

Semiconductor Manufacturing Technology

Chapter 5

Chemicals in Semiconductor Fabrication

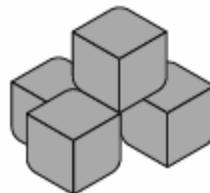
Objectives

After studying the material in this chapter, you will be able to:

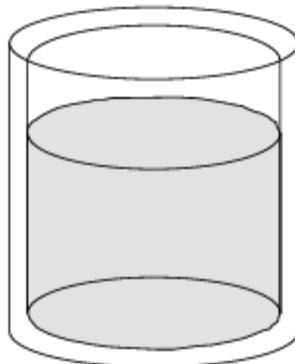
- Identify and discuss the four states of matter.
- Describe the important chemical properties relevant to semiconductor manufacturing.
- State how the different process chemicals are categorized and used in a wafer fab.
- Explain how an acid, base and solvent are used in chip manufacturing.
- State whether a gas is a bulk or specialty gas and how each type of gas is delivered and used in wafer fabrication.

Four States of Matter

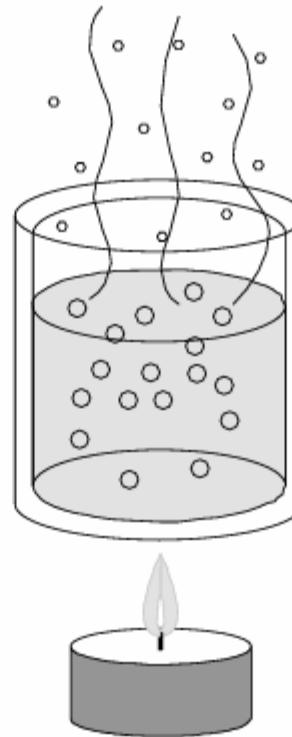
Solid



Liquid



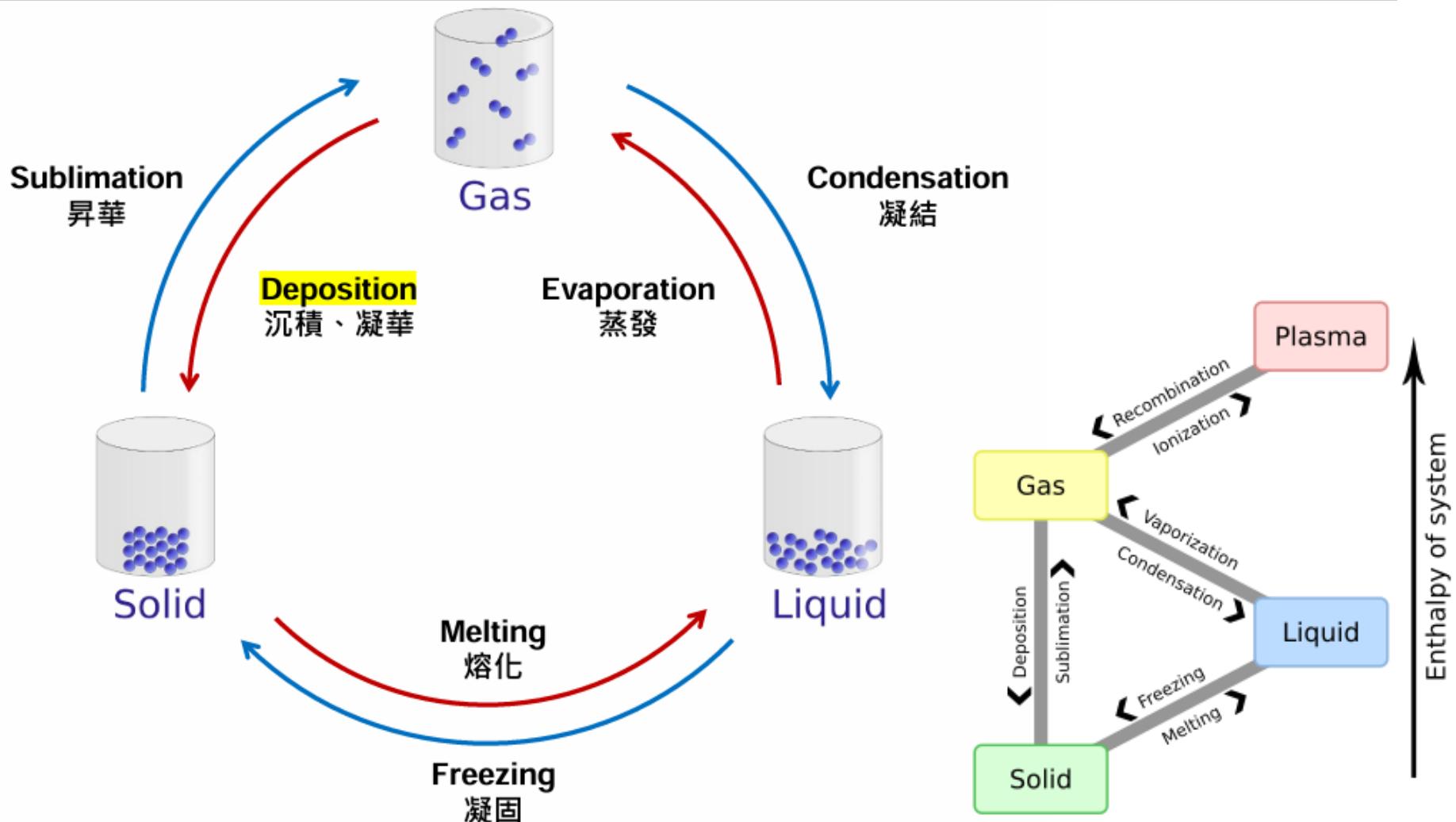
Gas



Plasma

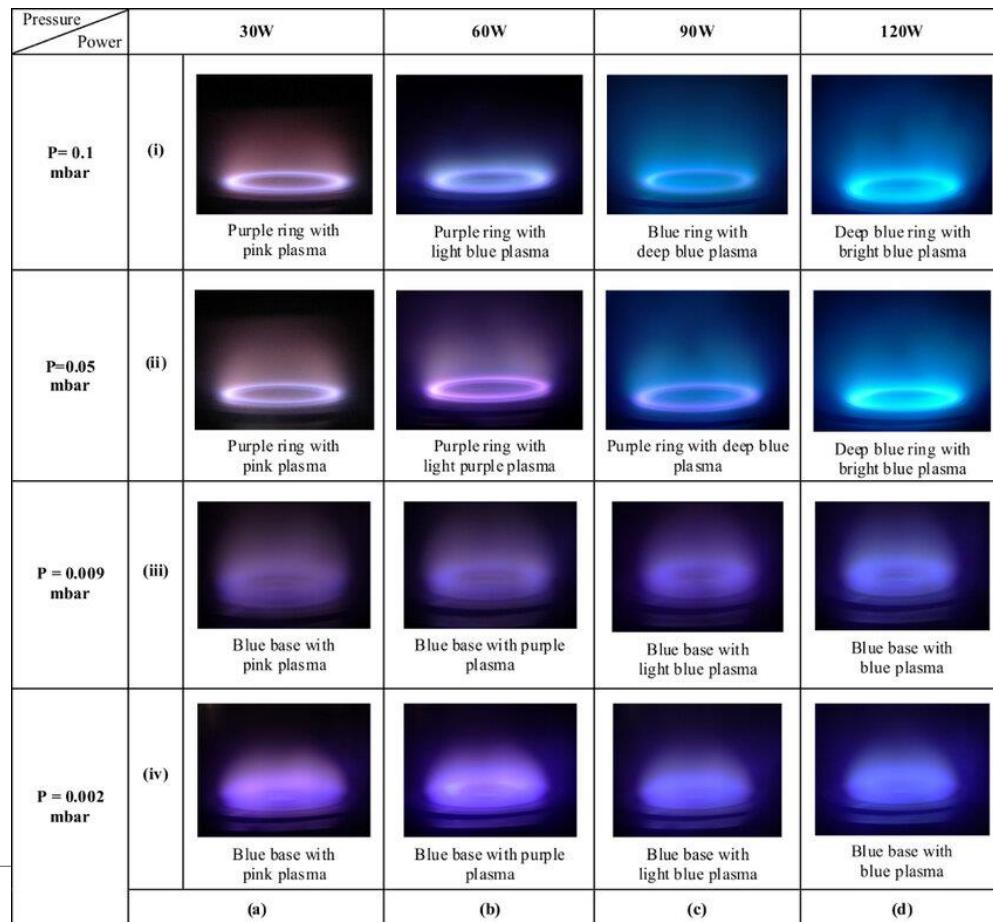


Phase change of the matter



Plasma phase

- 電漿（或稱等離子體）是物質的第四態，相較於固態、液態和氣態具有獨特的性質。電漿是一種由帶電粒子（如正離子和電子）組成的高能量、高溫狀態
- 當氣體受到足夠高的能量時，電子會從原子或分子中被移除，形成自由電子和正離子。這些帶電粒子會互相碰撞並形成電漿
- 性質：
 - 帶電性
 - 高能量
- 應用：
 - 自然界：閃電、極光等
 - 人造：半導體製造等



Argon plasma

Source: Debashis Maji, Analysis of plasma-induced morphological changes in sputtered thin films over compliant elastomer, Journal of Physics D: Applied Physics, Feb 2014

Physical properties of material

- **密度 (Density)**: 指單位體積內物質的質量，是衡量材料緻密程度的重要參數。密度高的材料通常結構較緊實，反之則較輕盈。
 - **熔點 (Melting Point)**: 指固態材料轉變成液態時的溫度。
 - **沸點 (Boiling Point)**: 指液態材料轉變成氣態時的溫度。通常用來評估材料在加熱條件下的穩定性。
 - **熱導率 (Thermal Conductivity)**: 衡量材料傳遞熱能的能力。高熱導率材料在散熱系統中具有重要應用；而低熱導率材料則常用作隔熱材料。
 - **比熱 (Specific Heat Capacity)**: 表示使單位質量的材料溫度上升一度所需吸收的熱量。比熱高的材料在加熱或冷卻過程中變化較慢，適合作為熱穩定材料。
 - **電導率 (Electrical Conductivity)**: 衡量材料允許電流通過的能力。
 - **硬度 (Hardness)**: 表示材料抵抗局部塑性變形（如刮痕、壓痕）的能力。
 - **彈性 (Elasticity)**: 指材料在受力變形後能恢復原狀的能力。
 - **韌性 (Toughness)**: 表示材料在受到外力作用時吸收能量而不斷裂的能力。
-

Physical properties of material

- 延展性 (Ductility) 與 可鍛性 (Malleability)

➤ 延展性：指材料在拉伸時能夠產生顯著塑性變形而不斷裂

➤ 可鍛性：指材料在受到壓力時能夠變形（如錘打或壓延）而不破裂，常用於金屬加工和成形。

- 热膨胀係數 (Coefficient of Thermal Expansion): 衡量材料隨溫度變化而膨脹或收縮的速率。不同材料熱膨胀係數的差異在結構設計中必須考慮，以避免因溫度變化引起的應力和損壞。

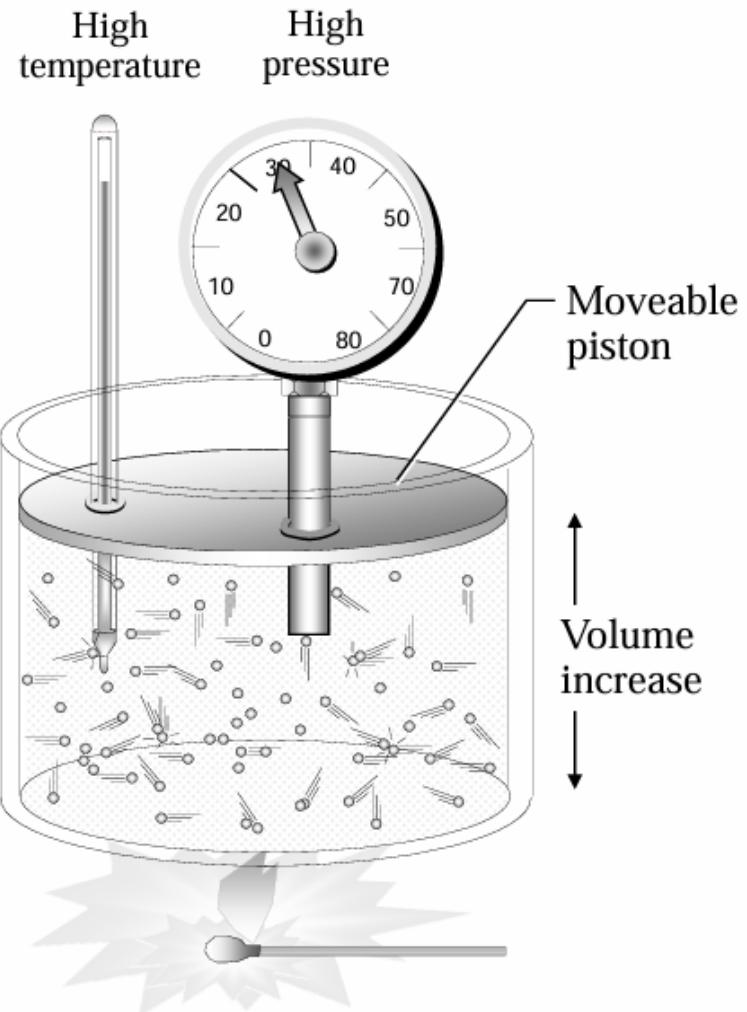
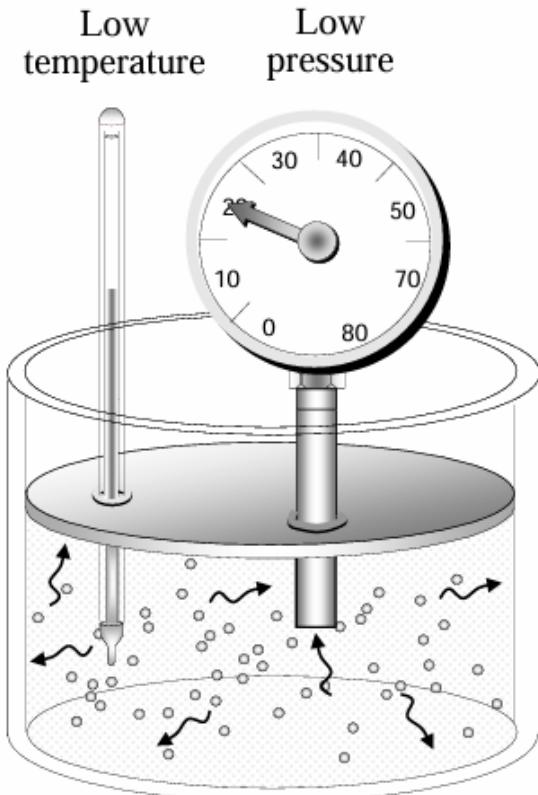
- 折射率 (Refractive Index): 描述光在材料中傳播時速度相對於真空中速度的比例。折射率是光學材料設計中的關鍵參數。

- 磁性 (Magnetic Properties): 材料對磁場的反應能力，可分為順磁性、反磁性、鐵磁性等。這些特性在電子、記憶體等領域有著廣泛應用。

Chemical properties of material

- 反應性(Reactivity)：材料與其他物質發生化學反應的傾向
- 氧化性(Oxidation State)：材料在與氧氣接觸時是否容易氧化
- 酸鹼性(Acidity or Basicity)：材料在溶液中是否表現為酸性或鹼性
- 腐蝕性(Corrosiveness)：材料在接觸水、空氣或其他化學物質時是否容易腐蝕
- 可燃性(Flammability)：材料是否容易燃燒
- 毒性(Toxicity)：材料在接觸或攝入時對生物體是否有毒害作用
- 電負度(Electronegativity)：材料的原子吸引電子的能力，這影響其在化學反應中的行為

Pressure



Vacuum level and pumping

	Torr
大氣壓力	760
粗略真空 (Rough Vacuum)	760 - 25
中度真空 (Medium Vacuum)	$25 - 10^{-3}$
高真空 (High Vacuum)	$10^{-3} - 10^{-9}$
超高真空 (Ultra-High Vacuum)	$10^{-9} - 10^{-12}$

	Torr	平均自由徑	分子密度 cm ⁻³
大氣壓力	760	66 nm	2.5×10^{19}
吸塵器	600	70 nm	10^{19}
液環真空泵	24	1.75 μm	10^{18}
LPCVD	0.075-0.75		
冷凍乾燥	$1 - 10^{-1}$	100 μm - 1 mm	$10^{16} - 10^{15}$
電燈泡	$10^{-1} - 10^{-2}$	1 mm - 1 cm	$10^{15} - 10^{14}$
保溫瓶的抽真空	$10^{-2} - 10^{-4}$	1 cm - 1 m	$10^{14} - 10^{12}$
HDP Etch	$10^{-3} - 0.075$		
Ion implant	10^{-6}		
真空管	$10^{-7} - 10^{-10}$	1 - 1,000 km	$10^9 - 10^6$
分子束外延	$10^{-9} - 10^{-11}$	100 - 10,000 km	$10^7 - 10^5$
月球大氣	10^{-11}	10,000 km	4×10^5

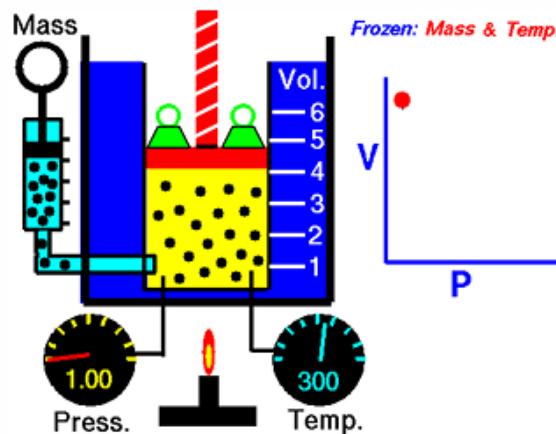
Vacuum level and pumping

- 排氣式pump:其作用為將低氣壓氣體排送至高氣壓的地方
 - 粗抽真空pump
 - 乾式真空pump
 - 擴散pump
 - Turbo pump
- 儲氣式pump:將被抽之氣體抽入pump中永久或暫時儲藏在pump中而不排出，原理為物理吸附或受高電壓離子化後結合成化合物(化學吸附)等
 - 低溫pump
 - Ion pump

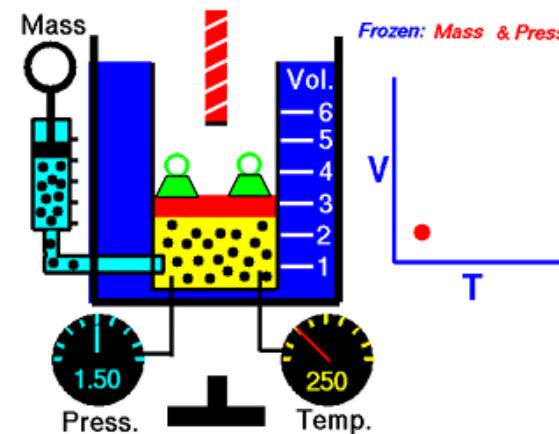
Ideal gas equation

- 波以耳定律：在密閉容器中的定量氣體，在恆溫下，氣體的壓力和體積成反比關係
- 查理-給呂薩克定律：當壓力不變時，理想氣體的體積和溫度成正比
- 亞佛加厥定律：同溫、同壓時，同體積的任何氣體含有相同數目之分子

$$PV = k$$



$$V \propto T$$



$$V \propto n$$



$$PV = nRT$$

n : 氣體數量 (莫耳)
 R : 理想氣體常數

Mean free path

- Mean Free Path (平均自由程) 指的是氣體中單位粒子在兩次碰撞之間所能行進的平均距離
- 應用：
 - 薄膜沉積 (Deposition)
 - 電漿製程與蝕刻
 - 級子植入 (Ion Implantation)
- **關鍵點：**壓力控制

半導體製程常在高真空或超高真空環境下進行，以確保平均自由程足夠長，從而達到預期的效果

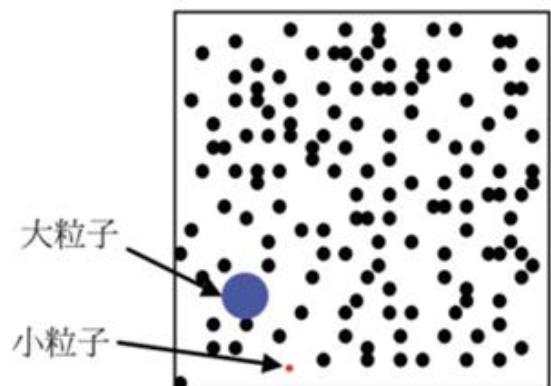
Mean free path

- 關鍵點：壓力控制

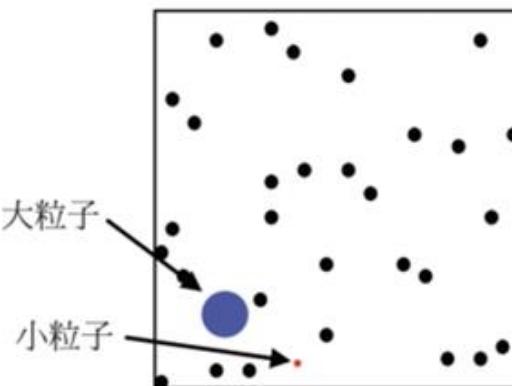
半導體製程常在高真空或超高真空環境下進行，以確保平均自由程足夠長，從而達到預期的效果

$$\lambda = \frac{k_B T}{\sqrt{2} \pi d^2 P} = \frac{1}{\sqrt{2} \sigma N}$$

σ : 單個粒子的有效碰撞截面積
 N : 每單位體積內的粒子數量



(a)

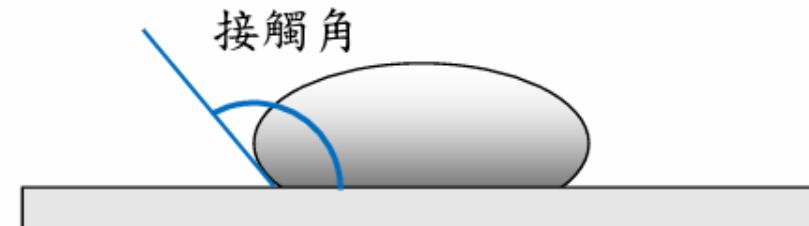


(b)

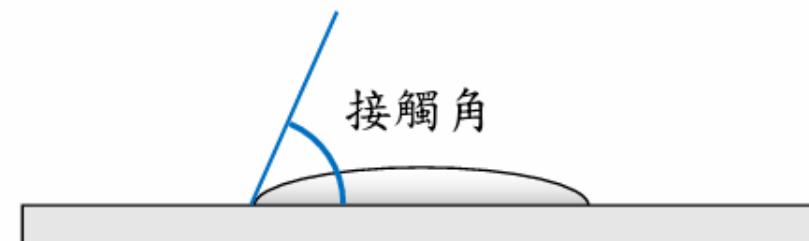
圖 7.6 (a) 具有較短 MFP 的高壓情況；(b) 具有較長 MFP 的低壓情況。

Surface tension

- 表面張力（Surface Tension）主要描述液體表面分子間的內聚力，這種力使液體表面趨向收縮以達到最小面積
- 表面張力直接影響到薄膜的均勻性、微結構的形成以及加工品質
- 應用：
 - 旋塗 (Spin Coating)
 - 濕式清洗



Si (疏水)

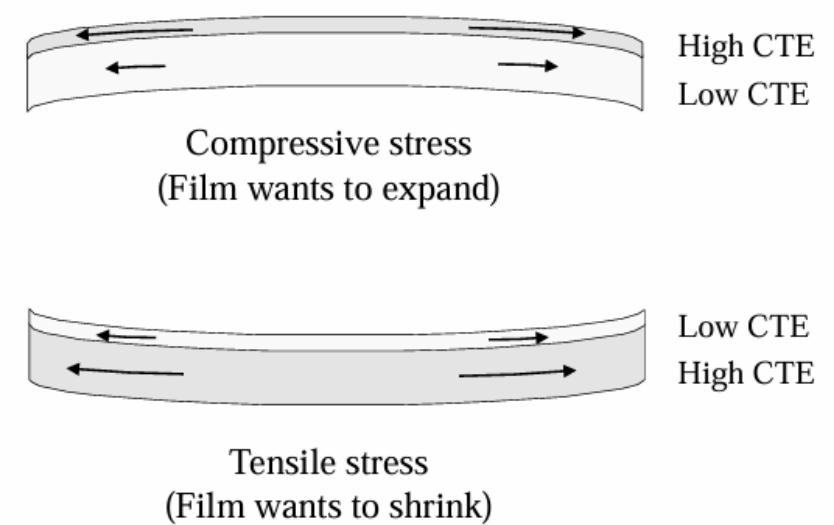


SiO₂ (親水)

Thermal expansion

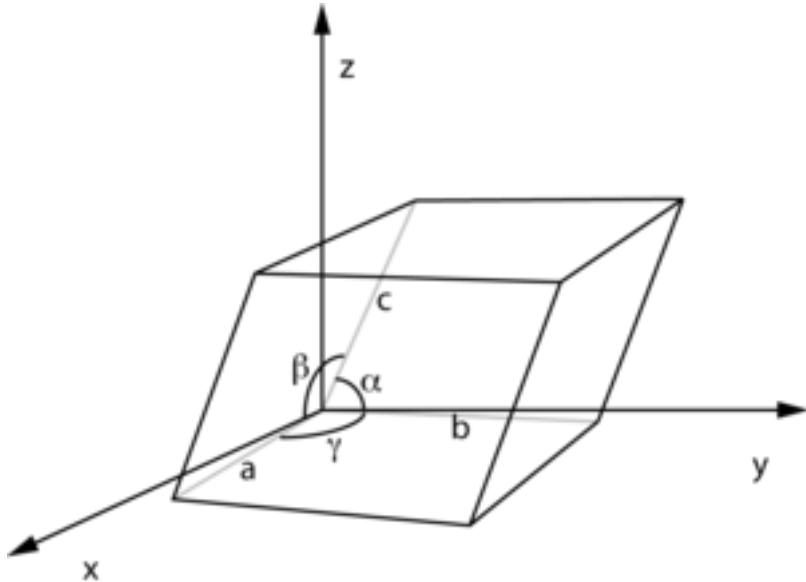
- Thermal Expansion (熱膨脹) 描述材料隨溫度升高而尺寸增大的現象
- The amount a material expands due to heating is known as its CTE (coefficient of thermal expansion)
- 應用：
 - The growth of heterojunction
 - Thermal process
 - Strain

材料	$10^{-6}/K$ (20 °C)
氧化矽 (SiO_2)	0.5
矽 (Si)	2.6
氮化矽 (Si_3N_4)	3.3
鎔 (W)	4.5
氧化鋁 (Al_2O_3)	8.5
鈦 (Ti)	8.6
氮化鈦 (TiN)	9.35
鎳 (Ni)	13.4
銅 (Cu)	16.5
鋁 (Al)	23.1



Lattice constant

- 晶格常數 (lattice constant) ，是指晶格中晶胞的物理尺寸。三維空間中的晶格一般有 3 個晶格常數，分別用 a , b 和 c 來表示
- 應用：
- 異質接面 (Heterojunction)
- Stress engineering
- Band structure engineering



Element or Compound	Type	Name	Crystal Structure	Lattice Constant at 300 K (Å)
C	Element	Carbon (Diamond)	Diamond	3.56683
Ge	Element	Germanium	Diamond	5.64613
Si	Element	Silicon	Diamond	5.43095
Sn	Element	Grey Tin	Diamond	6.48920
SiC	IV-IV	Silicon carbide	Wurtzite	$a=3.086; c=15.117$
AlAs	III-V	Aluminum arsenide	Zincblende	5.6605
AlP	III-V	Aluminum phosphide	Zincblende	5.4510
AlSb	III-V	Aluminum antimonide	Zincblende	6.1355
BN	III-V	Boron nitride	Zincblende	3.6150
BP	III-V	Boron phosphide	Zincblende	4.5380
GaAs	III-V	Gallium arsenide	Zincblende	5.6533
GaN	III-V	Gallium nitride	Wurtzite	$a=3.189; c=5.185$
GaP	III-V	Gallium phosphide	Zincblende	5.4512
GaSb	III-V	Gallium antimonide	Zincblende	6.0959
InAs	III-V	Indium arsenide	Zincblende	6.0584
InP	III-V	Indium phosphide	Zincblende	5.8686

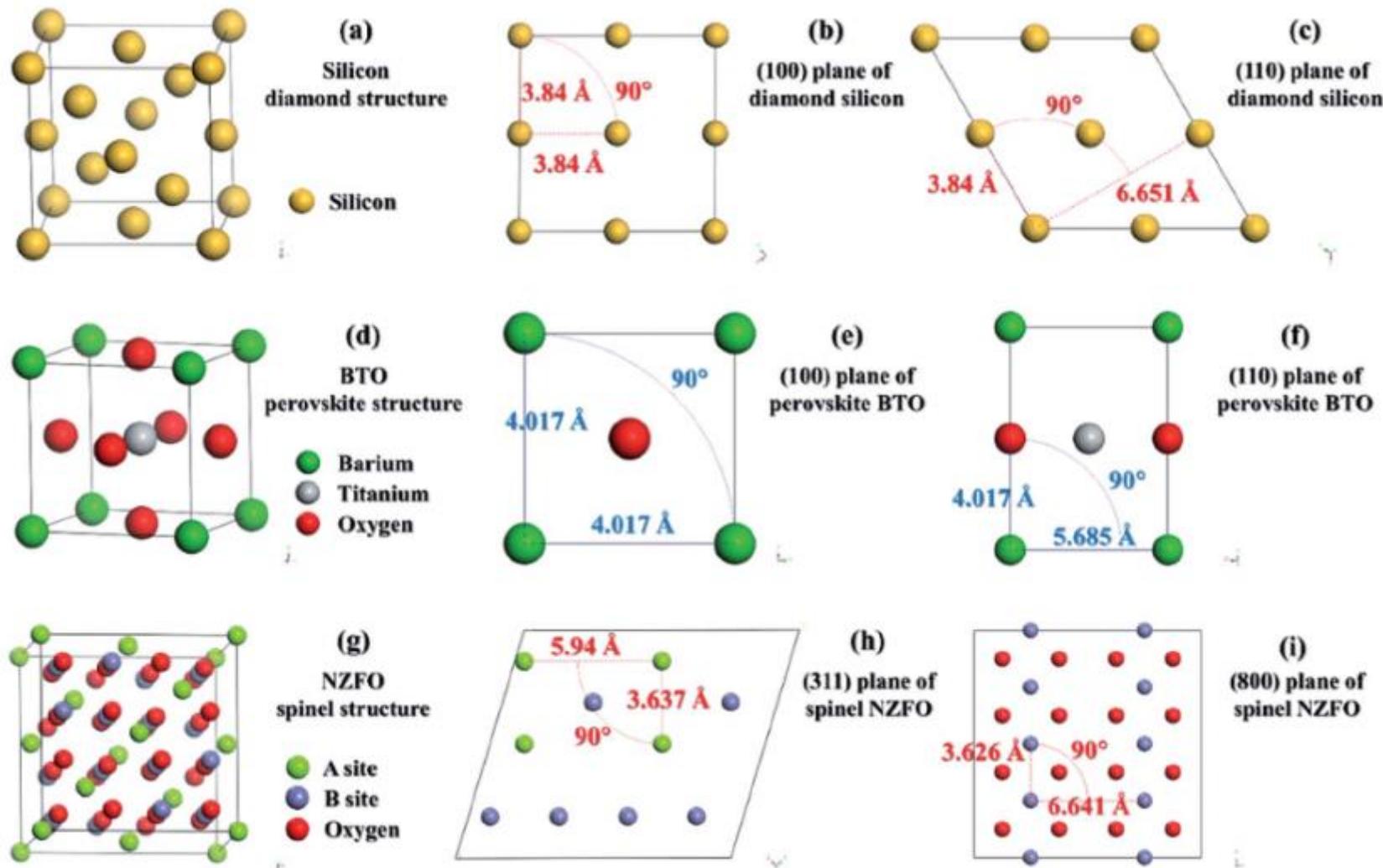
Source: K. Alfaramawi, Lattice Constants and Crystal Structures of some semiconductors

X-ray diffractometer (XRD)

- X射線繞射 (XRD) 是一種利用X射線與物質中**原子排列**所產生的繞射現象來研究晶體結構的分析技術，其基本原理是根據Bragg定律來探討晶格間距和晶體取向
- 常見的模式有 $\theta - 2\theta$ scan、XRR等
- 應用：
 - 晶體品質
 - 薄膜厚度 (fitting)
 - 組成分析
 - 應力
 - 材料晶相

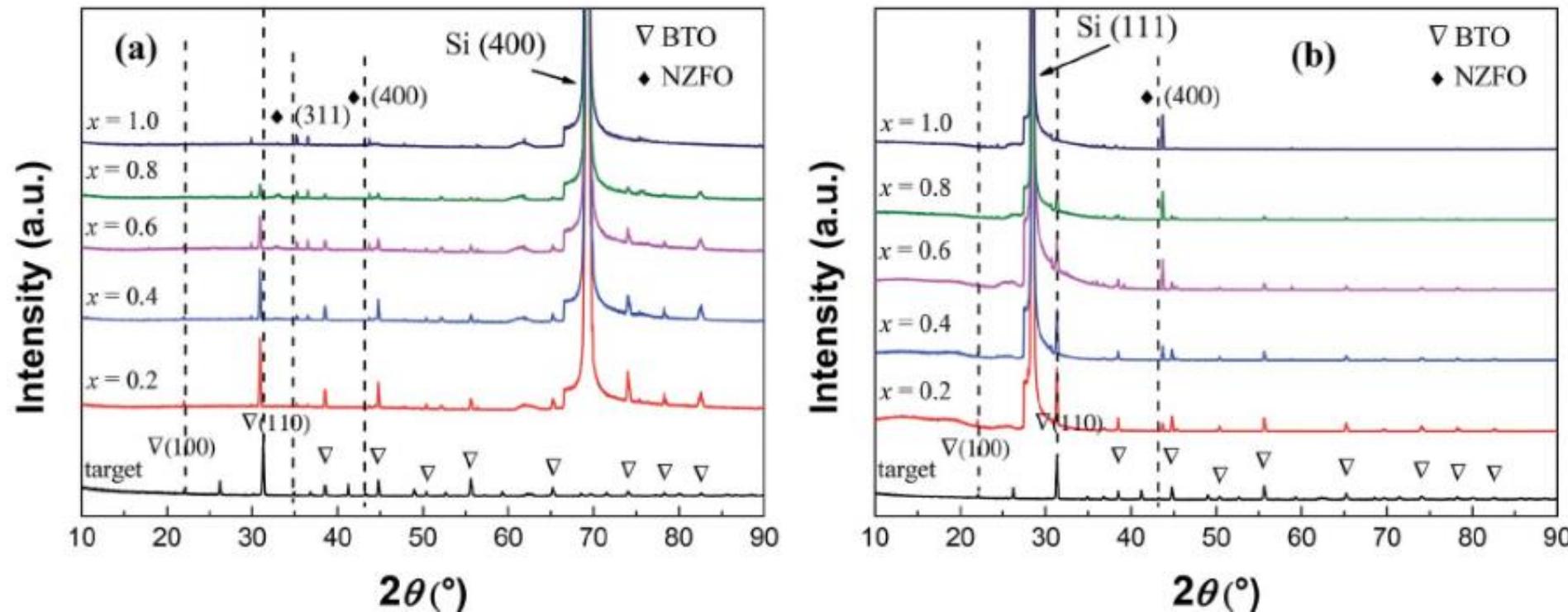


X-ray diffractometer (XRD)



Source: Yu Tang, Magnetoelectric coupling tailored by the orientation of the nanocrystals in only one component in percolative multiferroic composites, RSC Adv., 2019, 9, 20345–20355

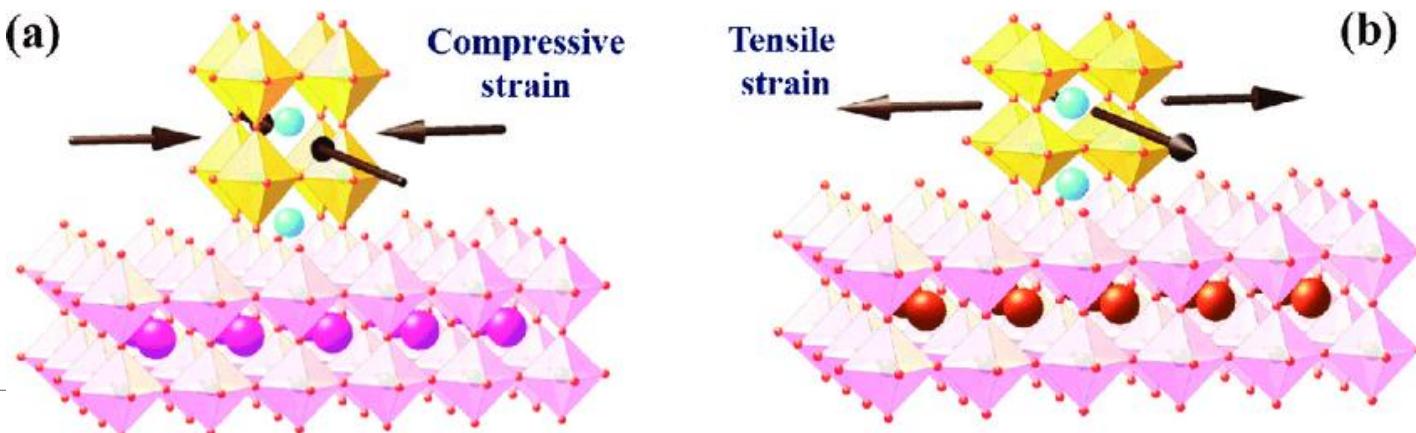
X-ray diffractometer (XRD)



Source: Yu Tang, Magnetoelectric coupling tailored by the orientation of the nanocrystals in only one component in percolative multiferroic composites, RSC Adv., 2019, 9, 20345–20355

Strain

- Strain (應變) 指的是由於外界或內部力量作用下，半導體晶體的原子排列發生輕微形變或扭曲的現象
- 常見類型：
 - 拉伸應變 (Tensile Strain)
 - 壓縮應變 (Compressive Strain)
- 影響：
 - 能帶結構
 - 界面品質
 - ✓ 適量的應變可以改善電性，但過大的應變可能會引入晶格缺陷或產生界面mismatch問題
- 應用：
 - Stress engineering



Source: Abhijit Biswas, Strain Effect in Epitaxial Oxide Heterostructures, Mar 2018

Stress (應力) engineering

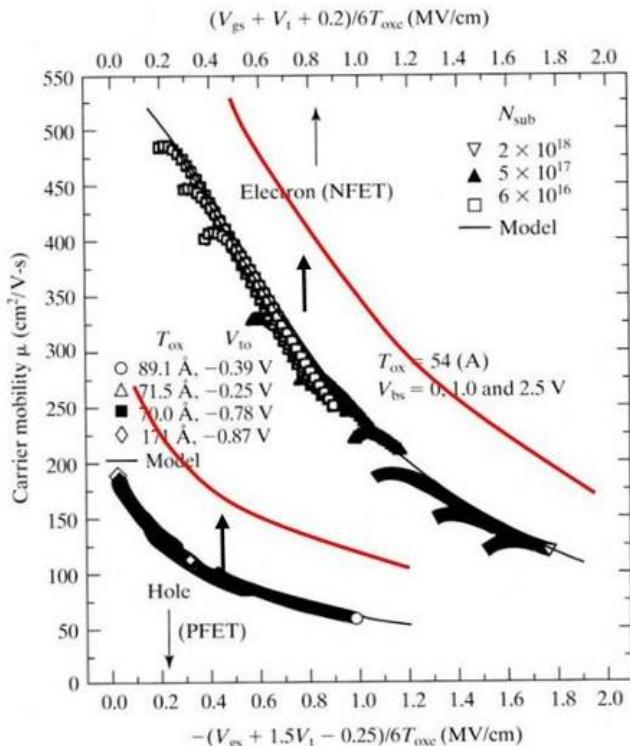


FIGURE 6-9 Electron and hole surface mobilities are determined by V_{gs} , V_t , and T_{oxc} . T_{ox} is the SiO_2 equivalent electrical oxide thickness. (From [4]. © 1996 IEEE.)

Black curves: un-strained Si (i.e. without stress)

Red curves: With desired mechanical stress applied

- MOSFET built on un-strained (i.e. without stress engineering) (100) Si
- In the mid-2000, people found out (by serendipity) that if we put some proper mechanical stresses on the MOSFET, the universal mobility can increase

The core is increasing the mobility for the carrier to improve the performance of the device, so how can we make it ?

Ans. Band diagram concept ! !

$$I_{\text{dsat}} = \frac{W}{2mL} C_{\text{oxe}} \mu_{ns} (V_{\text{gs}} - V_t)^2$$

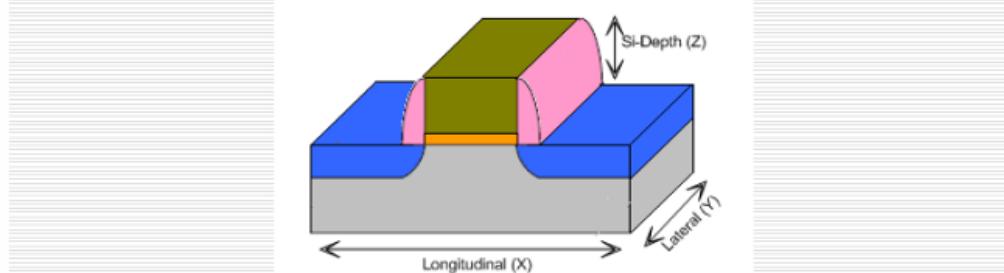
Stress engineering

- 半導體中的「stress engineering」是一項利用控制材料內部或界面處的應力來調整majority carrier性質和元件性能的重要技術
- 改變晶體結構中的原子排列和能帶結構，達到提升載子遷移率、提高速度等
- 技術原理：
 - Increasing the curvature of energy diagram
 - Decreasing the effective mass
 - Increasing the carrier mobility
- 技術核心概念：
 - The difference of lattice constant between two atom
 - Coefficient of thermal expansion

$$\text{Effective mass} \equiv \frac{\hbar^2}{d^2 E/d\mathbf{k}^2}$$

Stress engineering

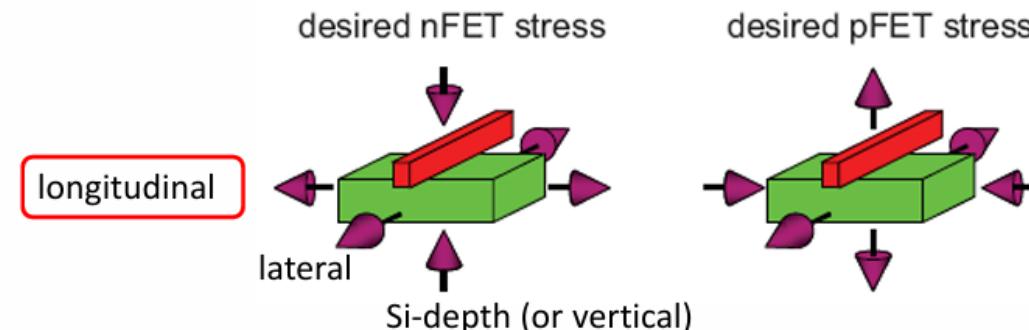
Desired Stress for CMOS Devices



	NMOS	PMOS
Longitudinal (X)	Tensile	Compressive
Lateral (Y)	Tensile	Tensile
Si-Depth (Z)	Compressive	Tensile

Stress engineering is mainly applied to (or along) this Longitudinal direction.

Be aware of the Lateral and Si-Depth (vertical) directions, but no engineering efforts.



	a_0 (nm)
C	0.356
Si	0.543
Ge	0.565

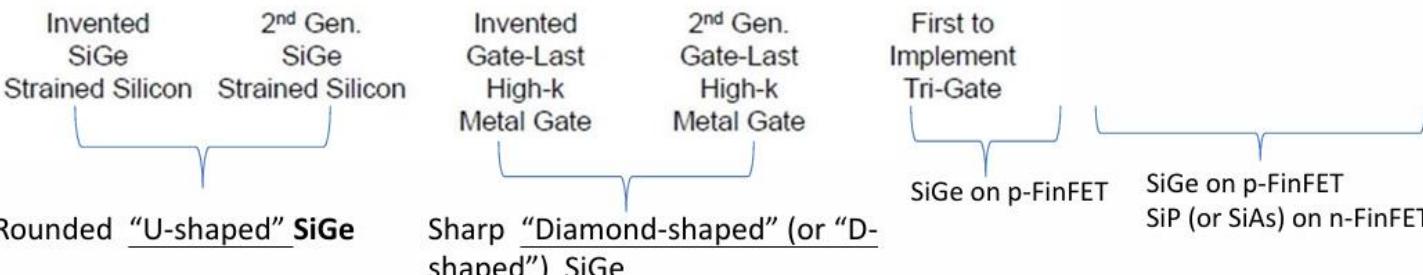
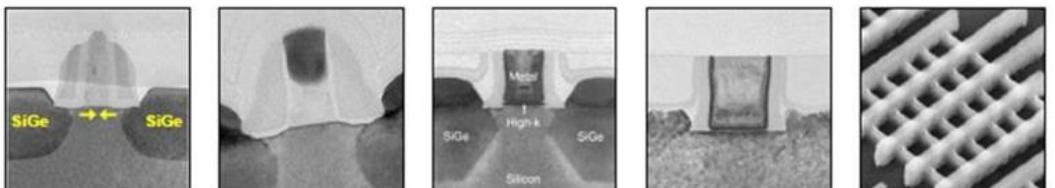
$$P : 0.539 \text{ nm}$$

Stress engineering

Embedded-SiGe for pFET

Intel

2003 90 nm	2005 65 nm	2007 45 nm	2009 32 nm	2011 22 nm	2014 14nm	2017 10nm	2018 7nm	2020 5nm
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- For foundries, 45G uses U-shaped SiGe (while 45LP has no SiGe). 28LP (the last Poly-SiON technology), 28HPM/HPC (1st HKMG), and 20nm (2nd HKMG) all use D-shaped SiGe.
- "D-shaped" SiGe is the pre-requisite of success for 28nm (and 20nm) – the last two planar CMOS !
- The U-shape or D-shape is referred to the S/D Si recess region (or cavity) where SiGe is deposited.
- For FinFET technologies, the epi-SiGe over the Si fin is usually Diamond shaped as well, but it's not the same as the above.

Source:

K. Rim et al., VLSI Symposium, June 2002, pg. 98-99

H. S. Yang et al., IEDM Tech. Dig., Dec 2004, pg. 1075-78

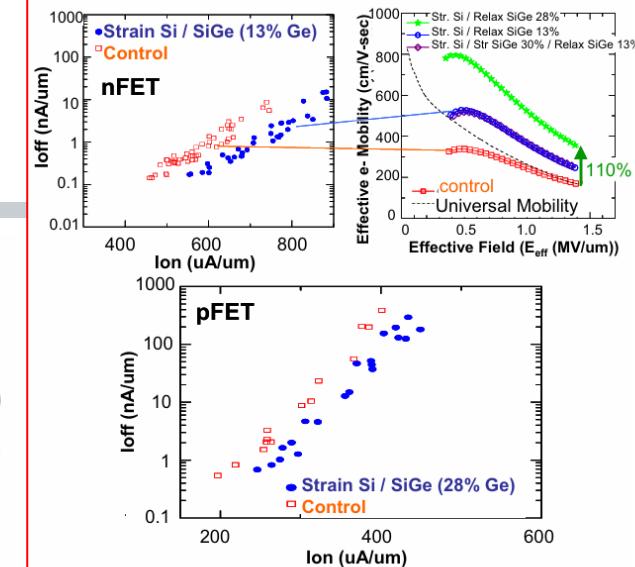


Fig. 5 NMOS and PMOS show benefits with biaxial tensile strained Si of 13 & 28% Ge respectively [2].

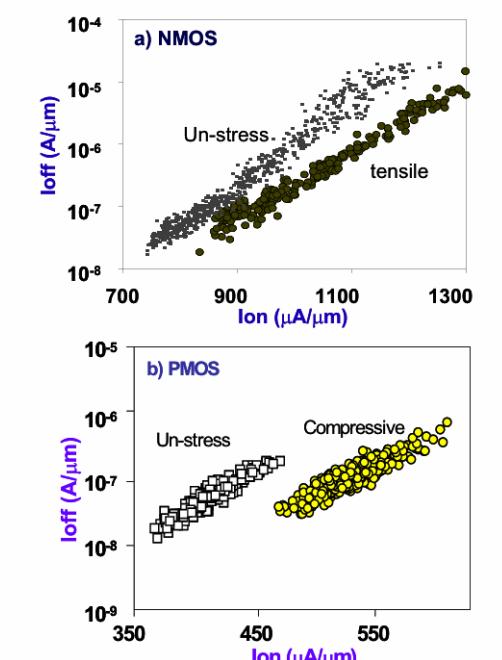


Fig.6 Ion enhancement using stress liner compared to neutral liner (non-stressed process) for a) nMOS and b) PMOS [9].

Stress engineering

Typical failure modes of tensile- or compressive-SiN

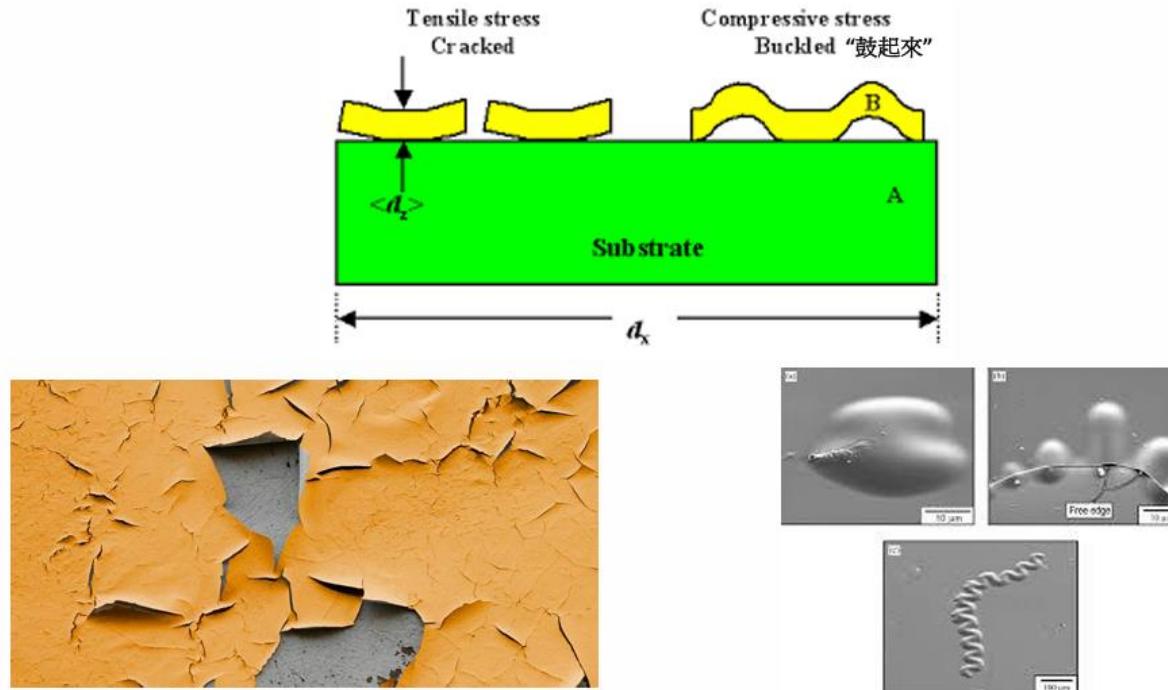


Fig. 1. Illustration of straight-edged, circular, and telephone cord buckles (Mose et al., 2002).

- Tensile SiN cracking looks similar to this (paint cracking) – all broken edges are curling upward, and tend to “peel off”.
- Cracked film flakes are particles – yield killers !!
- It’s obvious that cracked film will result in stress loss.
- Compressive film (if without enough adhesion) may buckle.
- Moderately compressive SiN usually does not buckle. Even if it does, usually no (or not many) particles are generated – much better than cracking.

Bulk Gases (99.9999%)

Type	Gas	Example of Use
Inert	Nitrogen (N ₂)	<ul style="list-style-type: none">清洗反應腔和吹掃管道 (Purge gas)，以確保沒有雜質和水分進入製程區域。高溫製程 (如退火) 中，氮氣提供無氧環境，防止氧化和不良反應。
	Argon (Ar)	<ul style="list-style-type: none">氩氣作為載體氣體，與其他反應氣體一起使用來生成電漿，有助電漿蝕刻。用於濺射製程 (Sputtering, PVD) 中，產生氩電漿體，將材料濺射到基板上。在一些退火過程中，氩氣作為惰性氣體，防止材料表面與氧氣反應。
	Helium (He)	<ul style="list-style-type: none">在化學氣相沉積 (CVD) 和其他製程中用於散熱。常用於真空系統中的漏檢測 (Leakage test)。
Reducing	Hydrogen (H ₂)	<ul style="list-style-type: none">在CVD製程中作為還原劑 $\text{SiCl}_{4(g)} + 2\text{H}_{2(g)} \rightarrow \text{Si}_{(s)} + 4\text{HCl}_{(g)}$ $\text{WF}_6 + \text{H}_2 \rightarrow \text{W} + 6\text{HF}$氫氣與氮氣混合用於矽片表面清洗和鈍化
Oxidizing	Oxygen (O ₂)	<ul style="list-style-type: none">用於生成矽片上的氧化層氧氣電漿用於光阻剝離，去除有機材料

Reducing and Oxidizing

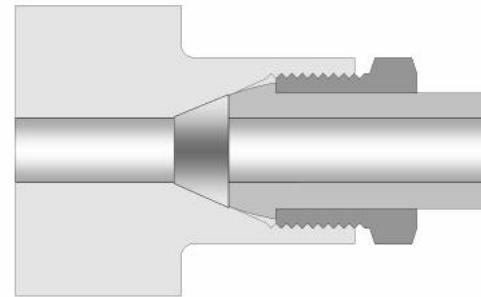
- 氧化 (Oxidizing) : 當原子或分子失去電子，或與氧結合時，稱為氧化
 - 例如: $\text{Si} + \text{O}_2 \rightarrow \text{SiO}_2$ (矽氧化形成二氧化矽)
- 還原 (Reducing) : 當原子或分子獲得電子，或移除氧時，稱為還原
 - 例如: $\text{CuO} + \text{H}_2 \rightarrow \text{Cu} + \text{H}_2\text{O}$ (氫氣將氧化銅還原為銅)
- 氧化與還原通常是同時發生的 (即氧化還原反應，Redox Reaction)
- 應用:
 - Thermal Oxidation (produce oxide / protection layer)
 - Oxidizing Etching (cleaning / removing / selective etching)
 - Annealing (recovering)
 - Deposition

Specialty Gases (99.99%)

Class	Gas	Symbol	Process	Example of Use
Hydrides 氫化物	Silane	SiH ₄	CVD	$\text{SiH}_4 \rightarrow \text{Si} + 2\text{H}_2$ (poly Si)
	Dichlorosilane (DCS)	SiH ₂ Cl ₂	CVD	$\text{SiH}_2\text{Cl}_2 \rightarrow \text{Si} + 2\text{HCl}$ (poly Si)
	Trichlorosilane (TCS)	SiHCl ₃	CVD	$\text{SiHCl}_3 + \text{H}_2 \rightarrow \text{Si} + 3\text{HCl}$ (Epitaxial Si)
	Silicon tetrachloride	SiCl ₄	CVD	$\text{SiCl}_4 + 2\text{H}_2 \rightarrow \text{Si} + 4\text{HCl}$ (Epitaxial Si)
	Tetraethyl Orthosilicate (TEOS)	Si(OC ₂ H ₅) ₄	CVD	$\text{Si}(\text{OC}_2\text{H}_5)_4 \rightarrow \text{SiO}_2 + 4\text{C}_2\text{H}_5\text{OH}$
	Arsine	AsH ₃	Doping	Source of dopant
	Phosphine	PH ₃	Doping	Source of dopant
	Diborane	B ₂ H ₆	Doping	Source of dopant
Fluoride 氟化物	Tungsten hexafluoride	WF ₆	CVD	$\text{WF}_6 + \text{H}_2 \rightarrow \text{W} + 6\text{HF}$
	Carbon tetrafluoride	CF ₄	Etching	
	Tetrafluoromethane)	C ₂ F ₄	Etching	
	Nitrogen trifluoride	NF ₃	Etching	
	Silicon tetrafluoride	SiF ₄	Etching	
	Chlorine trifluoride	ClF ₃	Etching	
Acid Gases	Boron triflouride	BF ₃	Doping	Source of dopant
	Boron trichloride	BCl ₃	Doping	Source of dopant
	Fluorine	F ₂	Etching	
	Chlorine	Cl ₂	Etching	
	Hydrogen chloride	HCl	Etching	
Other Gases	Ammonia	NH ₃	CVD	$3\text{SiH}_4 + 4\text{NH}_3 \rightarrow \text{Si}_3\text{N}_4 + 12\text{H}_2$
	Nitrous oxide	N ₂ O	CVD	$\text{SiH}_4 + 2\text{N}_2\text{O} \rightarrow \text{SiO}_2 + 2\text{N}_2 + 2\text{H}_2$
	Carbon monoxide	CO		

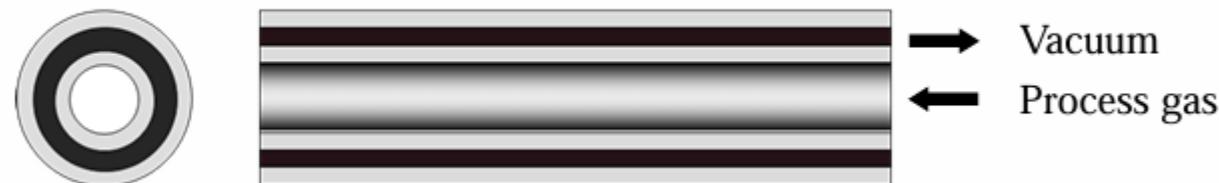
CGA Gas Line Connector

Number	Gas
CGA 580	氮氣 (N_2) 、 氩氣 (Ar) 、 氦氣 (He) 等
CGA 320	二氧化碳 (CO_2)
CGA 540	氧氣 (O_2)
CGA 350	氫氣 (H_2) 等
CGA 632 / 660 / 670	半導體級高純度氣體
CGA 722 / 724	劇毒或腐蝕性氣體



Double-Walled Tubing

- Double-Walled Tubing（雙層管）是一種具有內外兩層結構的管路系統，主要用於氣體與液體輸送
- 應用：
 - 高純度氣體輸送
 - ✓ 雙層管的內層通常使用不鏽鋼（SS316L）
 - 腐蝕性化學品輸送
 - ✓ 雙層管的內層通常使用不鏽鋼（SS316L）（氣體）
 - ✓ 雙層管的內層通常使用PTFE/PFA（氟塑料）（液體）
 - 安全與洩漏偵測



Double-Walled Tubing

