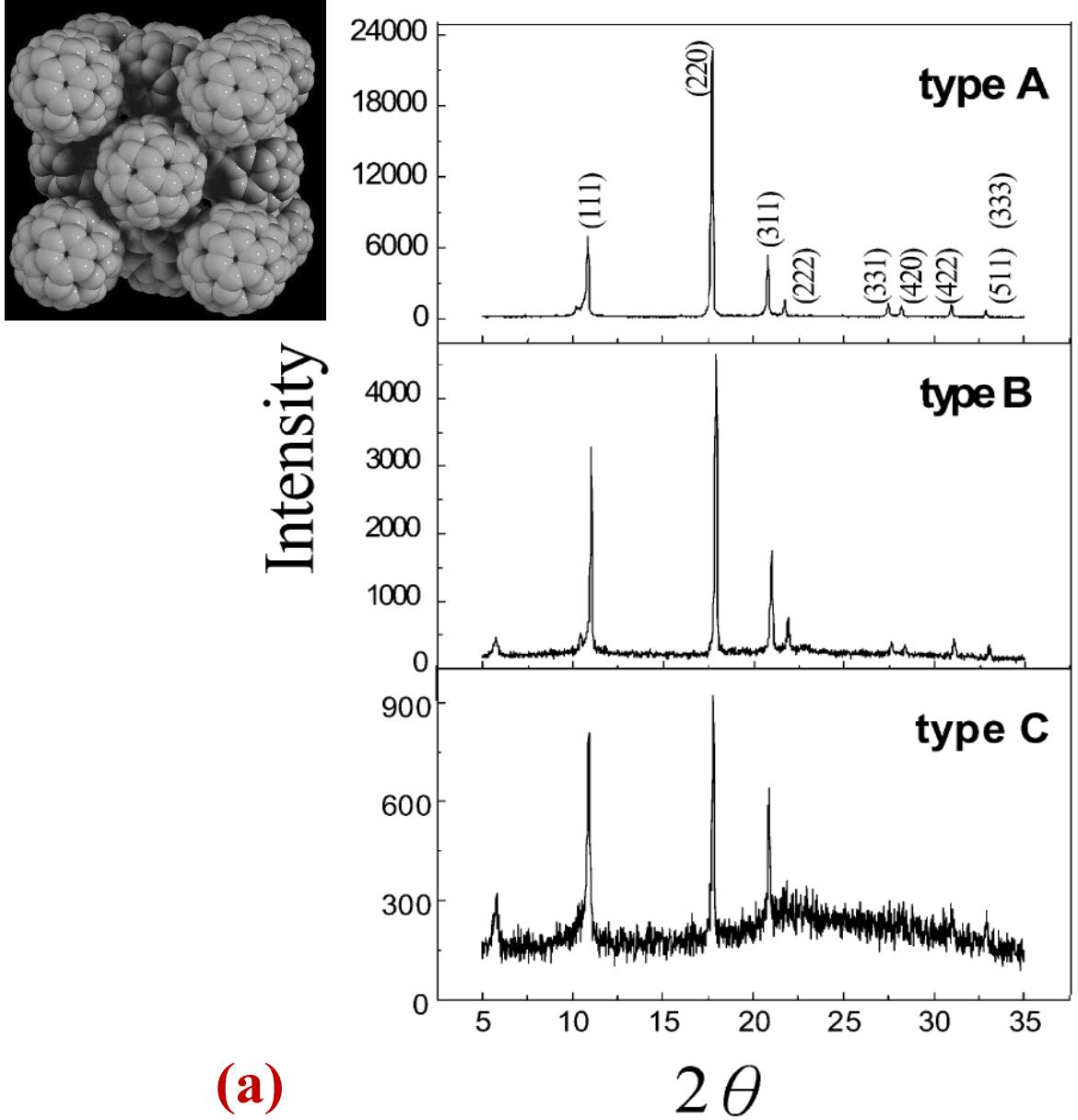
Useful for measuring wavelengths (λ) and for determining the lattice spacings (d) of crystals.



The second-order diffraction of X-ray (with wavelengths $\lambda = 2.20 \text{ \AA}$) occurs at $\theta = 36^\circ$. Find the distance d between the adjacent Miller planes.

Solution: Using **Bragg's law**, $n = 2$, $\lambda = 2.20 \text{ \AA}$, $\theta = 36^\circ$, we get $d = 3.74 \text{ \AA}$.





XRD patterns correspond to (a) three types of **C₆₀ polycrystalline films in fcc structure**; (b) five types of **α-HgI₂ (tetragonal)** polycrystalline films.

1.2.4 The diamond lattice:

- The **diamond lattice** can be thought of as an fcc structure with an extra atom places at $a/4 + b/4 + c/4$ from each of the **fcc** atoms.

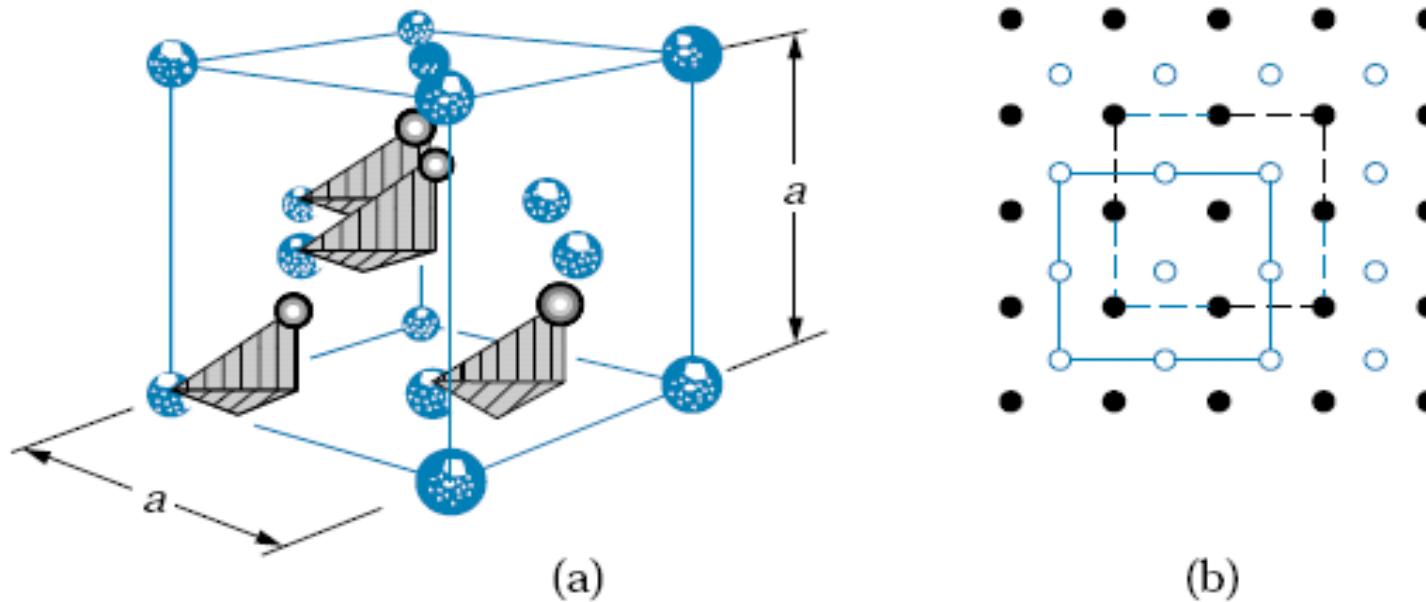
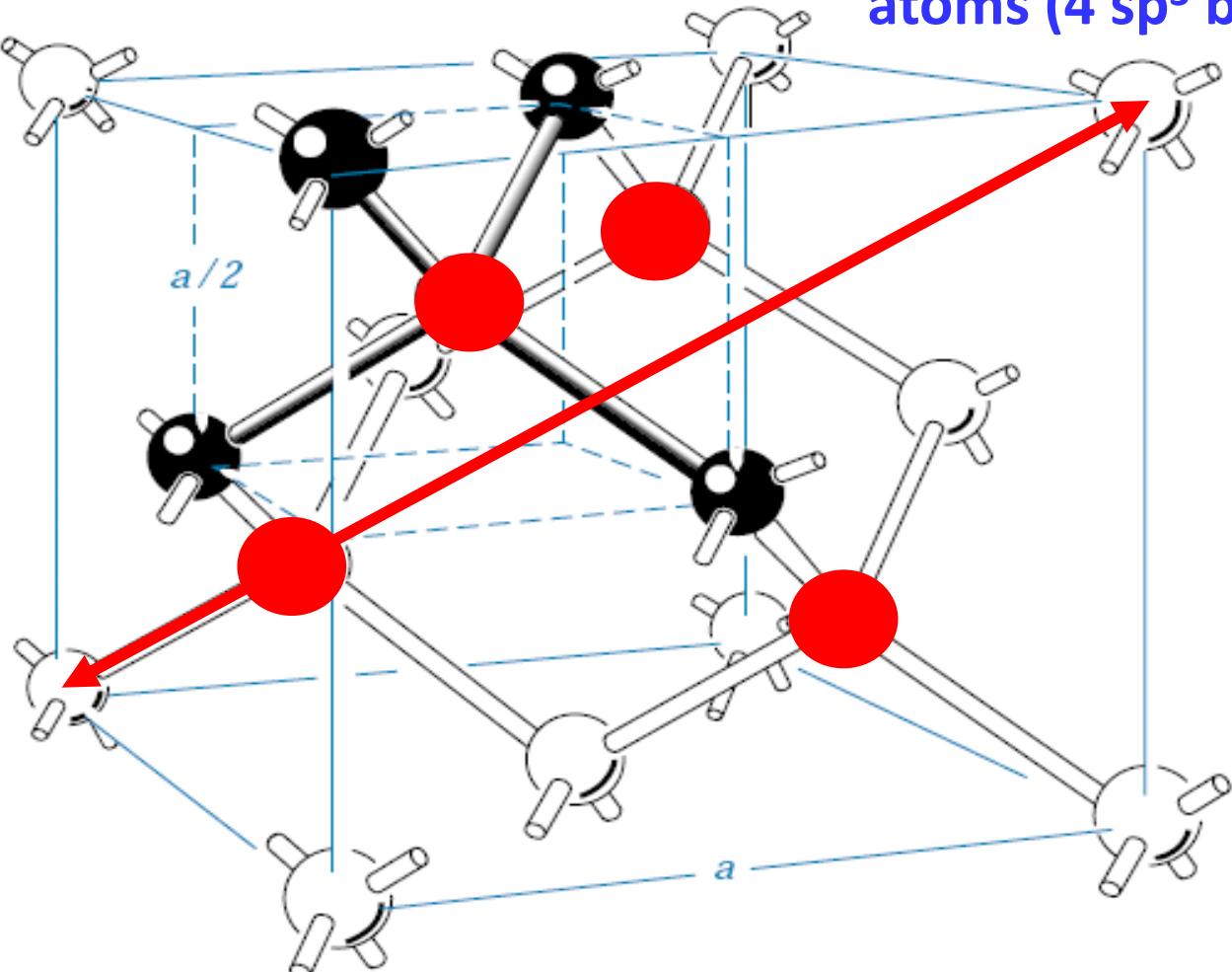
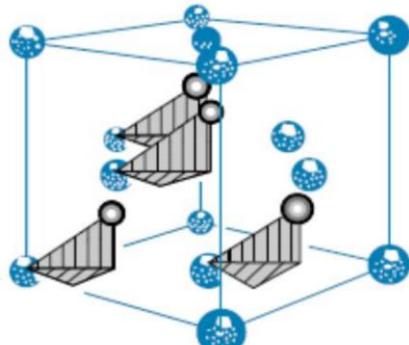
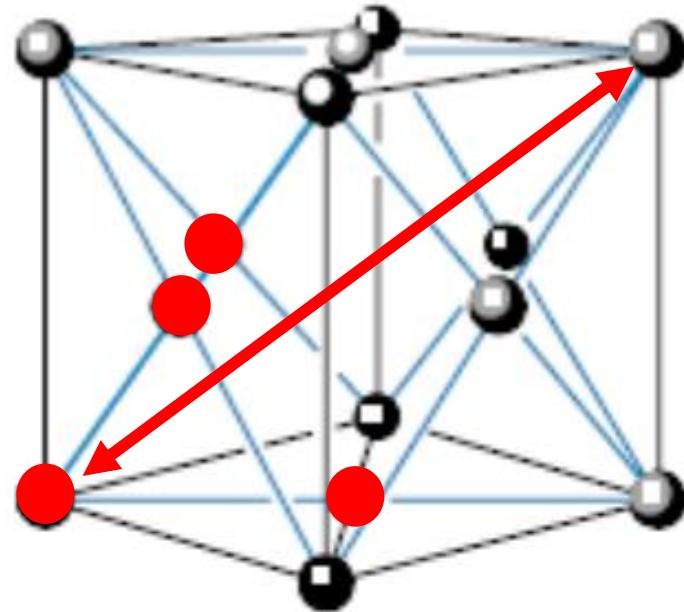


Figure 1-8

Diamond lattice structure: (a) a unit cell of the diamond lattice constructed by placing atoms $\frac{1}{4}$ from each atom in an fcc; (b) top view (along any $\langle 100 \rangle$ direction) of an extended diamond lattice. The colored circles indicate one fcc sublattice and the black circles indicate the interpenetrating fcc.

Diamond lattice: C, Si, and Ge; covalent bonding.

Nearest neighboring atoms (4 sp^3 bonds)

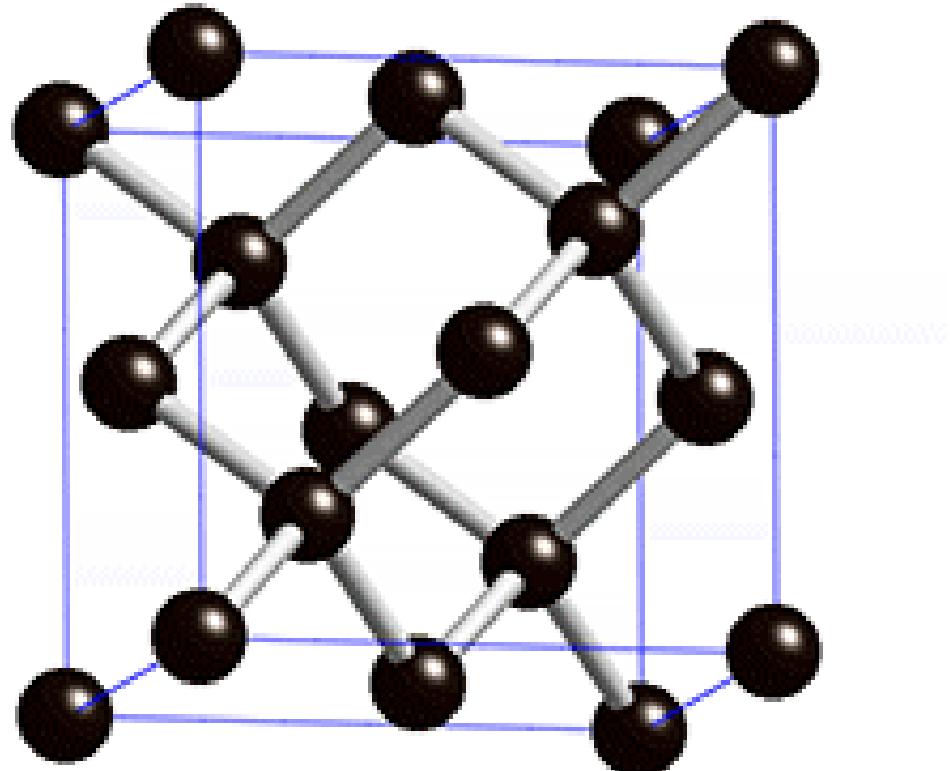


For diamond, 8 atoms/unit cell,
coordination number = 4, APF = ?

Figure 1-9

Diamond lattice unit cell, showing the four nearest neighbor structure. (From *Electrons and Holes in Semiconductors* by W. Shockley, © 1950 by Litton Educational Publishing Co., Inc.; by permission of Van Nostrand Reinhold Co., Inc.)

Rotating model of the diamond cubic crystal structure



固態晶體(如鑽石結構)具有各向異性(Anisotropic property)

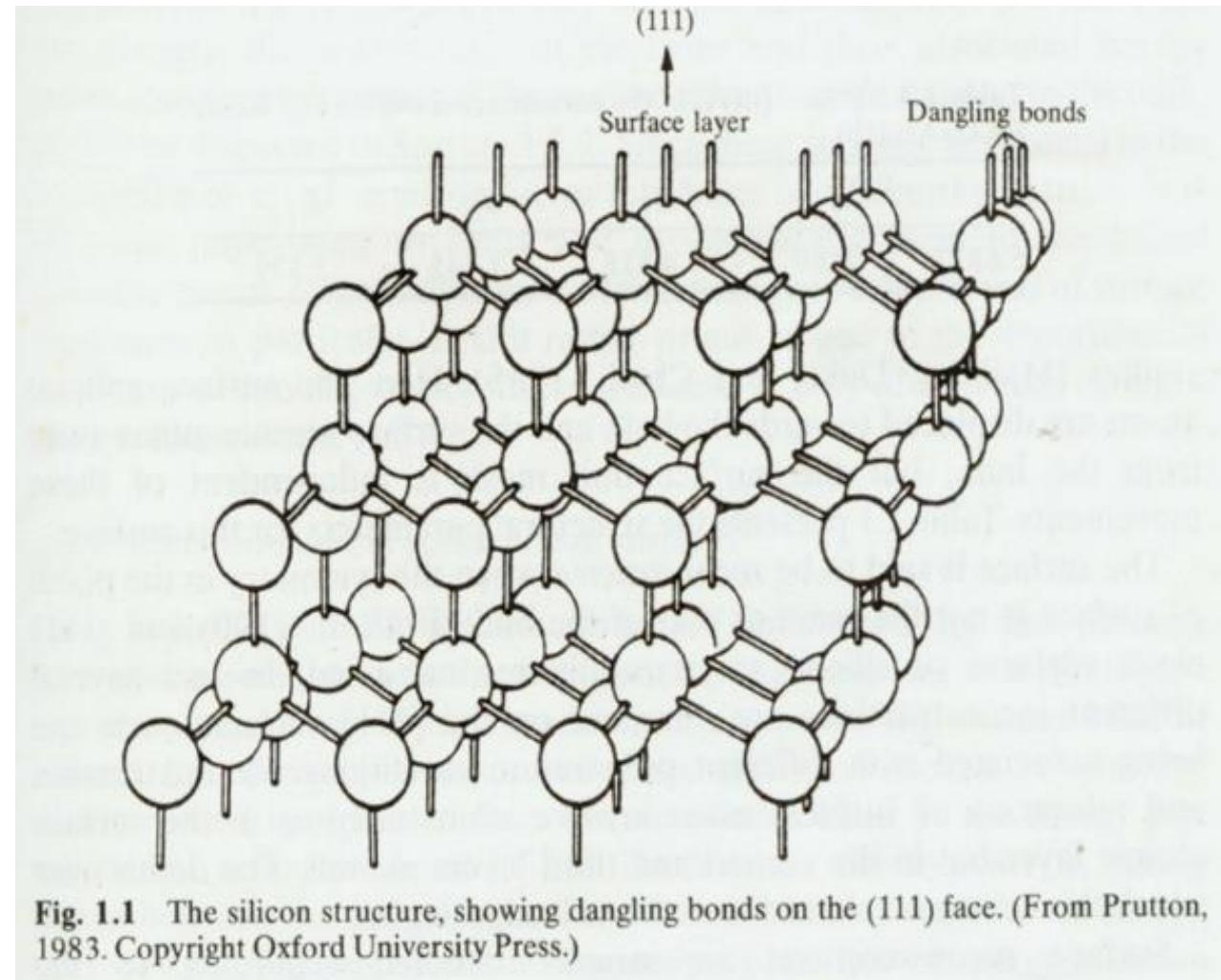
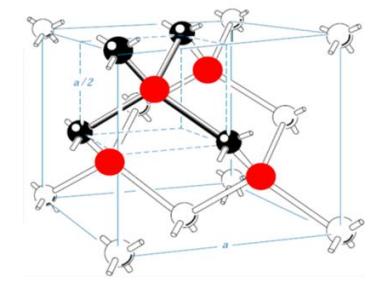


Fig. 1.1 The silicon structure, showing dangling bonds on the (111) face. (From Prutton, 1983. Copyright Oxford University Press.)

From crystal structure \Rightarrow Volume density (atoms/cm³) and areal density (atoms/cm²)



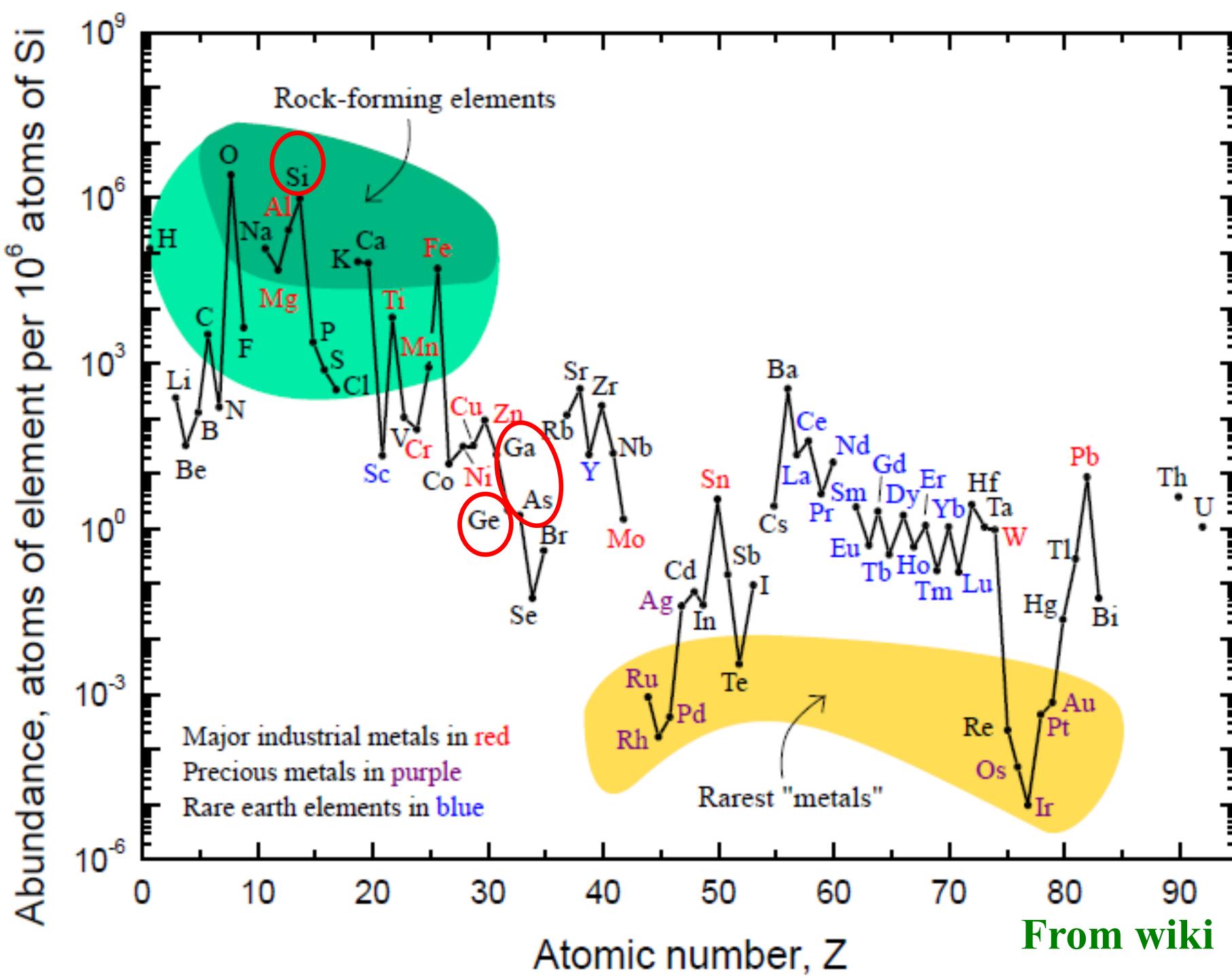
Ex. 1-3 Given that the lattice constant of Si in diamond structure is $a = 5.43\text{\AA}$, please calculate (a) the volume density (Si-atoms/cm³), and (b) the areal density (Si-atoms/cm²) on the (001) plane.

(a) 8 atoms/unit cell, volume density = $8/(5.43 \times 10^{-8})^3 = 5.00 \times 10^{22} \text{ atoms/cm}^3$, with atomic mass \Rightarrow the mass density is 2.33 g/cm^3 .

(b) 2 atoms/unit areal cell, areal density = $2/(5.43 \times 10^{-8})^2 = 6.8 \times 10^{14} \text{ atoms/cm}^2$.

Q: 在地殼中，含量最多 (週期表上) 的元素依序為何？

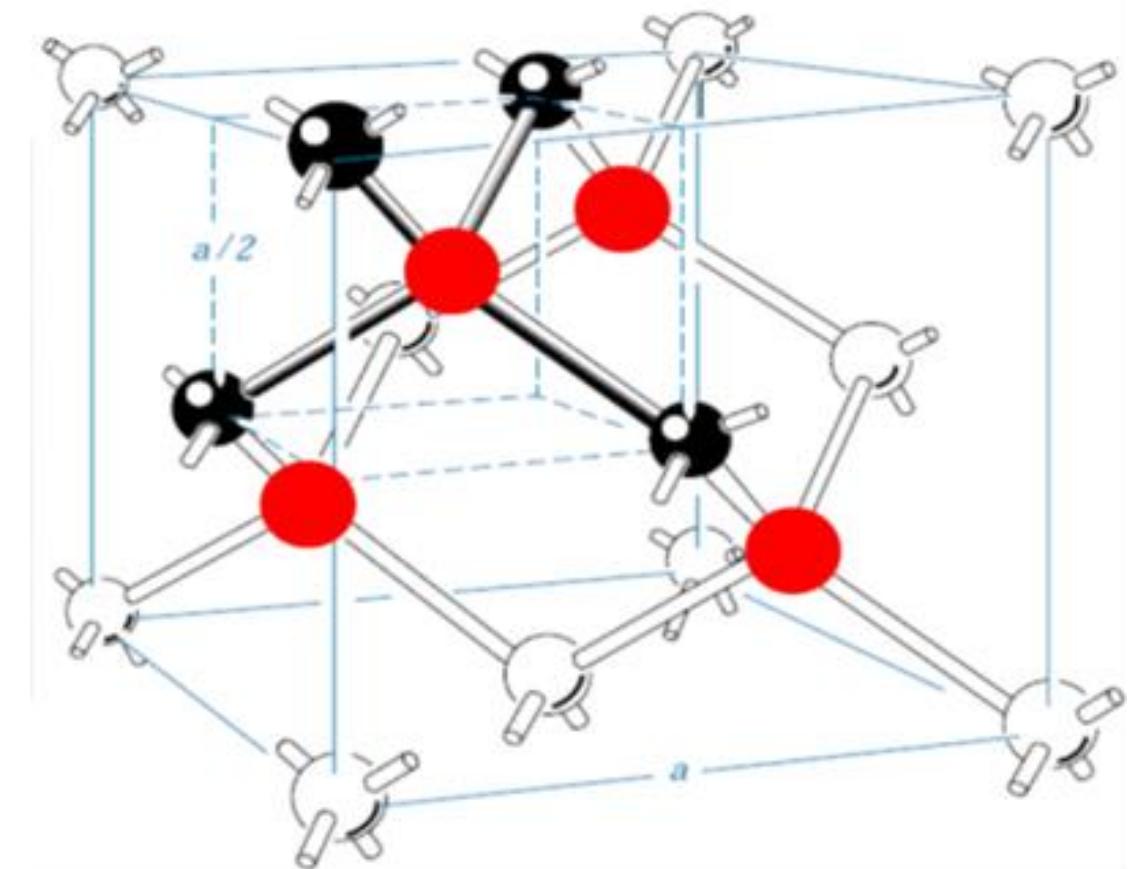
A: 地殼中含量 (Abundance of elements in Earth's crust) 最高的元素依序是氧 (46.6%)，矽 (27.7%)，鋁 (8.1%)，鐵 (5.0%)，鈣 (3.6%)，鈉 (2.8%)，鉀 (2.6%)，鎂 (2.1%)。



The **diamond** (*D*) lattice for Si or Ge \leftrightarrow

The **Zincblende** (Z, 閃鋅礦) lattice for III-V or II-VI compounds

- In many **binary III-V compound semiconductors** (GaAs, GaP, etc), III and V atoms are arranged in a basic diamond structure but are different on alternating sites \Rightarrow 4 III-atoms and 4 V-atoms per cell in Zincblende lattice.
- **II-VI compounds** (ZnSe, CdTe, etc) \Rightarrow 4 II-atoms and 4 VI-atoms per cell in Zincblende lattice.



**Indirect (*i*) or
direct (*d*) E_G**

	/ lattice	E_g (ev)	μ_n ($\text{cm}^2/\text{V}\cdot\text{s}$)	μ_p ($\text{cm}^2/\text{V}\cdot\text{s}$)	m_n^*/m_o (m_l/m_i)	m_p^*/m_o (m_{lh}/m_{hh})	a (Å)	ϵ_r	Density (g/cm^3)	Melting point (°C)
Si	(<i>i/D</i>)	1.11	1350	480	0.98, 0.19	0.16, 0.49	5.43	11.8	2.33	1415
Ge	(<i>i/D</i>)	0.67	3900	1900	1.64, 0.082	0.04, 0.28	5.65	16	5.32	936
SiC (α)	(<i>i/W</i>)	2.86	500	—	0.6	1.0	3.08	10.2	3.21	2830
AlP	(<i>i/Z</i>)	2.45	80	—	—	0.2, 0.63	5.46	9.8	2.40	2000
AlAs	(<i>i/Z</i>)	2.16	1200	420	2.0	0.15, 0.76	5.66	10.9	3.60	1740
AlSb	(<i>i/Z</i>)	1.6	200	300	0.12	0.98	6.14	11	4.26	1080
GaP	(<i>i/Z</i>)	2.26	300	150	1.12, 0.22	0.14, 0.79	5.45	11.1	4.13	1467
GaAs	(<i>d/Z</i>)	1.43	8500	400	0.067	0.074, 0.50	5.65	13.2	5.31	1238
GaN	(<i>d/Z, W</i>)	3.4	380	—	0.19	0.60	4.5	12.2	6.1	2530
GaSb	(<i>d/Z</i>)	0.7	5000	1000	0.042	0.06, 0.23	6.09	15.7	5.61	712
InP	(<i>d/Z</i>)	1.35	4000	100	0.077	0.089, 0.85	5.87	12.4	4.79	1070
InAs	(<i>d/Z</i>)	0.36	22600	200	0.023	0.025, 0.41	6.06	14.6	5.67	943
InSb	(<i>d/Z</i>)	0.18	10^5	1700	0.014	0.015, 0.40	6.48	17.7	5.78	525
ZnS	(<i>d/Z, W</i>)	3.6	180	10	0.28	—	5.409	8.9	4.09	1650*
ZnSe	(<i>d/Z</i>)	2.7	600	28	0.14	0.60	5.671	9.2	5.65	1100*
ZnTe	(<i>d/Z</i>)	2.25	530	100	0.18	0.65	6.101	10.4	5.51	1238*
CdS	(<i>d/W, Z</i>)	2.42	250	15	0.21	0.80	4.137	8.9	4.82	1475
CdSe	(<i>d/W</i>)	1.73	800	—	0.13	0.45	4.30	10.2	5.81	1258
CdTe	(<i>d/Z</i>)	1.58	1050	100	0.10	0.37	6.482	10.2	6.20	1098
PbS	(<i>i/H</i>)	0.37	575	200	0.22	0.29	5.936	17.0	7.6	1119
PbSe	(<i>i/H</i>)	0.27	1500	1500	—	—	6.147	23.6	8.73	1081
PbTe	(<i>i/H</i>)	0.29	6000	4000	0.17	0.20	6.452	30	8.16	925

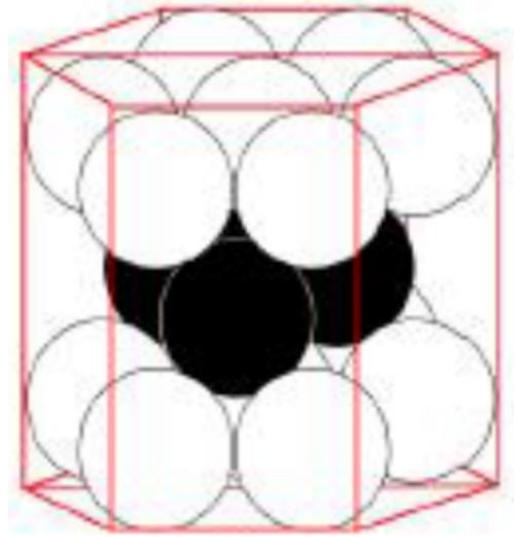
All values at 300 K.

*Vaporizes

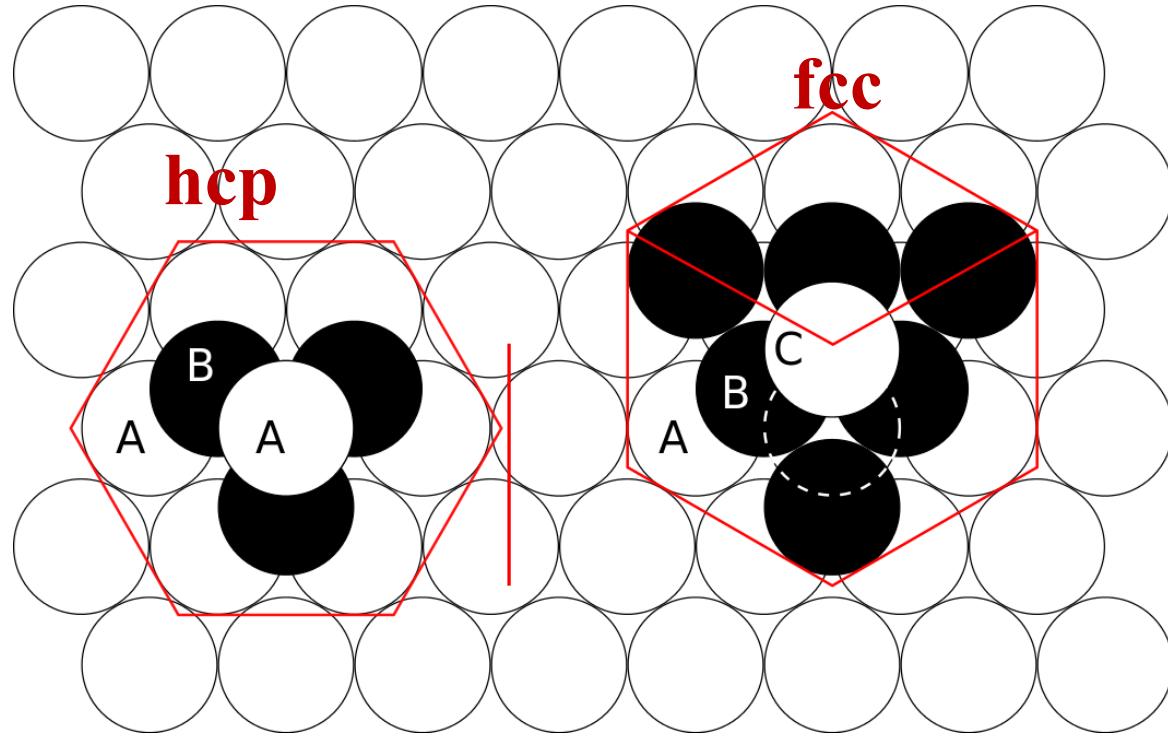
Hexagonal close-packed (**hcp**: 六方緊密堆積) versus **fcc**



hcp



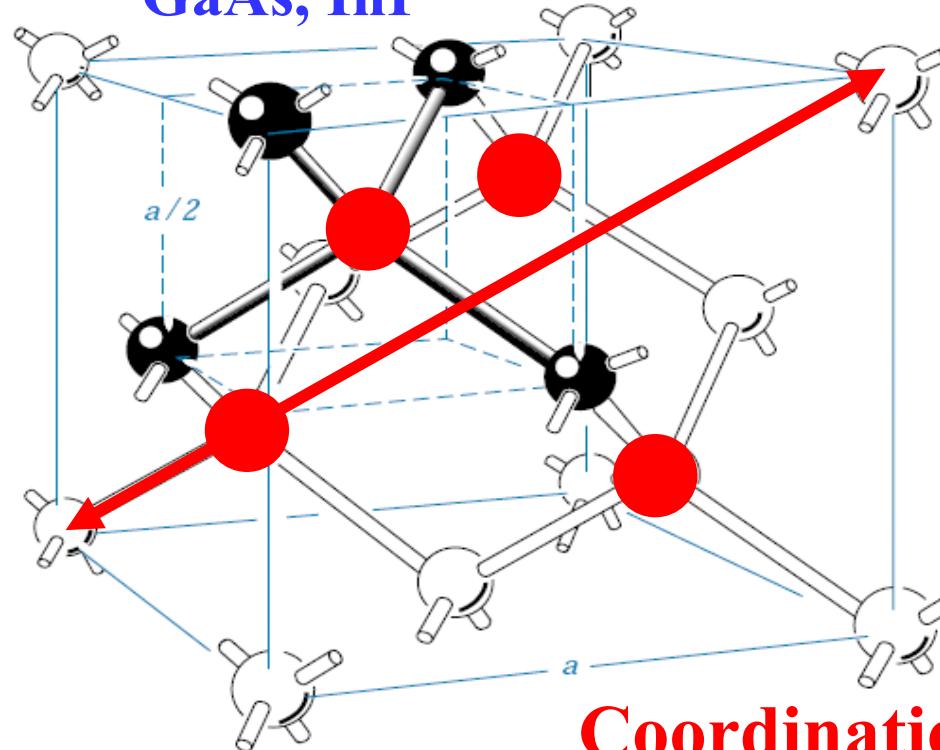
Both (hcp & fcc) have coordination number = 12 and packing density = 74.04%.



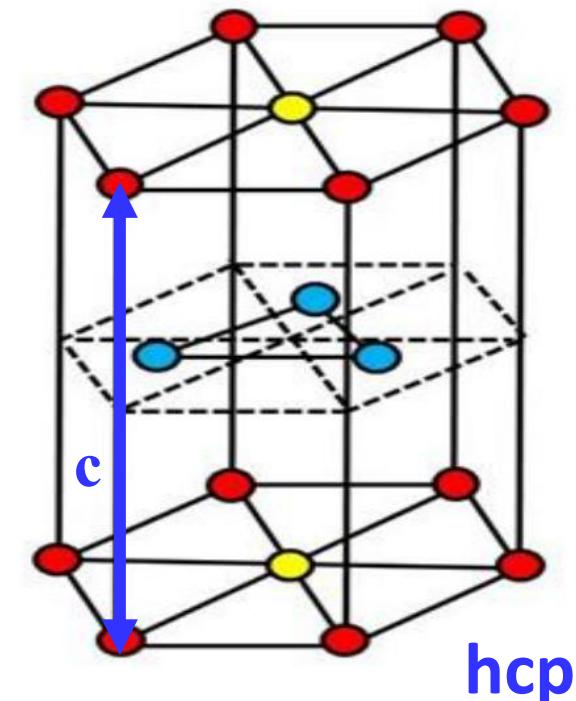
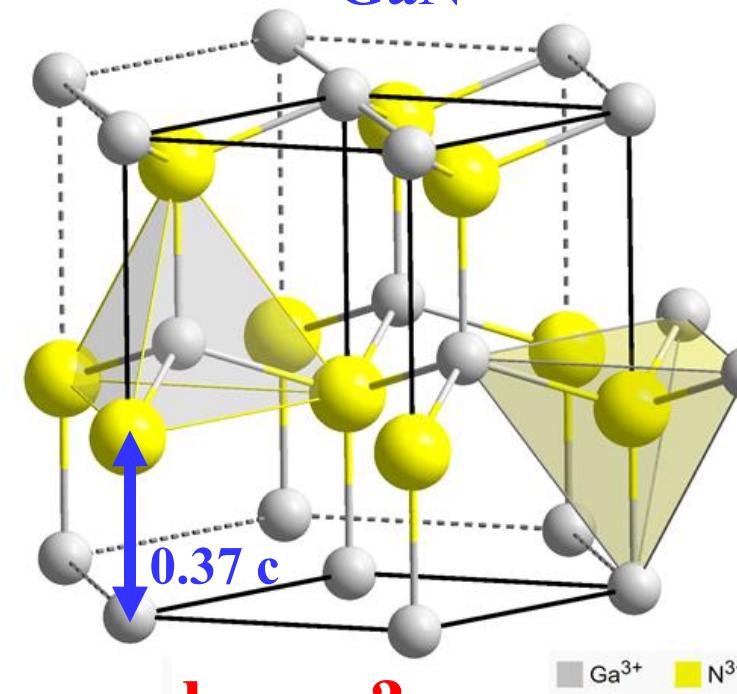
- The letters indicate which layers are the same.
- There are two "A" layers in the **hcp** matrix, where all the spheres are in the same position.
- All three layers in the **fcc** stack are different.
- Note the **fcc** stacking may be converted to the **hcp** stacking by translation of the upper-most sphere, as shown by the dashed outline.

Compare the difference between Zincblende (Z, 閃鋅礦) \leftrightarrow Wurtzite (W, 織鋅礦)

GaAs, InP



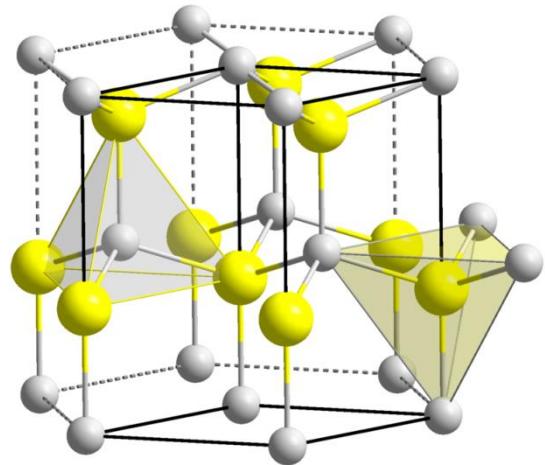
GaN



Coordination number = ?

The **zincblende lattice** in many binary III-V compounds (GaN, GaP, etc) has III-atoms and V-atoms arranged in **a basic diamond structure** but different on alternating sites.

The **wurtzite lattice** in some binary III-V (GaN) or II-VI compounds (CdS, ZnS, etc) has III-atoms and V-atoms (or II-VI atoms) occupied on alternating sites of **two interpenetrating hcp structures shifting with $0.37 c$ along the c-axis.**



Space group: P6₃mc

Bravais lattice and Wyckoff positions:

Hexagonal

S in 2b: 1/3,2/3,0 2/3,1/3,0.5

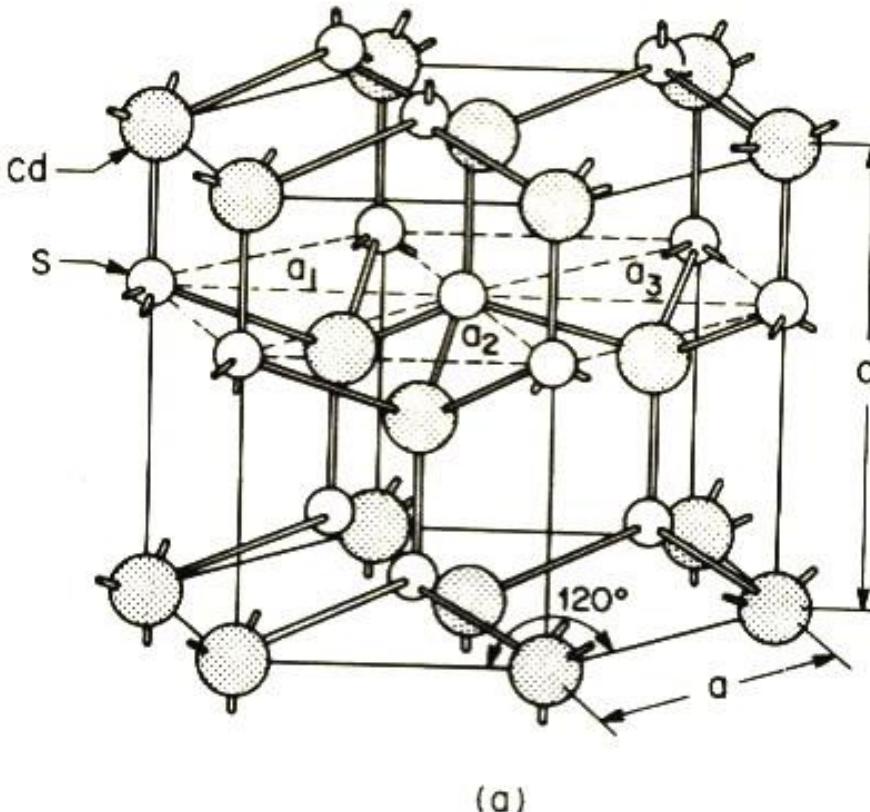
Zn in 2b: 1/3,2/3,0.371 2/3,1/3,0.871

Structure description:

Interpenetrating hexagonal close-packed sublattices of the anion and the cation displaced along [0001] (by 0.371c for ZnS).

Cations occupy tetrahedral sites in the h.c.p. anion sublattice. Bonding is a mix of sp³ covalent bonds and ionicity due to the large electronegativity difference.

**Wurtzite (*W*, 纖鋅礦) lattice
for CdS and ZnS, etc.**
anion: 陰離子; cation: 陽離子
hexagonal: 六邊形的



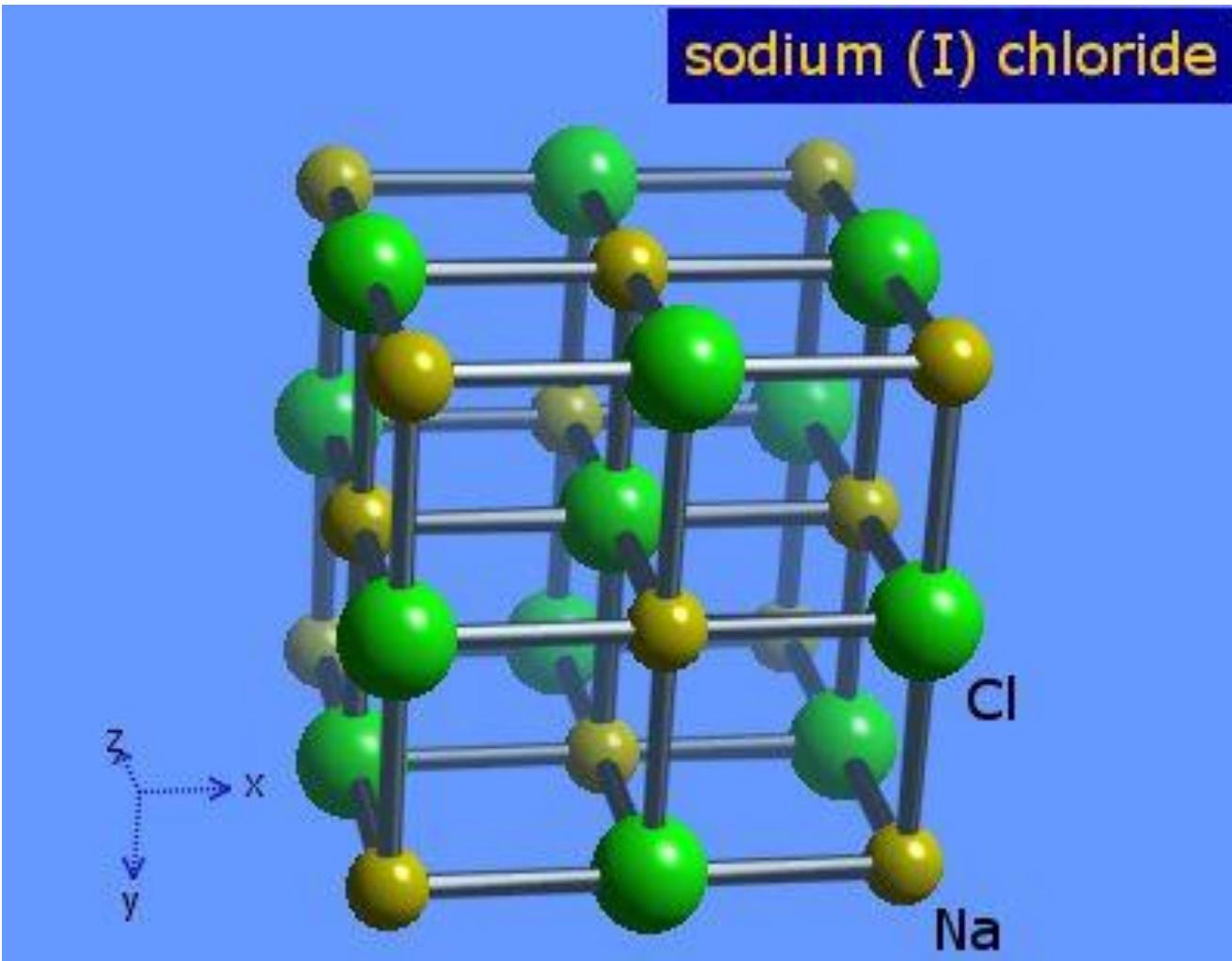
**Indirect (*i*) or
direct (*d*) E_G**

	/ lattice	E_g (ev)	μ_n ($\text{cm}^2/\text{V}\cdot\text{s}$)	μ_p ($\text{cm}^2/\text{V}\cdot\text{s}$)	m_n^*/m_o (m_l/m_i)	m_p^*/m_o (m_{lh}/m_{hh})	a (Å)	ϵ_r	Density (g/cm^3)	Melting point (°C)
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AlAs	(<i>i/Z</i>)	2.16	1200	420	2.0	0.15, 0.76	5.66	10.9	3.60	1740
AlSb	(<i>i/Z</i>)	1.6	200	300	0.12	0.98	6.14	11	4.26	1080
GaP	(<i>i/Z</i>)	2.26	300	150	1.12, 0.22	0.14, 0.79	5.45	11.1	4.13	1467
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PbTe	(<i>i/H</i>)	0.29	6000	4000	0.17	0.20	6.452	30	8.16	925

All values at 300 K.

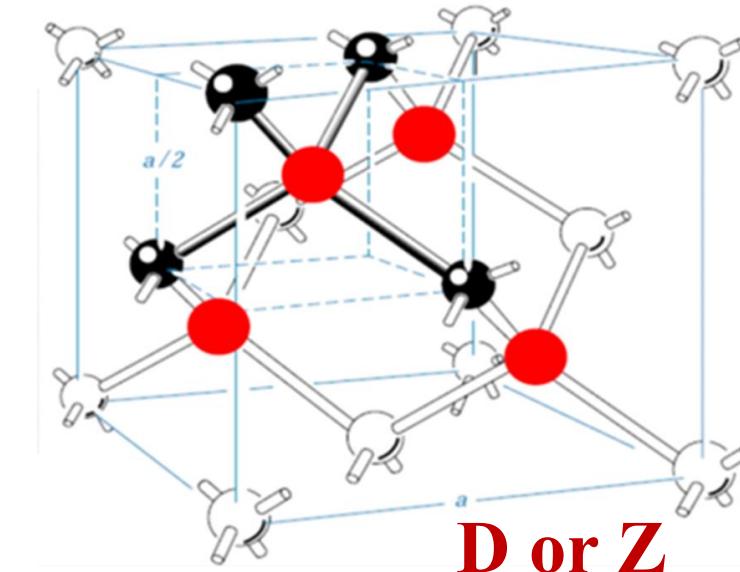
*Vaporizes

Halite crystal (*H*, 石鹽晶體)



Halite, commonly known as **rock salt** (岩鹽), is **the mineral form of sodium chloride (NaCl)**. Halite forms isometric (cubic) crystals. The NaCl mineral is typically **colorless or white**, but may also be **light blue, dark blue, purple, pink, red, orange, yellow or gray** depending on **the amount and type of impurities**.

Various crystallographic directions (or planes, facets) possess different properties



- The facets of a diamond reveal clearly the triangular, hexagonal, and rectangular symmetries of intersecting planes in various crystallographic directions.
- Semiconductors with diamond (D) and zincblende (Z) lattices have similar cleavage planes (劈裂面). A cleavage plane is a smooth, flat surface along which a crystal or material breaks, due to weak bonds or planes of weakness within its internal atomic structure.
- Chemical reactions, e.g., etching (蝕刻) of the crystal, often take place preferentially along certain directions. These properties play important roles in fabrication processes for many semiconductor devices.

Homework #1 for Chapter 1 (A1, 3, 5, 10, 13, 15,)

A1. In a unit cell, **an atom's coordination number** is the number of atoms it is touching (the closest vicinity of the atom). (配位數是晶格中與某一原子相距最近的原子個數.) What are the coordination number for sc, bcc, fcc, hcp, and diamond lattices?

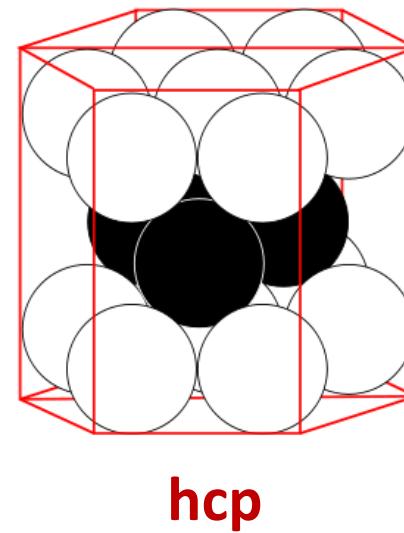
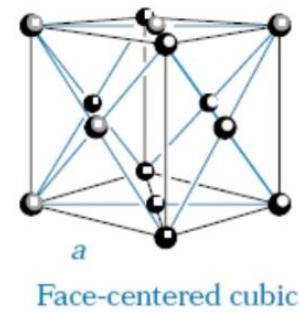
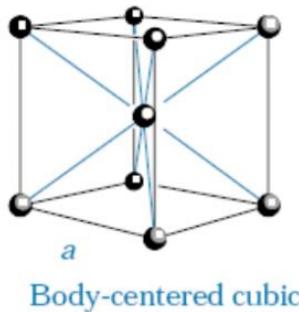
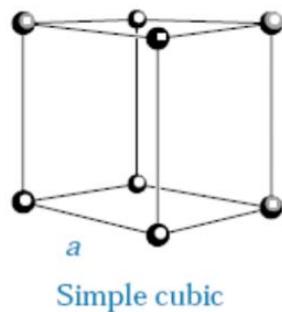


Figure 1-3

Unit cells for three types of cubic lattice structures.

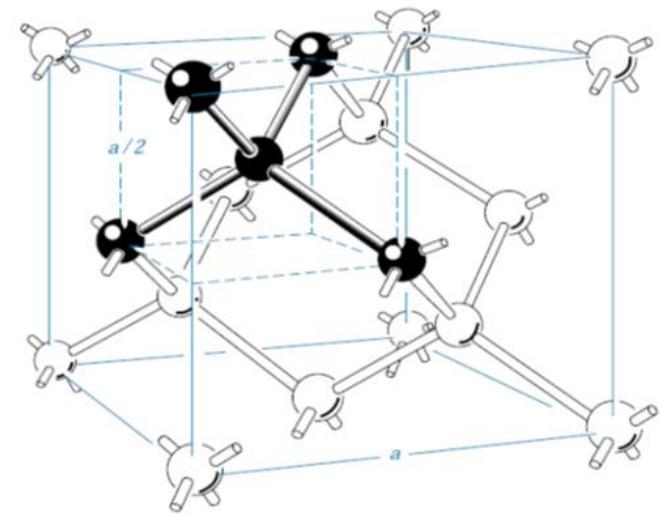
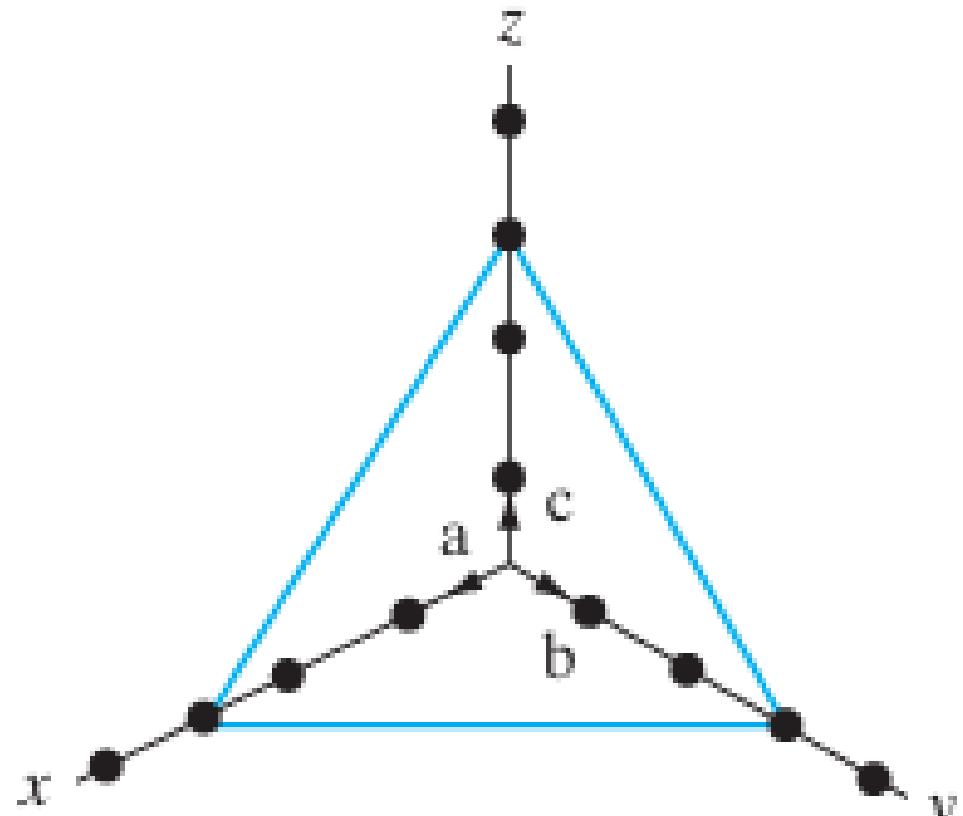


Figure 1-9

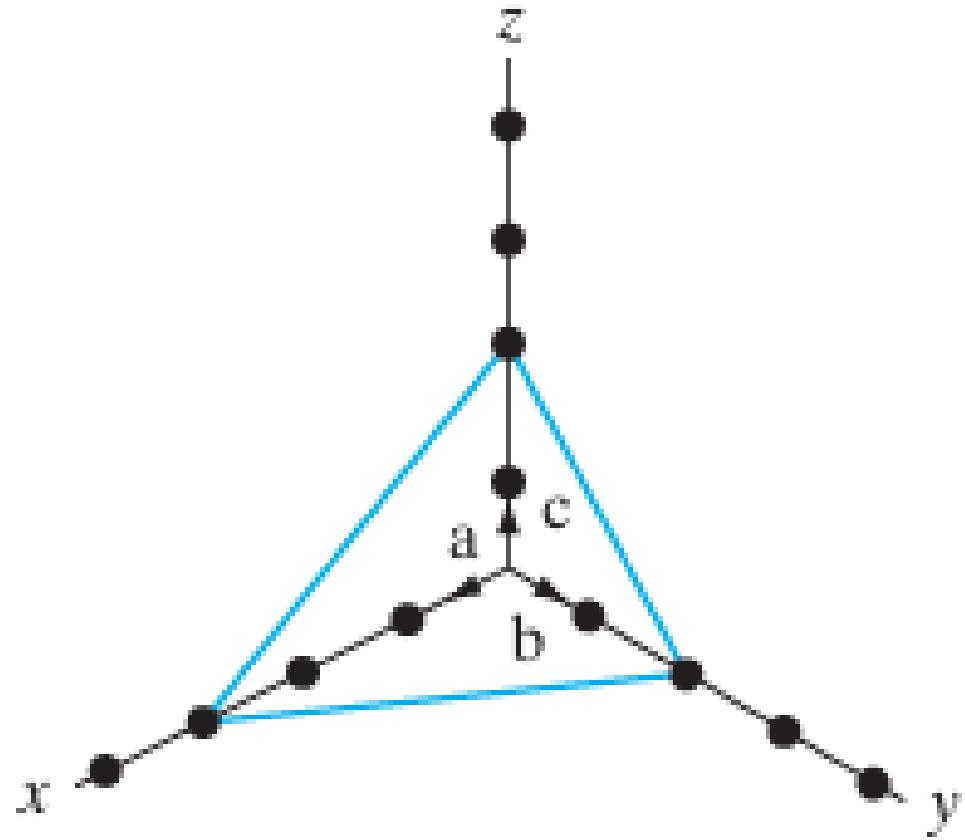
Diamond lattice unit cell, showing the four nearest neighbor structure. (From *Electrons and Holes in Semiconductors* by W. Shockley, © 1950 by Litton Educational Publishing Co., Inc.; by permission of Van Nostrand Reinhold Co., Inc.)

1.3 Label the planes illustrated in Fig. P1-3.

In terms of Miller indices (密勒指數) (hkl)



(a)



(b)

1.5 Calculate the densities of Si and GaAs from the lattice constants (Appendix III), atomic weights, and Avogadro's number. Compare the results with densities given in Appendix III. The atomic weights of Si, Ga, and As are 28.1, 69.7, and 74.9, respectively.

1.10 (a) Find the number of atoms/cm² on the (100) surface of a Si wafer.
(b) What is the distance (in Å) between nearest In neighbors in InP.

1.13 How many atoms are found inside a unit cell of an sc, a bcc, and an fcc crystal? How far apart in terms of lattice constant a are the nearest neighbor atoms in each case, measured from center to center?

1.15 Find the maximum fractions of the unit cell volume that can be filled by hard spheres in the sc, fcc, and diamond lattices.



Appendix III

		E_g (eV)	μ_n (cm ² /V-s)	μ_p (cm ² /V-s)	m_n^*/m_o (m_l/m_i)	m_p^*/m_o (m_{lh}/m_{hh})	a (Å)	ϵ_r	Density (g/cm ³)	Melting point (°C)
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ZnSe	(d/Z)	2.7	600	28	0.14	0.60	5.671	9.2	5.65	1100*
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PbSe	(i/H)	0.27	1500	1500	—	—	6.147	23.6	8.73	1081
PbTe	(i/H)	0.29	6000	4000	0.17	0.20	6.452	30	8.16	925

All values at 300 K.

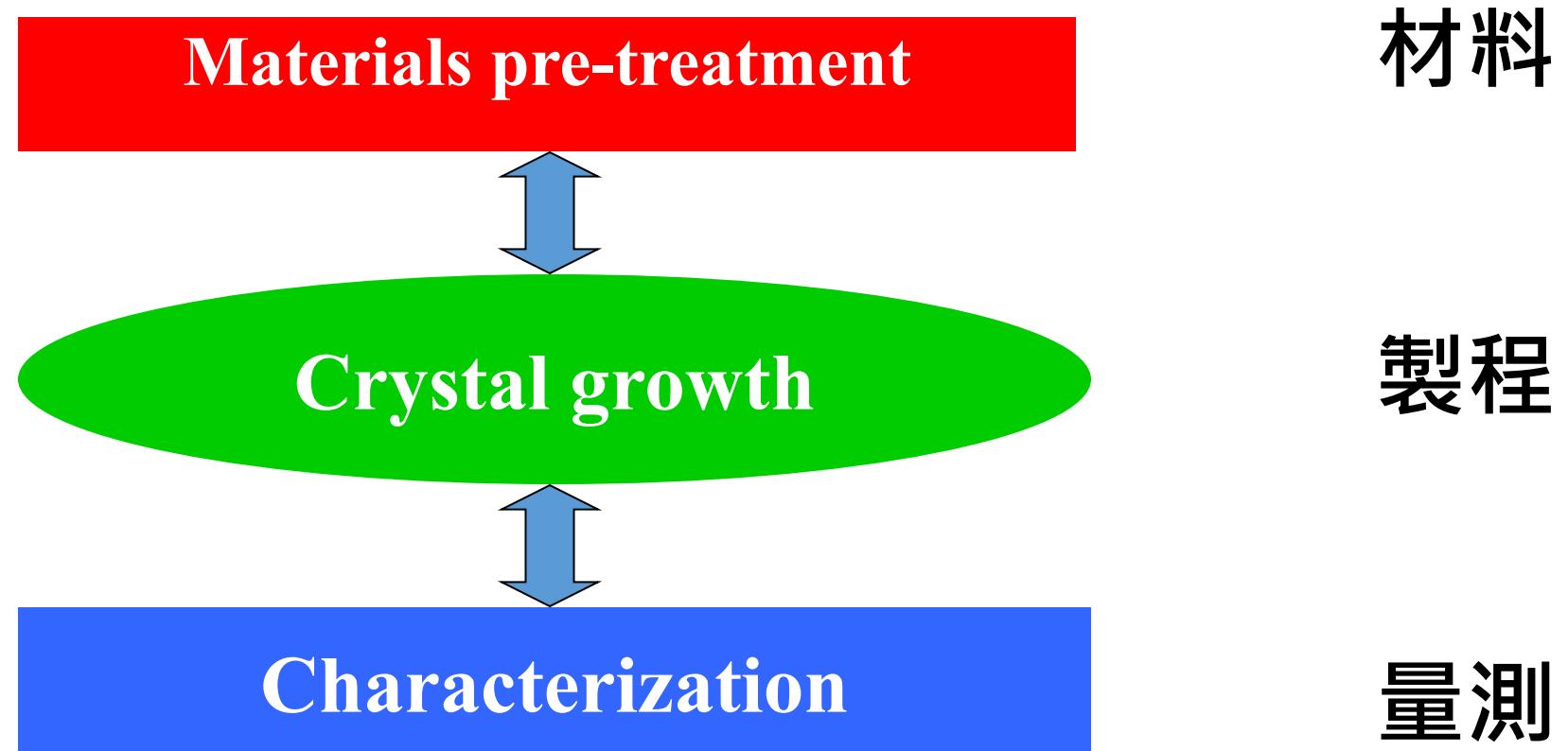
*Vaporizes

p. 580

Contents

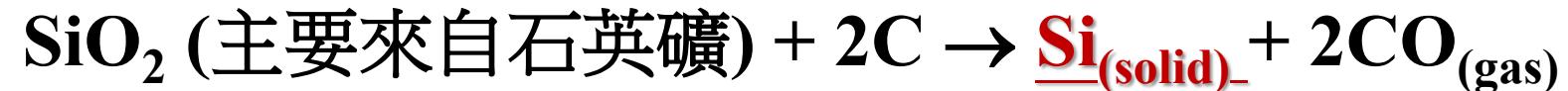
- 1.1 Semiconductor Materials
- 1.2 Crystal Lattices
- 1.3 Bulk Crystal Growth
 - Starting materials;
 - Czochralski, Bridgman, Floating zone pulling;
 - Wafers; Doping
- 1.4 Epitaxial Layer Growth
- 1.5 Wave propagation in discrete, periodic structures

Crystal Growth: an interdisciplinary (跨學科的) effort from physics, chemistry, chemical and mechanical engineering, etc



1.3.1 Starting materials for Si

- In an arc furnace at 1800°C, **metallurgical (冶金) grade Si (MG-Si)** (~ 98% purity, major impurities: Fe, Al, Ca, P, etc.) is formed by



Impurity Concentrations in MG-Si (ppm)

Element	Concentration	Element	Concentration
Al	1000-5000	B	35-50
P	20-50	Ca	250-600
Cr	50-200	Cu	15-60
Fe	1600-6500	Mn	50-100
Mo	2-20	Ni	20-100
Ti	150-300	V	50-250
Zr	20-30		

Silicon metal manufacturers /
Silicon metal 553/441 custom size
US\$ 2980 / 1 Ton (US)
24 Tons (US) Minimum order

List of countries by silicon production (各國矽產量列表)

	<u>2021</u>	<u>2022</u>
United States	313	310
Australia	50	50
Bhutan ⁹	85	85
Brazil	389	400
Canada	49	49
China	6,400	6,000
France	127	120
Germany	63	63
Iceland	111	110
India ⁹	59	59
Kazakhstan	122	120
Malaysia ⁹	85	92
Norway	362	360
Poland ⁹	49	49
Russia	644	640
Spain	60	57
Ukraine ⁹	49	19
Other countries	128	210
World total (rounded)	9,150	8,800

- Based on USGS figures (美國地質調查局統計資料).
- https://en.wikipedia.org/wiki/List_of_countries_by_silicon_production

(2016)

排名	國家/地區	矽產量 (千噸)
—	世界	7,200
1	中華人民共和國	4,600
2	俄羅斯	747
3	美國	396
4	挪威	380
5	法國	121
6	巴西	100
7	南非	84
8	西班牙	81
9	不丹	78
10	冰島	75
	其他國家	538

Haishiwan Town (海石
灣鎮), Honggu District
(紅古區), Lanzhou City,
Gansu (甘肅) Province

In 2024, China accounted for almost 80% of total global estimated silicon production (from wiki).

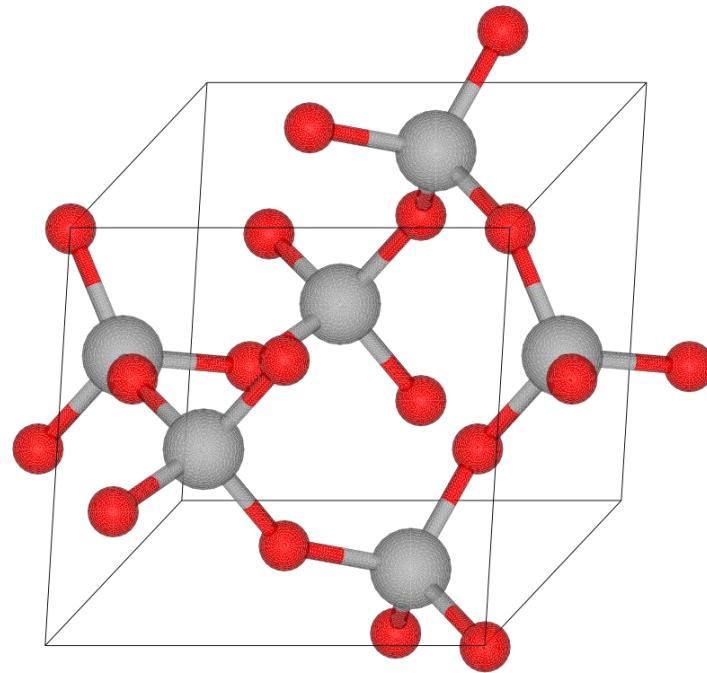
Rank	Country /region	Ferrosilicon (FeSi) production (thousands of metric tons per year)	Silicon metal (MG-Si) production (thousands of metric tons per year)	Total silicon production (thousands of metric tons per year)
—	<u>World</u>	5100	4600	9700
1	<u>China</u>	3500	3900	7400
2	<u>Russia</u>	470	50	520
3	<u>Brazil</u>	200	190	390
4	<u>United States</u>	-	-	310 ^[3]
5	<u>Norway</u>	180	120	300
6	<u>Kazakhstan</u>	130	7	137
7	<u>Malaysia</u>	130	-	130
8	<u>France</u>	20	90	110
9	<u>Iceland</u>	70	20	90
10	<u>Bhutan</u>	80	-	80
11	<u>India</u>	~ 90% 之間, 用 於鋼鐵製造和鑄 造行業.	60	60
12	<u>Canada</u>	20	30	50
13	<u>Spain</u>	40	5	45
14	<u>Australia</u>	-	40	40
15	<u>Poland</u>	30	-	30
	Other countries	130	78	208

矽鐵 (FeSi) 是一種主要由鐵和矽組成的鐵，其矽含量通常在 15% ~ 90% 之間，用於鋼鐵製造和鑄造行業。

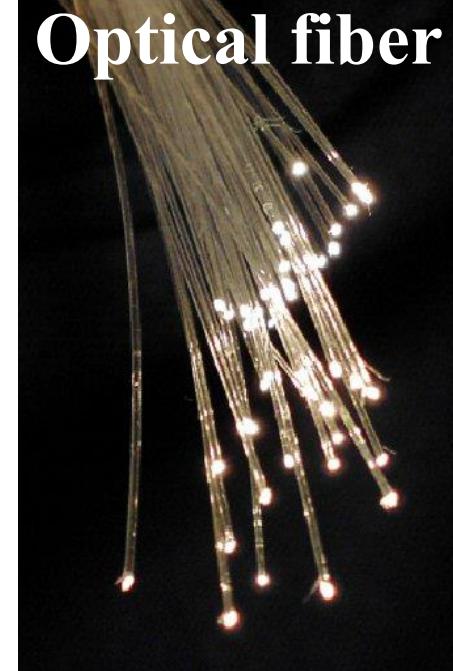
金屬矽 (MG-Si)
內矽純度為
97~98%



石英
(Quartz)



Optical fiber



Silicon dioxide



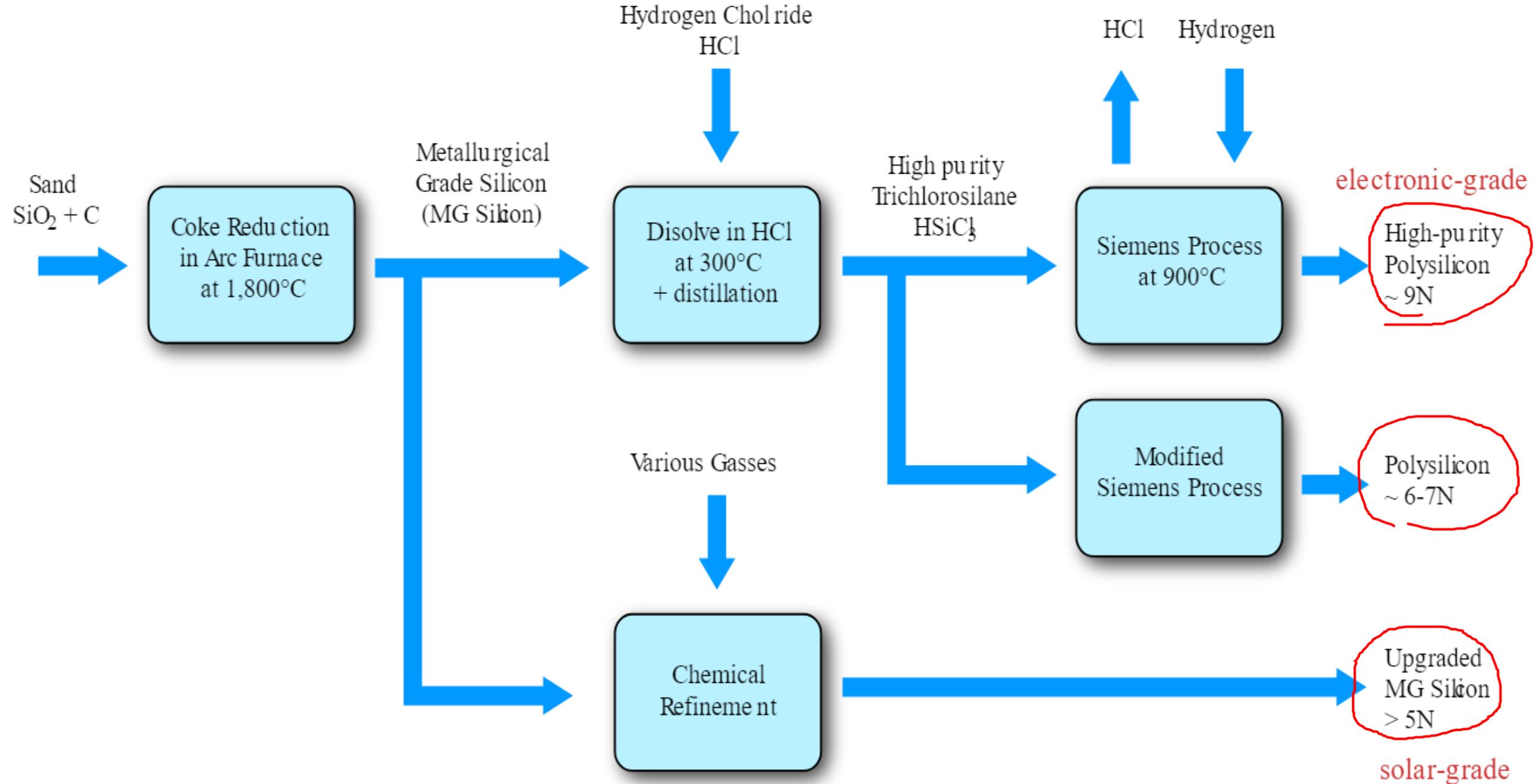
- 石英 (Quartz) 是地殼數量第二多的礦石，僅次於長石，其晶體結構是 SiO_4 (矽-氧四面體) 的連續框架，其中每個氧在兩個四面體之間共享，得到 SiO_2 的總化學式。
- Crystal structure of **α -quartz** (red balls are oxygen, grey are silicon).
- An optical fiber is a flexible, transparent fiber made by drawing glass (silica is an oxide of silicon with the chemical formula SiO_2 , most commonly found in nature as quartz).
- 石英粉可以做為有效的金屬拋光劑，常應用於研磨機、噴砂機中。(Wiki)
- 將石英與焦炭混合後，在電弧爐加熱下即生成粗矽 (MG-Si)：
 SiO_2 (主要來自石英礦) + 2C → $\text{Si}_{(\text{solid})}$ + 2CO_(gas). MGS 是半導體產業重要的原料之一。

1.3.1 Starting materials for Si

- In an arc furnace at 1800°C, metallurgical (冶金) grade Si (MG-Si) ($\sim 98\%$ purity, major impurities: Fe, Al, Ca, P, etc.) is formed by



- At 300°C, $\text{Si}_{(\text{solid, MG})} + 3\text{HCl} \rightarrow \text{SiHCl}_{3(\text{liquid})}$ (三氯氫矽) + H_2
- By fractional distillation (分餾) to obtain pure $\text{SiHCl}_{3(\text{liquid})}$ (B.P.: 32 °C, different from, e.g., FeCl_3 of 315°C) with impurities level down to 1×10^{-9} (the update technology $\sim 10^{-11}$), then converted to highly pure electronic grade Si (EG-Si) by: $\text{SiHCl}_{3(\text{liquid})} + \text{H}_2 \rightarrow \text{Si}_{(\text{solid, EG})} + 3\text{HCl}$ 。
- The minimum dopant concentration (in Si with 9N purity, 0.999999999) >> $5\times 10^{22} \text{ atoms/cm}^3 \times 10^{-9} (10^{-11}) \doteq 5\times 10^{13} (5\times 10^{11}) \text{ atoms/cm}^3$.



世界最大的金磚為250公斤，由三菱原料股份公司製造。2017年6月19日，其價值約1125萬美金。此金磚純度約為 99.99% (4N)，在冶金級材料而言算是高純度，但在電子級材料 (需 9N ~ 11N) 而言，其純度仍然不夠。

High-purity silicon (EG-Si) 主要供應廠商：
Hemlock Semiconductor Corporation (HSC)

HSC is the largest producer of hyper-pure polysilicon owned by Corning Inc. (康寧) and Shin-Etsu Handotai (信越半導體) and headquartered in the United States.

Renewable Energy Corporation, Norway

SunEdison, USA

Tokuyama Corporation, Japan

Wacker Chemie AG, Germany

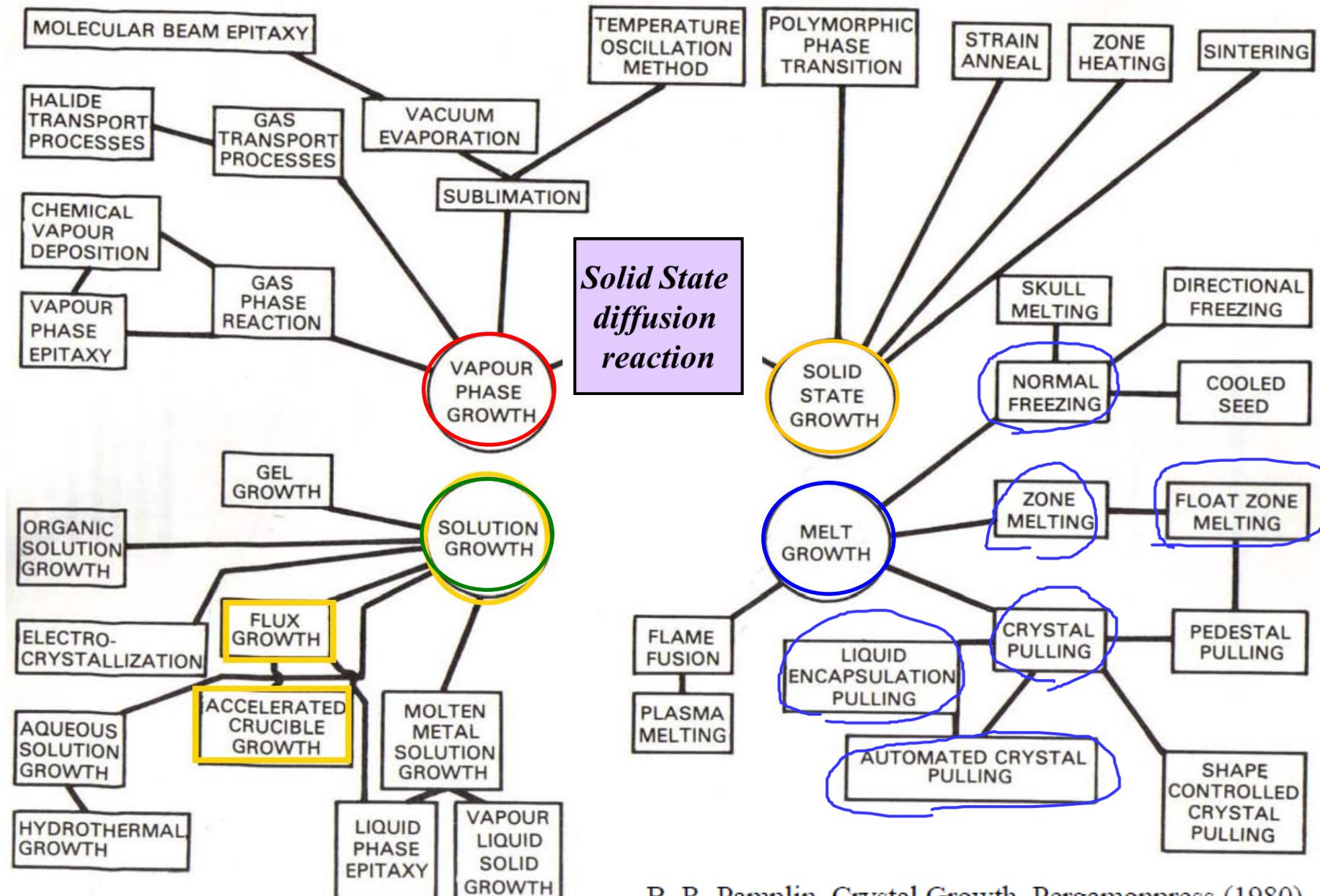
https://en.wikipedia.org/wiki/List_of_silicon_producers#High-purity_silicon



Crystal growth

- A control of phase transition to form a solid phase: nucleation and growth (凝核與生長)
- *Physics, Materials Science, Chemistry, Mechanical and Chemical engineering (Multidisciplinary sciences, 跨領域學科)*
- Thermodynamics, phase diagram, chemical reactions, heat and mass transfer, interface kinetics and stability, etc.
- $dG = -SdT + VdP$; the Gibbs function (or Gibbs free energy) remains constant during a reversible process taking place at constant temperature and pressure. Hence, for a change of phase from i to f at T and P , $G^{(i)} = G^{(f)}$.

□ What are the crystal growth techniques?



Crystal growth techniques

*Vapor phase
growth*

(蒸汽態成長)

*Solid State
diffusion
reaction*

*Solid
state
growth*

(固態成長)

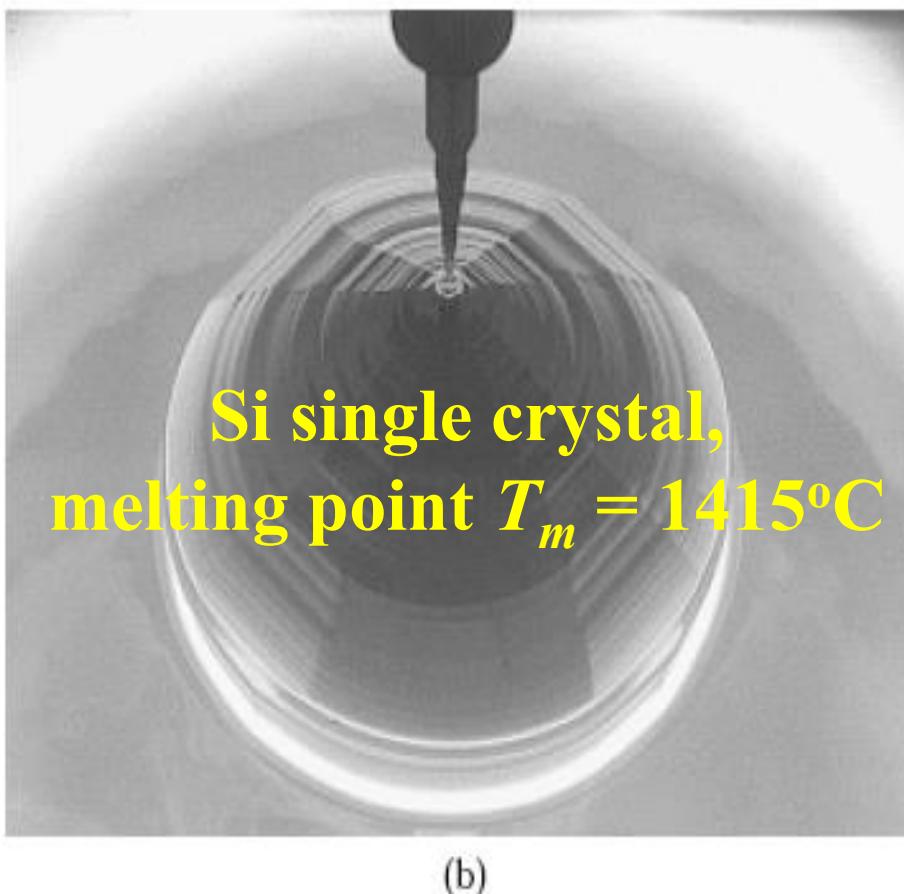
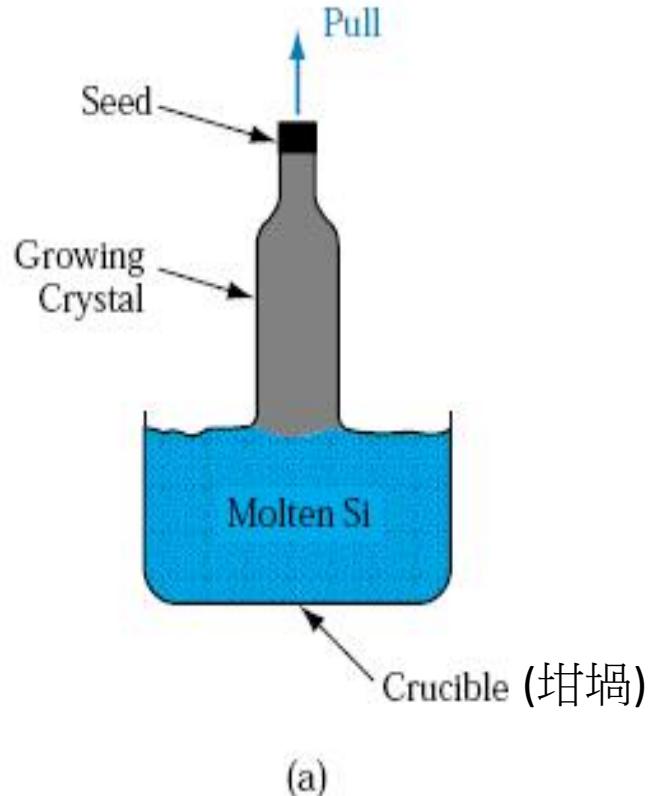
Solution growth
(溶液態成長)

Melt Growth
(熔融態成長)

Crystal growth techniques

- **Melt growth** ($T > T_{\text{Melt}}$): crystal pulling (Czochralski, CZ), Bridgman method (normal freezing), floating zone melting (FZ), etc, **for single crystals**
- **Solution growth** ($T < T_{\text{Melt}}$): liquid phase epitaxy (溶液相磊晶術, 溶質+溶劑), flux growth, hydrothermal growth, for epitaxial- or poly-films, nano-crystals
- **Solid state growth** ($T < T_{\text{Melt}}$): annealing (退火), sintering (燒結), etc, for polycrystalline materials
- **Vapor growth** ($T < T_{\text{Melt}}$): PVT, CVT for single crystal; **PVD, CVD, MOCVD, MBE** for epitaxial-layers, poly-films, or nano-crystals
- **Organic materials:** Spin-coating; ink-jet printing; **vacuum deposition**; MBE.

1.3.2 Bulk crystal growth: Czochralski method



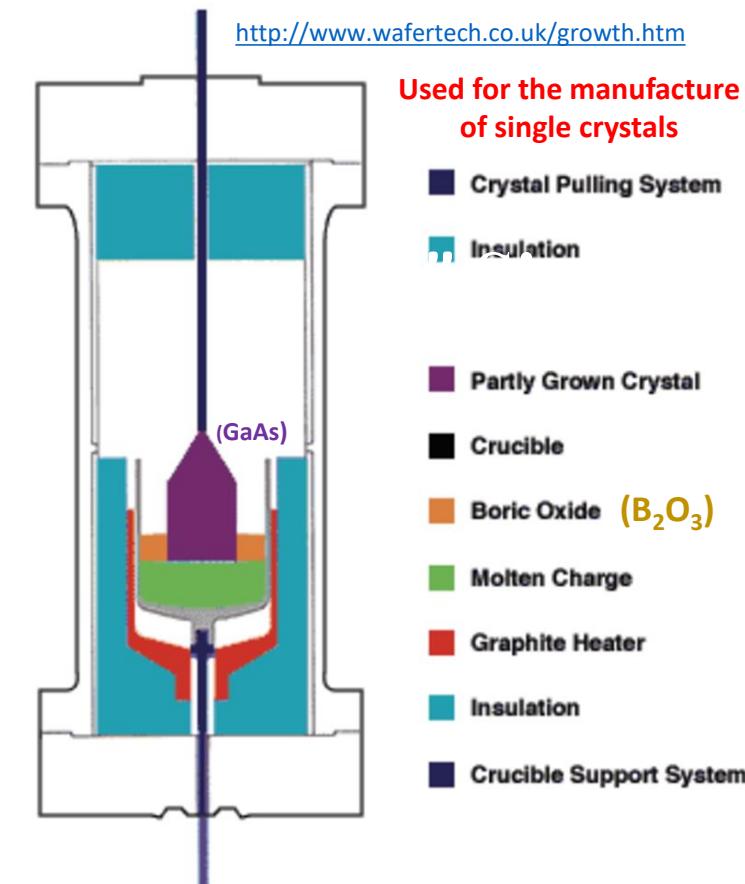
Crucibles were made from ceramics such as **alumina** (Al_2O_3 , 氧化鋁, 2072°C), **zirconia** (ZrO_2 , 二氧化鋯, 2715°C), **boron nitride** (BN, 氮化硼, 2700°C), etc.

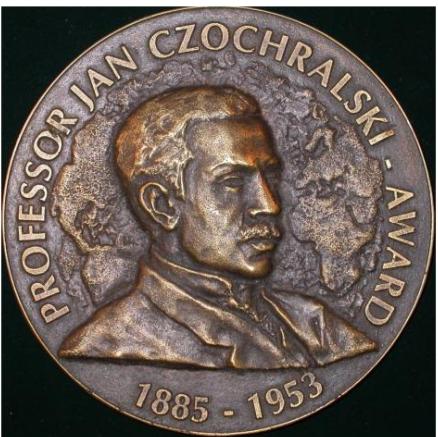
Figure 1-10

Pulling of a Si crystal from the melt (Czochralski method): (a) schematic diagram of the crystal growth process; (b) an 8-in. diameter, $\langle 100 \rangle$ oriented Si crystal being pulled from the melt. (Photograph courtesy of MEMC Electronics Intl.)

For GaAs ($T_m = 1238^\circ\text{C}$),
encapsulated
 B_2O_3 liquid layer
Liquid Encapsulation

Czochralski Crystal Growth System (GaAs)

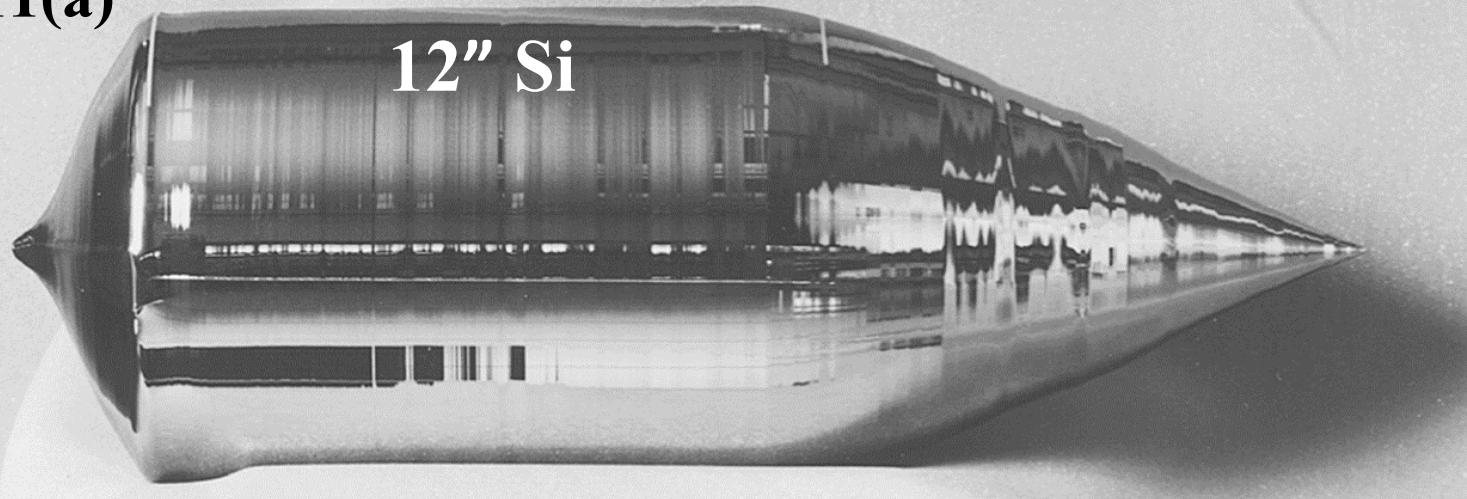




Jan Czochralski (1885 – 1953)

- A Polish chemist, he discovered the Czochralski method in 1916, when he accidentally dipped his pen into a crucible of molten tin (m.p. 232°C). He immediately pulled his pen out to discover that a thin thread of solidified metal was hanging from the nib. The nib was replaced by a capillary, and Czochralski verified that the crystallized metal was a single crystal.
- The Czochralski Award: Taking into account the merits of Czochralski for materials science, technology transfer to industry, and international collaboration, E-MRS (European Materials Research Society) established an award in the name of Jan Czochralski.

1–11(a)



Silicon ingot: 硅晶錠

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1–11(b)



Figure 1–11(a) Silicon crystal grown by the Czochralski method. This large single-crystal ingot provides 300 mm (12-in.) diameter wafers when sliced using a saw. The ingot is about 1.0 m long (including the tapered regions), and weighs about 140 kg. (b) A technician holding a cassette of **300 mm (12") wafers**. (Photographs courtesy of MEMC Electronics Intl.)



Ingot
(晶錠)

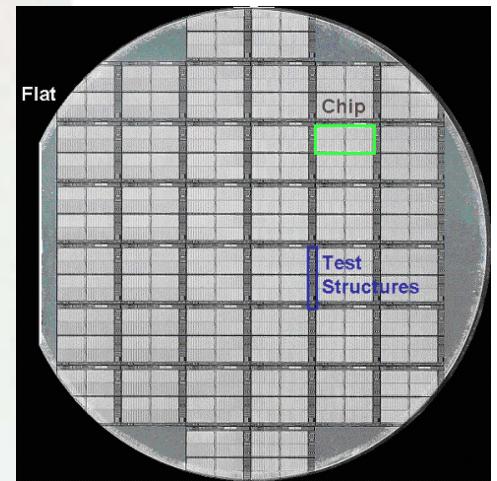
Freshly grown Si single crystal with 200 mm diameter



Si single crystal with 12"
(300 mm) diameter

Wafer (晶圓)

Wafer diameter:
8" ~ 12";
wafer thickness:
725 ~ 775 μm .



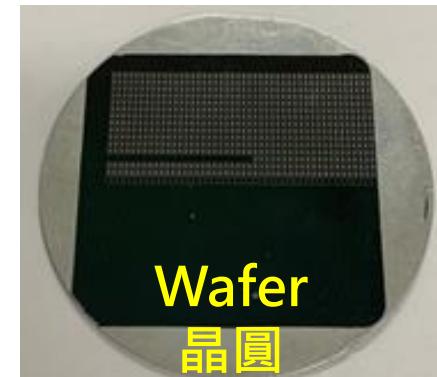
全球大約 16 家企業能夠製造產業用矽晶圓

<https://kknews.cc/zh-tw/news/p9gx438.html> (2018/11/05)

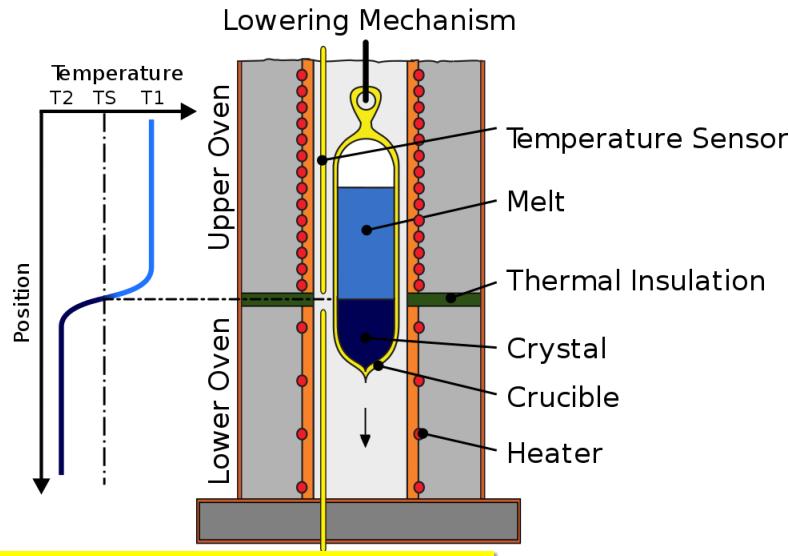
2021/02/09 德國反壟斷監管機構 批准環球晶 (GlobalWafers) 收購德商世創 (Silitronic) 50.8%的股份。2022/02/01 環球晶併世創卡關德國宣告失敗。

全球12大矽晶圓生產廠商排名

- (1) 日本信越半導體 (市占率 33%), (2) 日本勝高科技 (市占率 25%),
- (3) 台灣環球晶圓 (市占率 17%) (4) 德國 Silitronic (市占率 13%),
- (5) 南韓 SK Siltron,
- (6) 法國 (Soitec),
- (7) 台灣合晶 (Wafer Works),
- (8) 芬蘭 (Okmetic),
- (9) 台灣嘉晶 (Episil),
- (10) 上海新昇,
- (11) 重慶超矽,
- (12) 寧夏銀和,
- 2022年日商勝高 (Sumco) 會長橋本真幸在法人說明會表示，公司直到2026年底的產能已全數售完，未來五年所有12吋的晶圓產量已全被客戶包下，半導體矽晶圓供應將一路缺到2026年，



The **Bridgman method** is named after P. W. Bridgman (Nobel Prize in Physics, 1946). The method is **widely applied to grow high quality III-V semiconductors such as GaAs, InP, etc.**



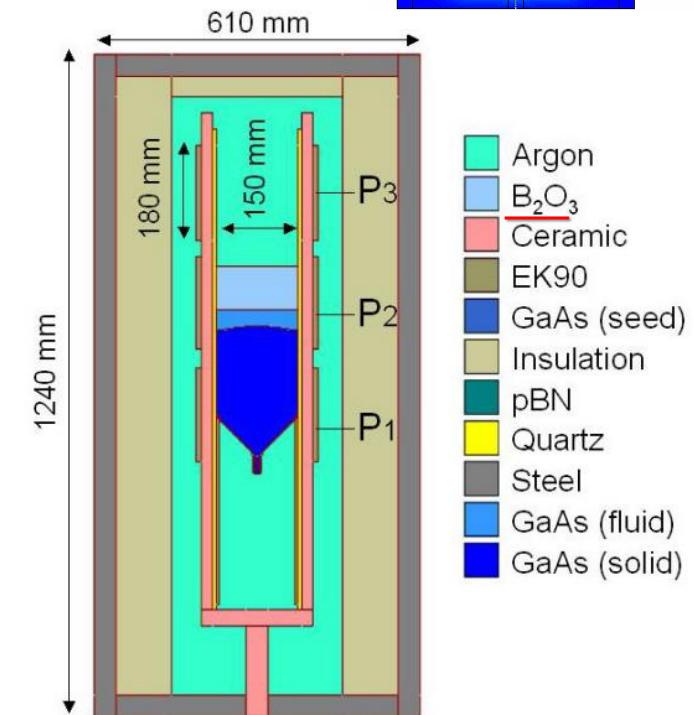
Bridgman method utilizes the relatively uncontrolled *temperature (T)-gradient*; **Bridgman- Stockbarger method** introduces a **baffle**, separating two coupled furnaces with T above and below the freezing point.

https://en.wikipedia.org/wiki/Bridgman%20Stockbarger_method

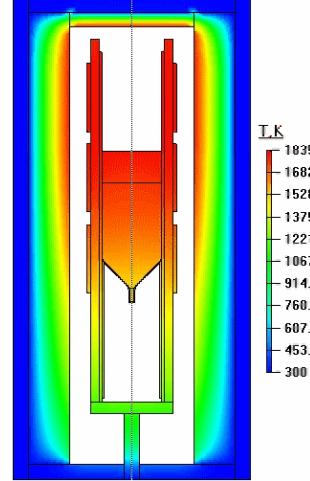
The **vertical gradient freeze method (VGF)** is a modification of the **conventional Bridgman method** without moving the ampoule or heaters. In this case, **the crystallization process is provided by changing the heat supply** in the electrodynamic gradient multi-zone furnace.

Optimization of heat transfer in the furnace is the key point in growing quality crystals.

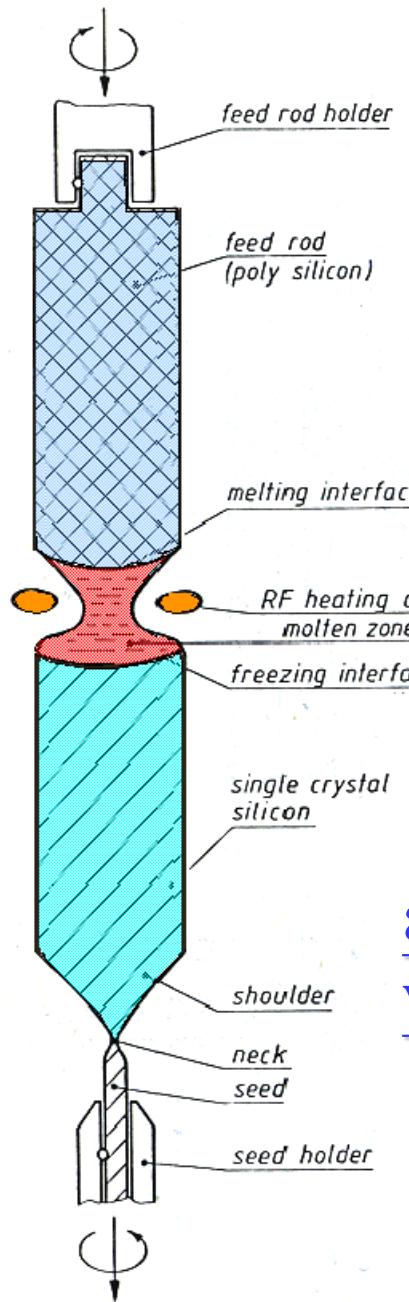
<https://str-soft.com/crystal-growth/vgf-iii-v/>



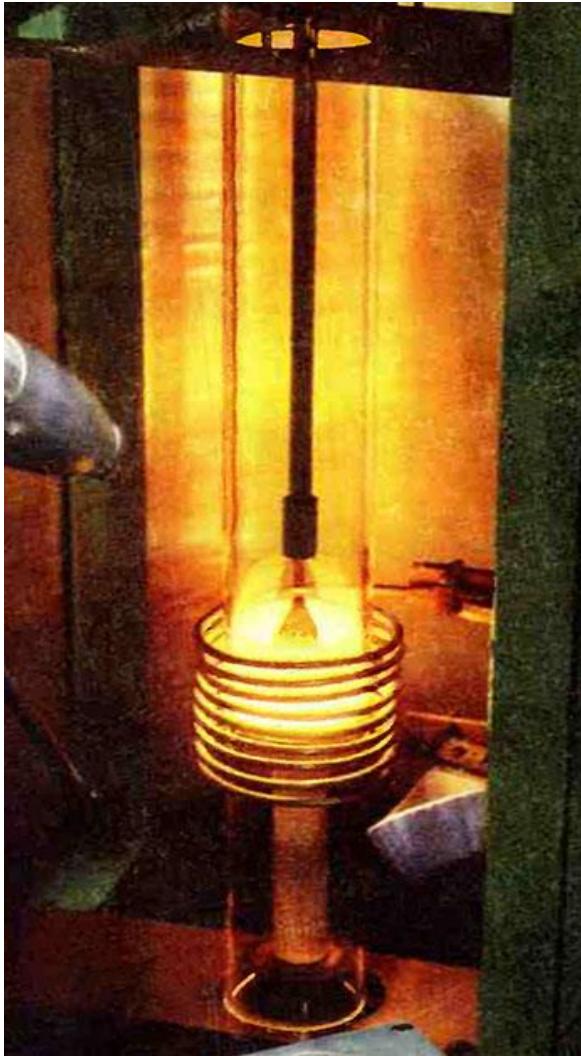
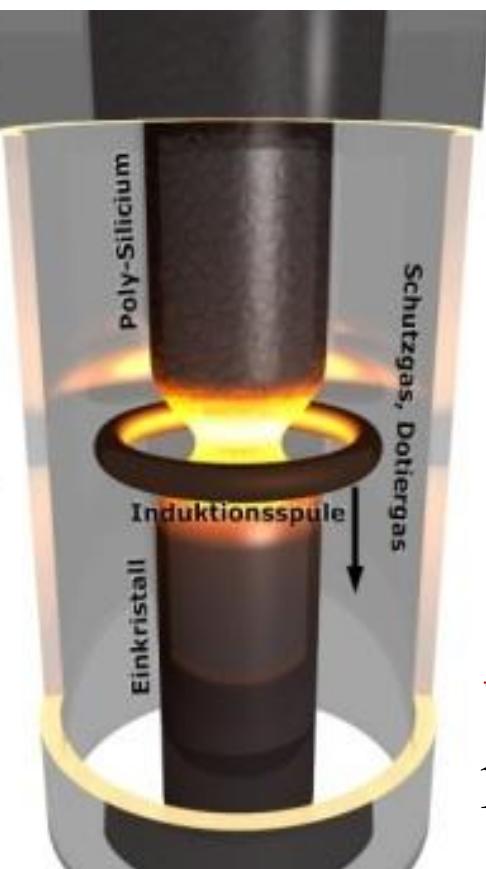
Schematic view of **the VGF setup** for growing 6 inch diameter GaAs crystals



Float-zone pulling



Floating zone pulling
adopted for purifying crystals
with distribution (segregation)
coefficient $k_d = C_s/C_L < 1$

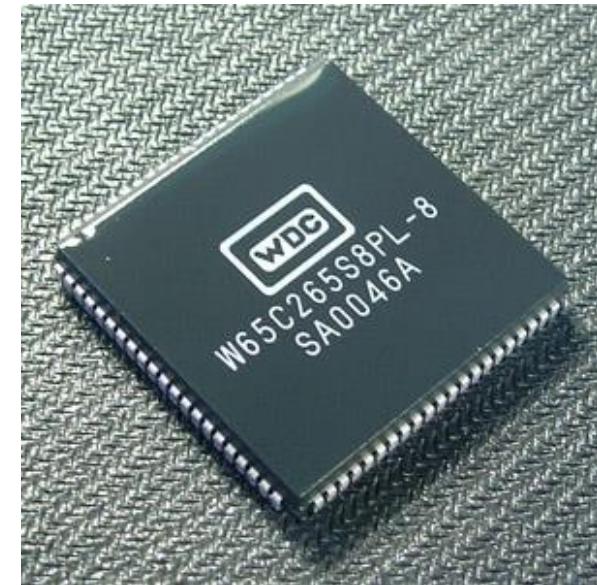


Induction RF heating
(感應加熱): Keeping Si
in crucible molten at
1,450°C for **Czochralski**
crystal growth, 1956

1.3.3 Wafers (晶圓)



Wafer: a thin slice of semiconductor used for the fabrication of integrated circuits



單晶片 (Single-chip microcomputer)



Chip: 晶片

Figure 1-12

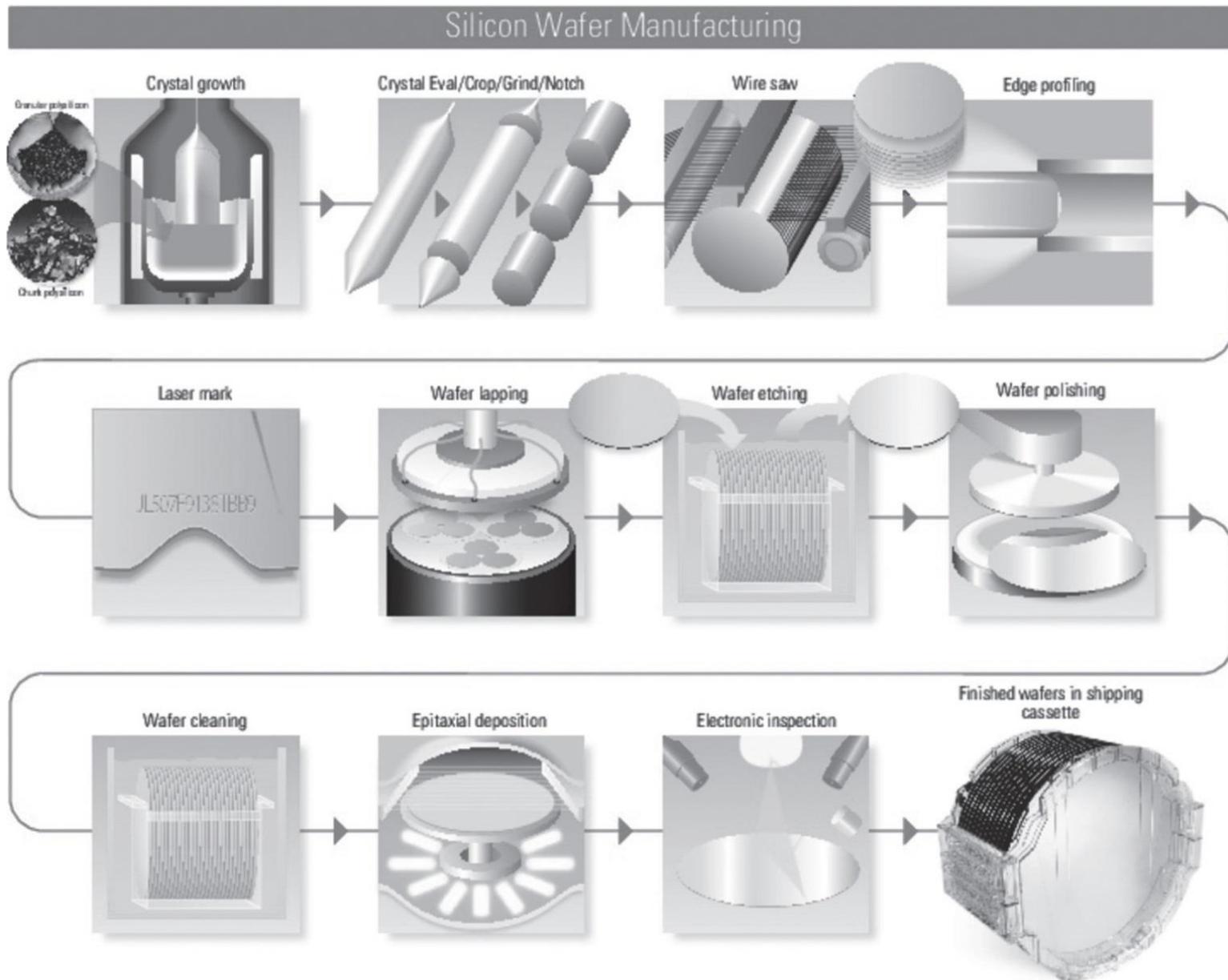
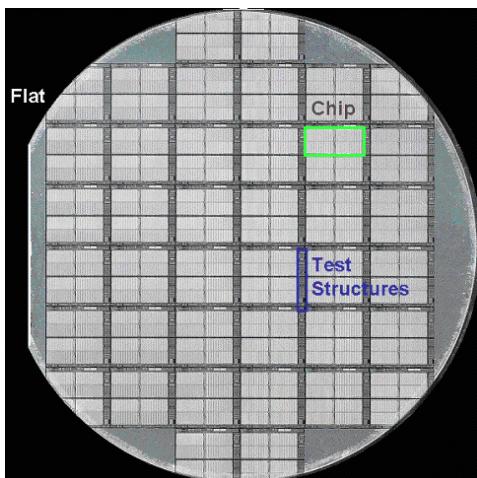
Steps involved in manufacturing Si wafers: (a) A 300 mm Si cylindrical ingot, with a notch on one side, being loaded into a wire saw to produce Si wafers; (b) a technician holding a cassette of 300 mm wafers. (Photographs courtesy of MEMC Electronics Intl.)

Fig. 1-12 Steps involved in manufacturing Si wafers.

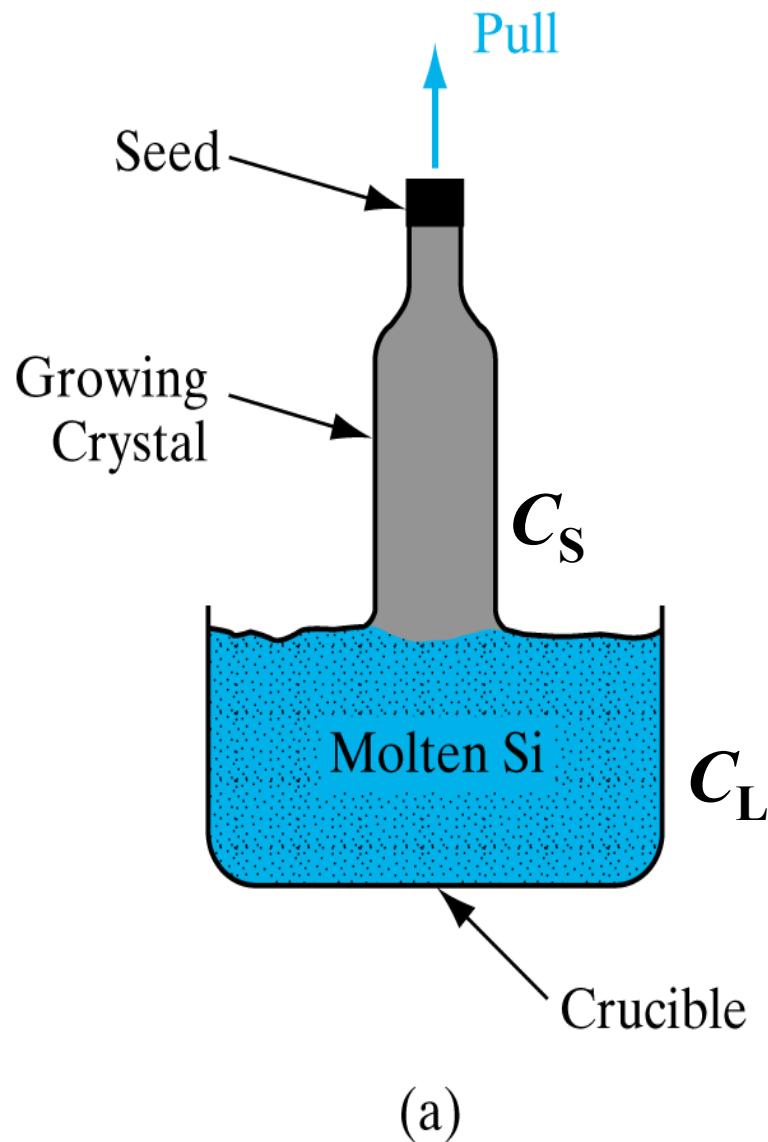
The five steps of wafer forming:

1. Slicing (切片);
2. Lapping (研磨);
3. Etching (蝕刻);
4. Polishing (拋光);
5. Cleaning and inspection
(清潔和檢查)

晶圓代工



1.3.4 Doping: add intentional (p- or n-type) dopants (掺雜物) to the Si melt to change its electronic properties

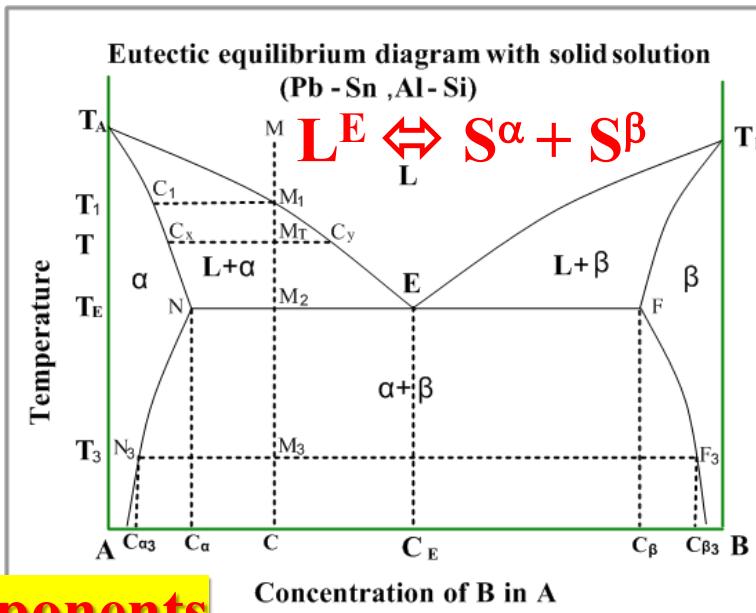
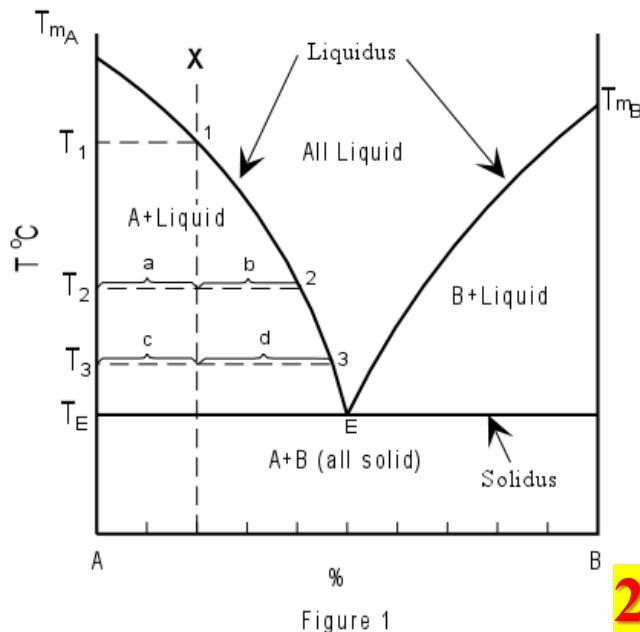
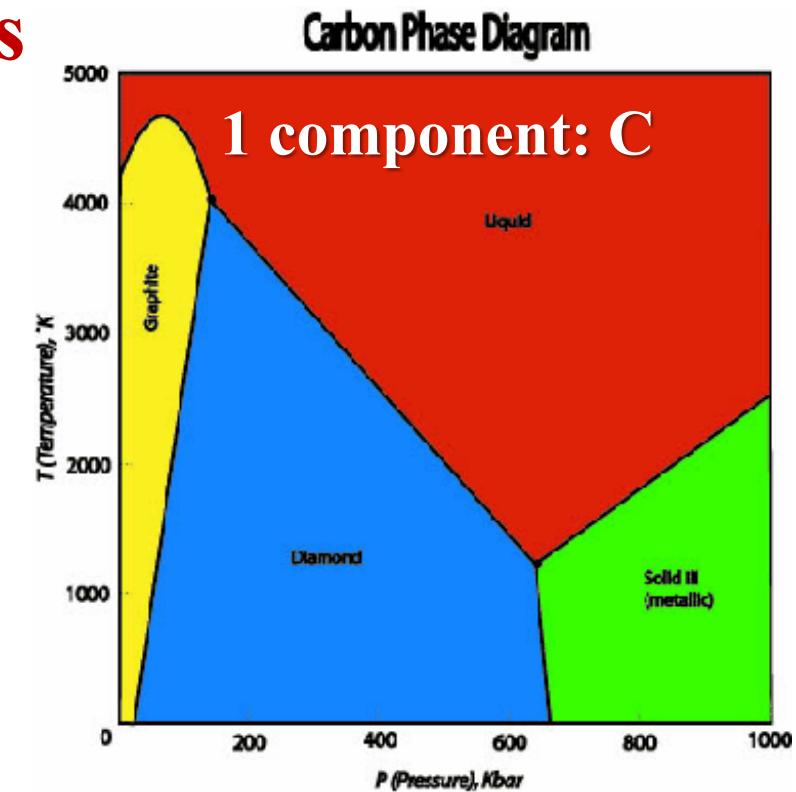
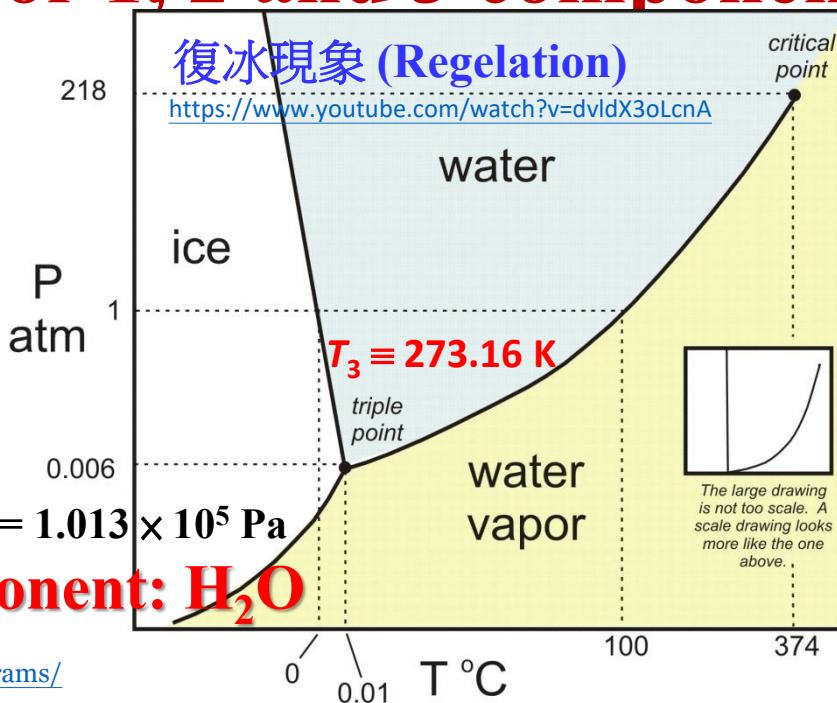
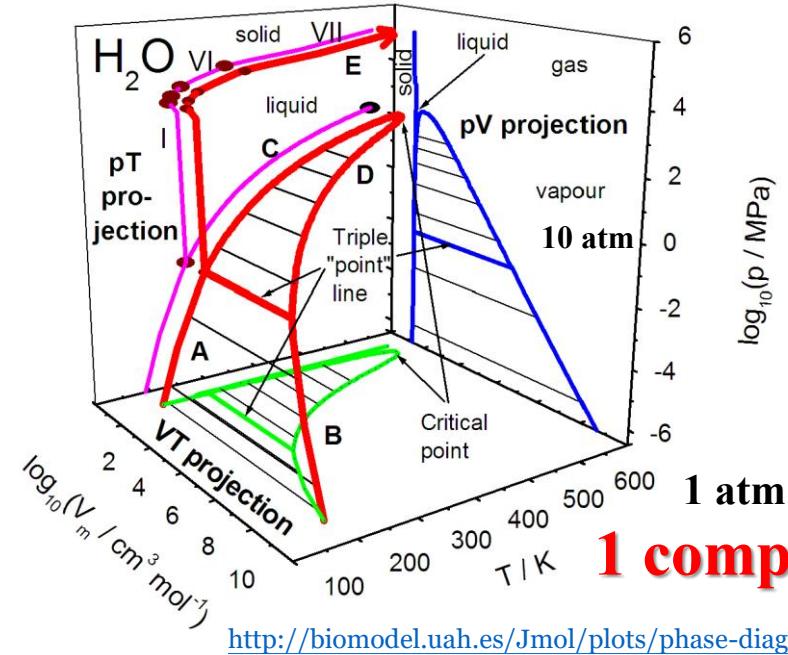


- Based on **distribution (segregation, 偏析) coefficient** : $k_d = C_S/C_L$; where C_S & C_L are the dopant concentration in the solid and liquid, respectively.
- k_d is a function of the host material (Si or GaAs), the dopants, the temperature of the solid-liquid interface, and the growth rate, etc.
- See Ex. 1-4 for As in Si with doping at $1.0 \times 10^{15} \text{ cm}^{-3}$.

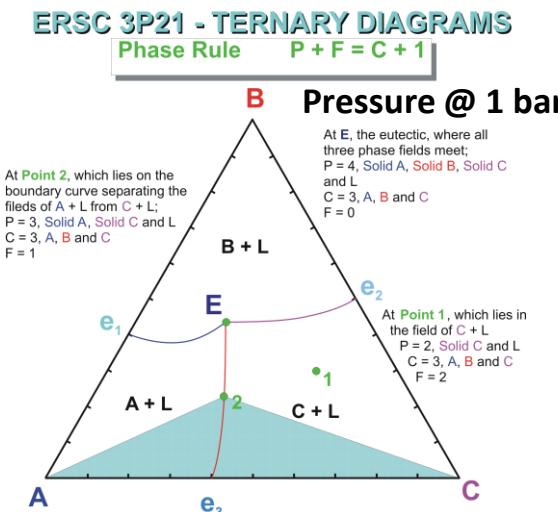
Segregation (or distribution) coefficient

- Add intentional impurities (dopants, 掺雜物) to Si-melt to adjust the electronic properties of the as-grown crystal.
- The segregation coefficient k_d is the ratio of the concentration of impurity atoms in the solid C_s to the concentration of the impurity atoms in the liquid C_L at equilibrium: $k_d = C_s/C_L$. It is usually much lower than 1 because impurity atoms “prefer” to stay in the melt. This can be seen from the liquidus and solidus lines (液相線和固相線) in the respective phase diagrams. In other words, the solubility of impurity atoms in the solid is smaller than that in the melt.
- "Equilibrium" refers to a growth speed of 0 mm/min or, more practically, very low growth rates. For finite growth rates, k_d becomes a function of the growth rate (called $k_{d,eff}$) and approximates 1 for high growth rates (whatever comes to the rapidly moving interface gets incorporated).

Phase diagrams for 1, 2 and 3 components



Gibbs phase rule:
Degree of freedom $f = c - p + 2$;
 c : component
 p : phase.



2 components

3 components

Solid solubilities (固體溶解度) of impurities in Si

Solid solubility
refers to
the maximum
concentration of
impurities one can place
into the substrate.



Solubility of NaCl (solute) in
water (solvent) => solution:
36 g/100 g at 25 °C

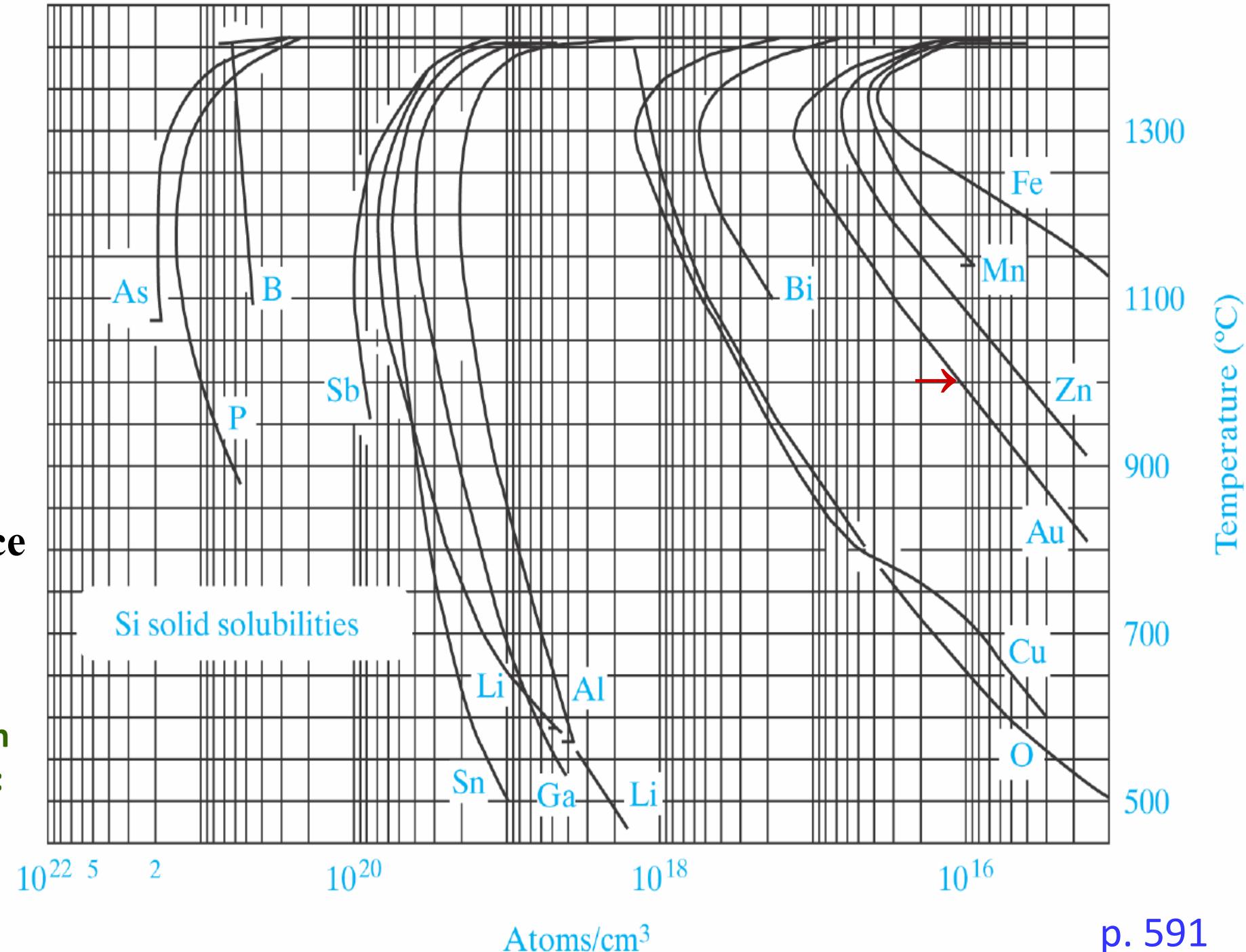


TABLE 1 Equilibrium Segregation Coefficients for Dopants in Si

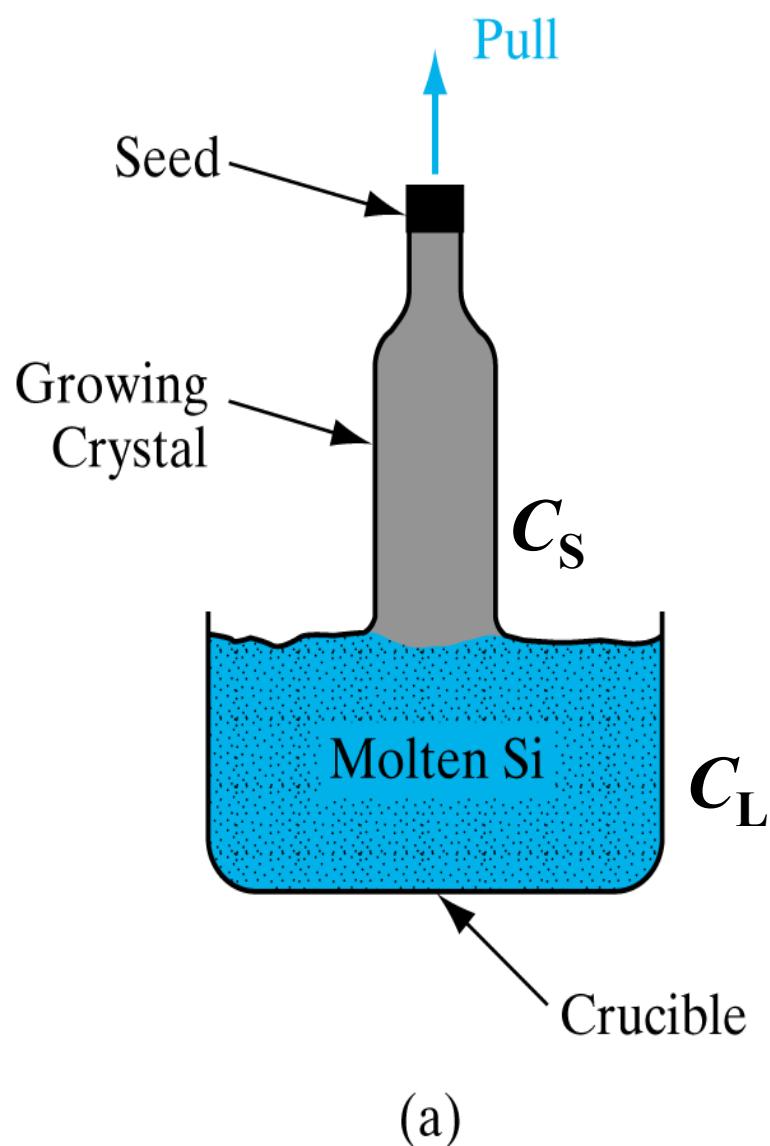
Dopant	k_0	Type	Dopant	k_0	Type
B	8×10^{-1}	p	As	3.0×10^{-1}	n
Al	2×10^{-3}	p	Sb	2.3×10^{-2}	n
Ga	8×10^{-3}	p	Te	2.0×10^{-4}	n
In	4×10^{-4}	p	Li	1.0×10^{-2}	n
O	1.25	n	Cu	4.0×10^{-4}	— ^a
C	7×10^{-2}	n	Au	2.5×10^{-5}	— ^a
P	0.35	n			

^aDeep-lying impurity level.

TABLE 2 Equilibrium Segregation Coefficients for Dopants in GaAs

Dopant	k_0	Type
Be	3	p
Mg	0.1	p
Zn	4×10^{-1}	p
C	0.8	n/p
Si	1.85×10^{-1}	n/p
Ge	2.8×10^{-2}	n/p
S	0.5	n
Se	5.0×10^{-1}	n
Sn	5.2×10^{-2}	n
Te	6.8×10^{-2}	n
Cr	1.03×10^{-4}	Semiinsulating
Fe	1.0×10^{-3}	Semiinsulating

A Si crystal is to be grown by the Czochralski method, and it is desired that the ingot contain 10^{16} phosphorus atoms/cm³.



- (a) What concentration of phosphorus atoms should the melt contain to give this impurity concentration in the crystal during the initial growth? For P in Si, $k_d = 0.35$.
- (b) If the initial load of Si in the crucible is 5 kg, how many grams of phosphorus should be added? The atomic weight of phosphorus is 31.

- (a) Assume that $C_s = k_d C_L$ throughout the growth. Thus the initial concentration of P in the melt should be

$$\frac{10^{16}}{0.35} = 2.86 \times 10^{16} \text{ cm}^{-3} \text{ (P-atoms/cm}^3 \text{ in melt)}$$

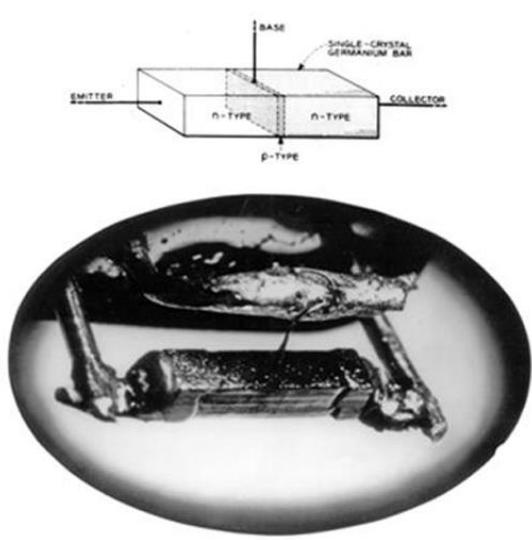
- (b) The P concentration is so small that the volume of melt can be calculated from the weight of Si. From Appendix III the density of Si is 2.33 g/cm³. In this example we will neglect the difference in density between solid and molten Si.

$$\frac{5000 \text{ g of Si}}{2.33 \text{ g/cm}^3} = 2146 \text{ cm}^3 \text{ of Si}$$

$$2.86 \times 10^{16} \text{ cm}^{-3} \times 2146 \text{ cm}^3 = 6.14 \times 10^{19} \text{ P atoms}$$

$$\frac{6.14 \times 10^{19} \text{ atoms} \times 31 \text{ g/mole}}{6.02 \times 10^{23} \text{ atoms/mole}} = 3.16 \times 10^{-3} \text{ g of P}$$

The fabrication of the 1st grown junction transistor (BJT)



- One of the 1st **microwatt** junction transistors (\Leftrightarrow 1 W @vacuum tube), made in 1951, by **G. K. Teal (left) and M. Sparks** at Bell Laboratories; and Bell Type M1752, commercial junction transistors, circa 1951. Teal built the needed crystal-growing equipment himself, based on techniques developed by J. Czochralski. Sparks fabricated **$n^+ \text{-} p \text{-} n$** junctions by growing a lightly **n** -doped Si, then dropping two successive pellets into the melt, the first with a **p** -type impurity (with thickness of 1 ~ 2 mil) and the second **n** -type, forming **$n^+ \text{-} p \text{-} n$** structures. Shockley later called this achievement "**the most important scientific development in the semiconductor field in the early days.**"

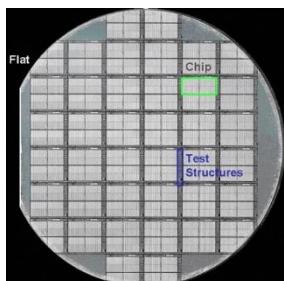
Contents

- 1.1 Semiconductor Materials
- 1.2 Crystal Lattices
- 1.3 Bulk Crystal Growth
- 1.4 Epitaxial Layer Growth

Lattice matching;
Liquid phase epitaxy (LPE);
Vapor-phase epitaxy (VPE);
Molecular Beam Epitaxy (MBE)
- 1.5 Wave propagation in discrete, periodic structures



⇒ 晶圓代工



1.4 Epitaxial layer growth (磊晶層生長或外延層生長)

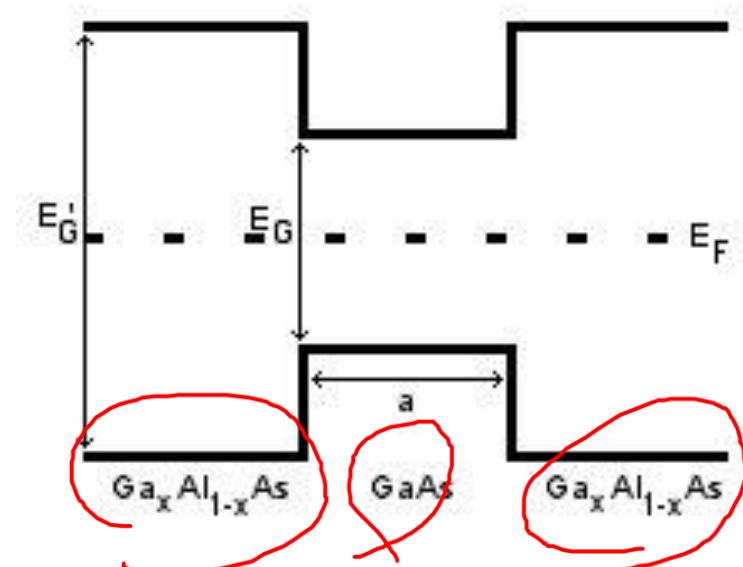
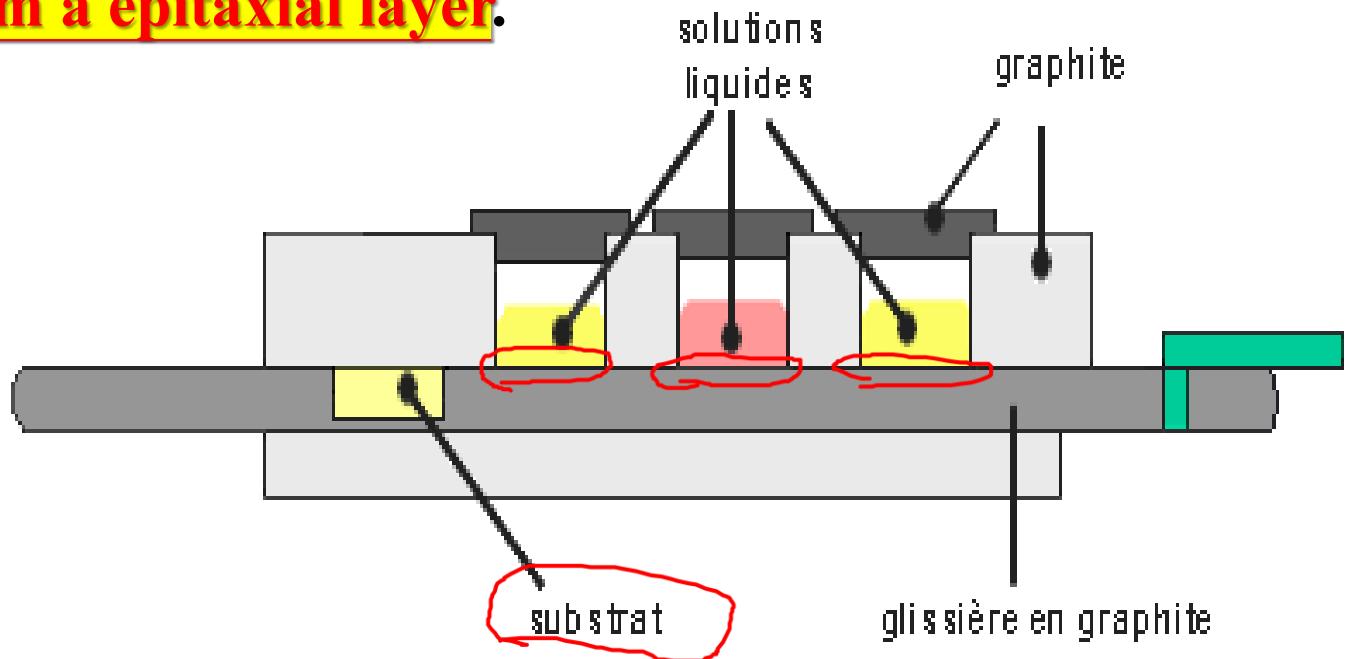
- Epitaxy from the Greek roots,
epi: upon, over, besides; *taxy* = *taxis*: order arrangement
- Growth of a thin crystalline layer (even on thickness of several lattice constants only) on a wafer of a compatible crystal.
- Growth techniques: liquid phase epitaxy (LPE); vapor phase epitaxy (VPE)
⇒ chemical vapor deposition (CVD); molecular beam epitaxy (MBE).
- 2D quantum well (AlGaAs-GaAs-AlGaAs) and superlattices (a periodic structure of layers of two or more materials with thickness of one layer being several nanometers, e.g., GaAs/Al_xGa_{1-x}As or Si_xGe_{1-x}).

Crystal growth techniques

- **Melt growth** ($T > T_{\text{Melt}}$): crystal pulling (Czochralski, CZ), Bridgman method (normal freezing), floating zone melting (FZ), etc, **for single crystals**
- **Solution growth** ($T < T_{\text{Melt}}$): liquid phase epitaxy (溶液相磊晶術, 溶質+溶劑), flux growth, hydrothermal growth, **for epitaxial- or poly-films, nano-crystals**
- **Vapor growth** ($T < T_{\text{Melt}}$): PVT, CVT for single crystal; PVD, CVD, MOCVD, MBE
for epitaxial-layers, poly-films, or nano-crystals
- **Solid state growth** ($T < T_{\text{Melt}}$): annealing (退火), sintering (燒結), etc, for polycrystalline materials
- **Organic materials:** Spin-coating; ink-jet printing; **vacuum deposition; MBE.**

Liquid phase epitaxy (LPE, 液相磊晶術)

LPE is a method to grow epitaxial layers on solid substrates from a solution (solute + solvent, 溶液 = 溶質 + 溶劑). This happens at temperatures well below the melting point T_M of the deposited semiconductor. For example. the solute (GaAs, or GaAs & AlAs) is dissolved in the solvent (Ga, MP = 29.76°C) at high enough temperature ($T \sim 700^\circ\text{C}$, but $T < T_M(\text{GaAs}) = 1238^\circ\text{C}$ or $T_M(\text{AlAs}) = 1740^\circ\text{C}$) with its saturated solubility. As T is lowering, the supersaturated solute (GaAs, or $\text{Ga}_x\text{Al}_{1-x}\text{As}$) may be deposited on the substrate to form a epitaxial layer.



LPE apparatus for the growth of III-V compound heterojunction bipolar transistor.

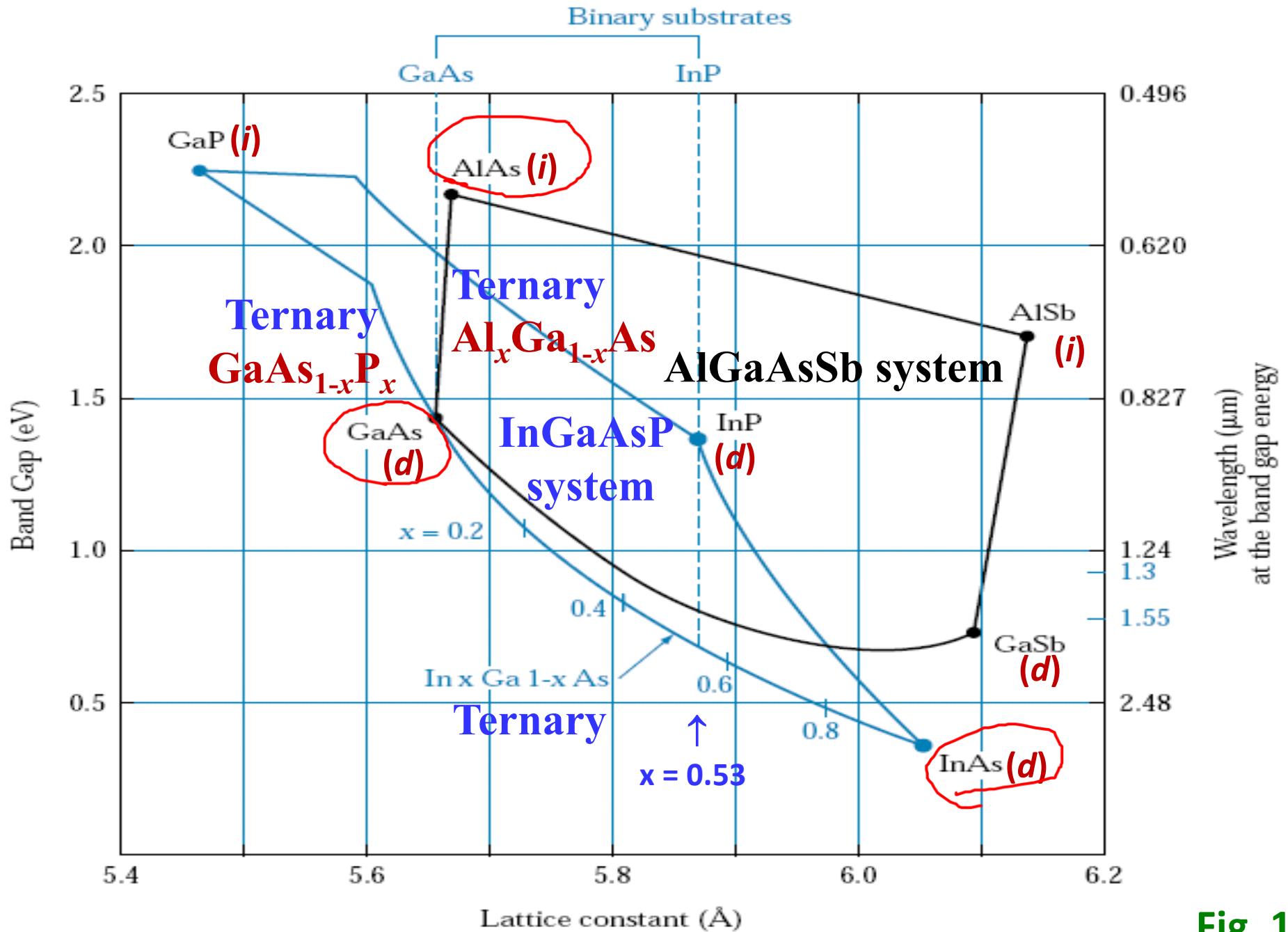
1.4.1 Lattice matching in epitaxial growth

- (i) **Si epitaxy on Si substrate => natural matching**
- (ii) **AlAs on GaAs** (both $a \approx 5.65\text{\AA}$) **heteroepitaxy** with **little lattice mismatch**
- (iii) **InAs (6.06\AA) on GaAs (5.65\AA)** **heteroepitaxy** with **7% lattice mismatch**

Figure 1-13

(四元)

Relationship between band gap and lattice constant for alloys in the InGaAsP and AlGaAsSb systems. The dashed vertical lines show the lattice constants for the commercially available binary substrates GaAs and InP. For the marked example of $\text{In}_x\text{Ga}_{1-x}\text{As}$, the ternary composition $x = 0.53$ can be grown tlattice-matched on InP, since the lattice constants are the same. For quaternary alloys, the compositions on both the III and V sub-lattices can be varied to grow lattice-matched epitaxial layers along the dashed vertical lines between curves. For example, $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$ can be grown on InP substrates, with resulting band gaps ranging from 0.75 eV to 1.35 eV. In using this figure, assume the lattice constant a of a ternary alloy varies linearly with the composition x .



		E_g (ev)	μ_n (cm ² /V-s)	μ_p (cm ² /V-s)	m_n^*/m_o (m_l/m_i)	m_p^*/m_o (m_{lh}/m_{hh})	a (Å)	ϵ_r	Density (g/cm ³)	Melting point (°C)
Si	(i/D)	1.11	1350	480	0.98, 0.19	0.16, 0.49	5.43	11.8	2.33	1415
Ge	(i/D)	0.67	3900	1900	1.64, 0.082	0.04, 0.28	5.65	16	5.32	936
SiC (α)	(i/W)	2.86	500	—	0.6	1.0	3.08	10.2	3.21	2830
AlP	(i/Z)	2.45	80	—	—	0.2, 0.63	5.46	9.8	2.40	2000
AlAs	(i/Z)	2.16	1200	420	2.0	0.15, 0.76	5.66	10.9	3.60	1740
AlSb	(i/Z)	1.6	200	300	0.12	0.98	6.14	11	4.26	1080
GaP	(i/Z)	2.26	300	150	1.12, 0.22	0.14, 0.79	5.45	11.1	4.13	1467
GaAs	(d/Z)	1.43	8500	400	0.067	0.074, 0.50	5.65	13.2	5.31	1238
GaN	(d/Z, W)	3.4	380	—	0.19	0.60	4.5	12.2	6.1	2530
GaSb	(d/Z)	0.7	5000	1000	0.042	0.06, 0.23	6.09	15.7	5.61	712
InP	(d/Z)	1.35	4000	100	0.077	0.089, 0.85	5.87	12.4	4.79	1070
InAs	(d/Z)	0.36	22600	200	0.023	0.025, 0.41	6.06	14.6	5.67	943
InSb	(d/Z)	0.18	10 ⁵	1700	0.014	0.015, 0.40	6.48	17.7	5.78	525
ZnS	(d/Z, W)	3.6	180	10	0.28	—	5.409	8.9	4.09	1650*
ZnSe	(d/Z)	2.7	600	28	0.14	0.60	5.671	9.2	5.65	1100*
ZnTe	(d/Z)	2.25	530	100	0.18	0.65	6.101	10.4	5.51	1238*
CdS	(d/W, Z)	2.42	250	15	0.21	0.80	4.137	8.9	4.82	1475
CdSe	(d/W)	1.73	800	—	0.13	0.45	4.30	10.2	5.81	1258
CdTe	(d/Z)	1.58	1050	100	0.10	0.37	6.482	10.2	6.20	1098
PbS	(i/H)	0.37	575	200	0.22	0.29	5.936	17.0	7.6	1119
PbSe	(i/H)	0.27	1500	1500	—	—	6.147	23.6	8.73	1081
PbTe	(i/H)	0.29	6000	4000	0.17	0.20	6.452	30	8.16	925

All values at 300 K.

*Vaporizes

Ternary (三元) and quaternary (四元) III-V polar semiconductor compounds

- Ternary: $\text{Al}_x\text{Ga}_{1-x}\text{As}$ (砷化鋁鎵), column III sublattice in the zincblende structure contains a fraction x of Al atoms and $1 - x$ of Ga atoms, with the interpenetrating column V sublattice occupied entirely by As atoms.
- Properties (E_g , a , μ_n , μ_p , etc) vary as GaAs ($x = 0, d$) $\Rightarrow \text{AlAs}$ ($x = 1, i$)
- Ternary: $\text{GaAs}_{1-x}\text{P}_x$, as GaAs (d) + GaP (i)
- Quaternary: $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$, wide range of properties.

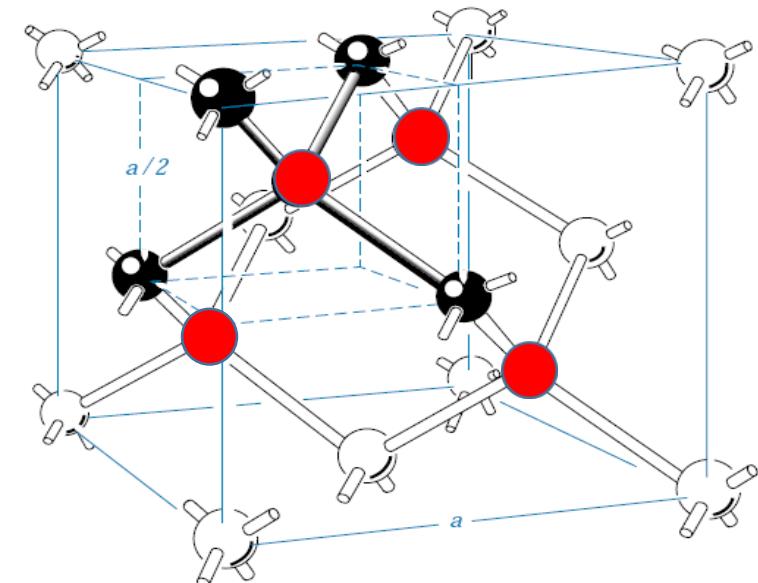
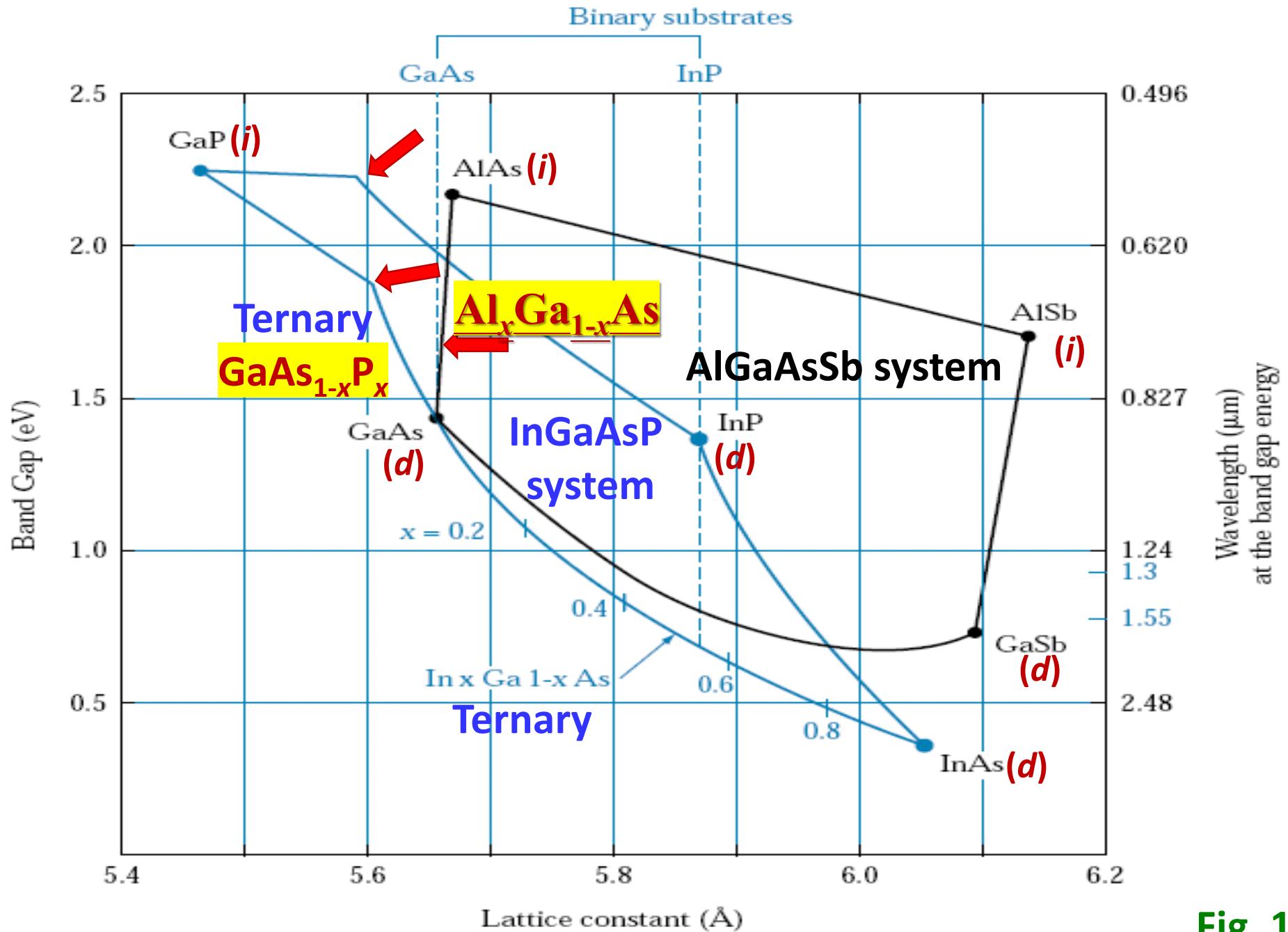
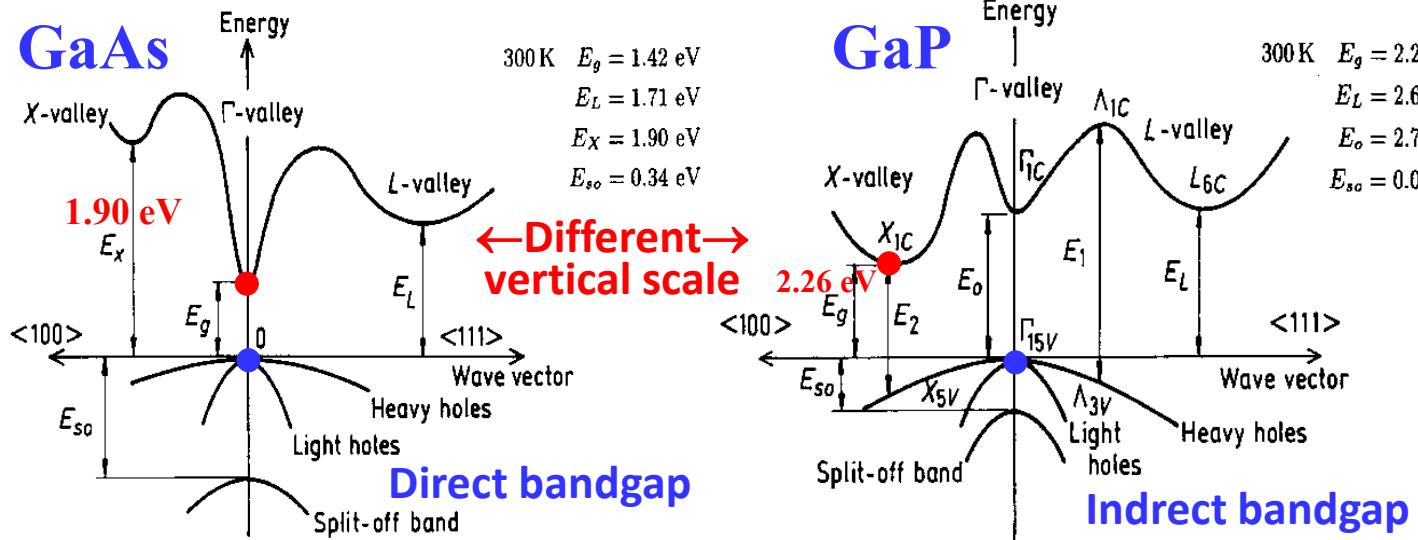


Figure 1-9

Diamond lattice unit cell, showing the four nearest neighbor structure. (From *Electrons and Holes in Semiconductors* by W. Shockley, © 1950 by Litton Educational Publishing Co., Inc.; by permission of Van Nostrand Reinhold Co., Inc.)

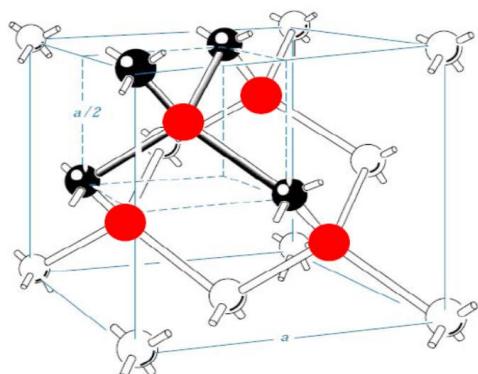


三元化合物半導體 $\text{GaAs}_{1-x}\text{P}_x$ 的 E_g 隨組成比 x 而變 => Bandgap engineering



<http://www.ioffe.ru/SVA/NSM/Semicond/GaAs/Figs/421.gif>

<https://www.ioffe.ru/SVA/NSM/Semicond/GaP/Figs/521.gif>

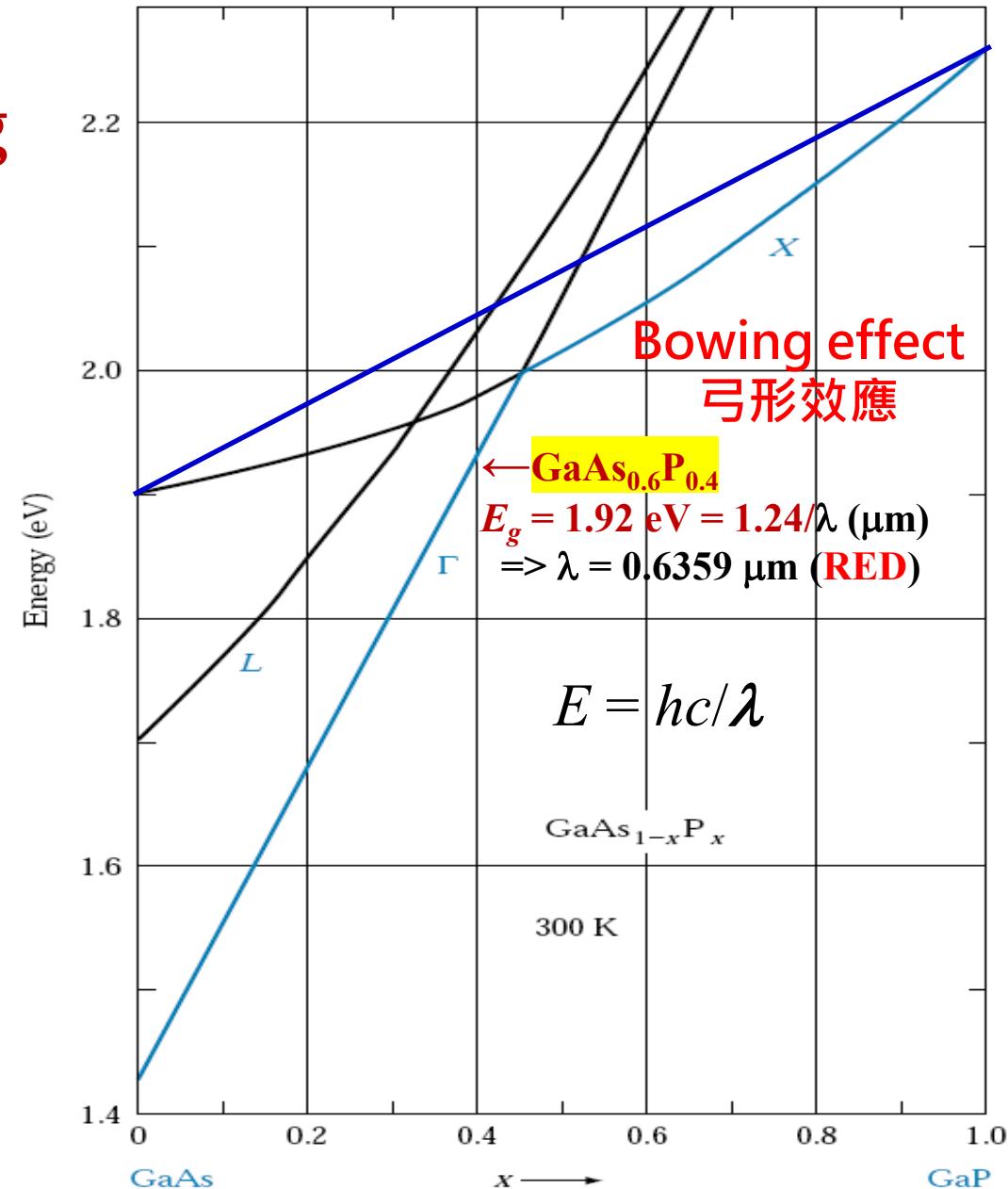


For Γ -band:

$$E_\Gamma(\text{GaAs}_{1-x}\text{P}_x) = [xE_\Gamma(\text{GaP}) + (1-x)E_\Gamma(\text{GaAs})] - b_\Gamma x(1-x)$$

For X-band:

$$E_X(\text{GaAs}_{1-x}\text{P}_x) = [xE_X(\text{GaP}) + (1-x)E_X(\text{GaAs})] - b_X x(1-x)$$



Bowing (彎如弓) of the defect formation energy in semiconductor alloys, *Phys. Rev. B* 87, 241201(R) (2013)

- Alloying different semiconductors is a popular approach to broaden the range of available material properties for specific applications (\Rightarrow Bandgap engineering).
- The compositional dependence of properties of isovalent $A_xB_{1-x}C$ (e.g., $Al_xGa_{1-x}As$) semiconductor alloys can be described as **a linear average** of the corresponding quantities in two pure constituents and **a quadratic term** (from entropy (熵) effect),

$$P(A_xB_{1-x}C) = [xP(AC) + (1 - x)P(BC)] - bx(1 - x),$$

where b is the so-called **bowing (弓形) coefficient**.

- For isovalent alloys with a **small size mismatch**, the **bowing coefficients** are **small constant numbers**; for alloys with a **large size mismatch**, the **bowing coefficients** could be **large and composition dependent**.

Graded (buffered) layer method for LED material

- **GaAs_{0.6}P_{0.4}**: an important **red LED** material (direct- E_g semiconductor with $a \cong 5.61\text{\AA}$)
- Using a **GaAs or Ge wafer** (both $a \cong 5.65\text{\AA}$) **as a substrate**, the growth is begun at a **composition near GaAs**. A **(graded) region $\sim 25 \mu\text{m}$ thick** is grown while gradually introducing P until the desired As/P ratio is achieved.
- The desired epitaxial layer **GaAs_{0.6}P_{0.4}** of $100 \mu\text{m}$ is then grown on this **graded layer**. By this method **epitaxial growth always occurs on a crystal of similar lattice constant**.
- Although **some crystal dislocations** (錯位) occur due to lattice strain in the graded region, such **epitaxial layer GaAs_{0.6}P_{0.4}** with high quality can be used in LEDs.

Strained-layer superlattice (SLS)

- If the mismatch is only a few % and the layer is thin (< critical thickness t_c), the epitaxial layer grows with a lattice constant in compliance with that of the seed crystal (Fig. 1-14). The resulting layer is in compression or tension along the surface plane as its lattice constant adapts to the seed crystal. Such a layer is called pseudo-morphic layer (偽形態層) because it is not lattice-matched to the substrate without strain.
- If the epitaxial layer exceeds t_c , which depends on the lattice mismatch, the strain energy leads to formation of defects called misfit dislocations.
- Using thin alternating layers of slightly mismatched layers, it is possible to grow a strained-layer superlattice (SLS) in which alternate layers are in tension and compression. The overall SLS lattice constant is an average of that of these two bulk materials.

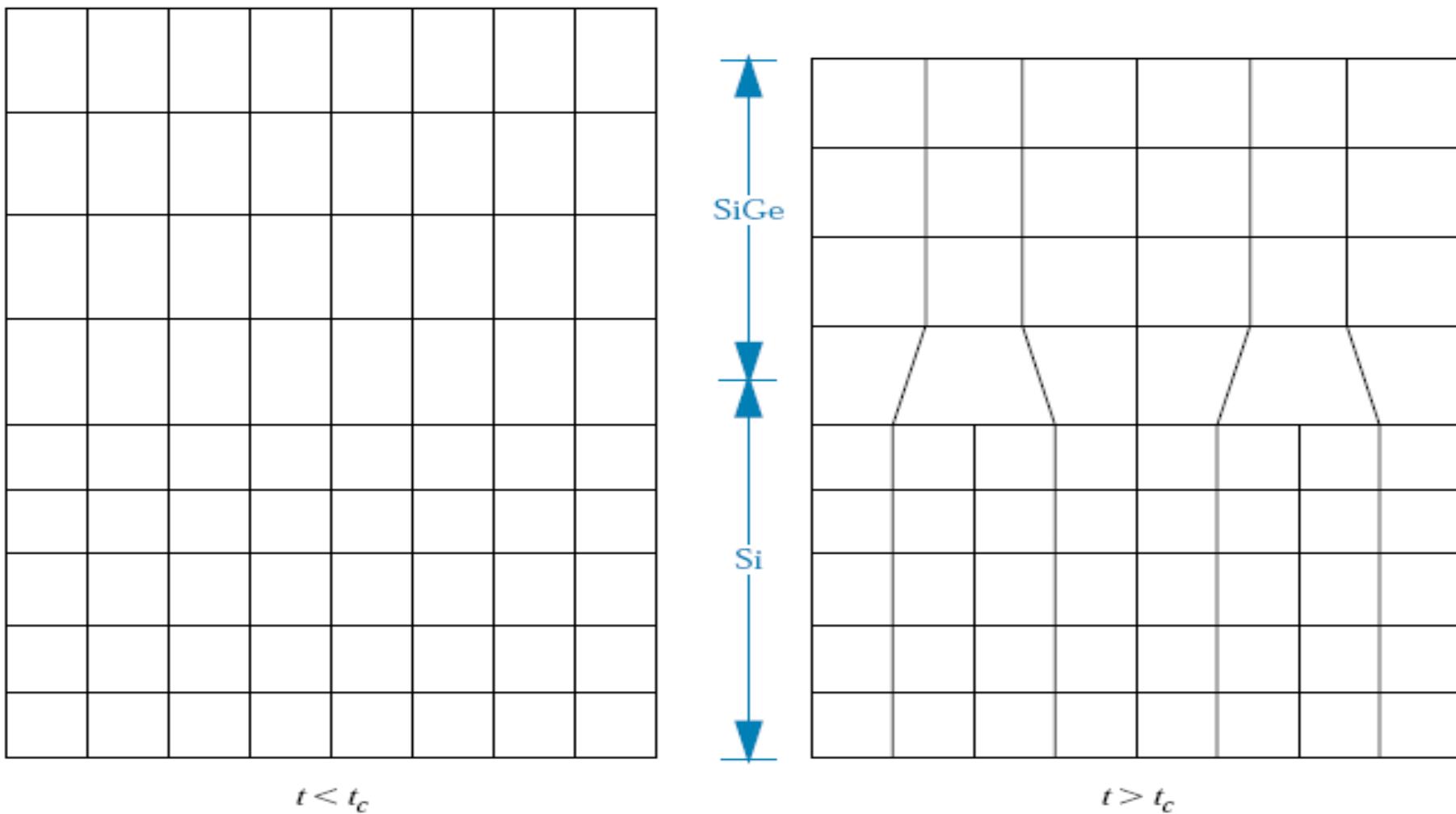


Figure 1–14

Heteroepitaxy and misfit dislocations. For example, in heteroepitaxy of a SiGe layer on Si, the lattice mismatch between SiGe and Si leads to compressive strain in the SiGe layer. The amount of strain depends on the mole fraction of Ge. (a) For layer thicknesses less than the critical layer thickness, t_c , pseudomorphic growth occurs. (b) However, above t_c , misfit dislocations form at the interface which may reduce the usefulness of the layers in device applications.

1.4.2 Vapor-phase epitaxy (VPE, 蒸汽相磊晶術)

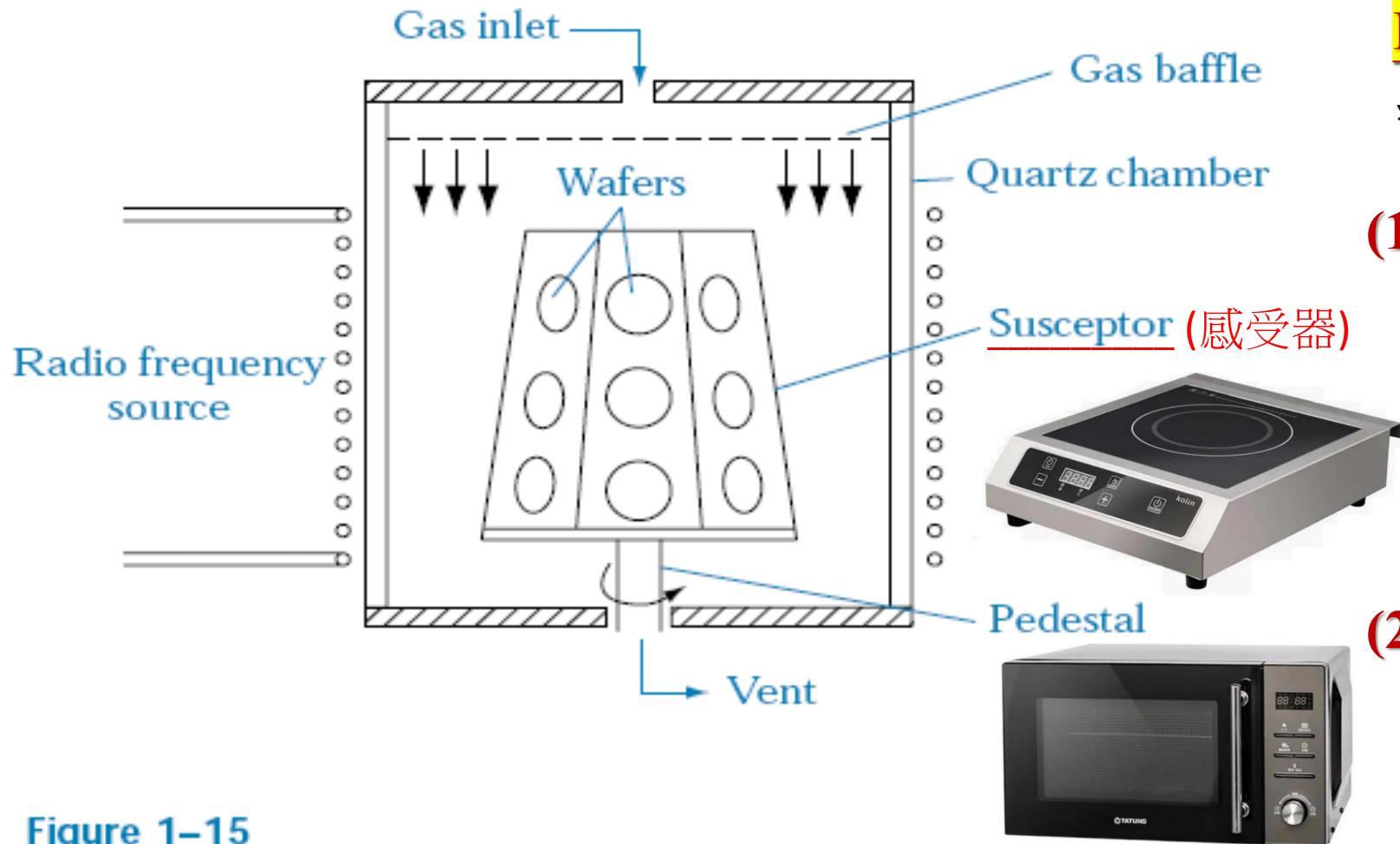


Figure 1-15

A barrel-type reactor for Si VPE. These are atmospheric pressure systems. The Si wafers are held in slots cut on the sides of a SiC-coated graphite susceptor that flares out near the base to promote gas flow patterns conducive to uniform epitaxy.

Radio-frequency heating: (RF:
射頻, 或無線電波的頻率, 介於
約 10 kHz ~ 300 GHz)

(1) **Induction heating:** 感應加熱
是一種利用電磁感應來加熱
電導體 (鐵磁性金屬效率高)
的方式，會在金屬中產生渦
電流，因電阻而讓金屬加熱；
如家用電磁爐 (20 ~ 27 kHz)。

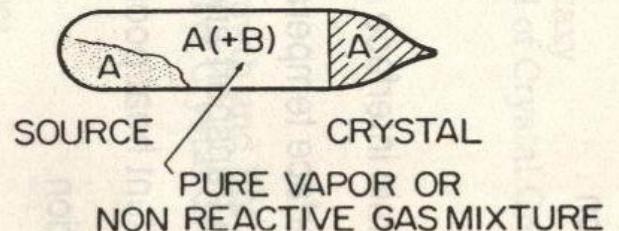
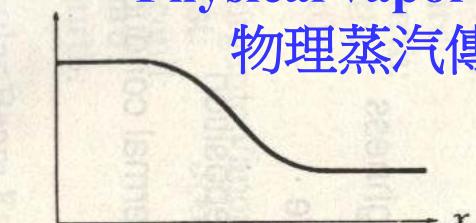
(2) **Dielectric heating:** 介電加熱
是利用 RF 無線電波 加熱 介電材料 的過程。食品中的 電偶極性分子 (如 H_2O max @
~ 10 GHz) 會在 微波震盪下旋轉，產生熱量。家用微波爐 (2.45 GHz ⇔ 12.24 cm)。

CRYSTALLIZATION FROM VAPORS

CLOSED TUBE TECHNIQUES

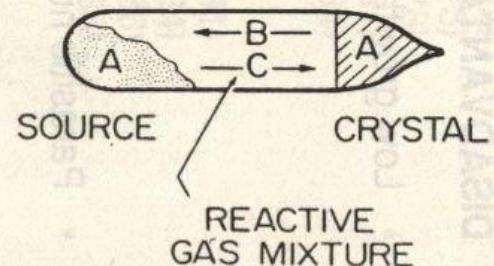
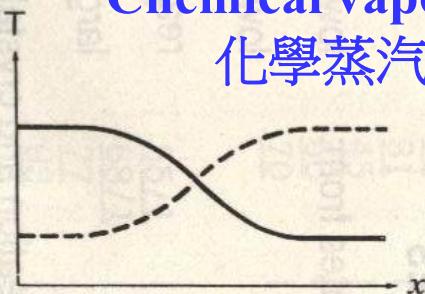
(a) PVT T Physical vapor transport

物理蒸汽傳輸法



(b) CVT T Chemical vapor transport

化學蒸汽傳輸法

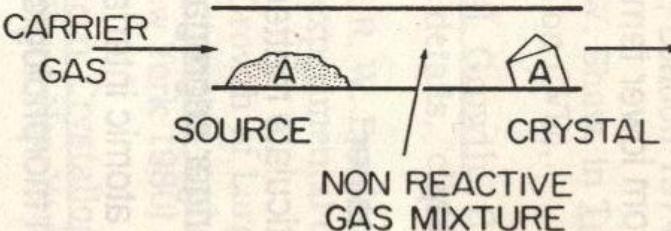
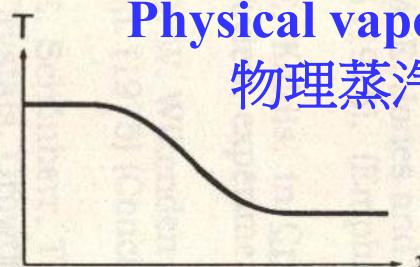


FLOW-THROUGH TECHNIQUES

(c) PVD T Physical vapor deposition

物理蒸汽沉積法

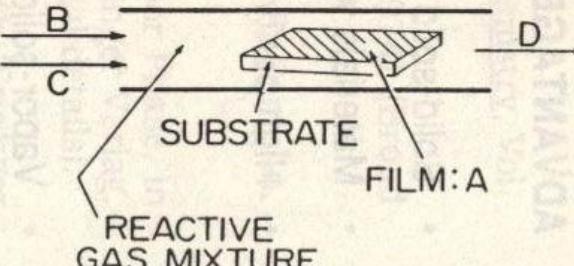
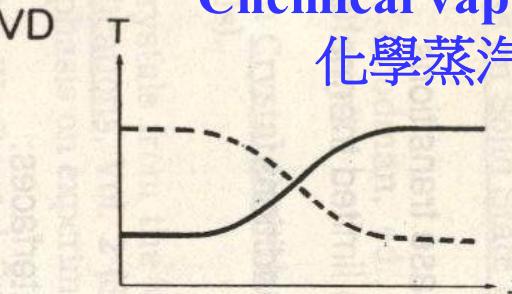
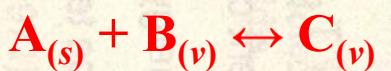
Sublimation and
re-condensation



(d) CVD T Chemical vapor deposition

化學蒸汽沉積法

Chemical reaction



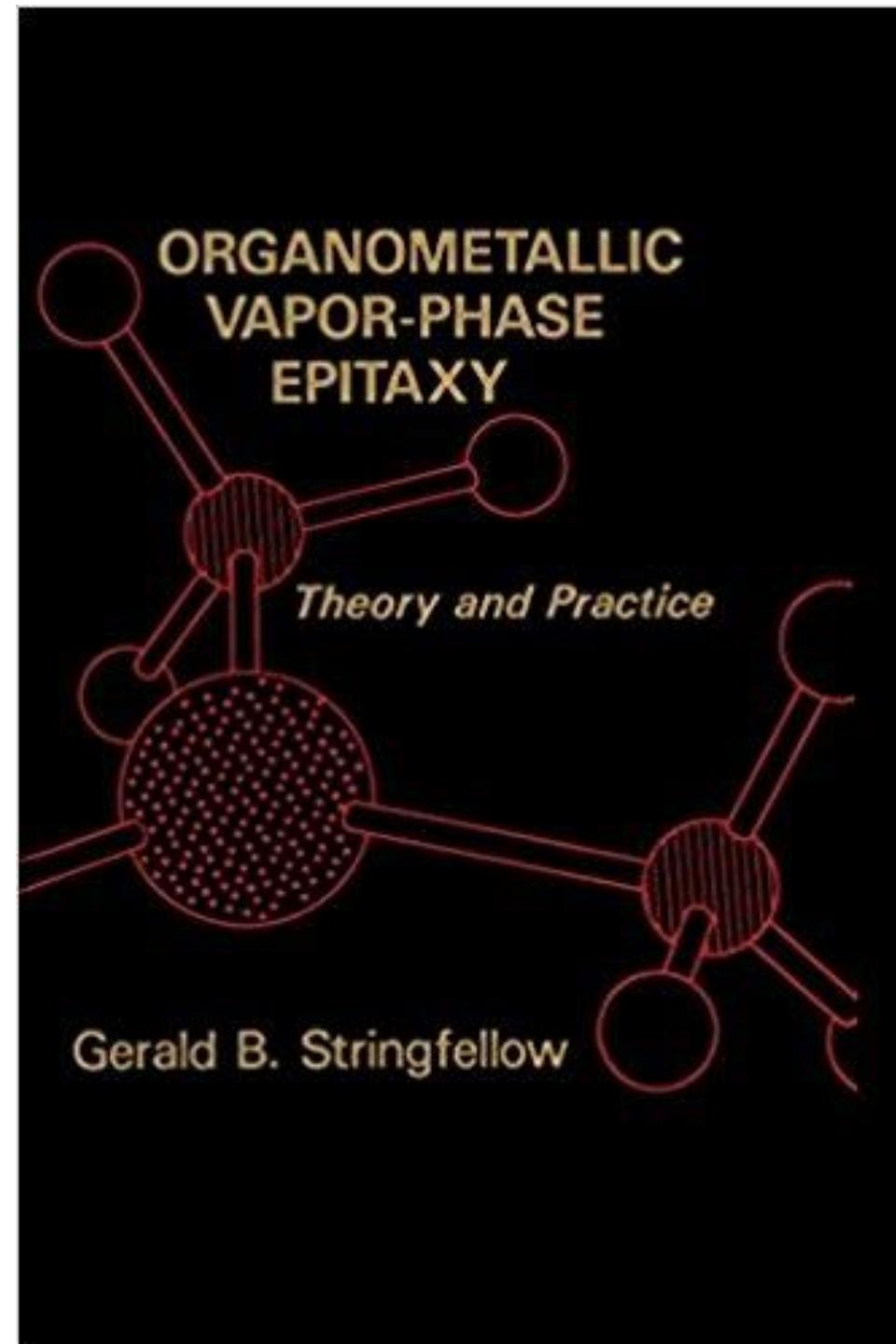
Selected examples for CVD

Chemical vapor deposition (CVD) processes are widely used for the preparation of electronically active and insulating layers for opto-electronic solid state devices.

Here are some selected examples:

Reaction	Temperature
$\text{GaCl} + \frac{1}{2} \text{As}_2 + \frac{1}{2} \text{H}_2 \rightarrow \text{GaAs}_{(s)} + \text{HCl}$	750°C
$(\text{CH}_3)_3\text{Ga} + \text{AsH}_3 \rightarrow \text{GaAs}_{(s)} + 3\text{CH}_4$	700°C
$(1-x)[(\text{CH}_3)_3\text{Ga}] + x[(\text{CH}_3)_3\text{Al}] + \text{AsH}_3$ $\rightarrow \text{Ga}_{1-x}\text{Al}_x\text{As}_{(s)} + 3\text{CH}_4$	700°C
$\text{SiH}_4 \rightarrow \text{Si}_{(s)} + 2\text{H}_2$	1050°C
$\text{SiCl}_4 + 2\text{H}_2 \rightarrow \text{Si}_{(s)} + 4\text{HCl}$	1050°C
$\text{SiH}_4 + \text{O}_2 \rightarrow \text{SiO}_2(s) + 2\text{H}_2$	400°C
$\text{TiCl}_4 + 2\text{BCl}_3 + 5\text{H}_2 \rightarrow \text{TiB}_2(s) + 10\text{HCl}$	900°C

MOCVD: metal-organic chemical vapor deposition,
OMVPE: organometallic vapor-phase epitaxy



Physics of
Semiconductor
Devices

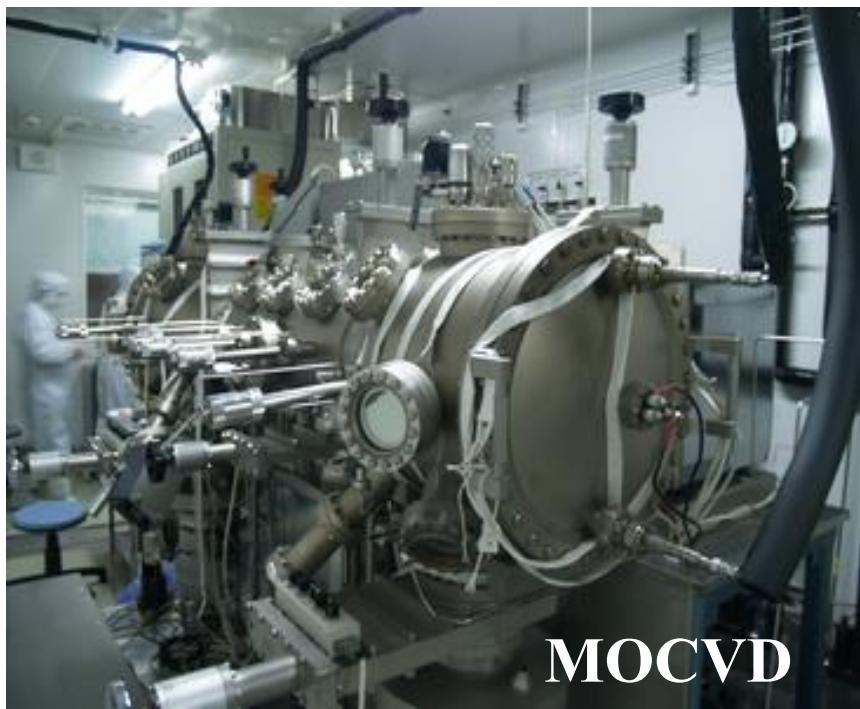
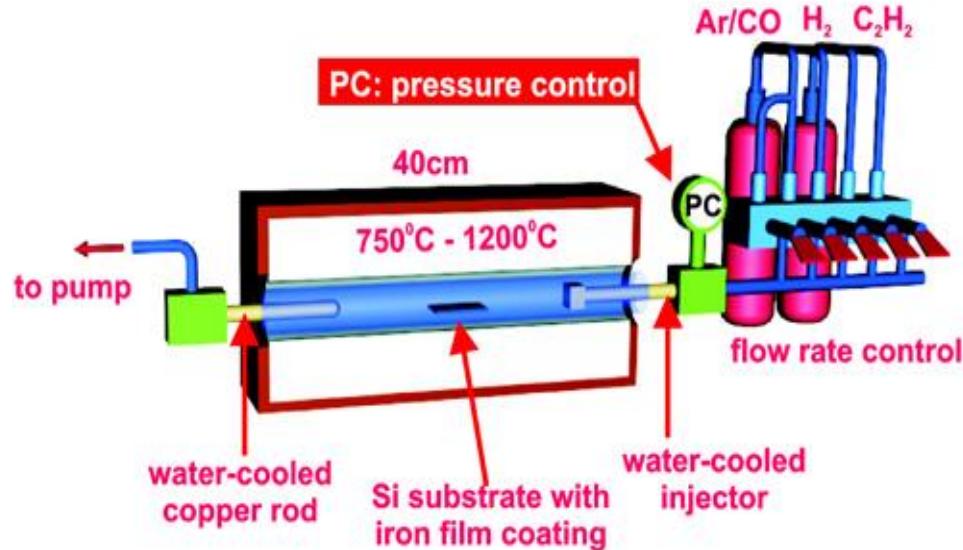
2nd Edition



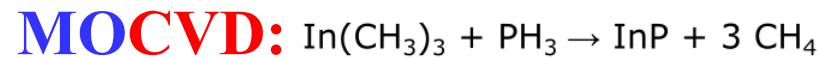
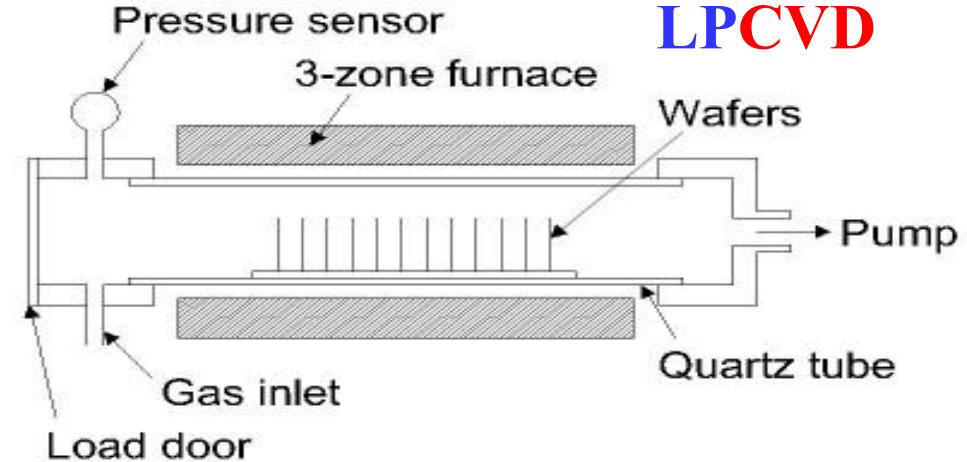
G. B. Stringfellow: Distinguished Professor, Materials Science and Engineering, University of Utah.

- The 1st single-author treatments of organometallic vapor-phase epitaxy (OMVPE ⇔ MOCVD) a leading technique for the fabrication of semiconductor materials and devices.
- Chinese Translation (2017), Peking University Press.

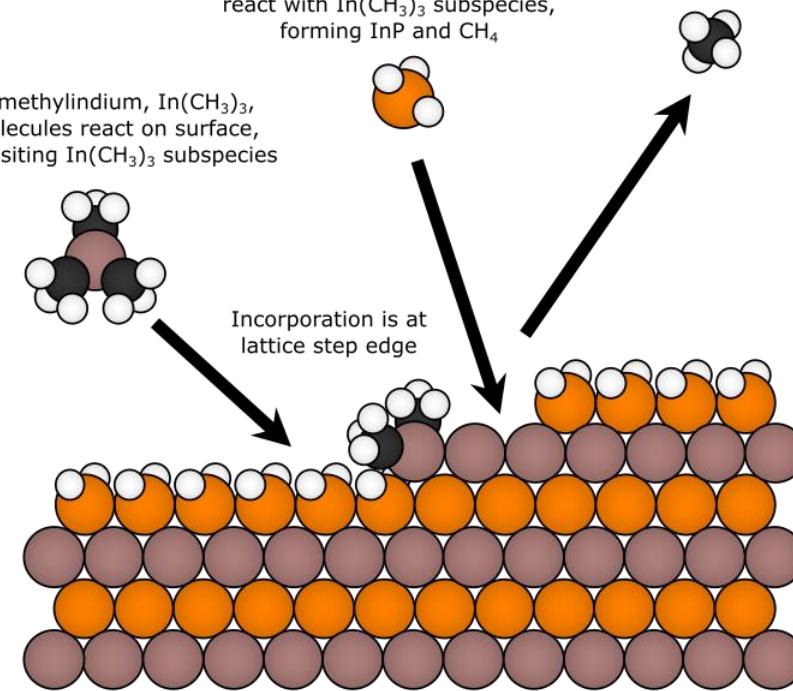
CVD reactors



MOCVD



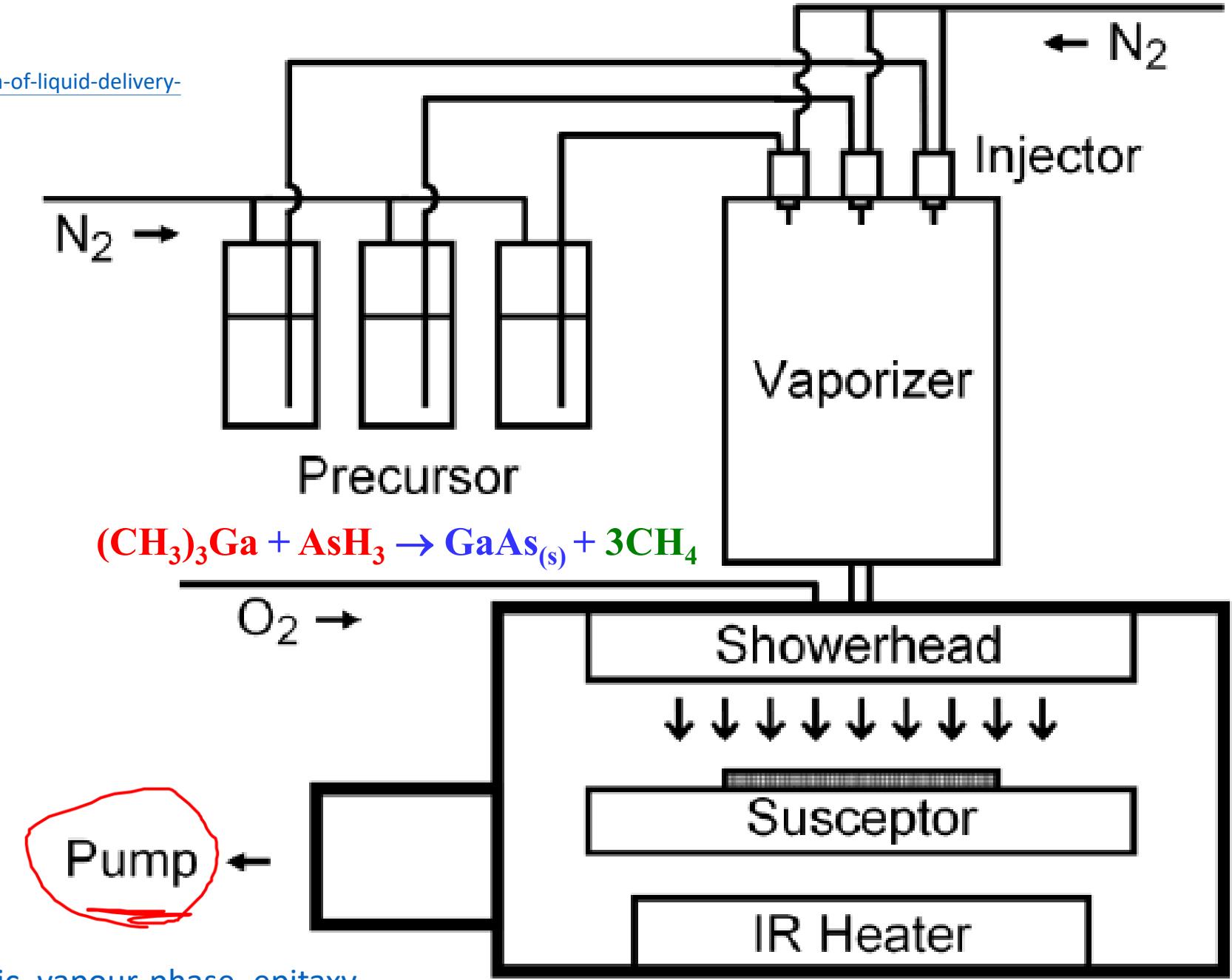
Phosphine (PH₃) molecules react on surface, leaving phosphorus to react with In(CH₃)₃ subspecies, forming InP and CH₄
Reaction byproducts (CH₄) leave reactor



MOCVD

https://www.researchgate.net/figure/Schematic-diagram-of-liquid-delivery-MOCVD-system_fig1_233652516

This equipment includes but is not limited to computer automated gas and chemical delivery systems, toxic and carrier gas sniffing sensors which can detect single digit ppb amounts of gas, and of course abatement equipment to fully capture toxic materials which can be present in the growth of arsenic containing alloys such as GaAs and InGaAsP.

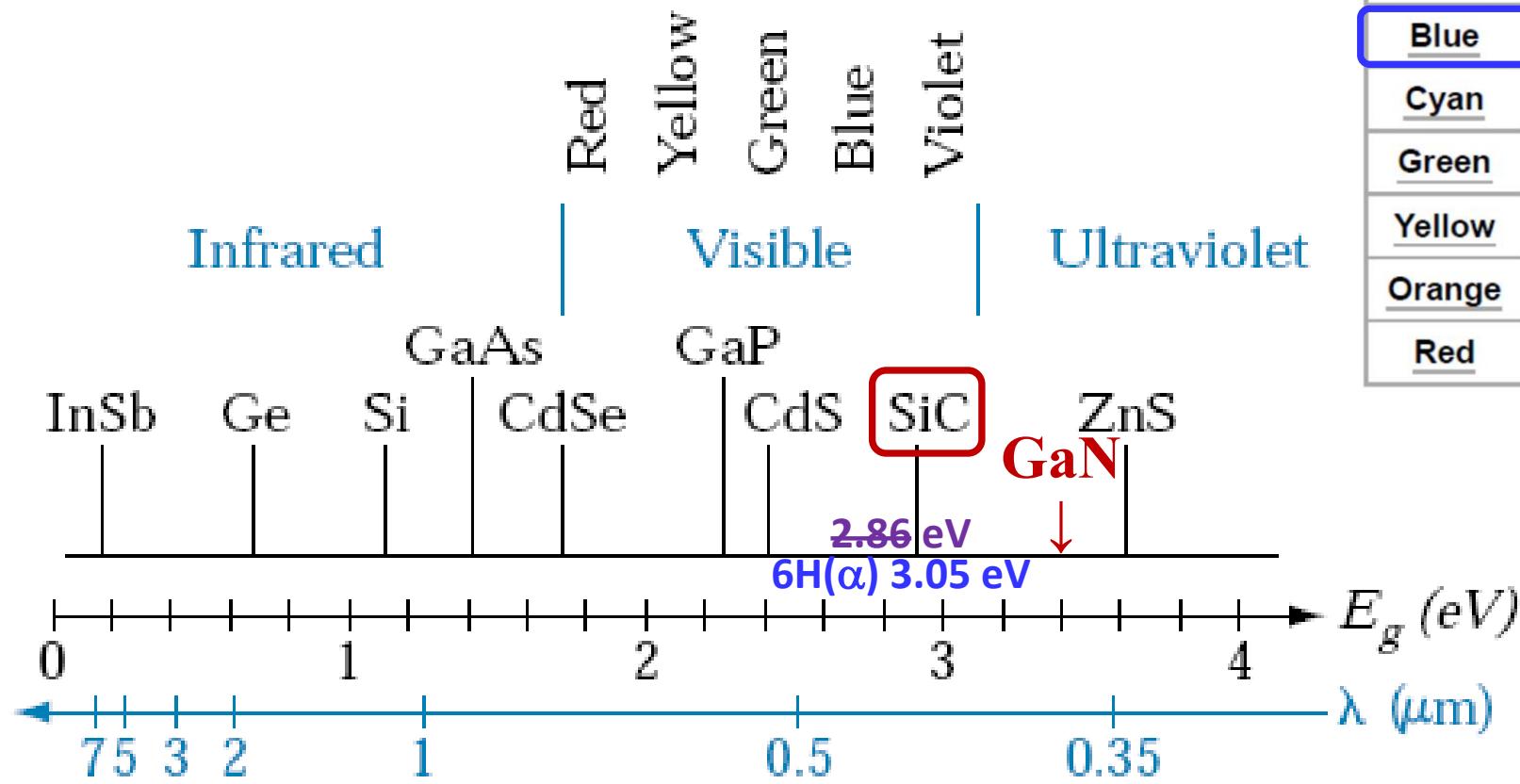


https://en.wikipedia.org/wiki/Metalorganic_vapour-phase_epitaxy

第三類(代)半導體:

GaN (3.4 eV),

4H-SiC (3.23 eV)



Blue LEDs by GaN (SiC in 1990s?)

Color	Wavelength	Frequency	Photon energy
Violet	380–450 nm	670–790 THz	2.75–3.26 eV
Blue	450–485 nm	620–670 THz	2.56–2.75 eV
Cyan	485–500 nm	600–620 THz	2.48–2.56 eV
Green	500–565 nm	530–600 THz	2.19–2.48 eV
Yellow	565–590 nm	510–530 THz	2.10–2.19 eV
Orange	590–625 nm	480–510 THz	1.98–2.10 eV
Red	625–700 nm	400–480 THz	1.65–1.98 eV

Human eye can respond to wavelengths from about **0.70 to 0.39 μm (1.77 ~ 3.18 eV, or 430 ~ 790 THz)**, $E = hc/\lambda = 1.24 / \lambda$, where E in eV and λ in μm.

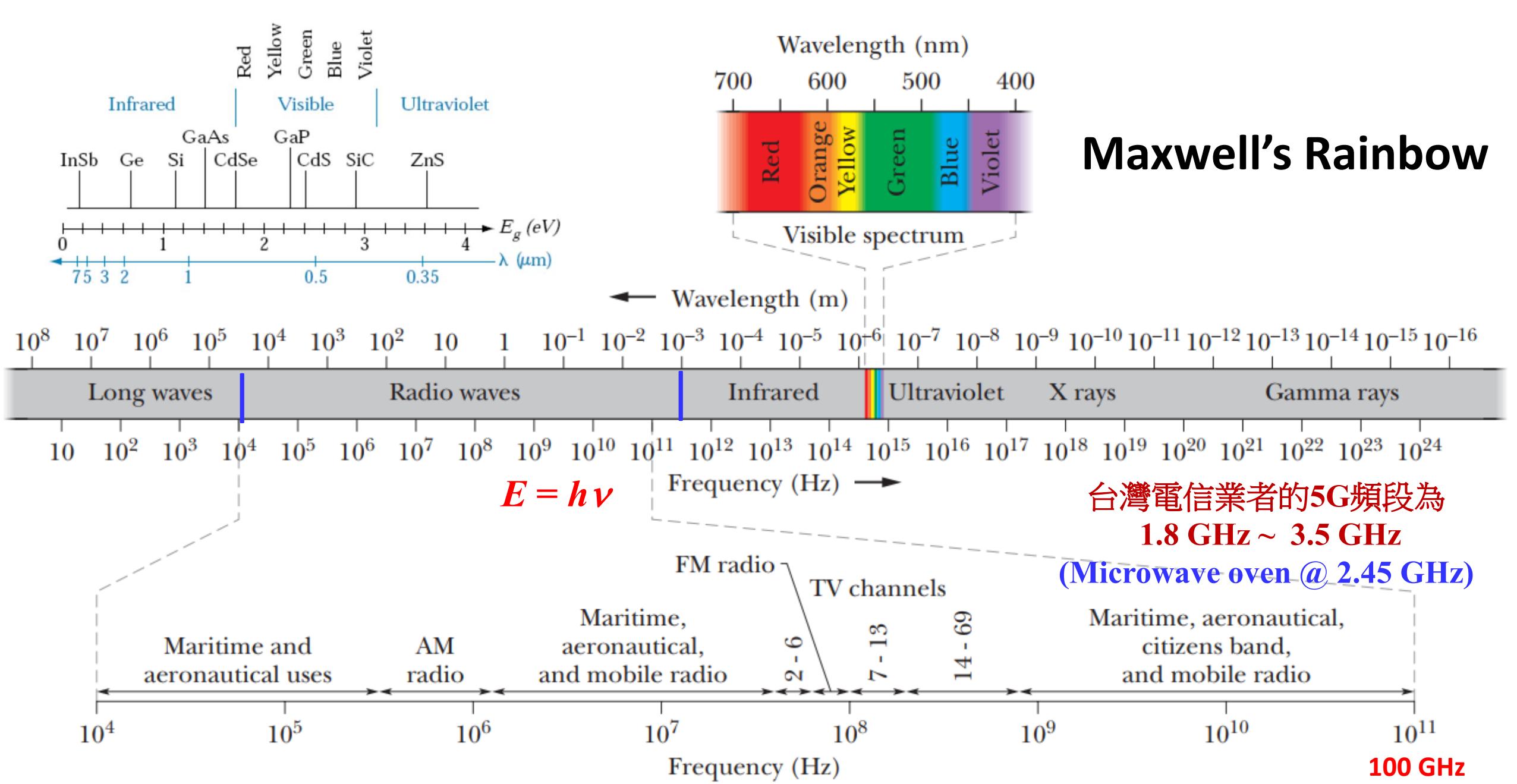
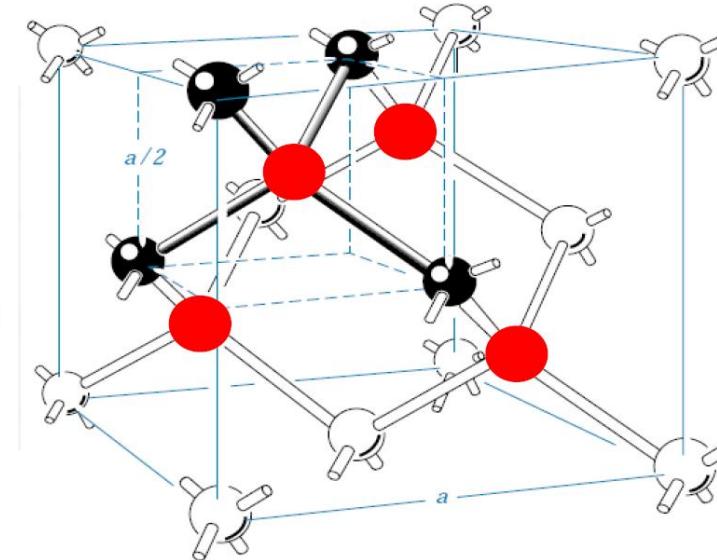
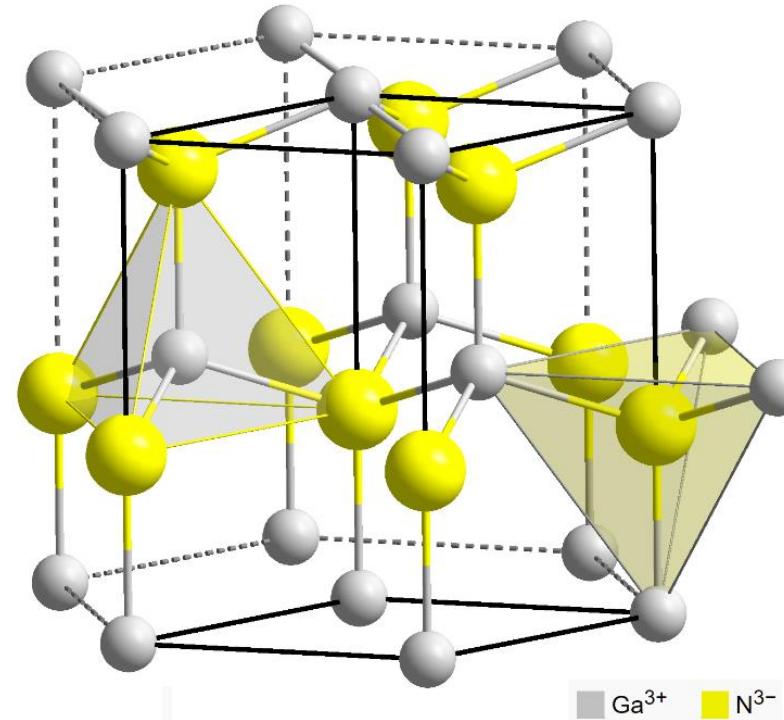
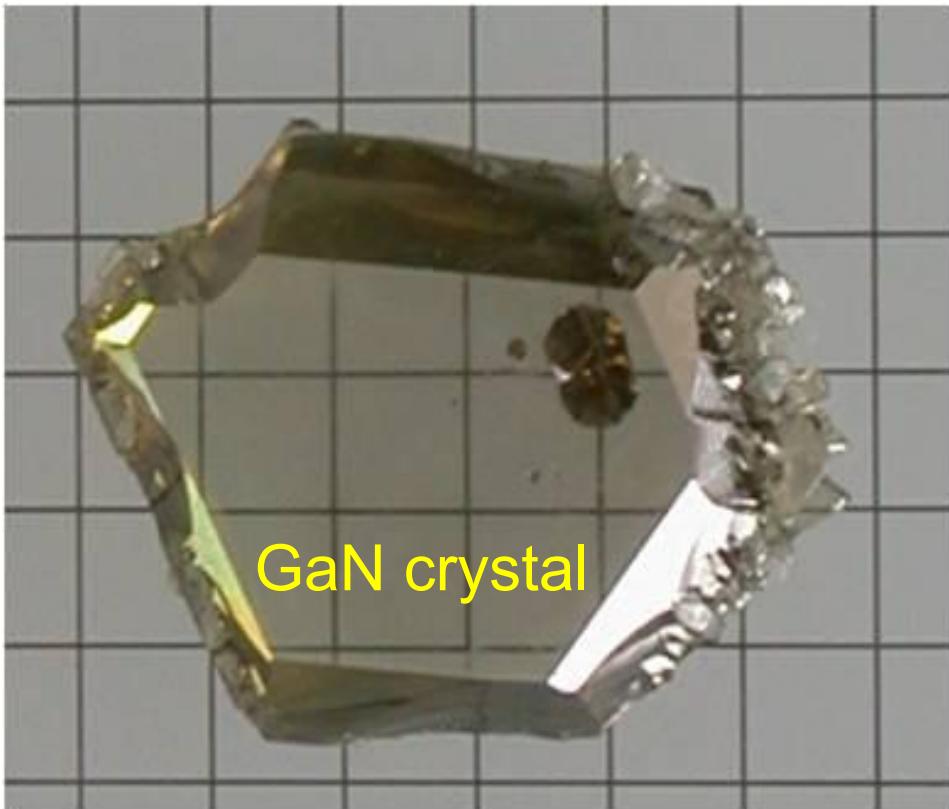


Fig. 33-1 The electromagnetic spectrum.

From “Fundamentals of Physics” by Halliday/Resnick/Walker, 8th Ed.

GaN is a binary III/V direct bandgap (3.4 eV) semiconductor used in light-emitting diodes since the 1990s. GaN is a very hard material (12 ± 2 GPa) that has a Wurtzite crystal structure



GaN

[d/Z, W]

3.4

The growth of **GaN** epitaxial layers adopted in blue LED by **MOCVD**

- GaN films were grown on (0001) GaN-on-sapphire (藍寶石, 氧化鋁, Al_2O_3) templates (模板) and free-standing GaN substrates in a 1×2 in. **MOCVD reactor** @ 975°C . Trimethylgallium (TMGa , $\text{Ga}(\text{CH}_3)_3$) and ammonia (NH_3) were used as the Ga and N precursors, respectively. Hydrogen (H_2) was used as the carrier gas. Silane (SiH_4) was used as an Si dopant (n-type).
- GaN can be doped with Si (\Rightarrow Ga-sublattice) or with O (\Rightarrow N) to n-type and with Mg (\Rightarrow Ga) to p-type. However, the Si and Mg atoms change the way the GaN crystals grow, introducing tensile stresses (拉應力) and making them brittle (易碎). GaN compounds also tend to have a high dislocation (錯位) density.
- The difficulty in making p-type doped GaN, p-type dopant Mg (\Rightarrow Ga)???

Akasaki & Amano discovered p-type GaN by doping with Mg and **subsequent activation by electron irradiation** to produce the 1st GaN p-n junction blue/UV LED in **1989**. **Nakamura** continued to develop the blue InGaN LED in **1993** by **MOCVD** and **thermal annealing processes** which was suitable for mass production and pointed out that H passivated acceptors (Mg) in GaN.



Nakamura solved the difficulty in making p-type doped GaN for mass production, and pointed out that H passivated acceptors in GaN.

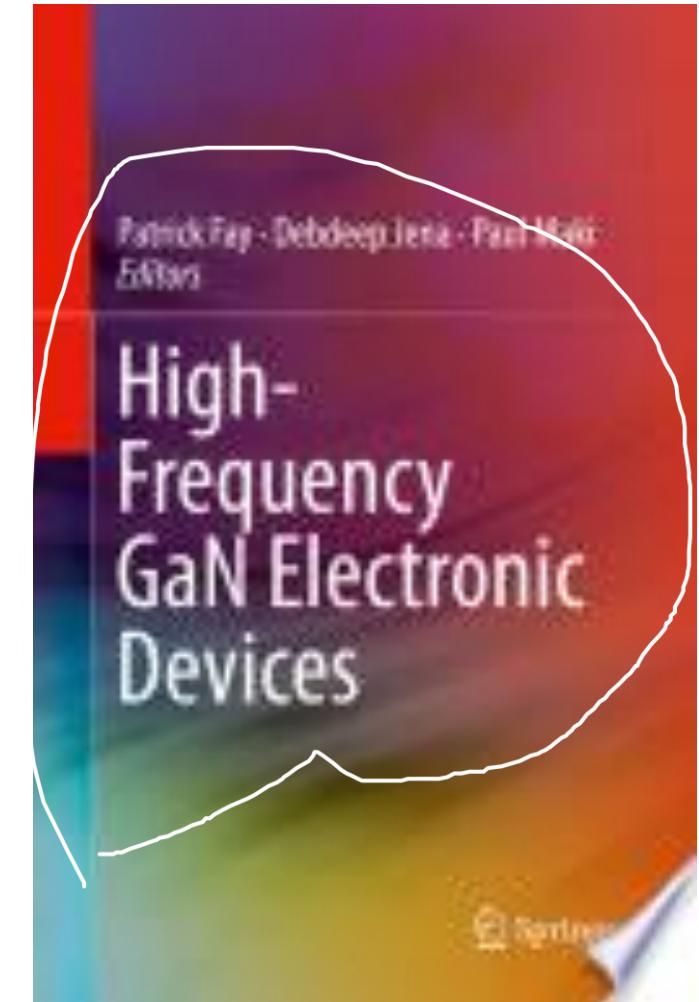
The Nobel Prize in Physics 2014

was awarded jointly to Isamu Akasaki (赤崎 勇), Hiroshi Amano (天野 浩) and Shuji Nakamura (中村 修二) "for the invention of efficient blue light-emitting diodes which has enabled bright and energy-saving white light sources".

GaN in **high frequency** devices:

恩智浦(NXP) 啟用美國境內最先進的射頻氮化鎵 (GaN) 晶圓廠

- 〔記者洪友芳／新竹報導〕**2020/10/12** 恩智浦半導體 (NXP) 宣佈正式啟用位於美國亞利桑那州錢德勒 (Chandler) 的 **6吋射頻氮化鎵 (GaN) 晶圓廠**，此為美國境內專注於 **5G 射頻功率放大器** 的最先進晶圓廠。恩智浦表示，這座**全新氮化鎵晶圓廠**已通過認證，首批產品將持續推出上市，預計**2020年底**將達到產能滿載。
- 恩智浦擁有近**20年**的氮化鎵開發專業知識和廣泛的無線通訊產業知識，將使其引領下**1波5G蜂巢擴展浪潮**。恩智浦已針對**氮化鎵技術**進行深度最佳化，改善半導體中的**電子陷阱 (electron trapping)** 問題，藉由一流的線性度提供高效率和增益，致力為恩智浦的客戶生產最高品質的氮化鎵裝置。



Infineon CEO Jochen Hanebeck holds one of the world's first 300 mm (12") GaN Power wafers produced in an existing and scalable high-volume manufacturing environment.



12" GaN wafer



Infineon is mastering all three relevant materials: Si, GaN and SiC."

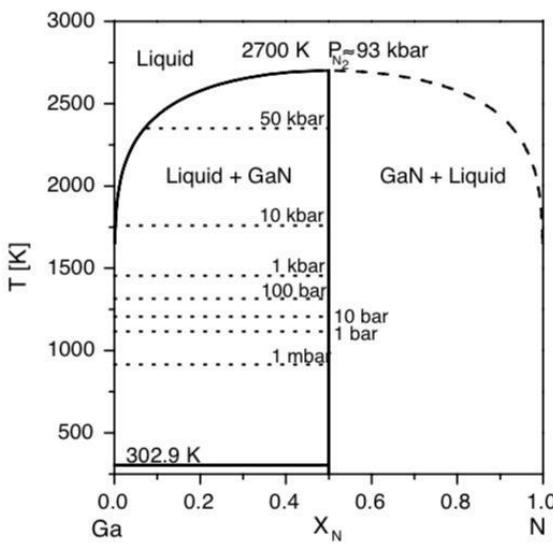
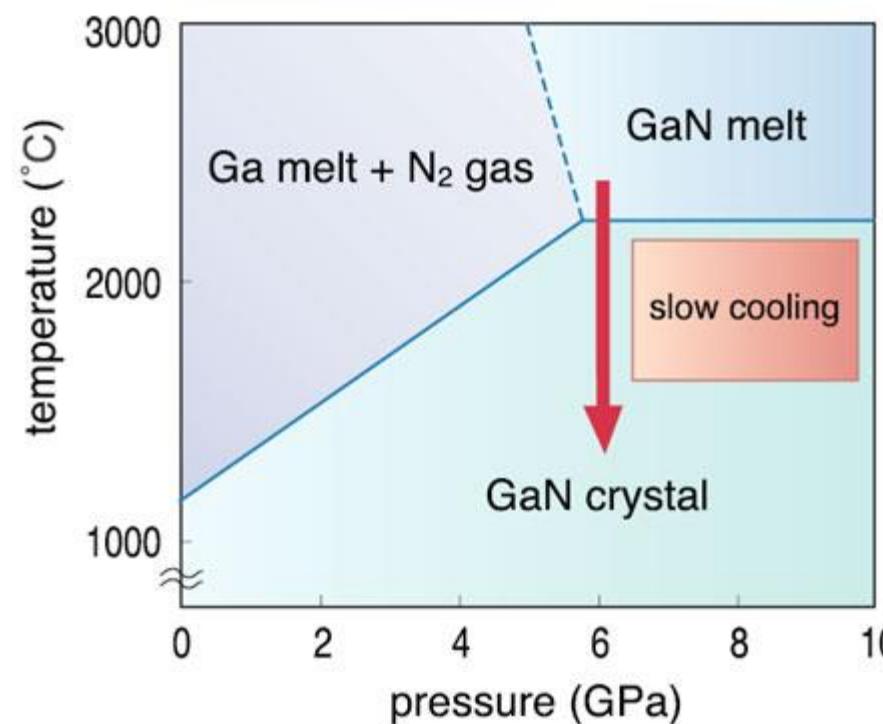


Fig. 12. Calculated condensed phase diagram of the Ga-N system, corresponding to Table 5. Equilibrium isobars of pressure P are superimposed.

<https://www.chegg.com/homework-help/questions-and-answers/help-confused-need-material-science-help-please-help-interpret-chart-phase-diagram-galliu-q88393460>

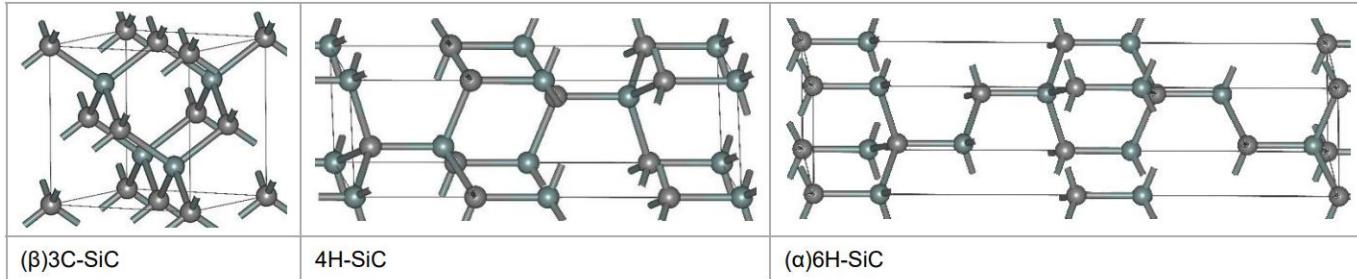


<https://rdreview.jaea.go.jp/tayu/ACT04E/05/0505.htm>

- **Gallium nitride (GaN)** is an important material for optoelectronic devices. These devices are usually fabricated by **epitaxial growth on sapphire substrates**. **Single crystals** are difficult to grow by the standard slow cooling method because at ambient pressure GaN usually **decomposes into Ga and N₂ before melting (left)**.
- **High-pressure** suppresses the decomposition of GaN and **allows congruent melting above 6.0 GPa (middle, 1 atm ~ 10⁵ Pa ~ 1 bar)**. A new method for single crystal growth of GaN by slow cooling of its melt under high pressure (**right**) have been successfully obtained. 2004 **Japan Atomic Energy Research Institute**

SiC in high power devices:

Structure of major SiC polytypes, https://en.wikipedia.org/wiki/Silicon_carbide



Polytype	3C (β)	4H	6H (α)
Crystal structure	Zinc blende (cubic)	Hexagonal	Hexagonal
Space group	T^2_d -F $\bar{4}3m$	C^4_{6v} -P6 $_3$ mc	C^4_{6v} -P6 $_3$ mc
Pearson symbol	cF8	hP8	hP12
Lattice constants (Å)	4.3596	3.0730; 10.053	3.0810; 15.12
Density (g/cm ³)	3.21	3.21	3.21
Bandgap (eV)	2.36	3.23	3.05
Bulk modulus (GPa)	250	220	220
Thermal conductivity (W·m ⁻¹ ·K ⁻¹) @ 300 K (see [36][37] for temp. dependence)	320	348	325



Characteristics of Silicon / SiC / GaN

Properties	Si	SiC	GaN	
Bandgap	eV	1.1	3.3	3.4
Electron Mobility	cm ² /Vs	1350	700	1500
Breakdown Electrical Field	MV/cm	0.3	3.0	3.3
Figure of Merit	$\epsilon \mu e E^3$	1	440	1130

SiC /GaN Compared to Silicon:

High Breakdown Voltage
Up to 10 Times Higher

High Heat Resistance
Up to 1000°C

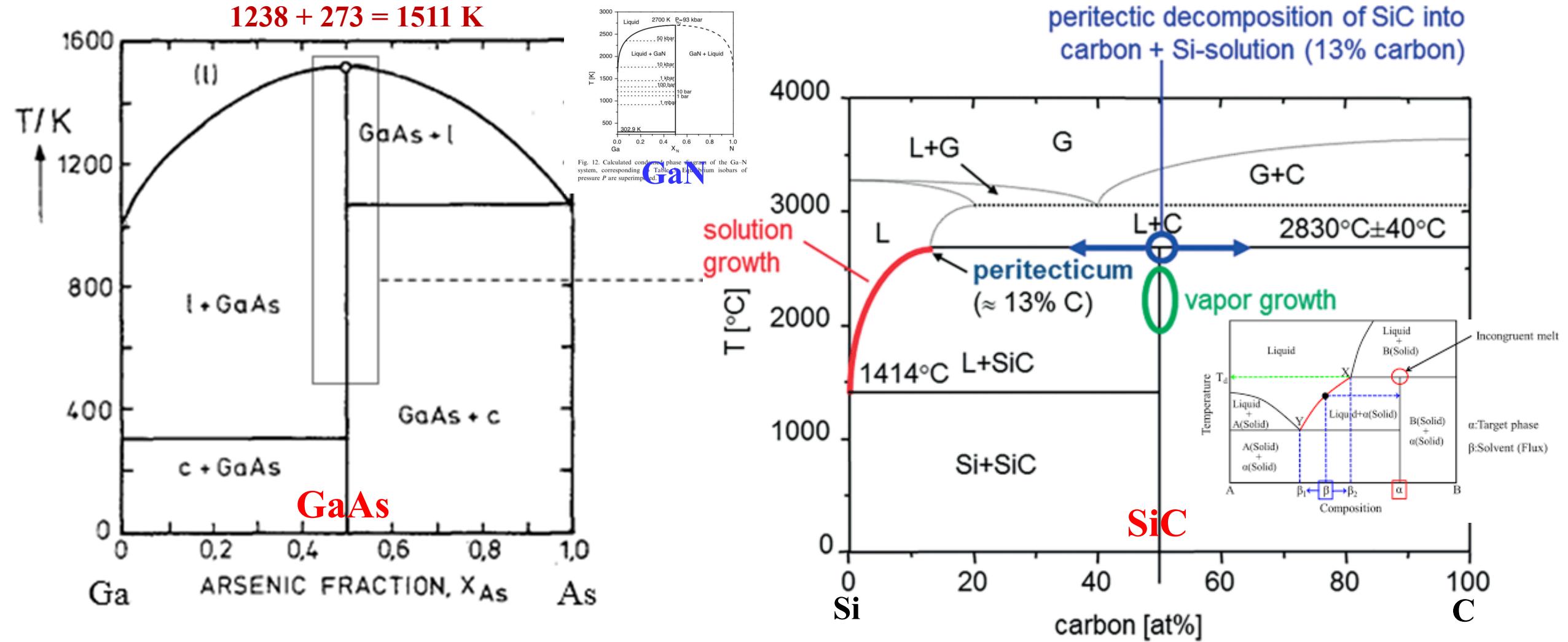
Compact
Reduced Up to 1/1000

High Speed
Up to 100 MHz

Physical properties (@ 300 K) of wide bandgap semiconductors for power electronic applications in comparison to classic semiconductor materials

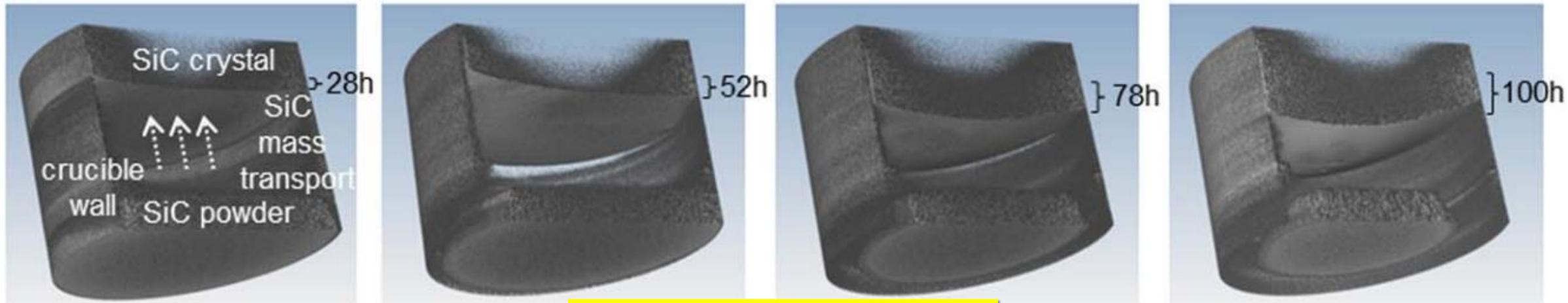
<https://iopscience.iop.org/article/10.1088/1361-6641/aad831>

	4H-SiC	GaN	$\beta\text{-Ga}_2\text{O}_3$	C	Si	GaAs
<i>lattice parameter</i> [Å]	a = 3.08 hexagonal	a = 3.19 hexagonal	a = 12.23 b = 3.04 c = 5.80 $\beta = 103.7^\circ$ monoclinic	3.57 cubic (diamond)	5.43 cubic	5.65 cubic
E_G [eV]	3.2	3.44	4.8	5.0	1.1	1.4
E_B [10^3 V cm $^{-1}$]	40	60	80	100	4	5
λ [Wcm $^{-1}$ K $^{-1}$]	3...5	1.3	0.23	20	1.5	0.5
v_S [10 7 cm s $^{-1}$]	2.5	2.5	2	2.7	1	2
μ_n [cm 2 V $^{-1}$ · s $^{-1}$]	400			2000	1500	9000
E_D [meV]	60 (N)	22 (Si)	20...30 (Sn)		45 (P)	6 (Si)
E_A [meV]	250 (Al)	160 (Mg)		400 (B)	44 (B)	26 (C)
T_S [°C]	2830	2500	1940	3900	1420	1250

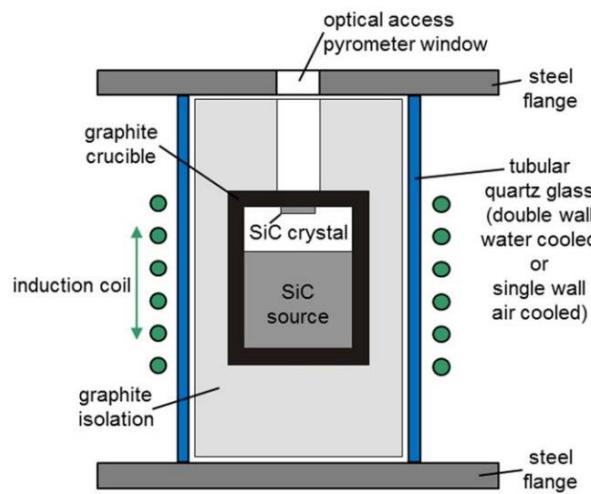


- **GaAs Crystals (Congruently melting binary, 共熔二元化合物)**
- **Phase diagram of Si-C-binary-system (Incongruently melting binary compound, 非一致熔化化合物).** At the peritectic decomposition temperature the compound, rather than melting, decomposes into another solid compound and a liquid ($\text{L} + \text{S}^{(1)} \leftrightarrow \text{S}^{(2)}$).

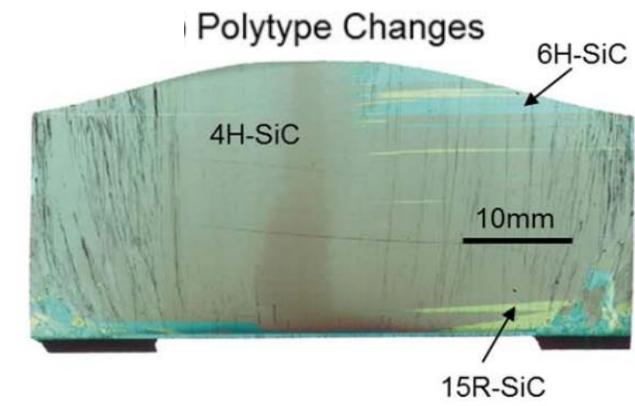
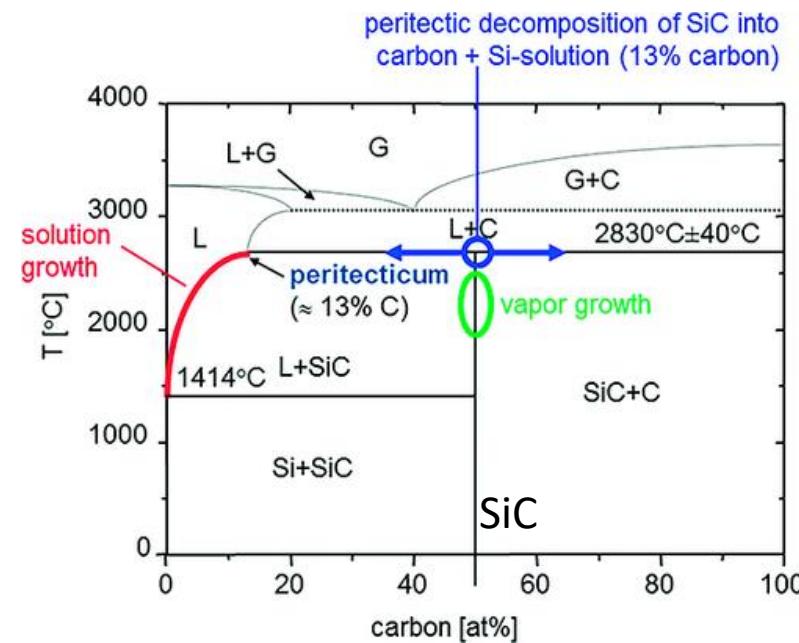
Live 3D X-ray computed tomography view of SiC PVT bulk growth at ca. 2200°C



3D in situ x-ray visualization of **the PVT growth process** using computed tomography:
Detailed visualization of the crystal's growth interface.



Sketch of a **PVT growth** machine
for the preparation of SiC boules



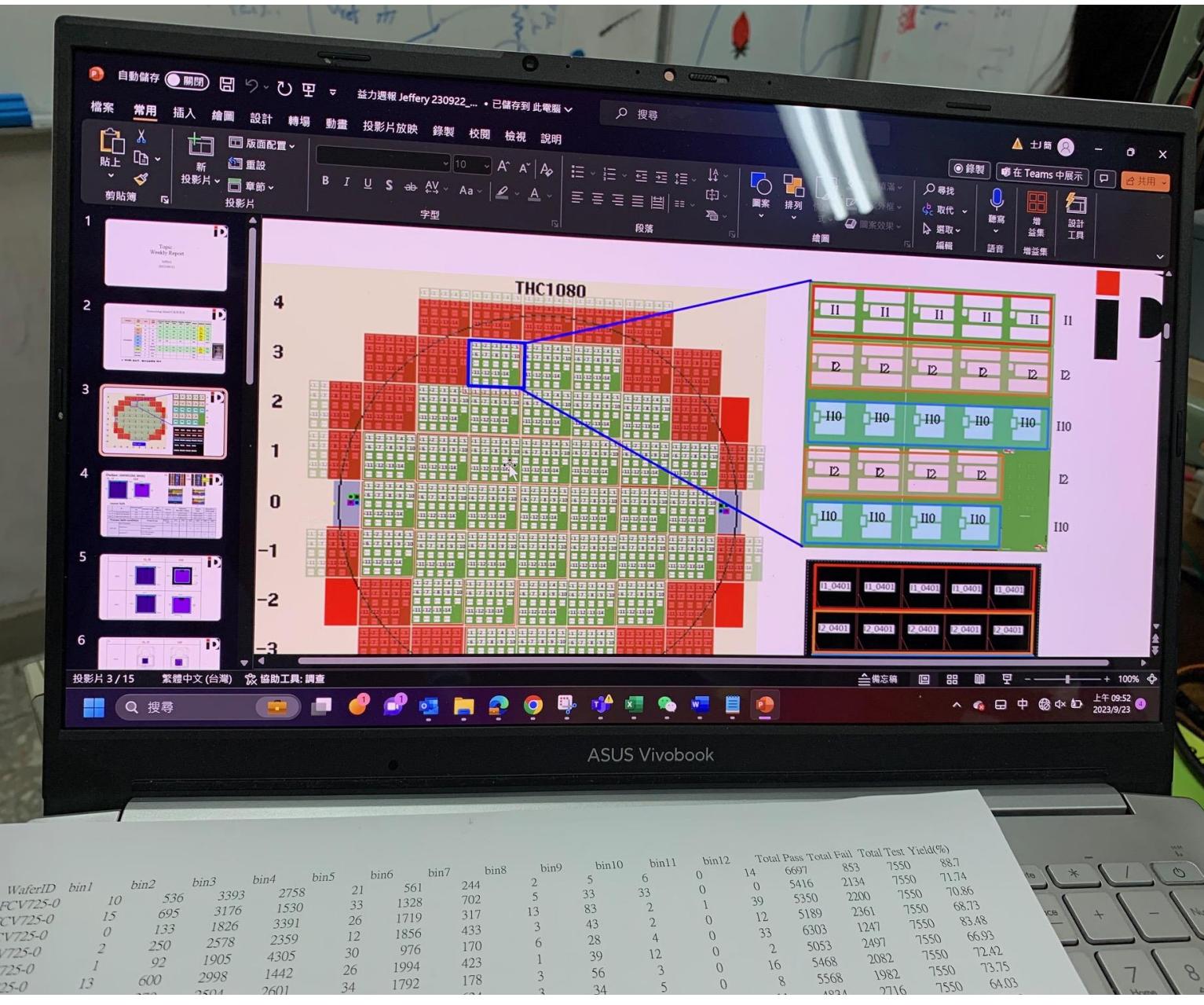
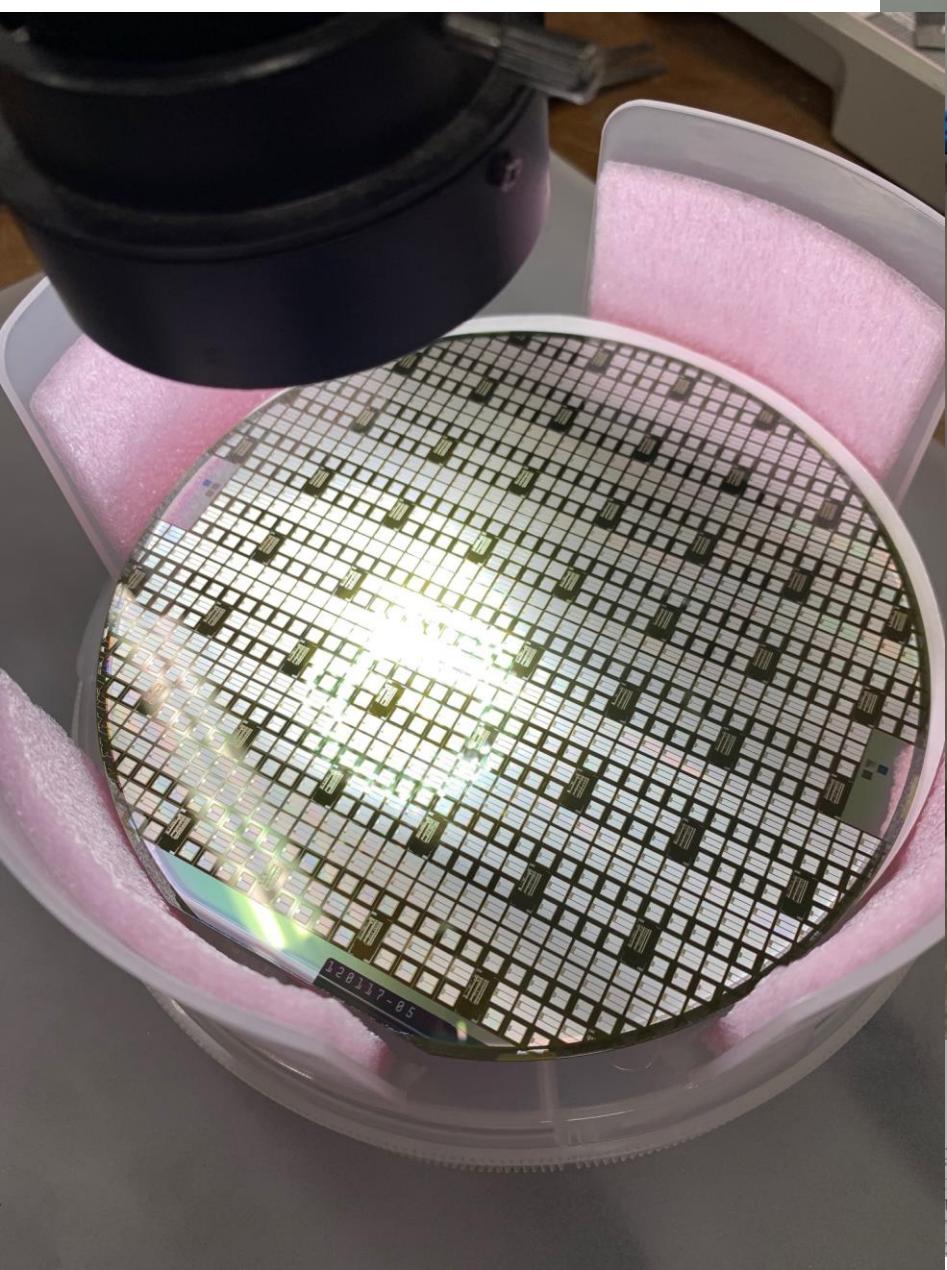
Phase diagram of SiC and
routes of crystal growth using
sublimation or **solution growth**.

		E_g (eV)	μ_n (cm ² /V-s)	μ_p (cm ² /V-s)	m_n^*/m_o (m_l, m_t)	m_p^*/m_o (m_{lh}, m_{hh})	a (Å)	ϵ_r	Density (g/cm ³)	Melting point (°C)
Si	(i/D)	1.11	1350	480	0.98, 0.19	0.16, 0.49	5.43	11.8	2.33	1415
Ge	(i/D)	0.67	3900	1900	1.64, 0.082	0.04, 0.28	5.65	16	5.32	936
SiC (α)	(i/W)	2.86	500	—	0.6	1.0	3.08	10.2	3.21	2830
AlP	(i/Z)	2.45	80	—	—	0.2, 0.63	5.46	9.8	2.40	2000
AlAs	(i/Z)	2.16	1200	420	2.0	0.15, 0.76	5.66	10.9	3.60	1740
AlSb	(i/Z)	1.6	200	300	0.12	0.98	6.14	11	4.26	1080
GaP	(i/Z)	2.26	300	150	1.12, 0.22	0.14, 0.79	5.45	11.1	4.13	1467
GaAs	(d/Z)	1.43	8500	400	0.067	0.074, 0.50	5.65	13.2	5.31	1238
GaN	(d/Z, W)	3.4	380	—	0.19	0.60	4.5	12.2	6.1	2530
GaSb	(d/Z)	0.7	5000	1000	0.042	0.06, 0.23	6.09	15.7	5.61	712
InP	(d/Z)	1.35	4000	100	0.077	0.089, 0.85	5.87	12.4	4.79	1070
InAs	(d/Z)	0.36	22600	200	0.023	0.025, 0.41	6.06	14.6	5.67	943
InSb	(d/Z)	0.18	10 ⁵	1700	0.014	0.015, 0.40	6.48	17.7	5.78	525
ZnS	(d/Z, W)	3.6	180	10	0.28	—	5.409	8.9	4.09	1650*
ZnSe	(d/Z)	2.7	600	28	0.14	0.60	5.671	9.2	5.65	1100*
ZnTe	(d/Z)	2.25	530	100	0.18	0.65	6.101	10.4	5.51	1238*
CdS	(d/W, Z)	2.42	250	15	0.21	0.80	4.137	8.9	4.82	1475
CdSe	(d/W)	1.73	800	—	0.13	0.45	4.30	10.2	5.81	1258
CdTe	(d/Z)	1.58	1050	100	0.10	0.37	6.482	10.2	6.20	1098
PbS	(i/H)	0.37	575	200	0.22	0.29	5.936	17.0	7.6	1119
PbSe	(i/H)	0.27	1500	1500	—	—	6.147	23.6	8.73	1081
PbTe	(i/H)	0.29	6000	4000	0.17	0.20	6.452	30	8.16	925

All values at 300 K.

*Vaporizes

Power devices on 6" SiC substrate (From 益力威芯)



第三代半導體潛力大 各路人馬紛搶進！

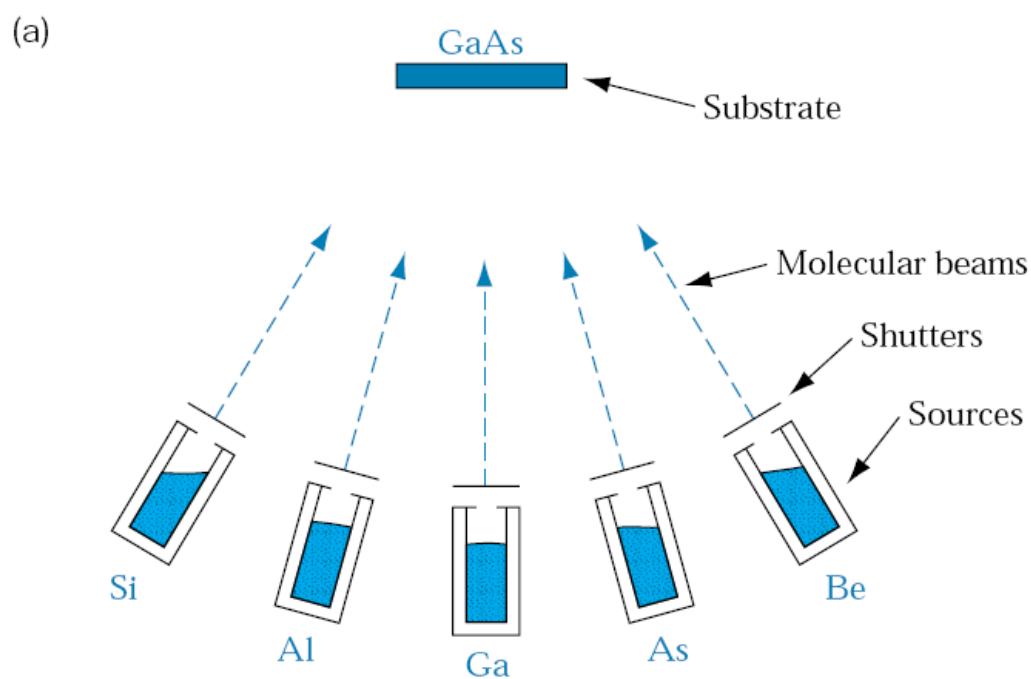
晶成半導體		世界先進	穩懋	三安積體電路
台灣LED晶片 龍頭廠晶電轉投資	晶圓代工龍頭 台積電轉投資	砷化鎵代工龍頭	中國LED晶片龍頭 廠三安光電轉投資	
策略 未來5G基地台、 電動車將衍生新需 求，因此晶電選擇 與環宇-KY策略合 作，布局通訊、充 電、感知領域	看好快充電源 市場，也與氮 化鎵矽基板廠 Qromis合作	因應5G手 機、 基地台的升級趨 勢，從砷化鎵跨 入氮化鎵代工	為加速半導體國 產化速度，從 LED產業跨入氮 化鎵代工	
優勢 6吋 廠 提 供 磚 晶 片、製程前段一條 龍服務	為全球首家提 供8吋矽基氮 化鎵代工服務 的業者	領導市場投入技 術 研 發，2013 年開始提供氮化 鎵代工服務	中國首家6吋化 合物半導體晶圓廠	

2021-02-24

整理：王子承

<https://www.businesstoday.com.tw/article/category/183015/post/202102240007/>

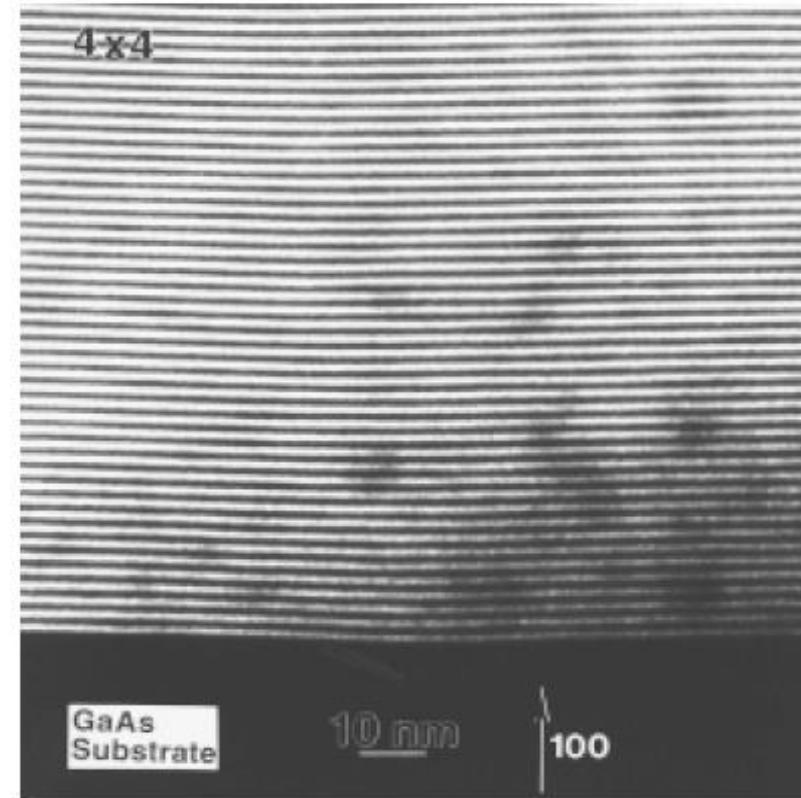
1.4.3 Molecular Beam Epitaxy, Stoichiometric ratio: III:V = 1:1



Replacing some of the solid sources with gaseous chemical sources, chemical beam epitaxy, or gas-source MBE

Figure 1-16

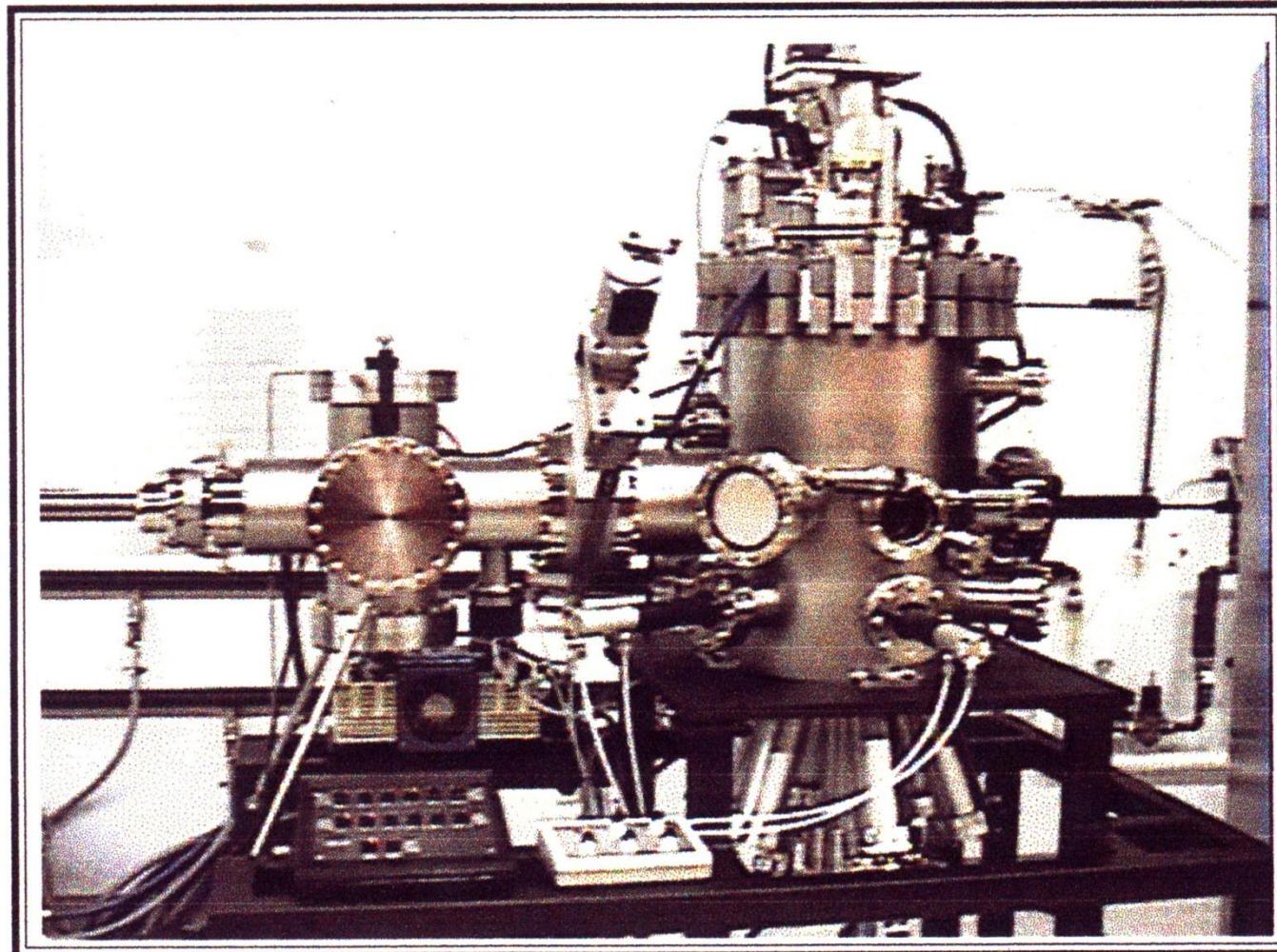
Crystal growth by molecular beam epitaxy (MBE): (a) evaporation cells inside a high - vacuum chamber directing beams of Al, Ga, As, and dopants onto a GaAs substrate; (b) scanning electron micrograph of the cross section of an MBE-grown crystal having alternating layers of GaAs (dark lines) and AlGaAs (light lines). Each layer is four monolayers ($4 \times a/2 = 11.3\text{\AA}$) thick. (Photograph courtesy of Bell Laboratories.)



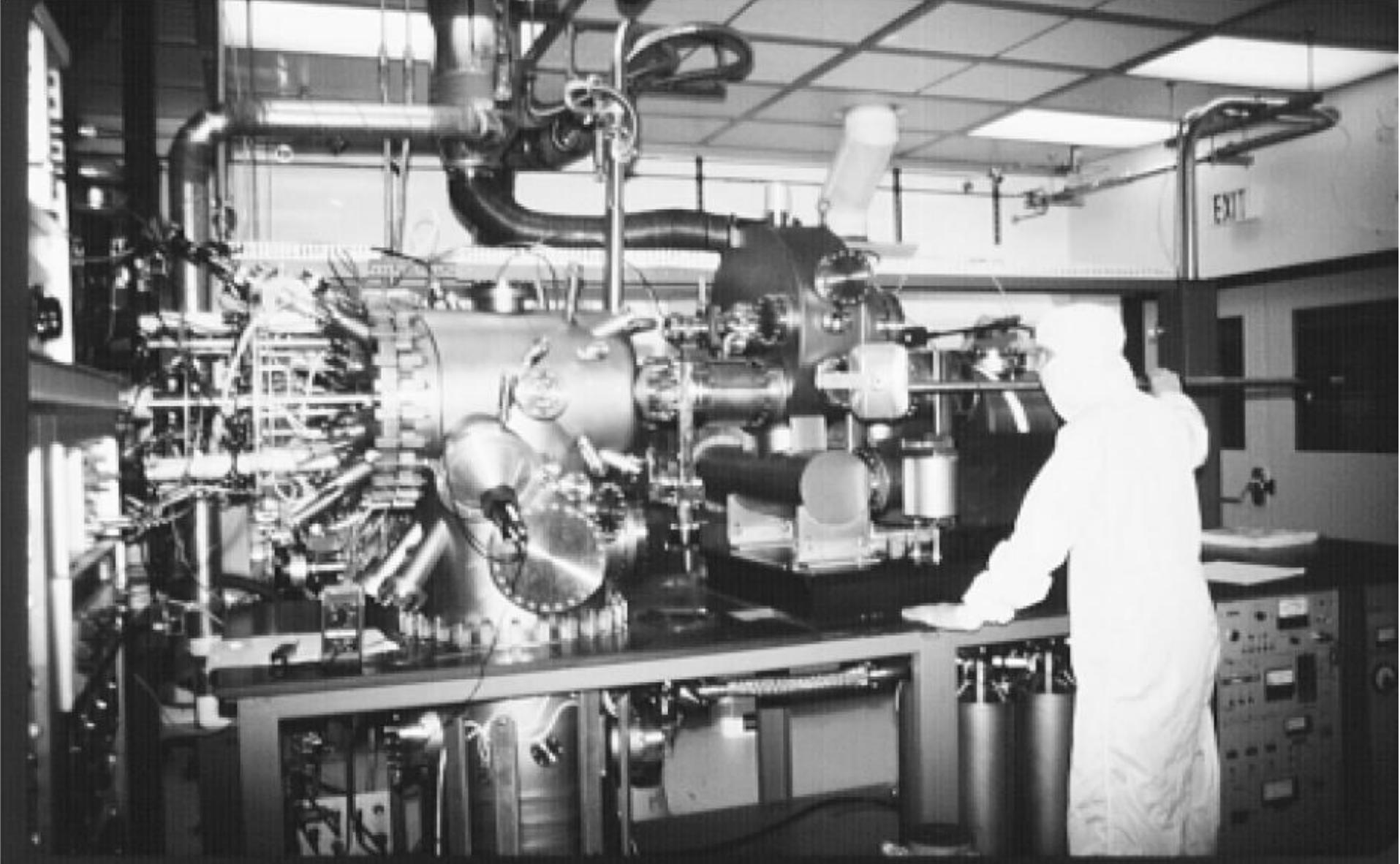
中原物理

<https://youtu.be/0t8M0nd10fo>

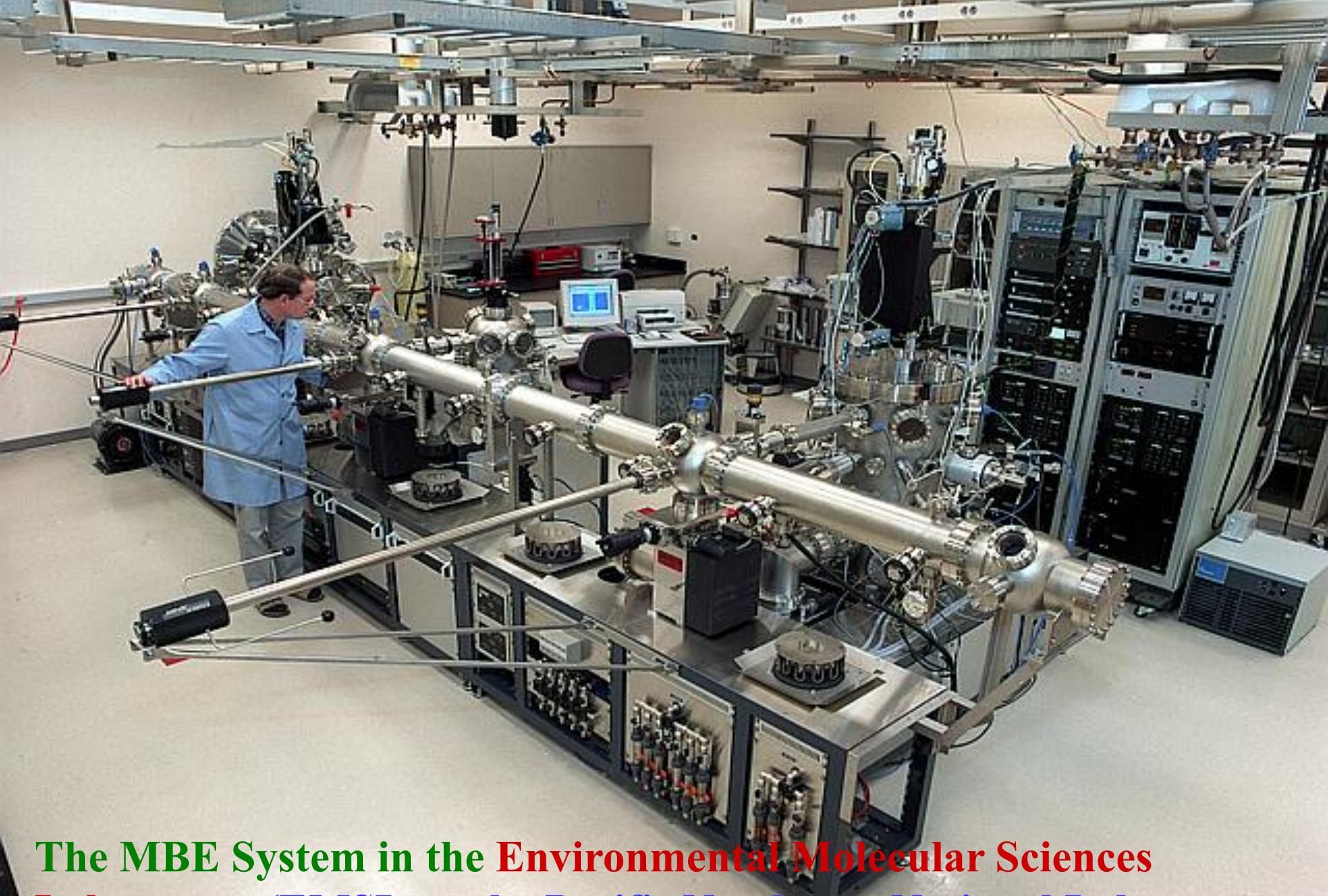
EPI
Model 620
Molecular Beam Epitaxy System



Rev Date: 11/96



Molecular beam epitaxy facility in the Microelectronics Research Center at the University of Texas at Austin.



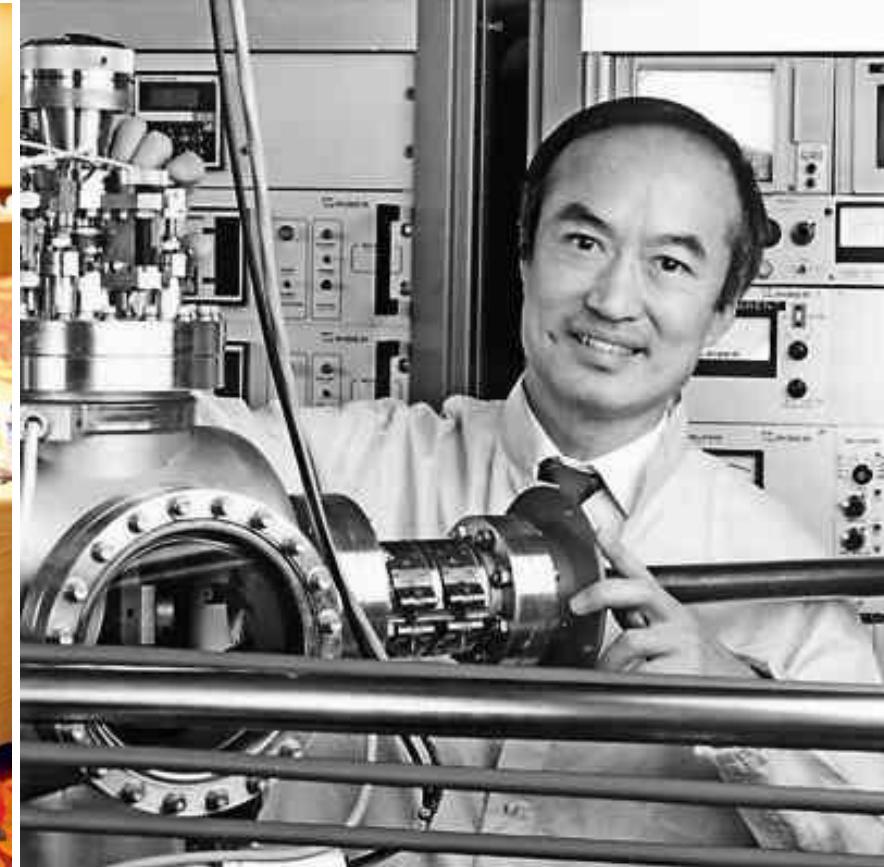
The MBE System in the Environmental Molecular Sciences Laboratory (EMSL, at the Pacific Northwest National Laboratory, Richland, Washington)

Molecular Beam Epitaxy: MBE

- MBE was invented in the late 1960s at Bell Telephone Laboratories by J. R. Arthur and Alfred Y. Cho (卓以和). MBE takes place in ultra high vacuum (10^{-8} Pa = 7.5×10^{-11} torr). The most important aspect of MBE is the slow deposition rate (typically less than 3 Å/sec), which allows the films to grow epitaxially at relatively low substrate temperature.
- In solid-source MBE, ultra-pure elements such as gallium and arsenic are heated in separate quasi-Knudsen effusion cells until they begin to slowly sublime. The gaseous elements then condense on the heated substrate, where they may react with each other to form epitaxial (single-crystal like) layer. The term “molecular beam” means that evaporated atoms do not interact with each other or vacuum chamber gases until they reach the substrate, due to the long mean free paths of the atoms.
- It has become common to replace some of the solid sources with gaseous chemical source. This approach, called chemical beam epitaxy, or gas-source MBE, combines many of the advantages of MBE and VPE.
- PIMBE: plasma-induced MBE.

卓以和 美國華裔 電機工程與物理學家

- 卓以和於1937年生於北京。1949年全家移住香港，就讀於培正中學。卓以和高中畢業後，在 University of Illinois at Urbana-Champaign 取得電機工程學士、碩士和博士學位。



- 卓以和的主要貢獻是發明分子束磊晶 (Molecular beam epitaxy, MBE) 技術和量子級聯雷射器 (Quantum cascade laser)。曾任貝爾實驗室助理副總裁 (Adjunct Vice President of Semiconductor Research at Alcatel-Lucent's Bell Labs)。

Contents

- 1.1 Semiconductor Materials
- 1.2 Crystal Lattices
- 1.3 Bulk Crystal Growth
- 1.4 Epitaxial Layer (磊晶) Growth
- 1.5 Wave propagation in discrete, periodic structures

Transport of electrons (Wave–particle duality) in crystal

https://en.wikipedia.org/wiki/Wave%20%E2%80%93particle_duality

1.5 Wave propagation in discrete, periodic structures

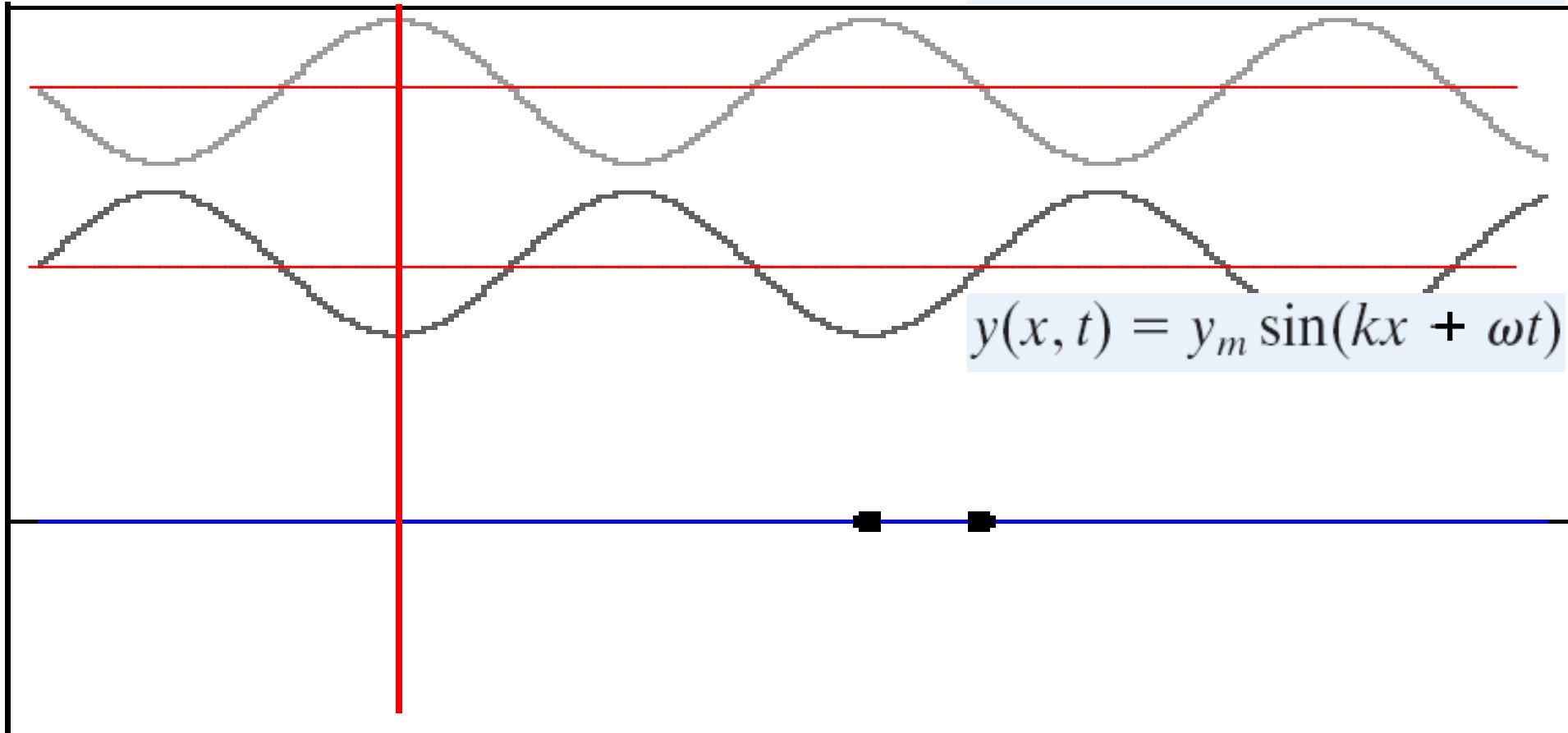
- Consider a plane wave $\psi(x,t) = A \exp\{j(kx \pm \omega t)\} = A\{\cos(kx \pm \omega t)\} + j\sin(kx \pm \omega t)\}$ (electron wave-function) in a medium made of discrete, periodic atoms. Traveling wave \Leftrightarrow standing wave. (see Fig. A)
- A transverse sinusoidal wave is characterized by various parameters: period T , frequency $f = 1/T$, angular frequency $\omega = 2\pi f = 2\pi/T$, wavelength λ , wave number $\kappa = 1/\lambda$, angular wave number $k = 2\pi\kappa = 2\pi/\lambda$, speed of wave $v_p = \lambda f$, group velocity of a wave packet $v_g = d\omega/dk$, ... (see Fig. B)
- A plane wave propagating in a finite crystal with lattice constant a and of length $L = Na$, where N is the number of atoms (see Fig. 1-18a). One may deal with not a single wave train, but a wave pack, made up of a superposition of various waves (Fig. 1-18b).

Fig. A

Traveling wave versus standing wave

Traveling wave (行進波)

$$y(x, t) = y_m \sin(kx - \omega t)$$

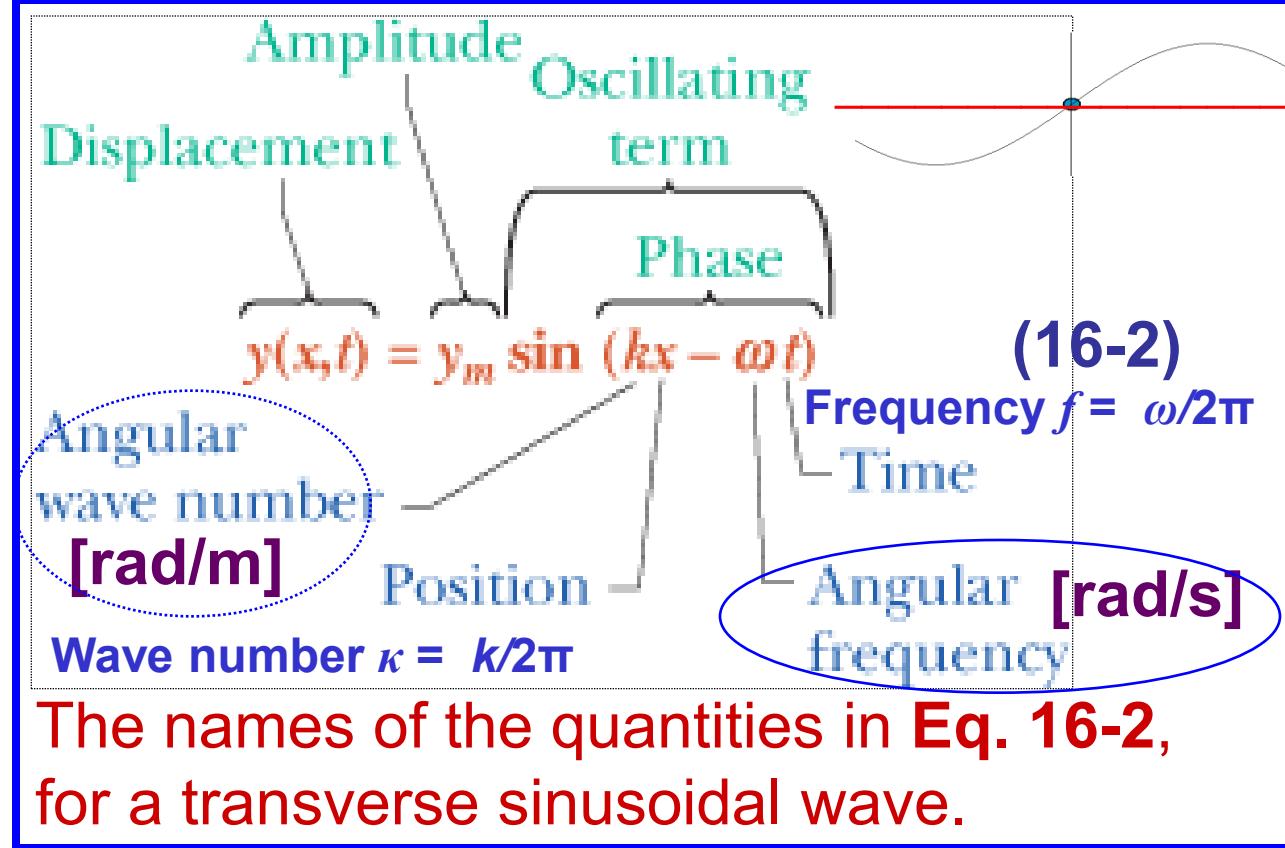


Standing wave (駐波)

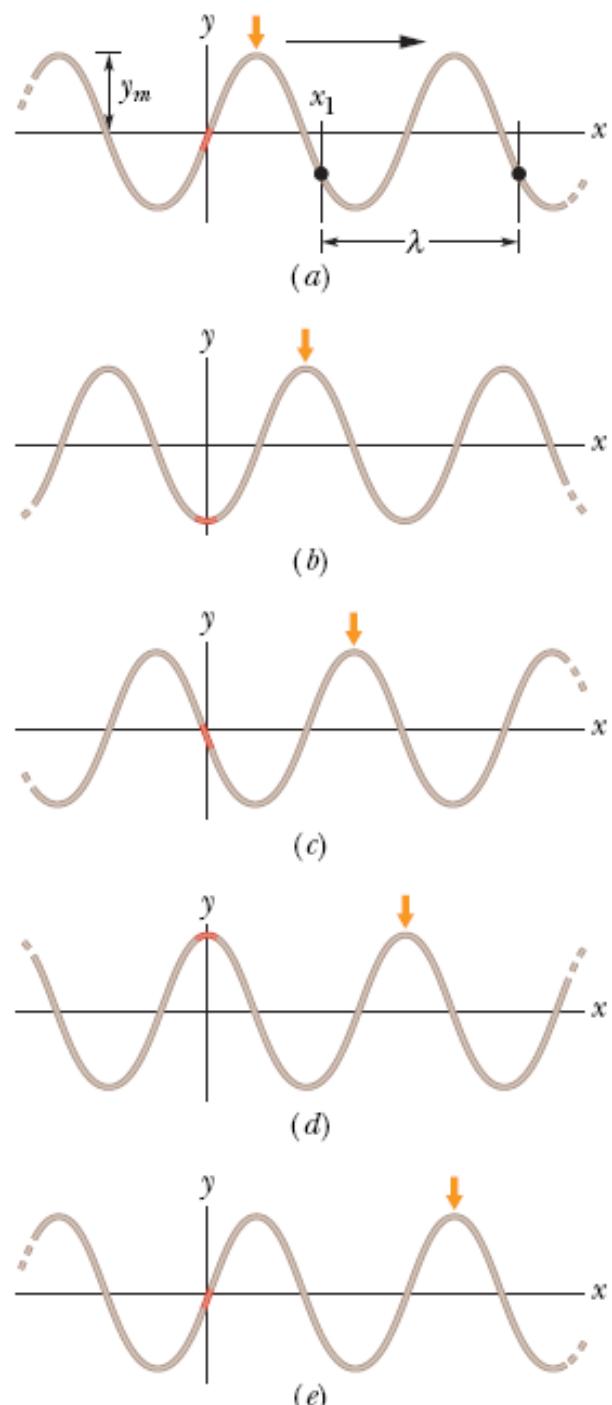
$$y'(x, t) = [2y_m \sin kx] \cos \omega t,$$

$$\Psi(x, t) = A \exp\{j(kx \pm \omega t)\} = A\{\cos(kx \pm \omega t)\} + j\sin(kx \pm \omega t)\}$$

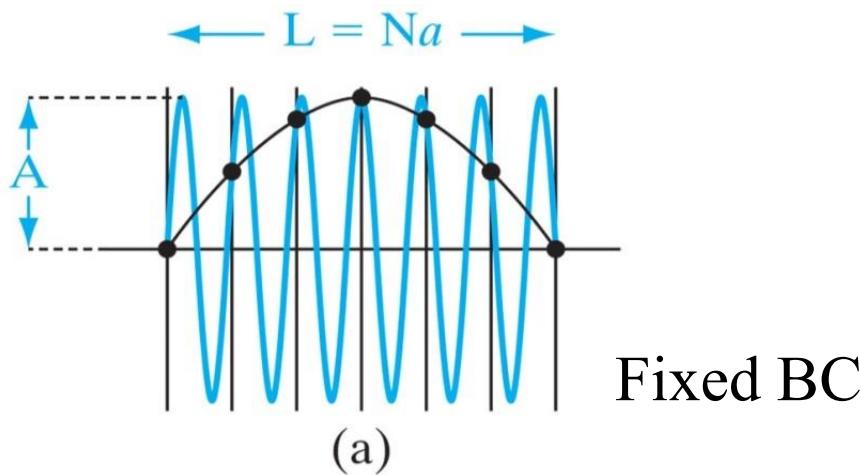
Fig. B



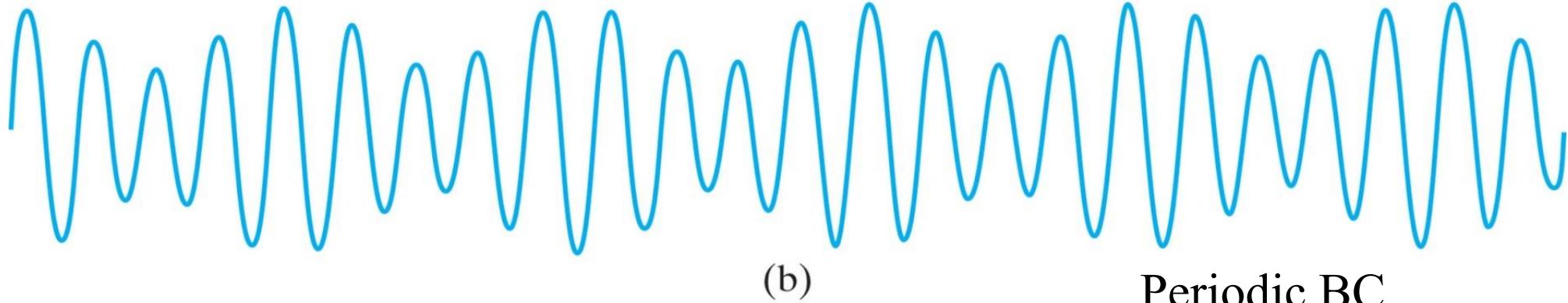
- Five “snapshots” of a string wave traveling in the positive direction of an x axis. The amplitude y_m is indicated. A typical wavelength λ , measured from an arbitrary position x_1 , is also indicated.
- From snapshot to snapshot, the short arrow moves to the right with the wave shape, but the string moves *only* parallel to the y axis.



A standing wave



A propagating wave

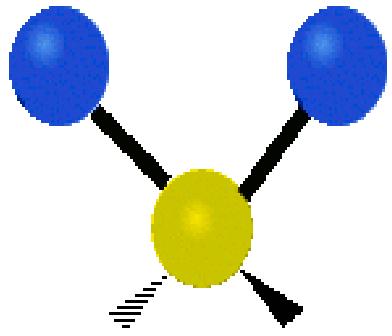


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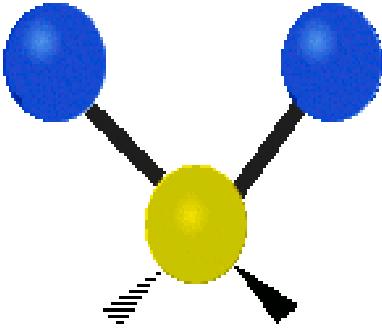
Periodic BC

Fig. 1–18 (a) **The displacement pattern of the atoms** (see next page) shown in a 1D crystal can be described equivalently by a longer or shorter wavelength. (b) A more complicated wave involving a mixing of two wavelengths (or Fourier components in k -space) giving rise to a beat pattern. By using a periodic boundary condition for the finite crystal in (a), one ends up with propagating waves rather than standing waves, making the math simpler.

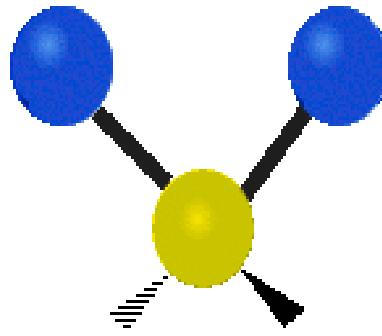
Intramolecular vibration (simply molecular modes)



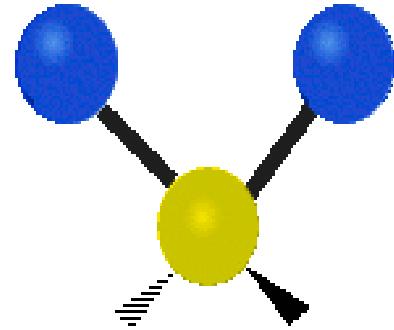
Symmetrical
stretching



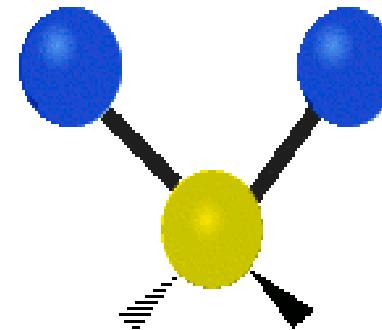
Anti-symmetrical
stretching



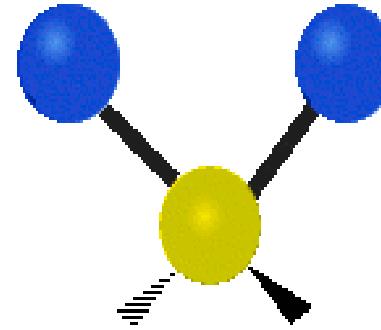
Rocking



Scissoring



Twisting



Wagging

Waves propagation in periodic structures

- Analogy to Fourier transform from a periodic signal in the time domain to the frequency domain, for periodic BCs one can use Fourier transform to describe the waves in real space, x , to its reciprocal k_x -space.
- In Chap. 3, the waves describing physical displacement of atoms correspond to sound waves propagating in the crystal, and are called phonons (聲子).
- In Chaps. 2 & 3, the electrons (fundamental particle) propagating in crystals can be described by a wave (matter wave) using the language of quantum mechanics, in term of a complex “wave-function”. Such electron wavefunctions are described by the plane wave mentioned above multiplied by another function $U(k_x, x) = U(k_x, x + a)$ having the same periodicity as the lattice. Such wavefunctions are known as Bloch functions.

Schrodinger equation in 1D

$$-\frac{\hbar^2}{2m}(\partial^2\Psi/\partial x^2) + U\Psi = -\frac{\hbar^2}{m}\frac{\partial^2\Psi}{\partial t^2}$$

Separation of variables $\Psi(x, t) = \psi(x)\varphi(t)$ leads

$$\frac{d\varphi(t)}{dt} + \frac{jE}{\hbar}\varphi(t) = 0; \text{ and}$$

Time-independent 1D Schrodinger equation

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}[E - U(x)]\psi(x) = 0.$$

For a particular potential energy form $U(x)$, one can solve the eigenfunctions $\psi_n(x)$ corresponding to the eigenvalues E_n .

Bloch function (Bloch wave):

A periodic function which appears in the solution of the Schrödinger equation with periodic potential

- In 1D time-independent Schrodinger equation, the wave function $\Psi_k(x)$ of a single electron (\because wave-particle duality) is assumed to be in the form of a plane wave moving, in x -direction with propagation constant (wave number) k , through a periodic lattice with potential $U(k, x)$ is (called the Bloch function)

$$\Psi_k(x) = U(k, x) e^{jkx}$$

$$(\Psi(x, t) = A e^{-j(\omega t - kx)} = A e^{-(j/\hbar)(Et - px)})$$

- In such a calculation, allowed values of energy E can be plotted vs. k , i.e., the (E - k) diagram (Remember that the electron momentum $\langle p \rangle = \hbar k$) can be considered as a plot of electron energy vs. momentum.

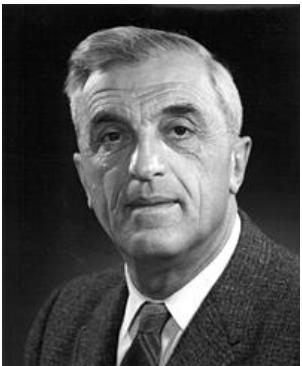
During 1924~1927 **Bloch** attended lectures and seminars given by Peter Debye and Hermann Weyl at ETH Zürich and Erwin Schrödinger at the neighboring University of Zürich.

Heisenberg and the early days of quantum mechanics

Felix Bloch

(Doctoral advisor: W. Heisenberg)

Citation: Phys. Today 29(12), 23 (1976); doi: 10.1063/1.3024633

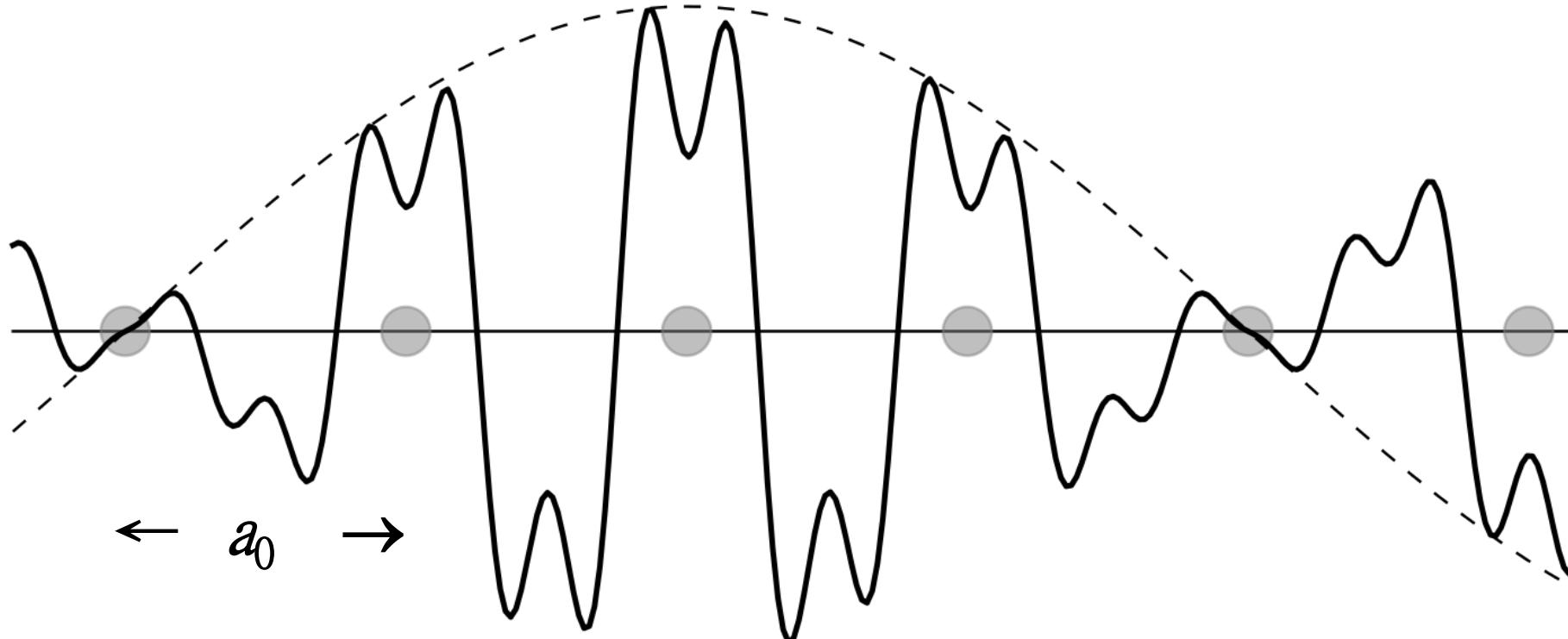


Felix Bloch (1905 – 1983) was a Swiss-American physicist and Nobel physics laureate who worked mainly in the U.S. He and **Edward Mills Purcell** were awarded the 1952 Nobel Prize for Physics for “their development of new ways and methods for nuclear magnetic precision measurements”.

Known for NMR, Magnon, Bloch wall, Bloch's Theorem, Bloch Function (Wave), Bloch sphere

1D Bloch function $\Psi = Ae^{j\mathbf{k}_x \cdot \mathbf{x}} u_{\mathbf{k}_x}(\mathbf{x})$ 示意圖

$$e^{j\mathbf{k}_x \cdot \mathbf{x}} = \cos(\mathbf{k}_x \cdot \mathbf{x}) + j \sin(\mathbf{k}_x \cdot \mathbf{x})$$



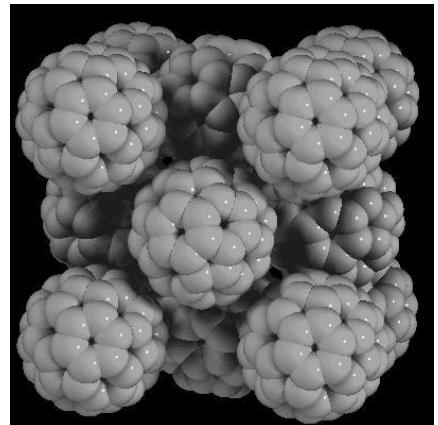
[Bloch function - Bloch's theorem – Wikipedia](#)

灰色圓點代表原子在 1D 的規則排列；實線代表 1D Bloch 複變函數 (Complex function) 實部；虛線來自 $e^{j\mathbf{k}_x \cdot \mathbf{x}}$ 的實部 (此函數之 $k_x = 2\pi/\lambda$, 波長 $\lambda = 8a_0$)。

Summary

- Elemental semiconductors \leftrightarrow compound semiconductors => more complicated alloy semiconductors are used to optimize optoelectronic properties.
- These devices are made in single-crystal, polycrystalline, and amorphous materials.
- Crystal lattices for common semiconductors: diamond (D), zinc blende (Z), wurtzite (W), and halite (H).
- Primitive cell: fundamental building block of a lattice.
- Miller indices.
- Defects in real crystals, some of which are benign, but many of which are harmful for device operation.
- Crystal growth: bulk crystals, epitaxial layers

Homework #2 for Chapter 1: A2, A3, A4, 18



A2: The solid phase for C₆₀ (molecular weight = $60 \times 12 = 720$ g/mole) has the crystal structure of *fcc* with a lattice constant of 14.17 Å, please calculate its mass density.

A3: In a Bragg diffraction analysis, the order of diffraction $n = 2$, the wavelength $\lambda = 154$ pm, and the diffraction angle $\theta = 22.2^\circ$. Solve for the spacing between the crystal planes $d = ?$

A4: A Si crystal is to be pulled from the melt and doped with P. If the Si crystal weighs 275 kg, how many grams of P should be introduced to achieve $5.0 \times 10^{16} \text{ cm}^{-3}$ doping during the initial growth? What happened with the doping concentration on the final growth part?

TABLE 1 Equilibrium Segregation Coefficients for Dopants in Si

Dopant	k_0	Type	Dopant	k_0	Type
B	8×10^{-1}	p	As	3.0×10^{-1}	n
Al	2×10^{-3}	p	Sb	2.3×10^{-2}	n
Ga	8×10^{-3}	p	Te	2.0×10^{-4}	n
In	4×10^{-4}	p	Li	1.0×10^{-2}	n
O	1.25	n	Cu	4.0×10^{-4}	— ^a
C	7×10^{-2}	n	Au	2.5×10^{-5}	— ^a
P	0.35	n			

^aDeep-lying impurity level.

Distribution coefficient k_d

TABLE 2 Equilibrium Segregation Coefficients for Dopants in GaAs

Dopant	k_0	Type
Be	3	p
Mg	0.1	p
Zn	4×10^{-1}	p
C	0.8	n/p
Si	1.85×10^{-1}	n/p
Ge	2.8×10^{-2}	n/p
S	0.5	n
Se	5.0×10^{-1}	n
Sn	5.2×10^{-2}	n
Te	6.8×10^{-2}	n
Cr	1.03×10^{-4}	Semiinsulating
Fe	1.0×10^{-3}	Semiinsulating

- 1.18 Assuming that the lattice constant varies linearly with composition x for a ternary alloy (e.g., see the variation for InGaAs in Fig. 1-13),
(a) what composition of $\text{AlSb}_x\text{As}_{1-x}$ is lattice-matched to InP?
(b) What composition of $\text{In}_x\text{Ga}_{1-x}\text{P}$ is lattice-matched to GaAs?
(c) What is the band gap energy in each case?
- [Note: Such linear variations of crystal properties (e.g., lattice constant and band gap) with mole fraction in alloys is known as Vegard's law. A second-order polynomial or quadratic fit to the data is called the bowing parameter.]

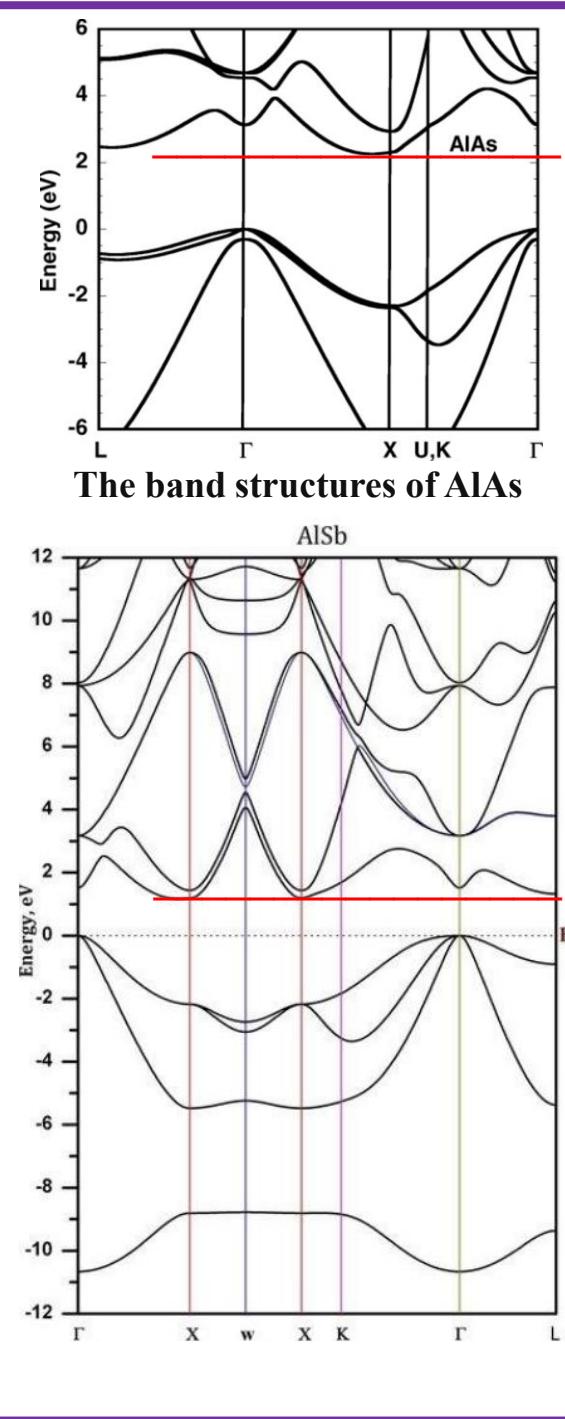
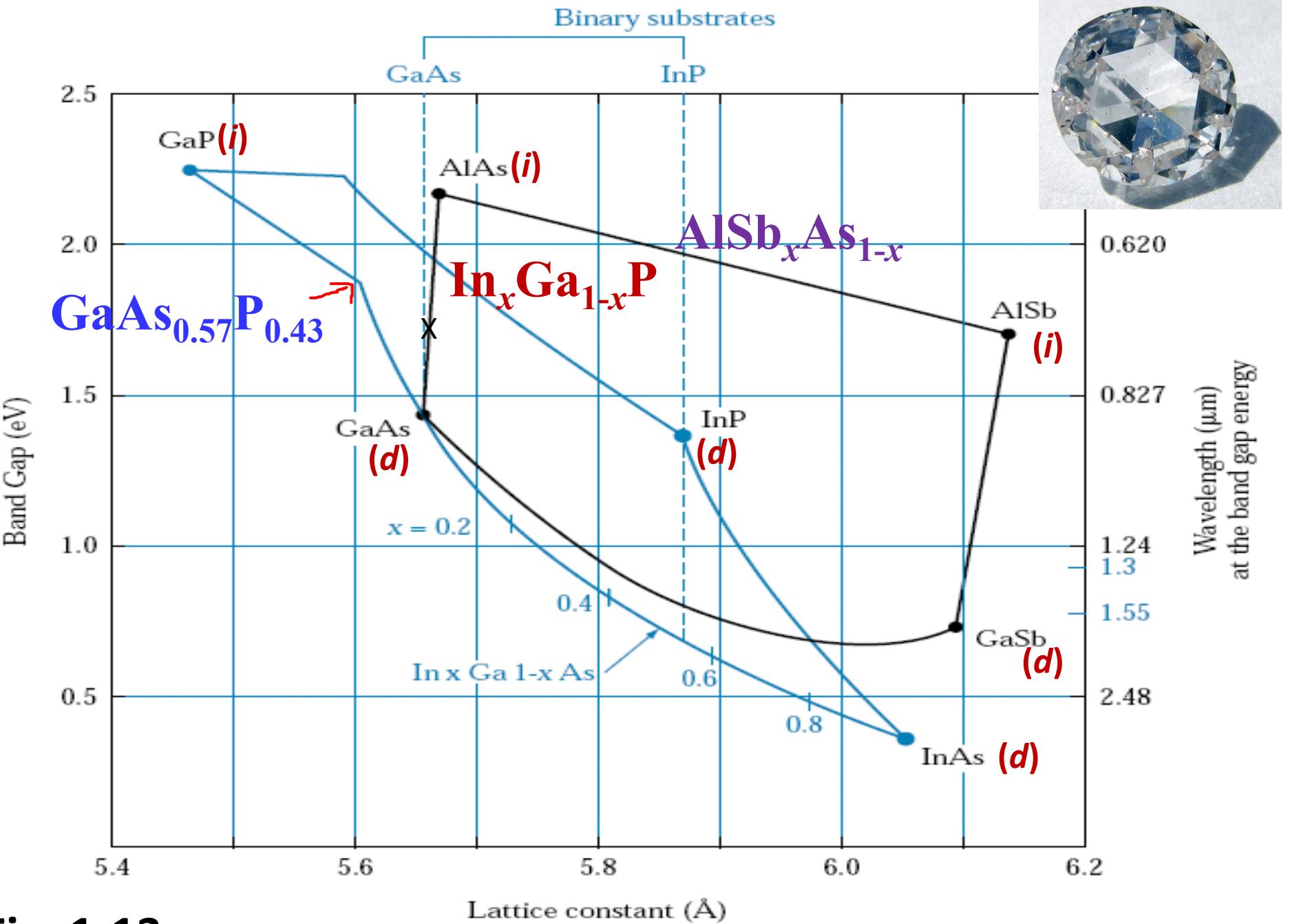
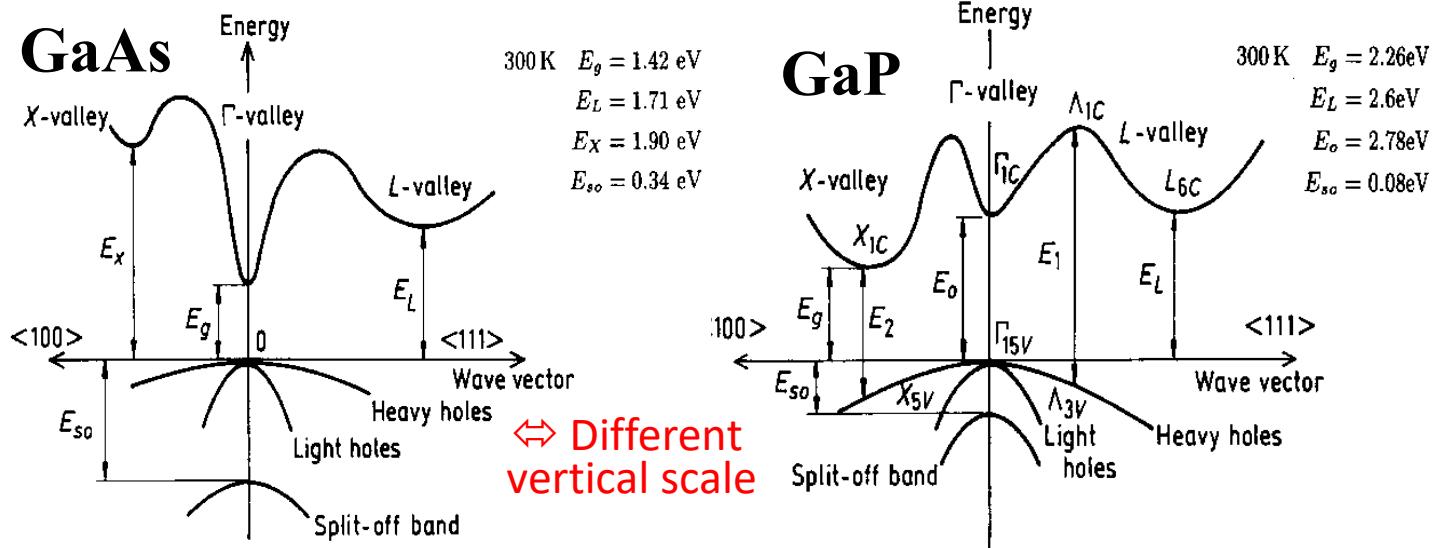


Fig. 1-13

三元化合物半導體 $\text{GaAs}_{1-x}\text{P}_x$ 的 E_g 隨組成比 x 而變 => Bandgap engineering



<http://www.ioffe.ru/SVA/NSM/Semicond/GaAs/Figs/421.gif>

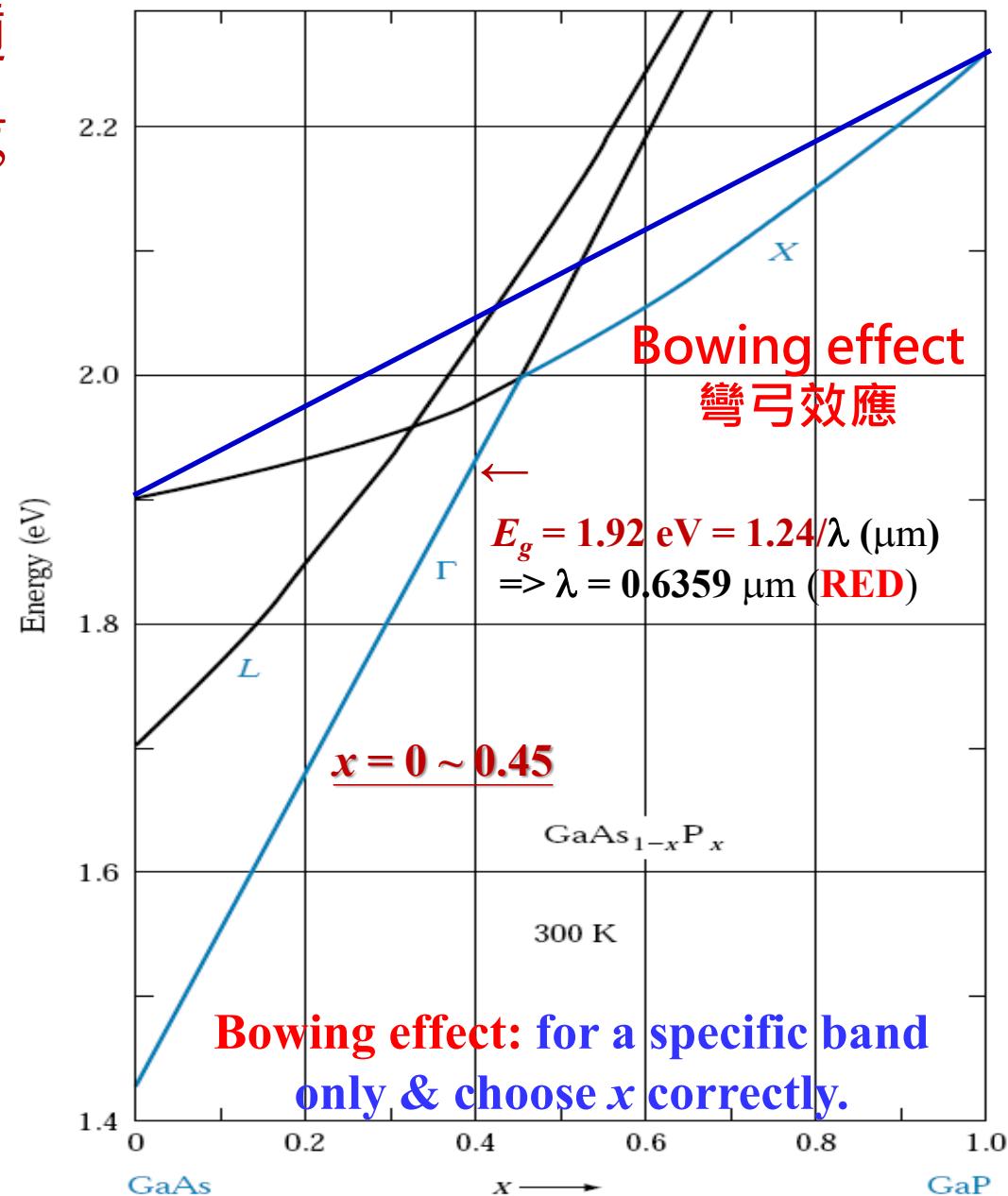
<https://www.ioffe.ru/SVA/NSM/Semicond/GaP/Figs/521.gif>

For the same Γ -band:

$$E_\Gamma(\text{GaAs}_{1-x}\text{P}_x) = [xE_\Gamma(\text{GaP}) + (1 - x)E_\Gamma(\text{GaAs})] - b_\Gamma x(1 - x)$$

For the same X-band:

$$E_X(\text{GaAs}_{1-x}\text{P}_x) = [xE_X(\text{GaP}) + (1 - x)E_X(\text{GaAs})] - b_X x(1 - x)$$



Bowing of the defect formation energy in semiconductor alloys, from *Phys. Rev. B* 87, 241201(R) (2013)

- Alloying different semiconductors is a popular approach to broaden the range of available material properties for specific applications. Considerable efforts have been made to understand **the compositional dependence of properties** of **isovalent $A_xB_{1-x}C$** (e.g., $\text{Al}_x\text{Ga}_{1-x}\text{As}$) semiconductor alloys. **Many alloy properties $P(A_xB_{1-x}C)$ can be described as a linear average of the corresponding quantities in two pure constituents and a quadratic term,**
- $$P(A_xB_{1-x}C) = [xP(AC) + (1 - x)P(BC)] - bx(1 - x),$$
 where **b** is the so-called **bowing coefficient**.
- Generally, **for isovalent alloys** with a **small chemical and size mismatch**, the **bowing coefficients are small constant numbers**; for alloys with a **large chemical and size mismatch**, the **bowing coefficients** could be **large and composition dependent**.

Avogadro's number	$N_A = 6.02 \times 10^{23}$ molecules/mole
Boltzmann's constant	$k = 1.38 \times 10^{-23} \text{ J/K}$ $= 8.62 \times 10^{-5} \text{ eV/K}$
Electronic charge (magnitude)	$q = 1.60 \times 10^{-19} \text{ C}$
Electronic rest mass	$m_0 = 9.11 \times 10^{-31} \text{ kg}$
Permittivity of free space	$\epsilon_0 = 8.85 \times 10^{-14} \text{ F/cm}$ $= 8.85 \times 10^{-12} \text{ F/m}$
Planck's constant	$h = 6.63 \times 10^{-34} \text{ J-s}$ $= 4.14 \times 10^{-15} \text{ eV-s}$
Room temperature value of kT	$kT = 0.0259 \text{ eV}$
Speed of light	$c = 2.998 \times 10^{10} \text{ cm/s}$

1 Å (angstrom) = 10^{-8} cm
 1 μm (micron) = 10^{-4} cm
 1 nm = 10 Å = 10^{-7} cm
 2.54 cm = 1 in.
 1 eV = 1.6×10^{-19} J

Prefixes:

milli-,	m-	$= 10^{-3}$
micro-,	μ-	$= 10^{-6}$
nano-,	n-	$= 10^{-9}$
pico-,	p-	$= 10^{-12}$
kilo-,	k-	$= 10^3$
mega-,	M-	$= 10^6$
giga-,	G-	$= 10^9$

A wavelength λ of 1 μm corresponds to a photon energy of 1.24 eV.

希臘字母 ⇔ 拉丁字母 ⇔ 英文字母

https://tw.dictionary.search.yahoo.com/_ylt=AwrsmD2DlaBY5SwAuQh9rolQ

希臘字母 (約在2900年前出現) 源自**腓尼基字母** (約在3100年前出現). **羅馬人**引進希臘字母, 略微改變為**拉丁字母** (約在2700年前). 現在**希臘字母**仍廣泛應用到學術領域, 如物理, 數學等, 以代表某個特定參數或物理量.

拉丁字母 主要有以下26 **(英文)字母**, 在19世紀時擴散為全世界最通行的字母.

A	B	C	D	E	F	G	H	I	J	K	L	M
N	O	P	Q	R	S	T	U	V	W	X	Y	Z

These 24 letters (**希臘字母**, in Times New Roman) are:

A α , B β , Γ γ , Δ δ , E ϵ , Z ζ , H η , Θ θ , I ι ,
K κ , Λ λ , M μ , N ν , Ξ ξ , O \circ , Π π , P ρ , Σ σ/ς ,
T τ , Y υ , Φ ϕ , X χ , Ψ ψ , and Ω ω .

Greek alphabet

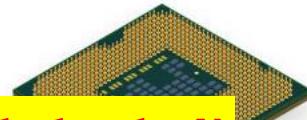
字母	名字			
	希臘語	拉丁語		
A α	Αλφα	Alpha	Κ κ	Καππα Kappa
B β	Βητα	Beta	Λ λ	Λαμδα Lambda
Γ γ	Γαμμα	Gamma	Μ μ	Μυ Mu
Δ δ	Δελτα	Delta	Ν ν	Νυ Nu
Ε ε	Εψιλον	Epsilon	Ξ ξ	Ξι Xi
Ζ ζ	Ζητα	Zeta	Ο ο	Ομικρον Omicron
Η η	Ητα	Eta	Π π	Πι Pi
Θ θ	Θητα	Theta	Ρ ρ	Ρω Rho
Ι ι	Ιωτα	Iota	Σ σ	Σιγμα Sigma
			Τ τ	Ται Tau
			Υ υ	Υψιλον Upsilon
			Φ φ	Φι Phi
			Χ χ	Ξι Chi
			Ψ ψ	Ψι Psi
			Ω ω	Ωμεγα Omega

https://officencycu-my.sharepoint.com/:f/g/personal/74181_o365tc_cycu_edu_tw/Et3dVELCERxDpdP6VILMwhYB4Gg38WFNgS30E67VG-vg7Q?e=LO7YMS

改變世界的半導體

半導體的歷史、原理、及科技發展

課外指定閱讀 (列入考試範圍)



1. 半導體科技的發展簡史 (4) (1.1 - 1.4)
2. 物理學的革命及半導體物理理論的發展 (6)
3. 半導體元件: p-n 二極體 (摻雜與接合) (8)
4. 除了電子, 還有光子! 半導體光電元件的發展
5. 雙極式接合電晶體 (Bipolar Junction Transistors)
6. 場效應電晶體 (Field-Effect Transistors, FETs)

物理一乙 (PH148B) 半導體元件發展史

授課教師 : 邱寬城

相關影片

- AMD (Advanced Micro Devices) CPU 製作過程 (中文, 10 min, 2011)

<https://youtu.be/wOuYLq6vfLE>

- 張忠謀大談和 IC 發明人的互動過程/旺宏電子盧志遠、鈺創盧超群、聯電簡山傑、科技部長陳良基揭開台灣IC產業的發展軌跡/非凡矽島台灣(上集) (2018年12月26日, 48:02 min) <https://www.youtube.com/watch?v=hqMAssDEdD4>

- 聯發科蔡明介、日月光吳田玉、環球晶徐秀蘭－台灣半導體關鍵人物揭開台灣如何迎戰全球競爭/非凡矽島台灣(下集) (2019年1月8日, 48:00 min)

<https://www.youtube.com/watch?v=Sd5J5YSZINQ>



The End

謝謝您的聆聽！



From snowcrystals.com