Semiconductor Manufacturing Technology

Chapter 2

Characteristics of Semiconductor Materials

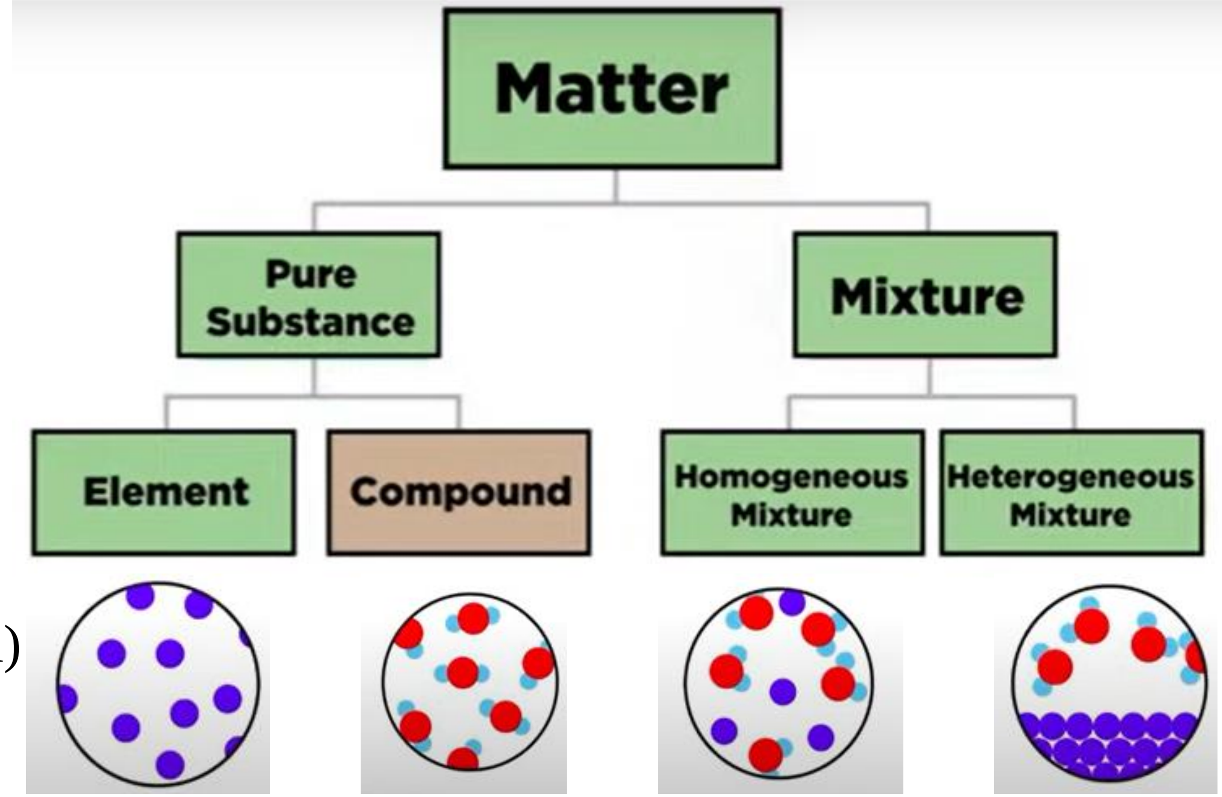
Objectives

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

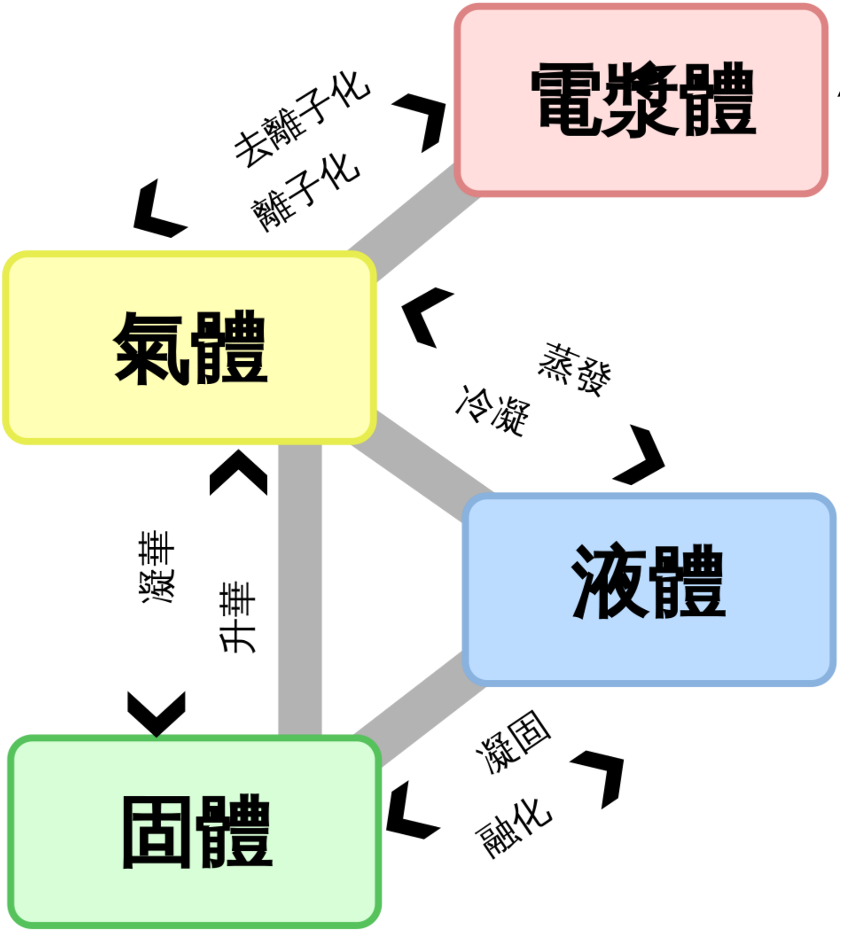
1. Describe the atom, including valence shell, band theory and ions.
2. Interpret the periodic table with regards to main group elements and explain how ionic and covalent bonds are formed.
3. State the three classes of materials and describe each one with regards to current flow.
4. Explain resistivity, resistance, capacitance and discuss their importance to wafer fabrication.
5. Describe pure silicon and give four reasons why it is the most common semiconductor material.
6. Explain doping and how the trivalent and pentavalent dopant elements make silicon a useful semiconductor material.
7. Explain p-type (acceptor) silicon and n-type (donor) silicon, how silicon resistivity changes with the addition of a dopant, and the PN junction.
8. Discuss alternative semiconductor materials.

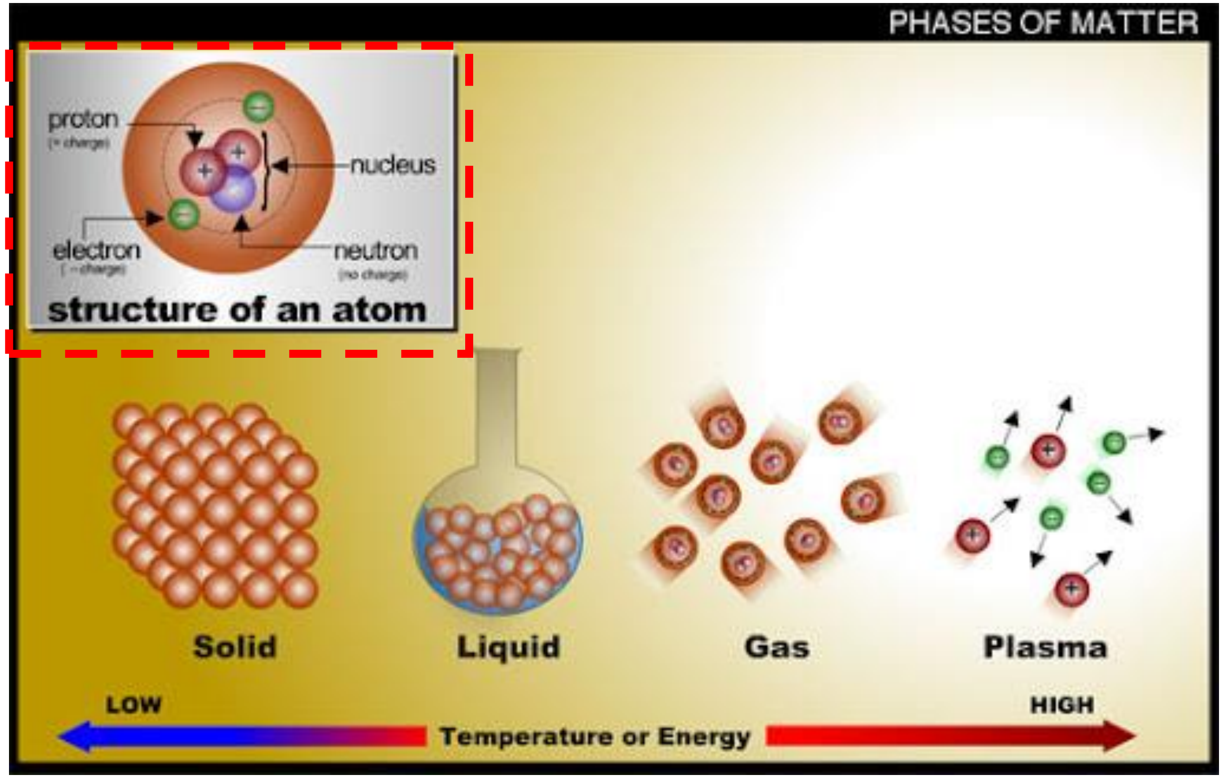
Atomic Structure

- Matter
  - ➢ Nucleus
    - ✓ Proton
    - ✓ Neutron
  - ➢ Orbital Shell
    - ✓ Electron
- Element
- Molecule
- Compound (substance different from individual)
- Electrons
  - ➢ Electron Energy
  - ➢ Valence Shells
  - ➢ Energy-Band Theory
  - ➢ Ions



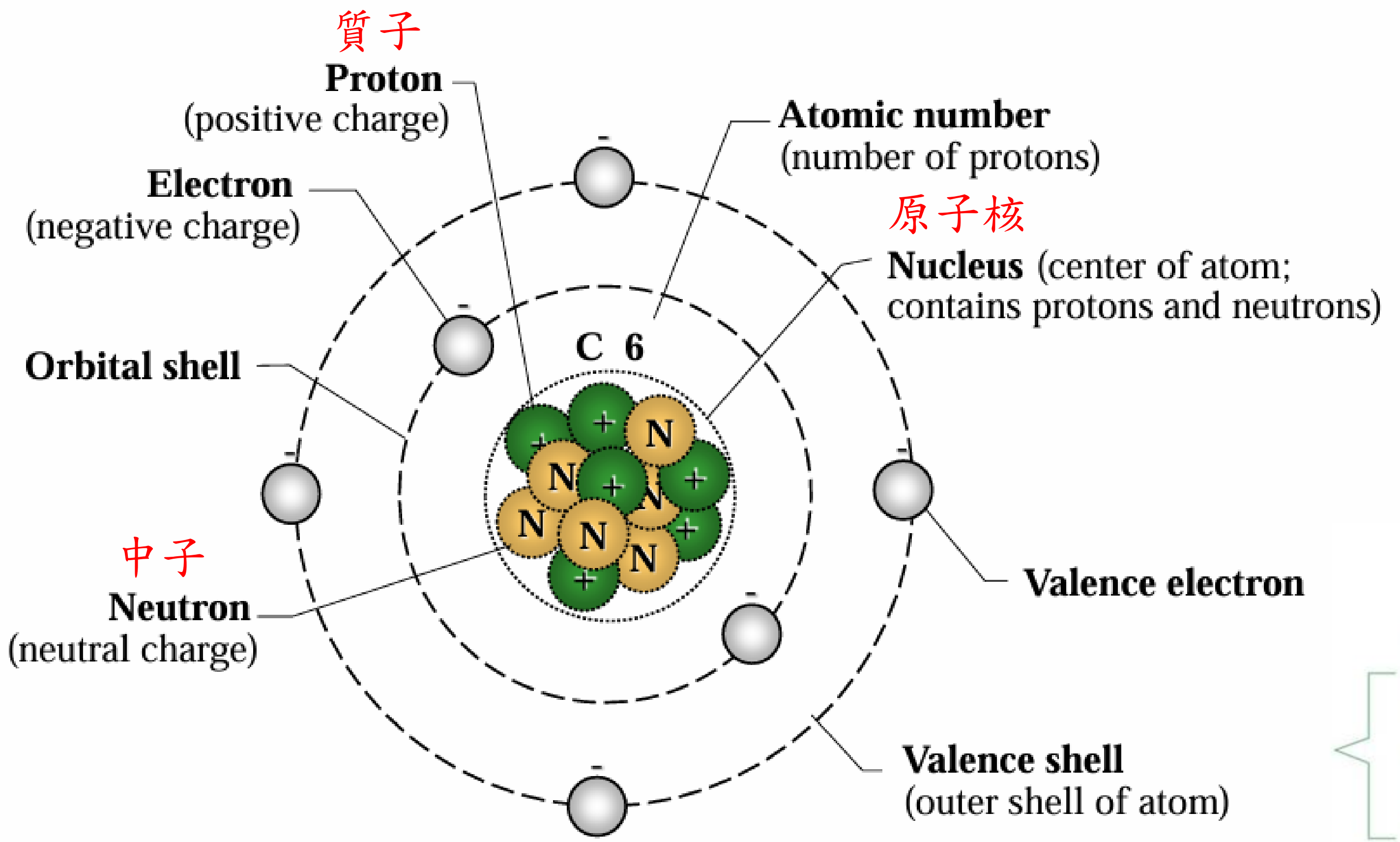
Matter





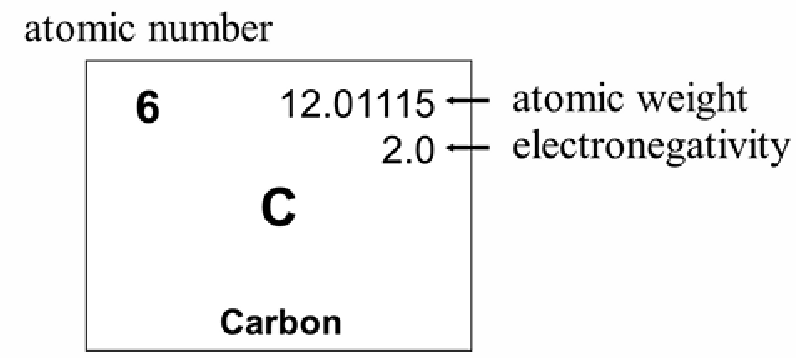
Source: Wikipedia、http://themis.ss.ncu.edu.tw/sun_earth_connecttion.htm

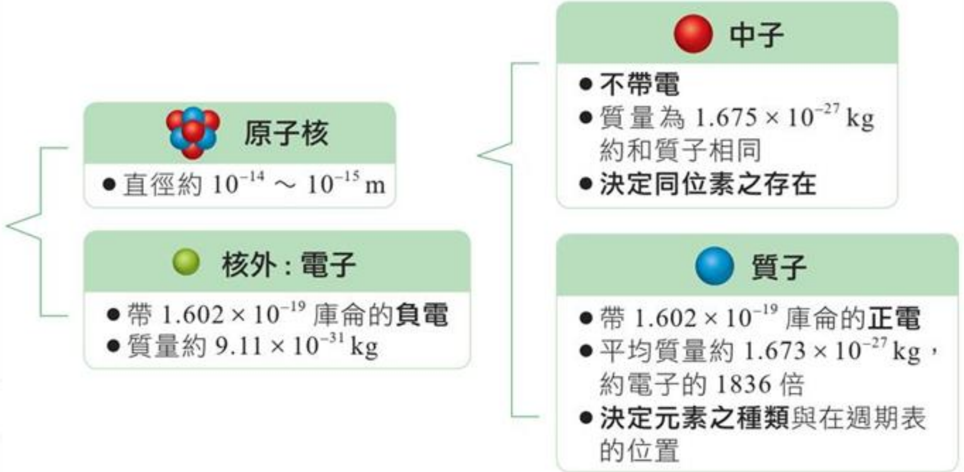
Elementary Model of the Carbon Atom



Carbon atom: The nucleus contains an equal number of protons (+) and neutrons (6 each). Six electrons (-) orbit around the nucleus.

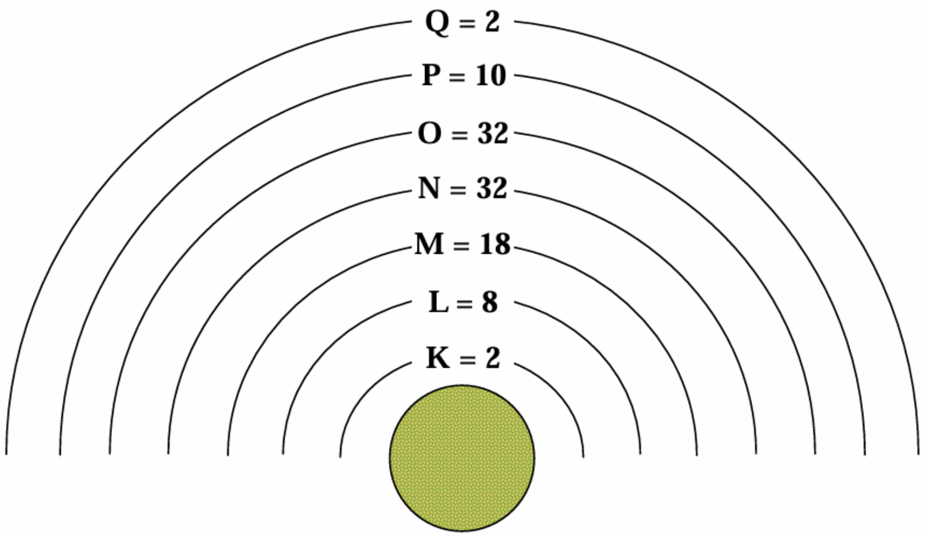
$\boxed{^{12}_{6}C}$





Electron Shells in Atoms

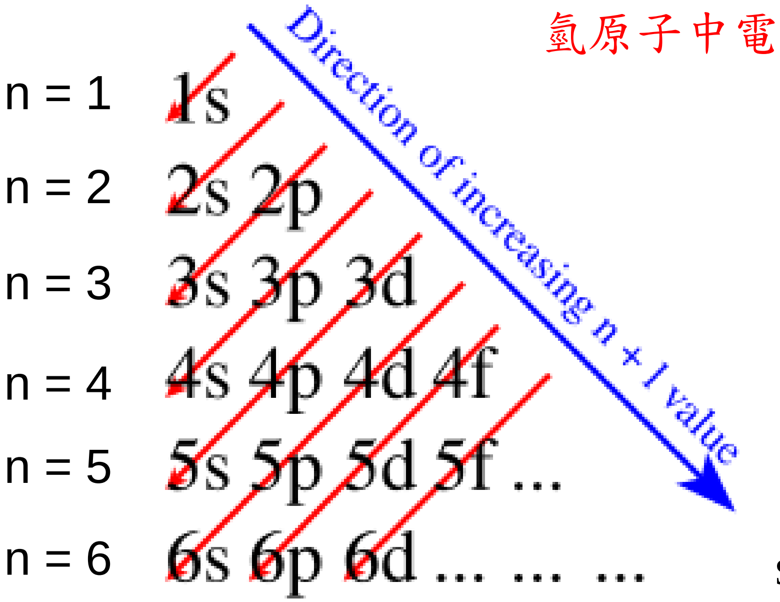
主量子數 n	1 (K)	2 (L)		3 (M)			4 (N)			
角動量量子數 l (n-1)	s	s	p	s	p	d	s	p	d	f
軌道容納電子數	2	2	6	2	6	10	2	6	10	14
總共容納電子數 $2n^2$	2	8		18			32			



Electron energy (eV): the kinetic energy gain by a electron in passing a 1V potential gap.

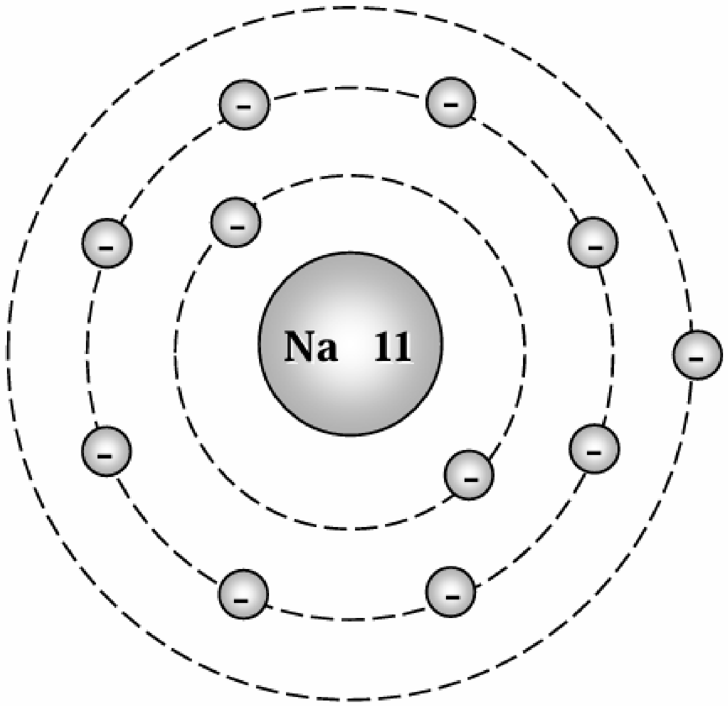
$$E_n = \frac{E_1}{n^2} = \frac{-13.6\ \mathrm{eV}}{n^2}, \quad n = 1, 2, 3, \ldots$$

氫原子中電子的束縛態能量



Source: Wikipedia

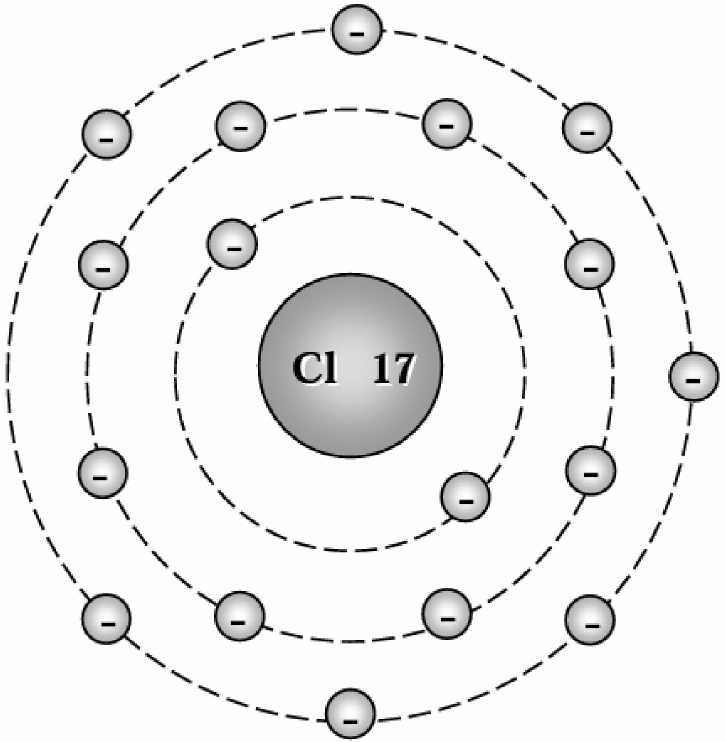
Electron Shells in Atoms



$1s^2\ 2s^2\ 2p^6\ 3s^1$

Sodium atom

Easy to give up a electron



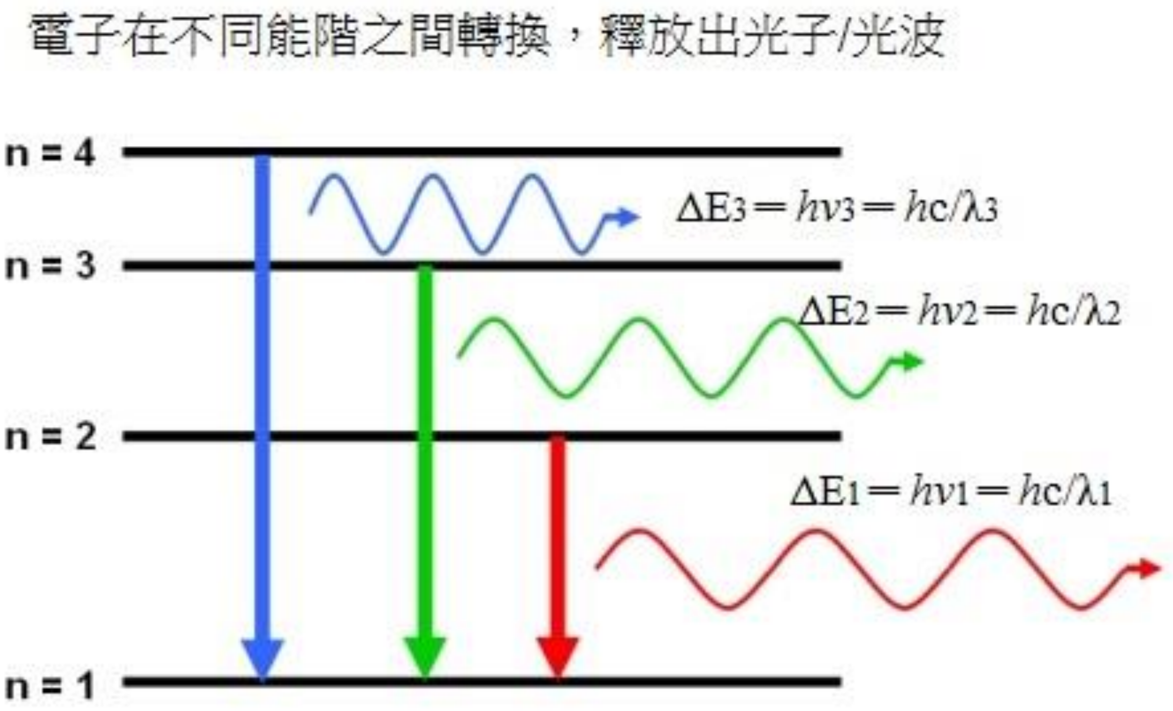
$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

Chlorine atom

It has an affinity to accept one electron

Energy level

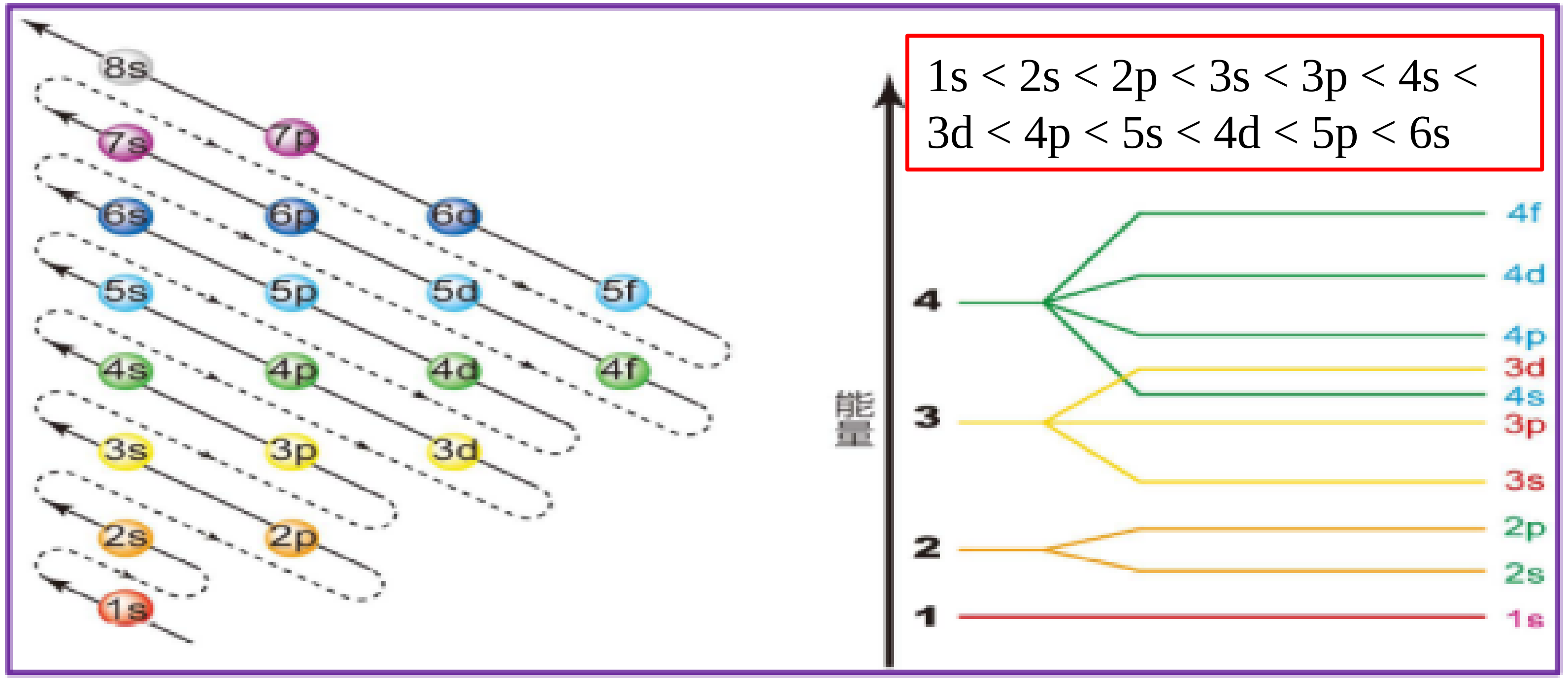
- 能階（Energy Level）是指電子在原子或分子內所能存在的**離散**能量狀態。能階是量子力學中的一個重要概念，描述了電子在原子內的排列和行為。
- 特點：
  - 離散性
  - 主量子數
  - 電子躍遷
  - 光譜線
  - 電子配置



Source: https://earthkart2011.blogspot.com/2012/04/atomic-spectrum-of-hydrogen_13.html

Energy level (Pauli exclusion principle)

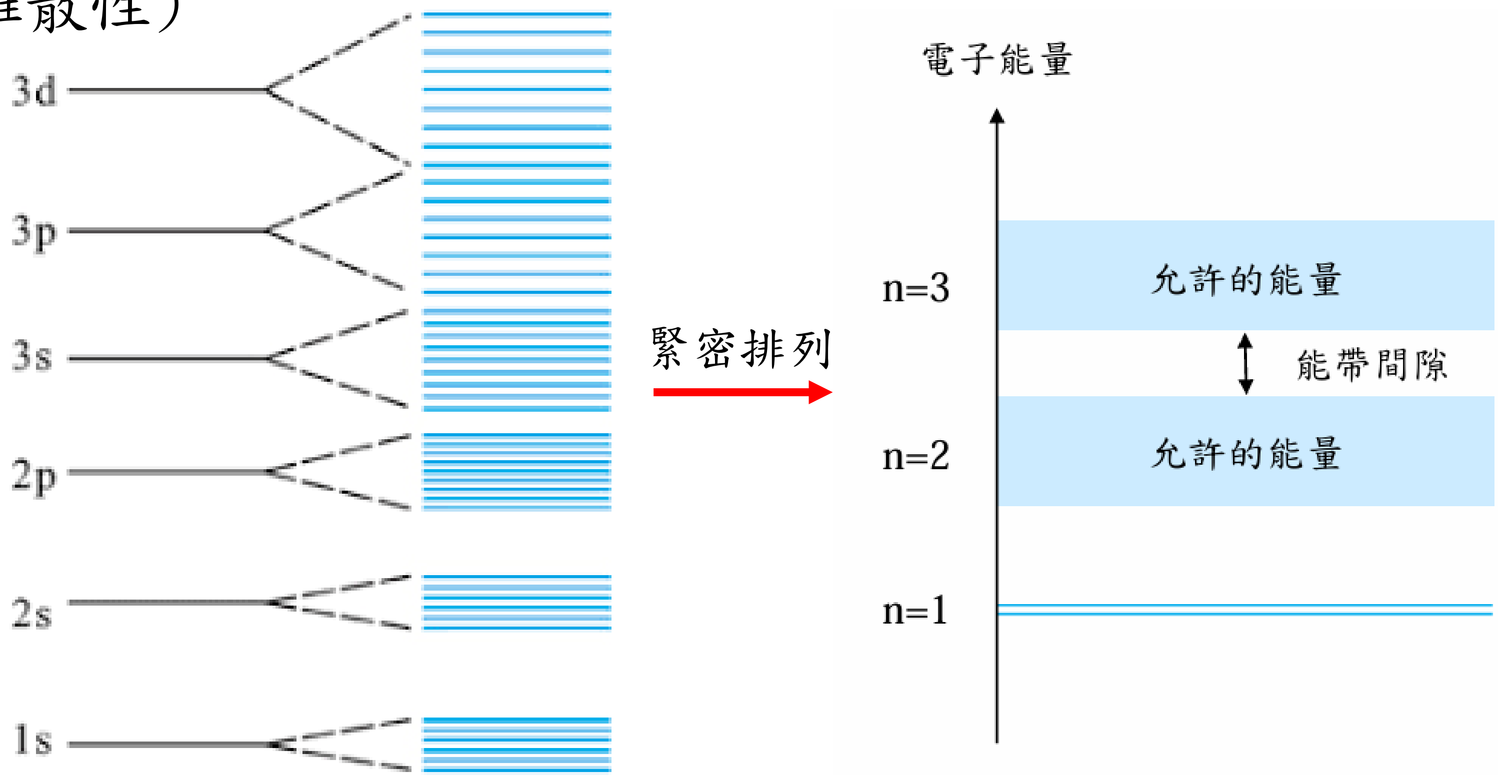
- 包利不相容原理（Pauli Exclusion Principle）是量子力學中的一個基本概念，由奧地利物理學家沃爾夫岡·包利（Wolfgang Pauli）於1925年提出。這個原理指出，在一個原子中，不能有兩個電子具有完全相同的一組四個量子數（主量子數 n、角動量量子數 l、磁量子數 m_l 和自旋量子數 m_s）
- 特點：
  - 獨特的量子數組合
  - 軌域最大容納電子數
  - 電子結構



Source:泰宇文化，選修化學上

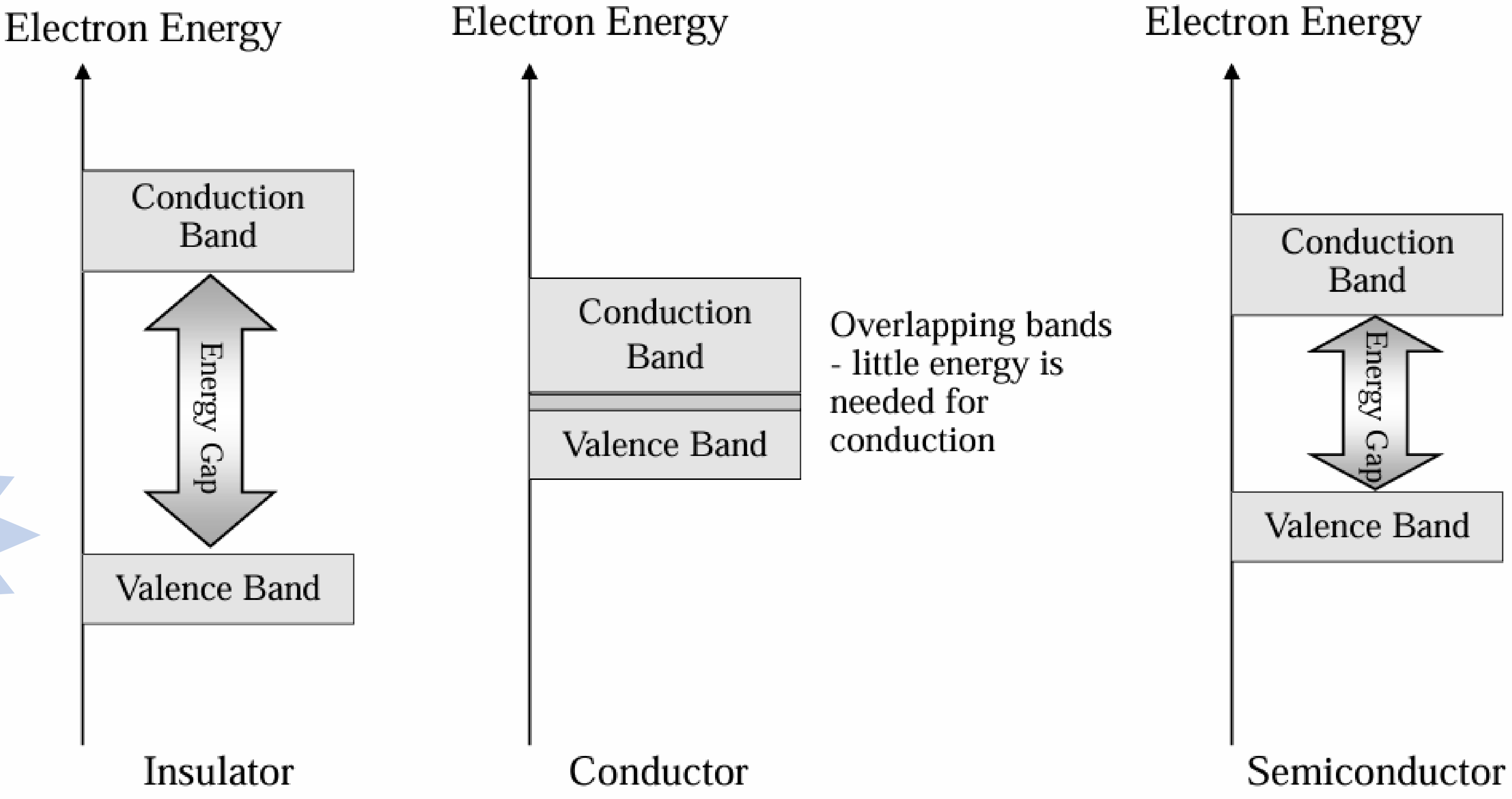
Energy Band

- 能帶的形成是由於大量原子緊密排列在一起時，其電子能級相互作用所致。這些能級互相重疊並形成連續的能量帶
- 特點：
  - 孤立原子的能級（離散性）
  - 原子靠近
  - 形成分子軌域
  - 能帶形成
  - 價帶和導帶



Energy Band Gaps

材料的導電性是由「傳導帶」中含有的電子數量決定



Eg > 2 eV

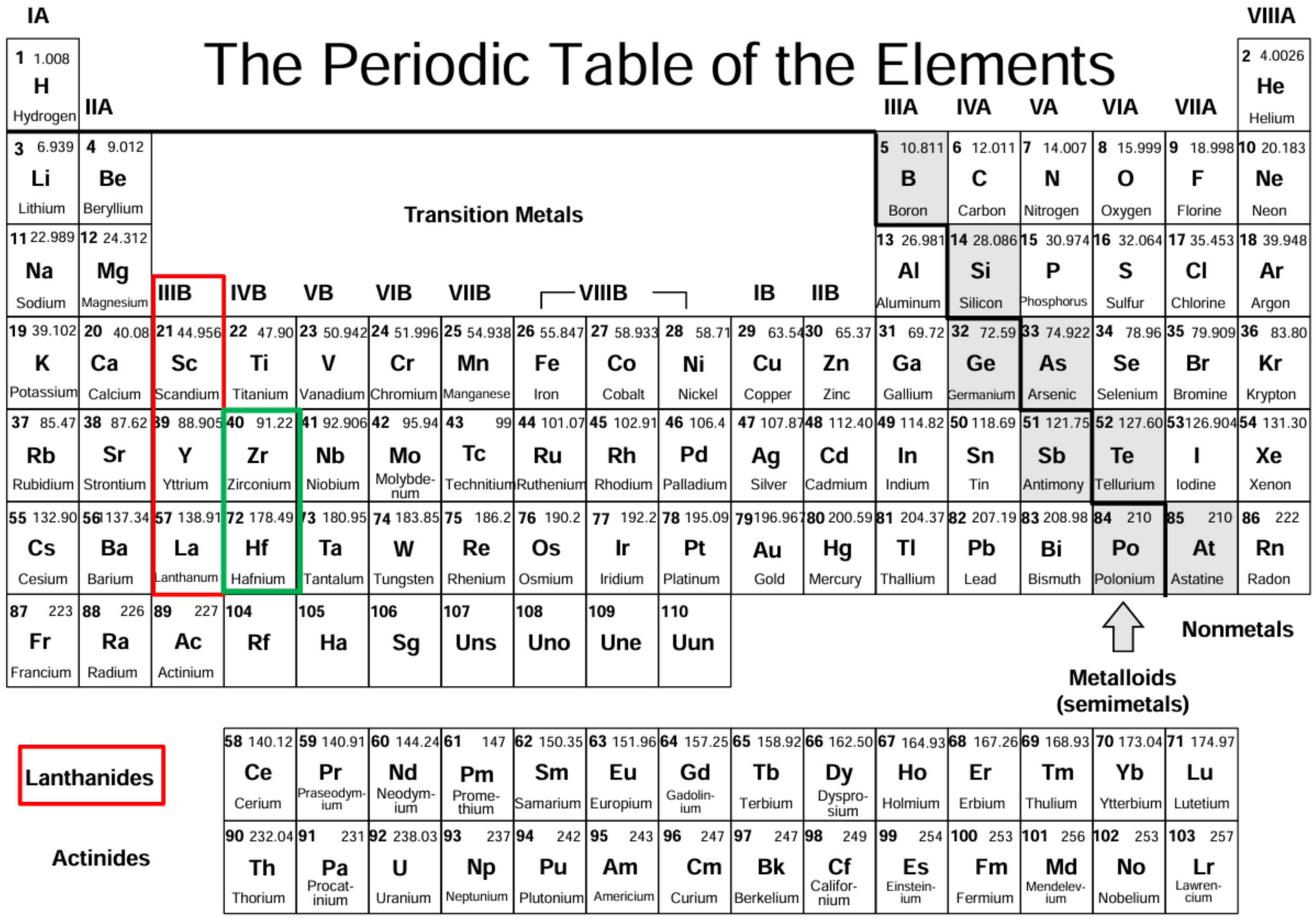
Overlap: no gap

Eg: moderate

The Periodic Table

- Characteristics of Commonly Used Elements
- Ionic Bonds
- Covalent Bonds

The Periodic Table



Characteristics of Chemicals used in Wafer Fabrication

Group Number	Characteristics
IA	• Low electronegativity • Highly unstable； Very reactive; explosive • Prefer not to use the metals in this group due to contamination issues
IIA	• Somewhat unstable； Quite reactive • Prefer not to use metals in this group
IIIA	• Dopant elements (primarily B) added to semiconductor material • Common interconnect conductor material (Al)
IVA	• Semiconductor materials
VA	• Dopant elements (primarily P and As)
VIA	• 6 valence electrons

Characteristics of Chemicals used in Wafer Fabrication

Group Number	Characteristics
VIIA	• Readily accepts electrons ; High electronegativity • Corrosive • Very reactive ； Useful in some semiconductor application: etching and cleaning compounds
VIIIA	• Stable; nonreactive (Inert gas) • Safe to use in semiconductor manufacturing
IB	• Best metal conductors (Cu is replacing Al as primary interconnect conductor material)
IVB – VIB	• Refractory (high melting temperature) metals commonly used in semiconductor manufacturing to improve metallization (especially Ti, W, Mo, Ta, and Cr) • Reacts well with silicon to form stable compound with good electrical characteristics

Ionic Bond

離子鍵（Ionic Bond）是一種化學鍵，由帶相反電荷的離子通過靜電引力相互吸引而形成。通常，這種鍵在金屬和非金屬原子之間形成

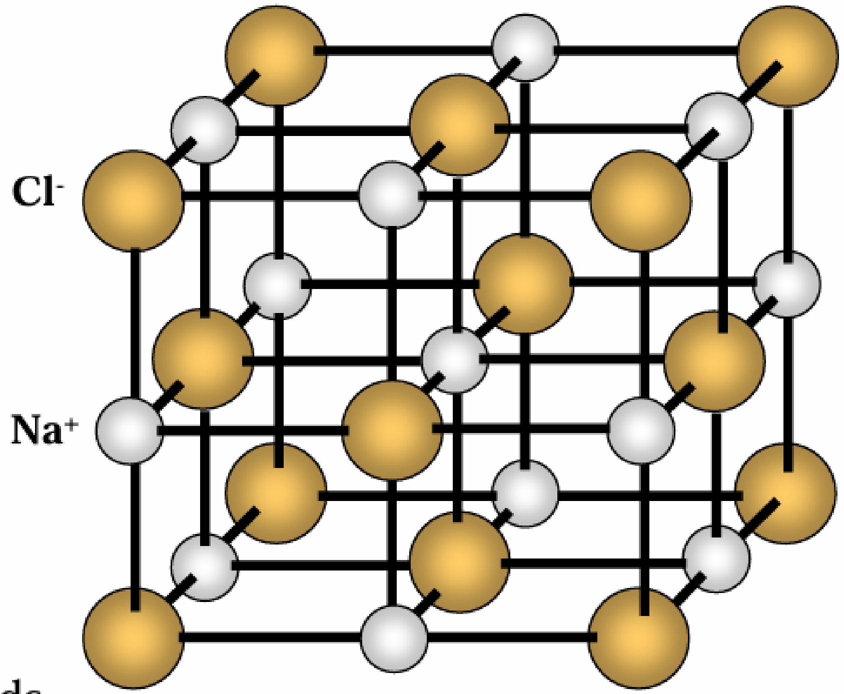
特徵:

- 電子轉移
- 靜電引力
- 結構特性
- 溶解性

氯化鈉（NaCl）

- 一種離子化合物。
  - ➢ 鈉（Na）原子失去一個電子形成Na^+陽離子
  - ➢ 氯（Cl）原子獲得一個電子形成Cl^-陰離子
  - ➢ 這些離子通過靜電力緊密結合，形成氯化鈉晶體。

Ionic Bond for NaCl



Formation of ionic bonds

- Oxidation: loss of electrons (Na^+)
- Reduction: gain of electrons (Cl^-)

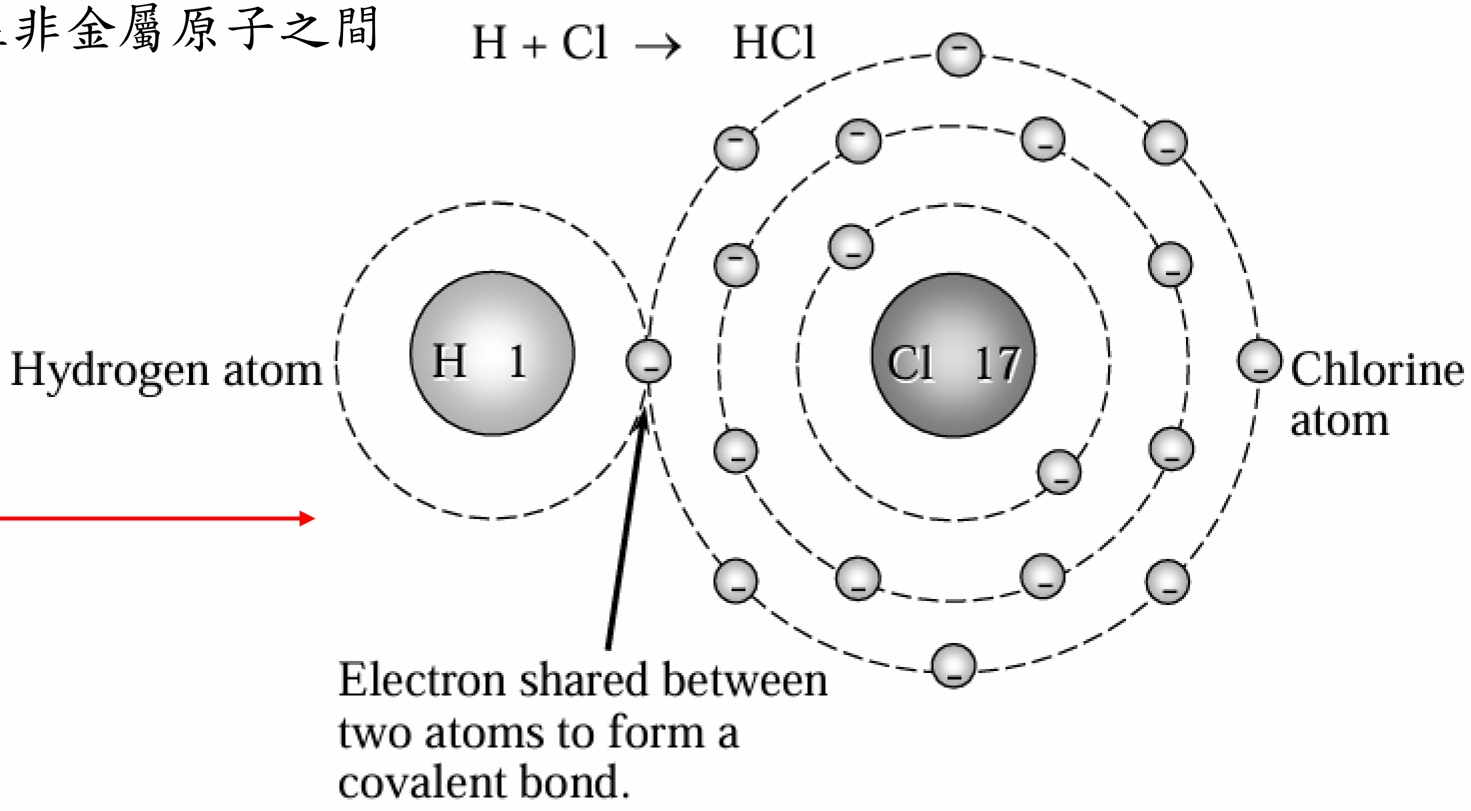
Covalent Bond

共價鍵（Covalent Bond）是指原子之間通過共享電子對形成的化學鍵。這種鍵通常發生在非金屬原子之間特徵：

- 電子共享（穩定）
- 單鍵、雙鍵和三鍵
- 極性

鹽酸（HCl）

- 極性共價鍵形成的分子
  - **極性共價鍵**：氯原子擁有部分負電荷（δ^-），氫原子擁有部分正電荷（δ^+）
  - **酸性**：在水中易解離形成氫離子（H^+）和氯離子（Cl^-）

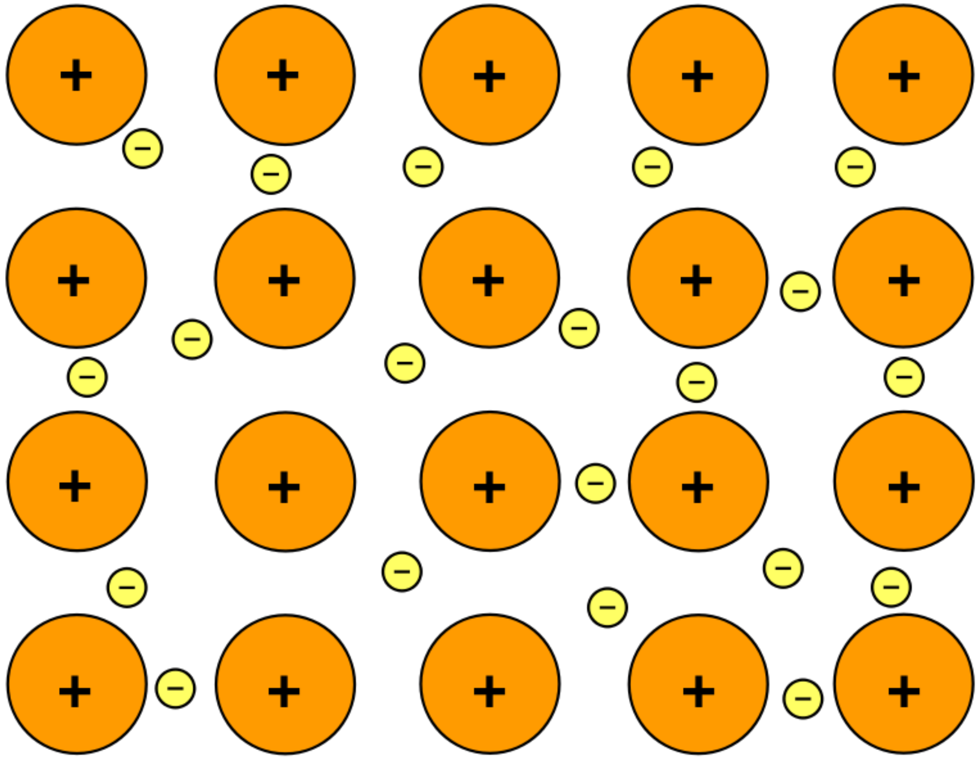


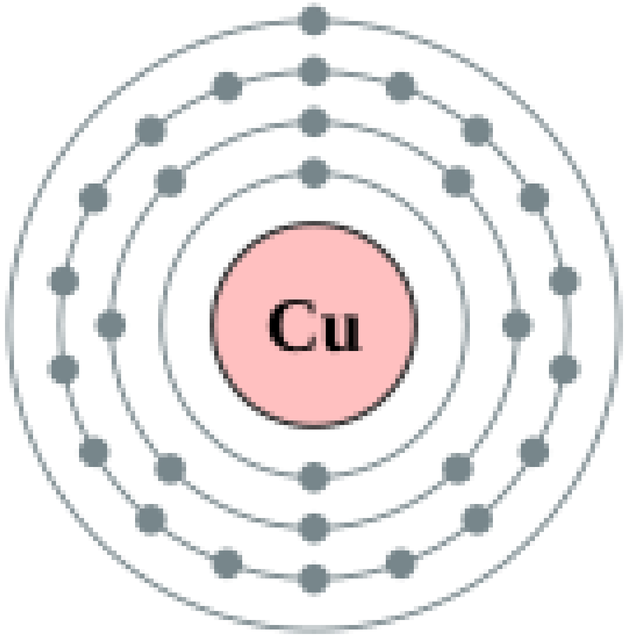
Metallic Bond

金屬鍵（Metallic Bond）是一種化學鍵，由金屬原子通過共用其價電子形成

特徵：

- 電子海模型
- 高導電性和導熱性
- 延展性和可塑性





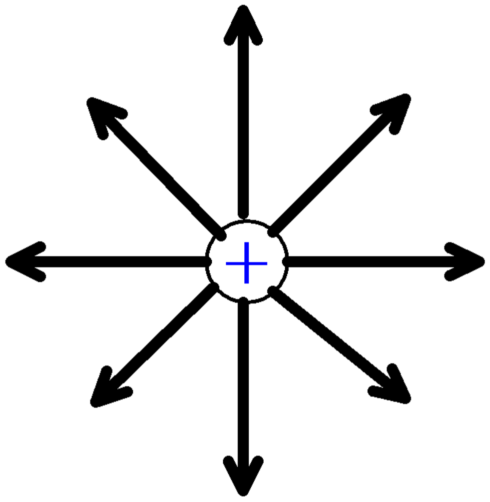
Source: Wikipedia

Classifying The Performance of Materials

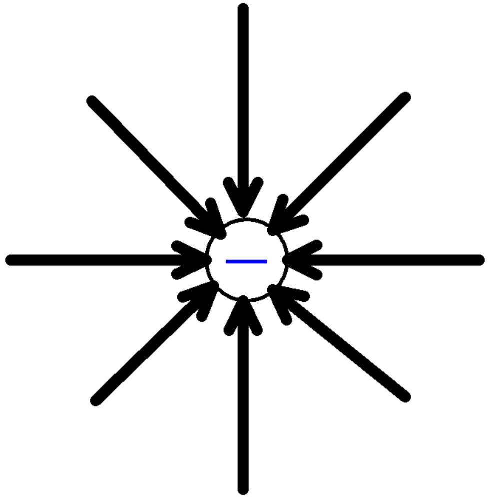
- Electric field & Electric potential
- Resistance
- Resistor
- Capacitance
- Capacitor

Electric field & Electric potential

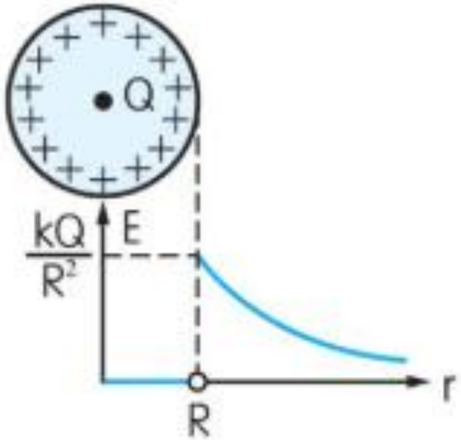
- 電場 (electric field) 是一種物理場，用來描述電荷之間的相互作用
- 電位 (electric potential) ，它描述了電荷在該點的潛在能量。電位的單位是伏特（V）

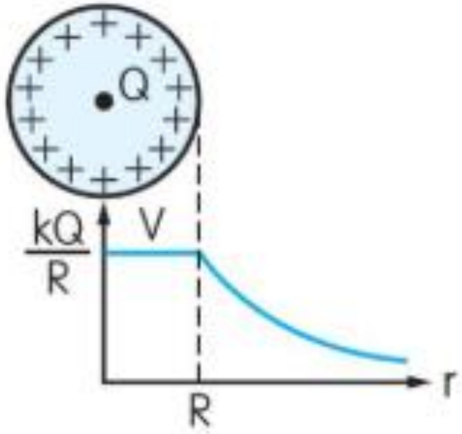


正電荷



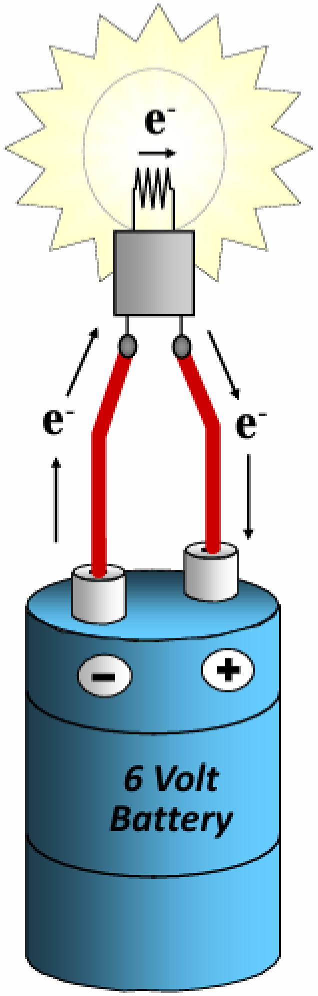
負電荷

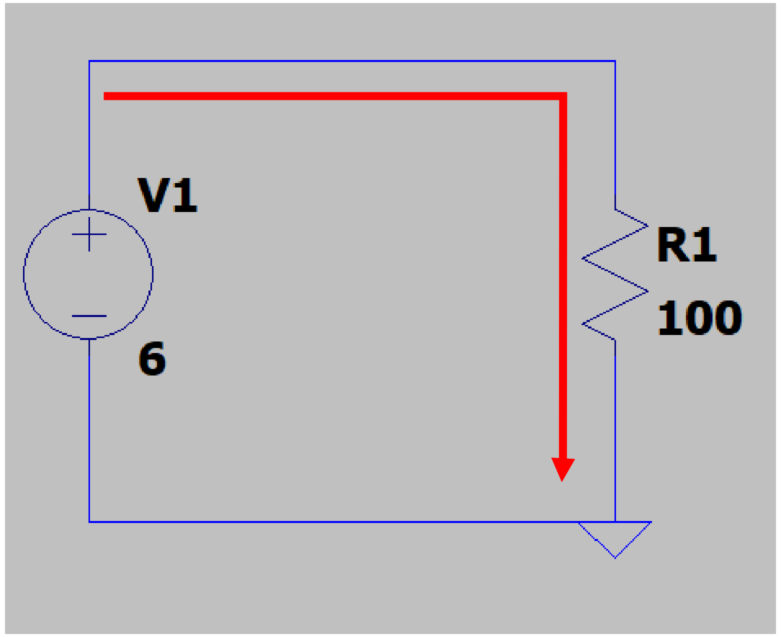




Electrical Current Flow

Copper wires provide connections that allow electrons to flow from the - terminal, through the filament inside the lamp, and back into the + terminal of the battery.





電流

$$I = \frac{Q}{t}$$

Q : 正電荷數

t ：時間

Resistance

- 電阻（Resistance）是指物質對電流流動的阻礙作用。它是電路中一個重要的參數，決定了電流在電路中的流動速度和電壓降。電阻的單位是歐姆（Ω）
- 特徵：
  - 電阻率（ρ）
  - 材料長度
  - 橫截面積
  - 溫度的影響

電阻推導：

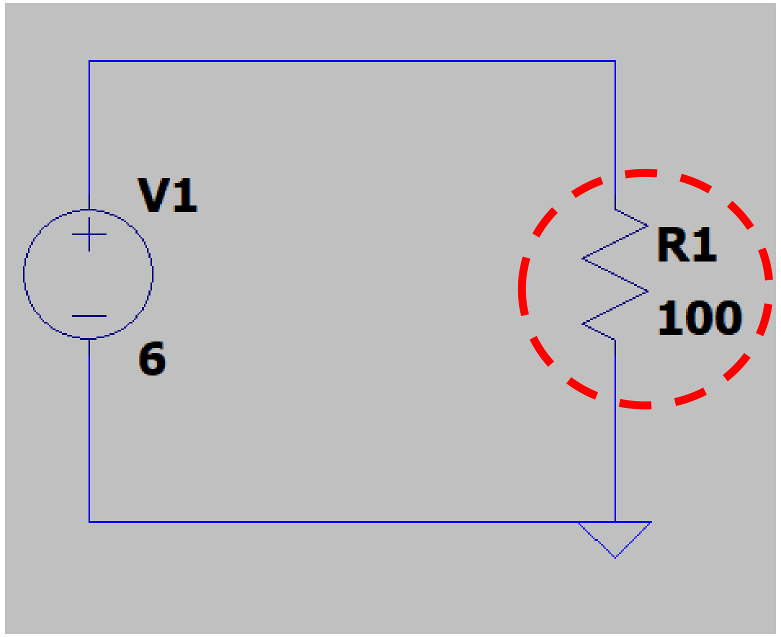
電流密度 $J = \frac{I}{A} = \sigma E = \frac{E}{\rho}$

電位/電壓 $V = EL$

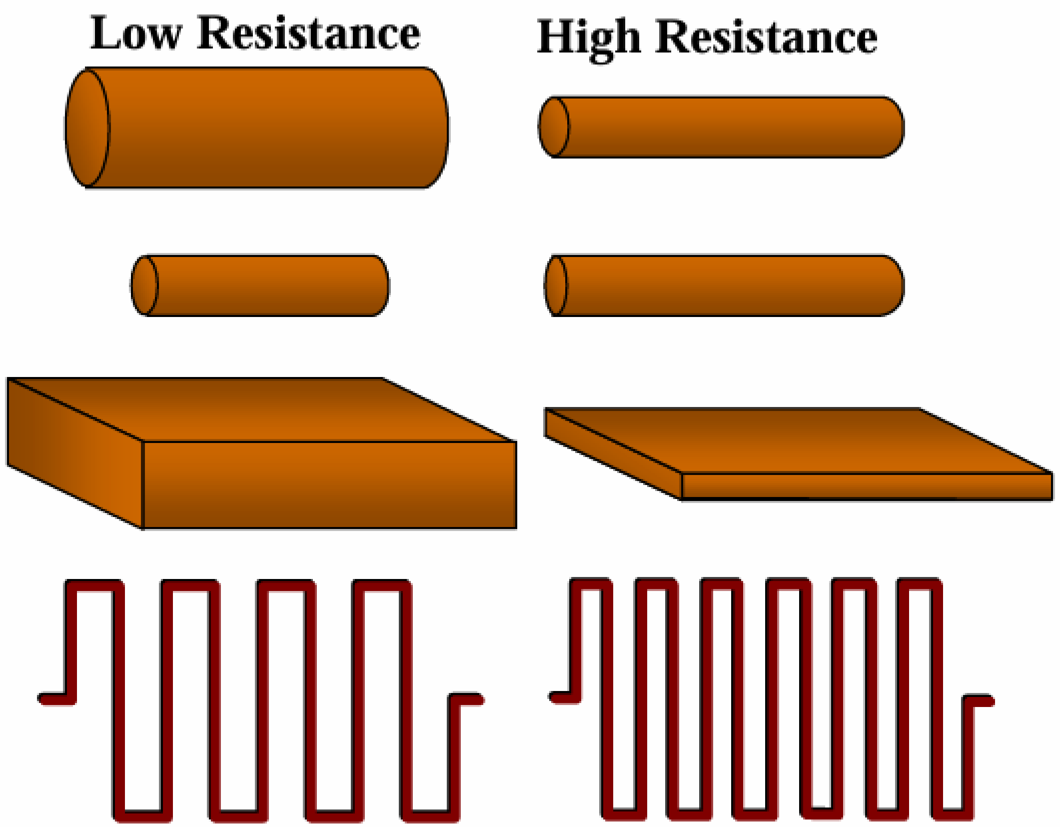
$$\frac{I}{A} = \frac{V}{\rho L}$$

歐姆定律 $V = IR$

電阻 $\boxed{R = \frac{\rho L}{A}}$



How Sizes Affect Resistance



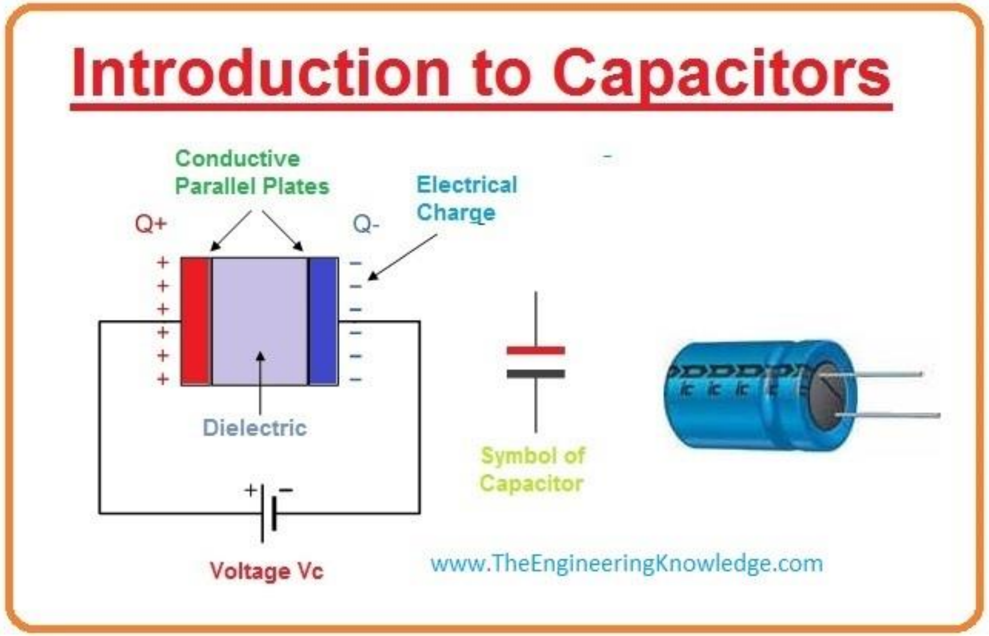
$$R = \frac{\rho L}{A}$$

$$\rho = \frac{1}{nq\mu}$$

Resistance is the opposition to current flow and is accompanied by the dissipation of heat

Capacitance

- A **capacitor** consists of two terminals, it stores electrical power or energy in the shape of an electrical field
- A capacitor has dielectric material among the electric plates this dielectric material do not allow direct current to pass instead it stores voltage in the shape of charge across the plates of a capacitor
- The motion of electrons over the electrode of the capacitor is recognized as the Charging Current of a capacitor, which flows till that point when applied voltage and voltage across the electrode of the capacitor become equal. This condition is said to be a fully charged condition of a capacitor
- A capacitance has a unit of Farad (F).



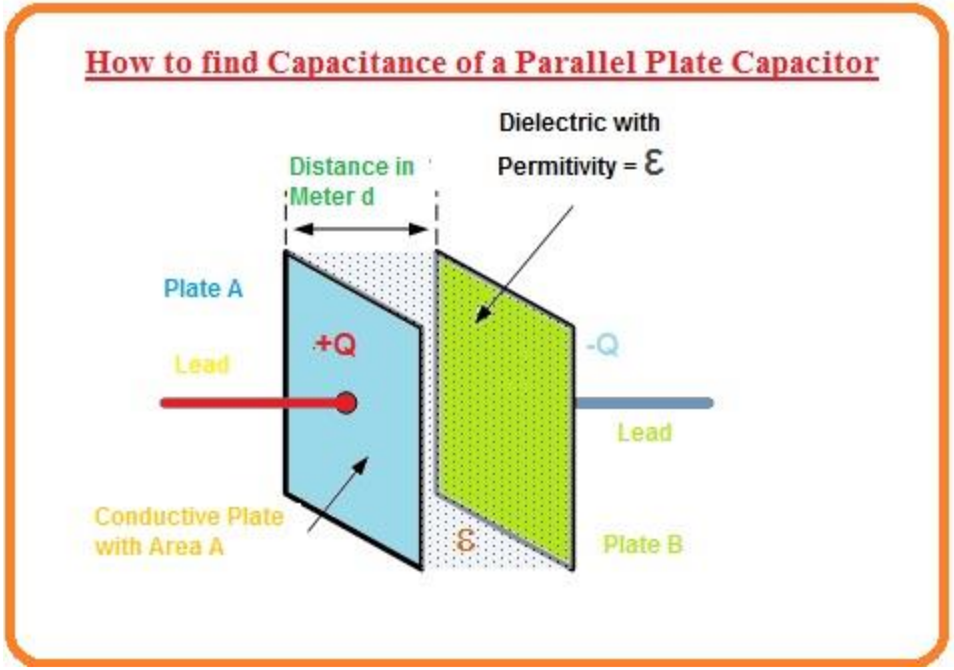
Capacitance

- 特徵：
  - 介電材料 / 介電系數 (ε_r)
  - 電極間距離
  - 橫截面積
  - 溫度的影響
  - 儲存電荷 / 儲存能量
  - 阻擋直流電
  - 頻率特性

電場 $E = \frac{V}{d}$

電荷 $Q = \varepsilon E * A = \frac{\varepsilon V * A}{d} = C * V$

$\boxed{電容\ C = \frac{\varepsilon * A}{d}}$



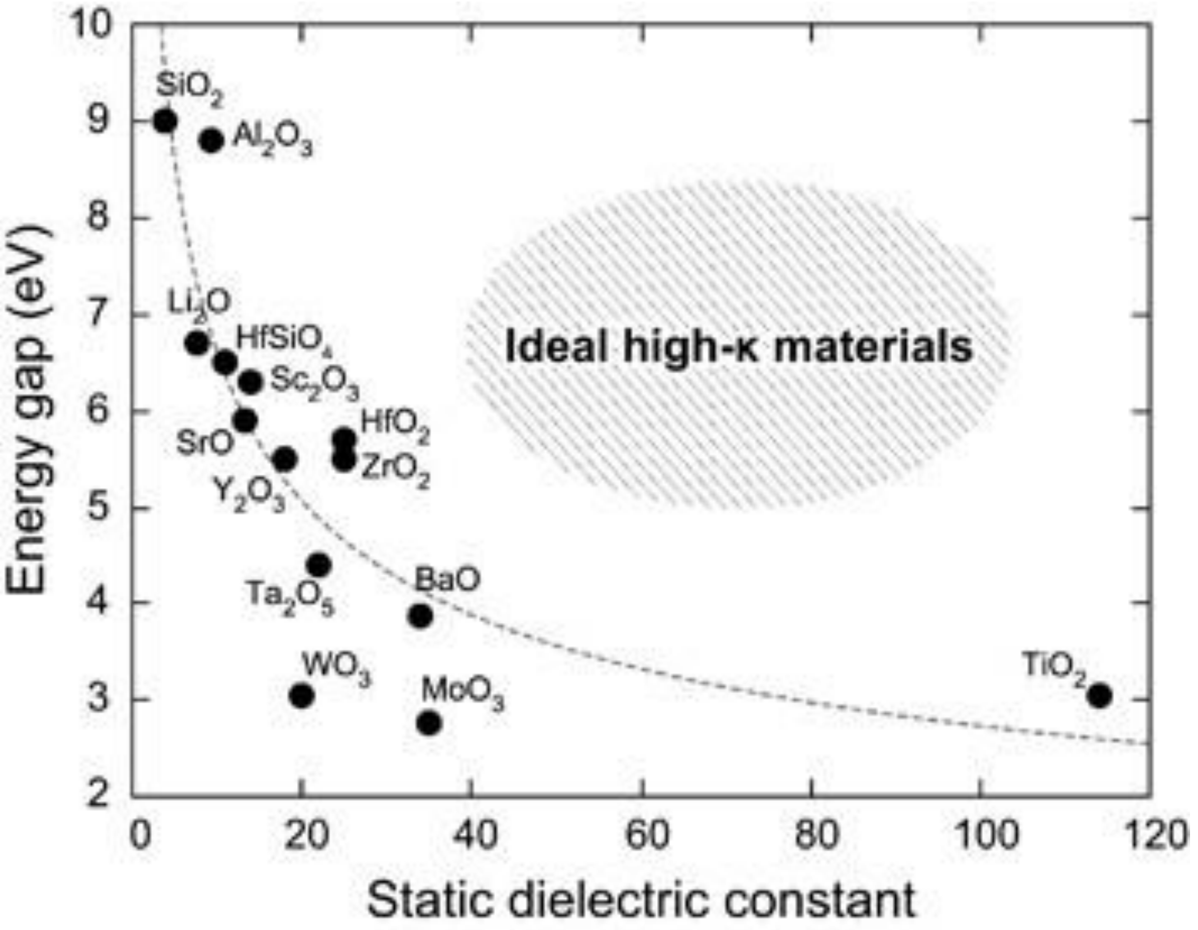
Low K vs. High K material

- 材料的介電常數（k / ε_r 值）決定了它們在電容和電隔離方面的性能

- 高介電常數（High-k）材料

- 特點：
  - 高介電常數（k值）
  - 降低漏電流
  - 減小等效厚度
  - 材料大部分為氧化物，因此需沉積一層很薄的SiO_2做為介面層

等效厚度 $EOT = dHigh_k * \frac{\varepsilon_{SiO2}}{\varepsilon_{High\,k}}$



Source: Kanghoon Yim et al, "**Novel high-κ dielectrics for next-generation electronic devices screened by automated *ab initio* calculations,**"
npg asia materials, 12 June 2015

Low K vs. High K material

- 低介電常數（Low-k）材料

- 特點：
  - ➢ 低介電常數（k值）
  - ➢ 降低信號延遲
  - ➢ 減少發熱 / 熱阻小

- Low k vs. ultra-low k material

Materials	Method	Electrical properties κ	Mechanical properties: Modulus (GPa)	Mechanical properties: Hardness (GPa)	Process Compatibility: CMP	Process Compatibility: Etching	Process Compatibility: Gap filling	Process Compatibility: CTE
SiO_2	CVD	4	55 - 70	3.5	O	X	X	O
FSG (Fluorinated silicon glass)	CVD	3.5 - 3.8	-50	3.36	O	X	X	O
SiCOH	PECVD	2.8	16.2	1.69	X	X	X	O
Fluorinated PI films	Scraping method	2.78	2.67	-	X	X	X	O
pSiCOH (pore <1.5 nm)	PECVD	2.4	4.2	0.28	X	X	X	O
Polyimide	Roll-to-roll	2.27	1.96	-	X	X	X	O
Porous HSQ(hydrogen silsesquioxane)	PECVD	2.2	-	-	X	X	X	X
Fluorocarbon	CVD	2.2	8	-	O	O	X	O
co-polyarylates with spiral ring	Solution-casting method	2.16	2.4	-	X	X	X	X
Triethoxyfluorosilane (TEFS)	spin-on process	2.1	12	1	X	X	X	X
pSiCOH (pore <2.5 nm)	PECVD	2.05	3.3	0.28	X	X	X	O
SiCOH	PECVD	2.02	5.3	-	X	O	X	X
Fluorinated graphene/polybenzoxazole composite	Scraping method	2.02	1.98	-	X	X	X	X
Porous oxycarbosilane	Spin coating	2.0	-	-	X	O	X	X
Fluorinated graphene/polyimide (FG/PI) composite	Laye by layer coating method	1.92	1.93	-	X	X	X	X
Decamethylcyclopentasiloxane and tetrakis (trimethylsilyloxy)silane	PECVD	1.91	2	0.3	X	X	X	X
2D covalent organic frameworks (COFs)	Templated colloidal method	1.6	-	-	X	X	X	X
MSQ with triblock copolymer	Spin coating	1.5	0.6	0.16	X	X	X	X
a-BN	CVD	1.16 - 1.78	Compared with bare Si wafer		X	X	X	X
Cross-linked SiO_2 aerogel	Spin coating	1.45 - 1.7	5.1	0.3	O	O	O	O

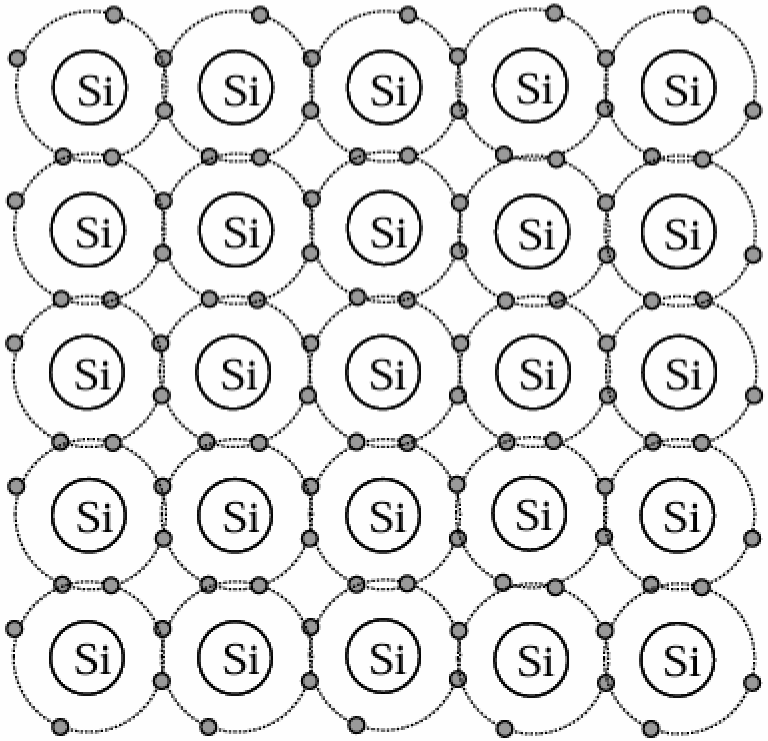
Source: Haryeong Choi et al, "Ultralow dielectric cross-linked silica aerogel nanocomposite films for interconnect technology ," Applied Materials Today, 2 June 2022

Silicon

- Pure Silicon
- Why Use Silicon?
- Doped Silicon
- Dopant Materials
  - n-type Silicon
  - p-type Silicon
  - Resistivity of Doped Silicon

Covalent Bonding of Pure Silicon

- Silicon is not found pure in nature ; it needs refined and purified
- Pure silicon is a poor conductor, no free electron, no use

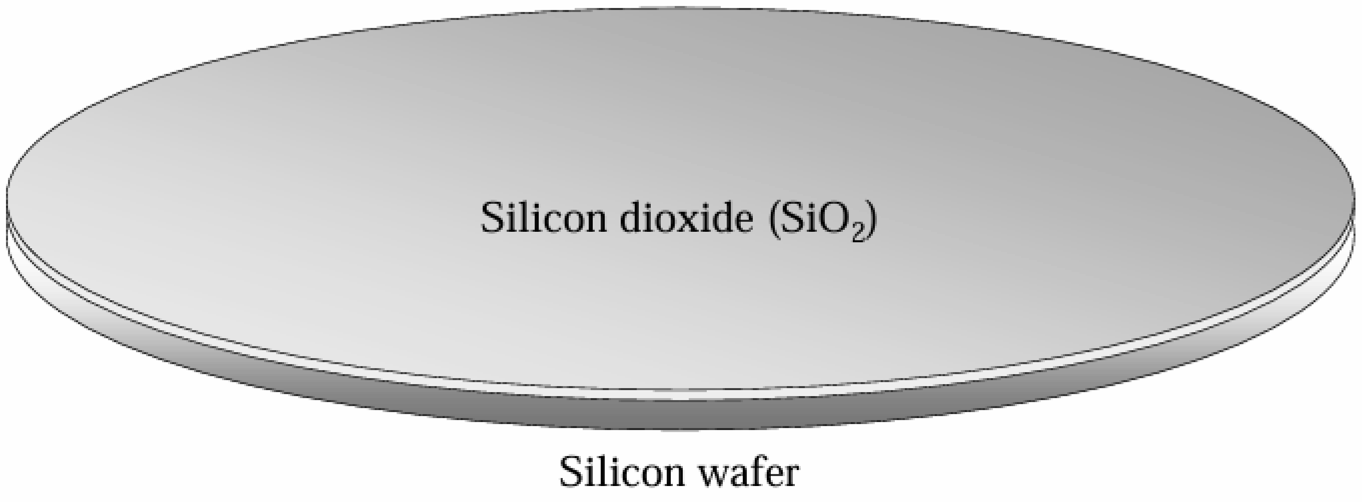


Silicon atoms share valence electrons to form insulator-like bonds.

SiO_2 on Silicon Wafer

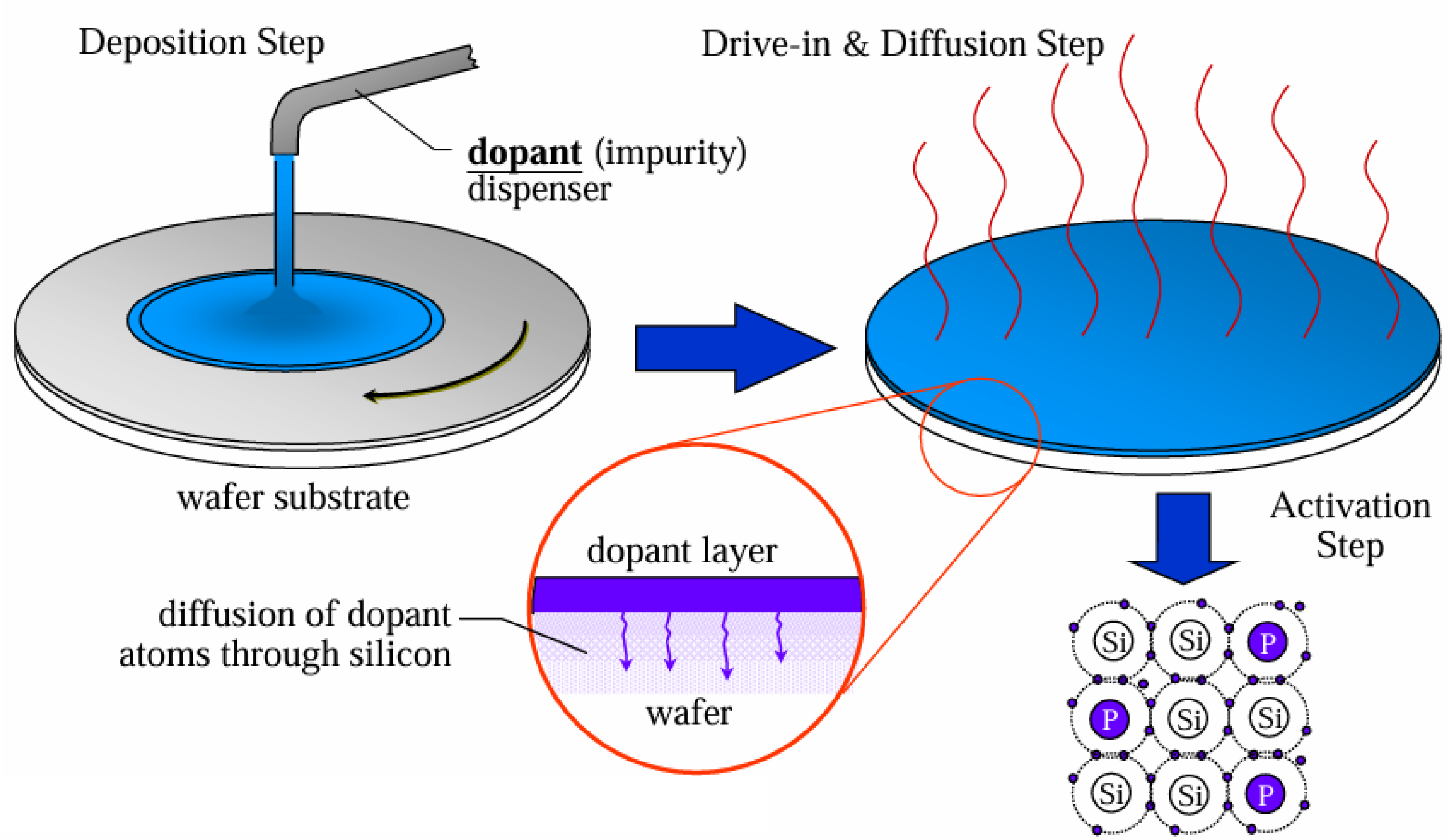
- Why Silicon:

1. Abundance of silicon (25%, the second)
2. Higher melting temperature for wider processing range (1412 °C)
3. Wider temperature range of operation (Eg> Ge)
4. Natural growth of silicon dioxide (MOS)



Doping of Silicon (intrinsic → extrinsic)

- Pure silicon : ρ = 2.5x10^5 ohm-cm
- If doped one in every 10^6 silicon atom, then ρ = 0.2 ohm-cm

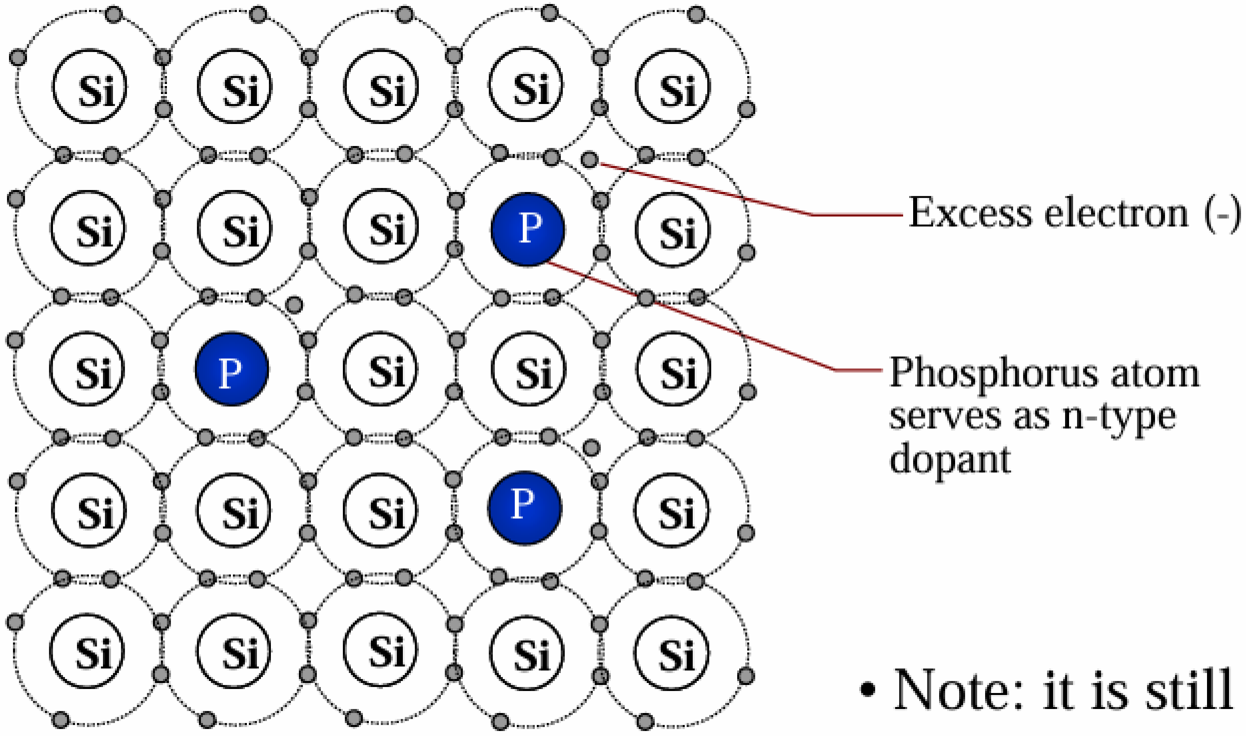


$$\boxed{diffusion\ fiux\ F = -D * \frac{dn}{dx}}$$

Acceptor Impurities		Semiconductor		Donor Impurities	
Group III (p-type)		Group IV		Group V (n-type)	
Boron	**5**	Carbon	6	Nitrogen	7
Aluminum	13	**Silicon**	**14**	**Phosphorus**	**15**
Gallium	31	Germanium	32	**Arsenic**	**33**
Indium	49	Tin	50	**Antimony**	**51**

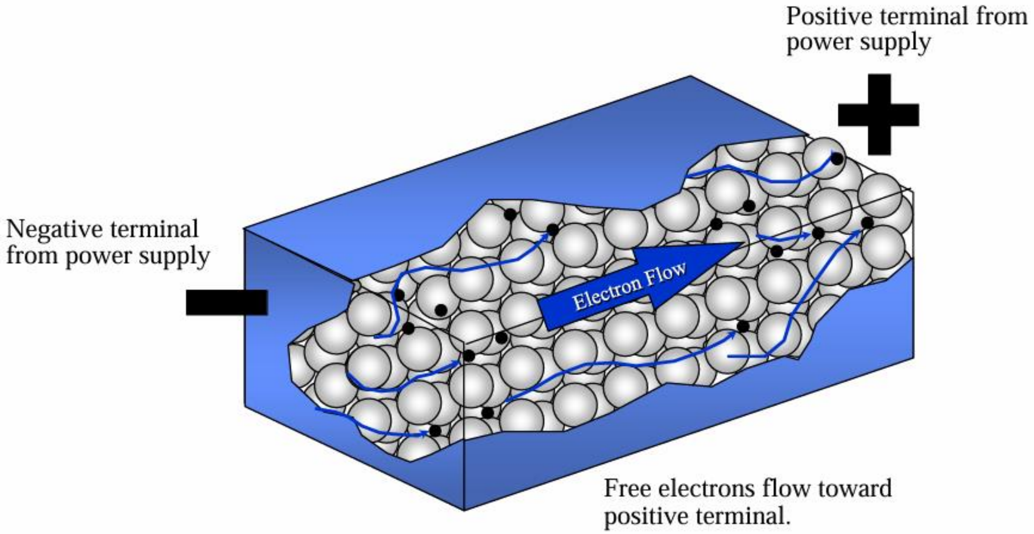
** Items underlined are the most commonly used in silicon-based IC manufacturing.*

Electrons in N-Type Silicon with Phosphorus Dopant

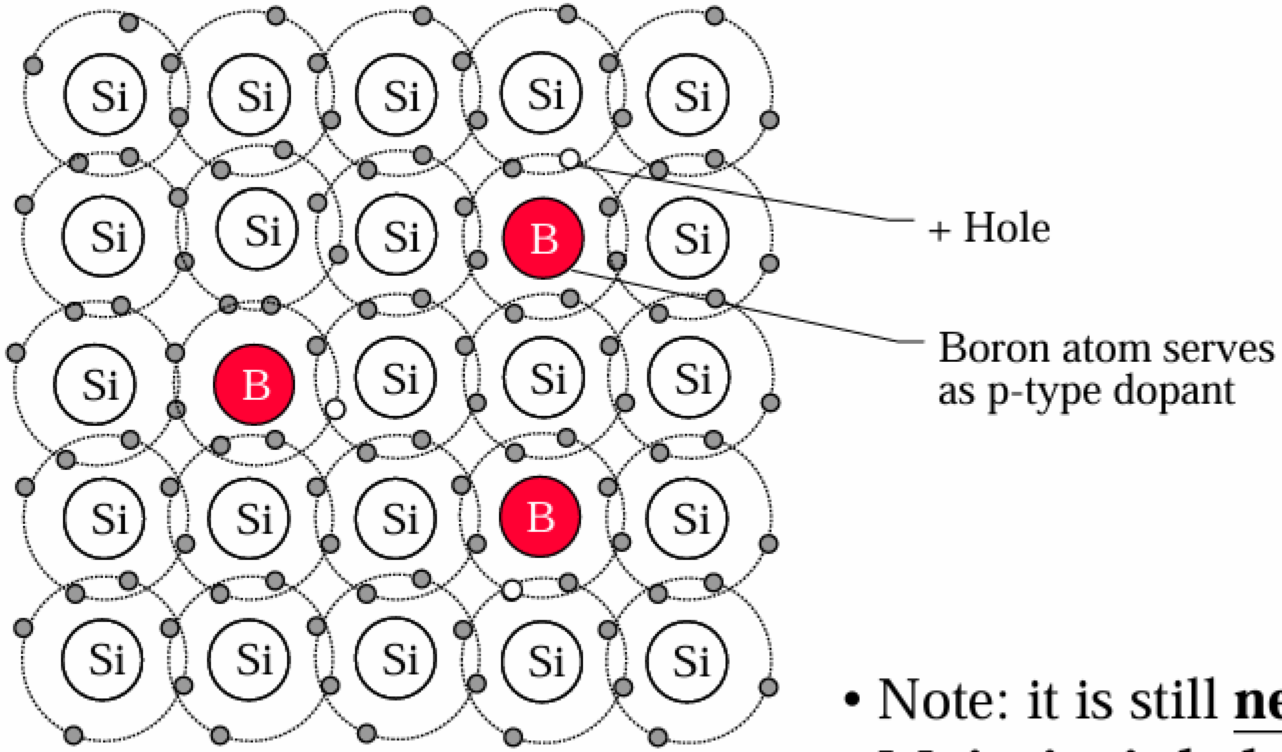


Donor atoms provide excess electrons to form n-type silicon.

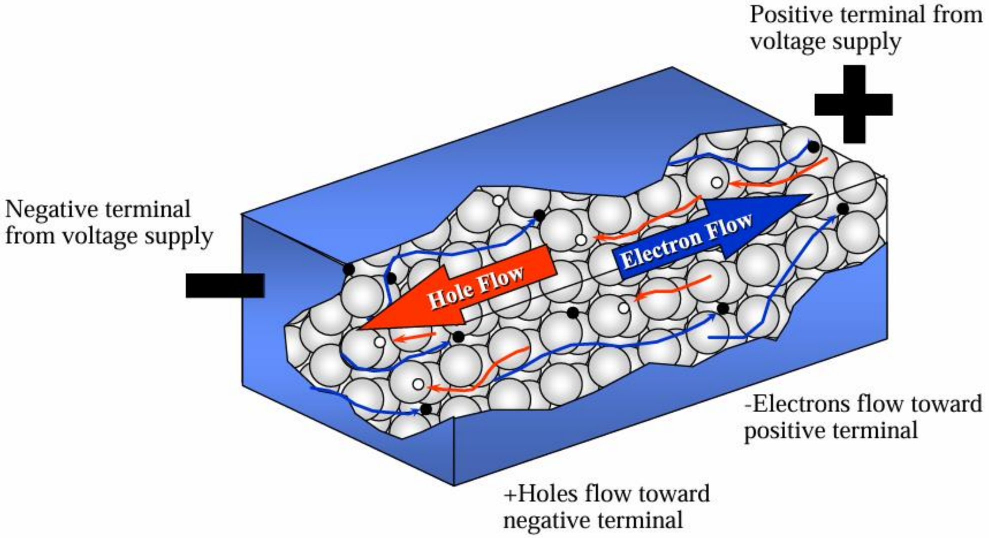
- Note: it is still **neutral**
- **Majority is electron**



Holes in p-Type Silicon with Boron Dopant

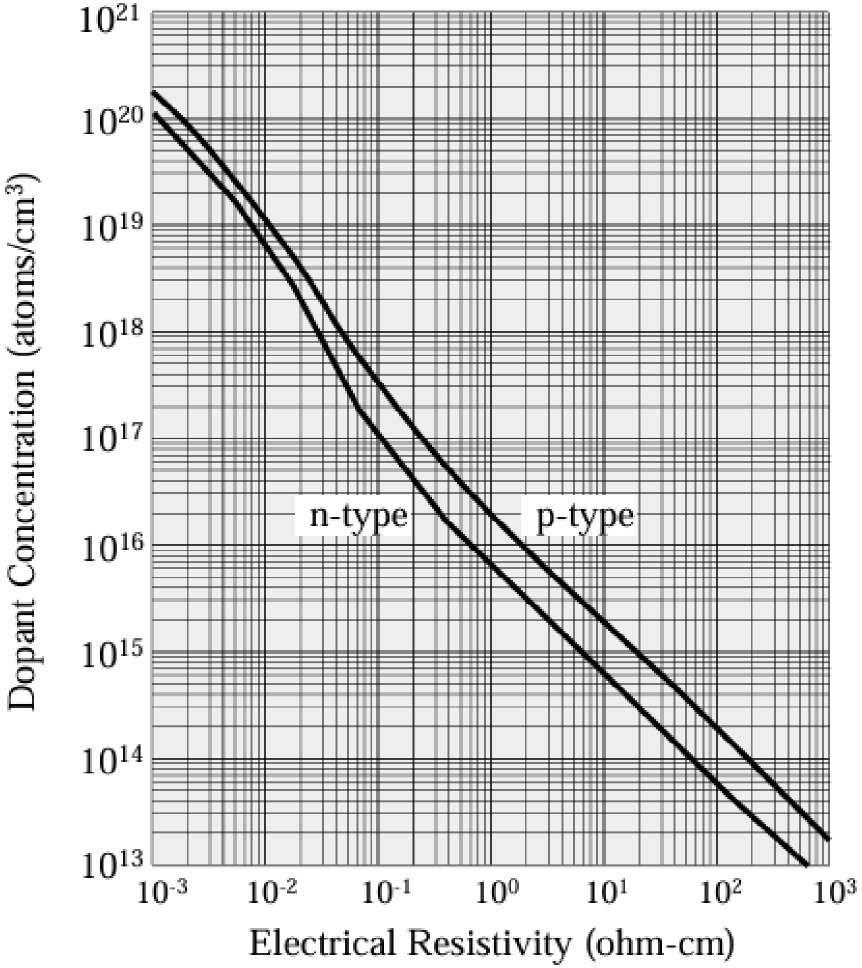


Acceptor atoms provide a deficiency of electrons to form p-type silicon.



- Note: it is still **neutral**
- **Majority is hole**
- **Minority is electron**

Silicon Resistivity Versus Dopant Concentration



Redrawn from *VLSI Fabrication Principles, Silicon and Gallium Arsenide*, John Wiley & Sons, Inc.

Alternative Semiconductor Materials

	第一代 (元素) 半導體		第二代 (化合物) 半導體	第三代 (寬能隙) 半導體	
	Ge	Si	GaAs	GaN	SiC
Melting point (°C)	937	1414	1238	2500+	~2700
Atomic Weight	72.63	28.09	144.64	83.73 (Ga) + 14.01 (N)	28.09 (Si) + 12.01 (C)
Atomic Density (10^{22} atoms/cm^3)	~4.42	~5.00	~4.42	~4.38	~4.91
Energy Bandgap (eV)	0.66	1.12	1.42	~3.4	~3.2
Bandgap type	間接	間接	直接	直接	間接
Electron Mobility (cm^2/V-s)	~3900	~1400	~8500	~1500	~900
Breakdown electric field (MV/cm)	~0.1	~0.3	~0.4	~3.3	~3.0
Thermal conductivity (W/m·K)	~60	~150	~46	~130	~370

第二代半導體 (Gallium Arsenide)

- 由砷 (As) 和鎵 (Ga) 兩種元素組成。它在電子和光電領域中擁有許多優異的特性
- 特性：
  - 高電子遷移率
  - 直接能隙
  - 寬能隙
- 優點：
  - 高頻性能優越
  - 高效率光電轉換
  - 良好的高溫穩定性
- 缺點：
  - 製造成本高
  - 材料稀有
  - 晶圓尺寸小
- 應用：
  - 高頻電子元件
  - 光電元件
  - 高效能計算

種　類	材　料	應　用
Si	Si	積體電路 (Integrated Circuits) 太陽能電池 (Solar Cell) 微機械元件 (Micromechanics)
化合物	GaAs	高速、高頻積體電路
	GaP	發光二極體 (Light Emitted Diode)
	InP	光測器 (Photo Detector)
	ZnSe	半導體雷射 (Semiconductor Laser)
	ZnS	平面顯示器 (Flat Panel Displays)

第三代半導體 (Gallium Nitride & Silicon Carbide)

	氮化鎵	碳化矽
能隙	3.4 eV	3.26 eV
開關速度	高	中高
熱導率	中	高
耐壓	高	更高
製造成本	較高	更高
應用領域	高頻電子設備、發光元件	高壓、大功率應用
體積	更小	中等

第三代半導體 (Gallium Nitride & Silicon Carbide)

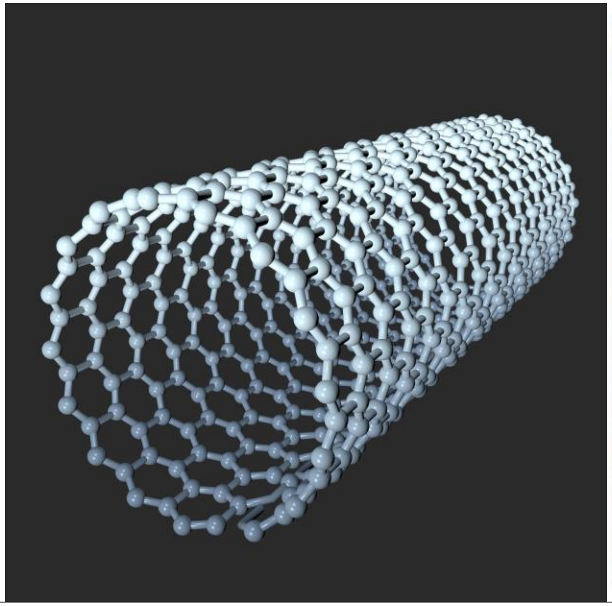
	GaN on Si	GaN on SiC
基板名稱	矽基氮化鎵	碳化矽基氮化鎵
特色	• 異質磊晶 • 高頻、中低頻 • 成本較低 • Si 長晶速度較快	• 異質磊晶 • 高溫高頻 • 性能較GaN on Si好，但成本較高 • SiC長晶速度慢
常用基板尺寸	6吋，未來往8吋邁進。 GaN on Si成品率普遍介於50-60%，較容易擴展到8吋晶圓。	6吋，未來往8吋邁進。
售價	500美元	1,300美元
應用內容	• RF射頻元件 • Power GaN，例如電源轉換器、整流器	• 5G基地台 • 電動車充電電池
特性	• 磊晶層和基板間熱膨脹 • 係數不同，「晶格不匹配」程度比GaN on SiC 大。	• 技術掌握在少數國際大廠，例如Cree、ROHM。 • SiC 材質硬且脆，切割、研磨難度更高。

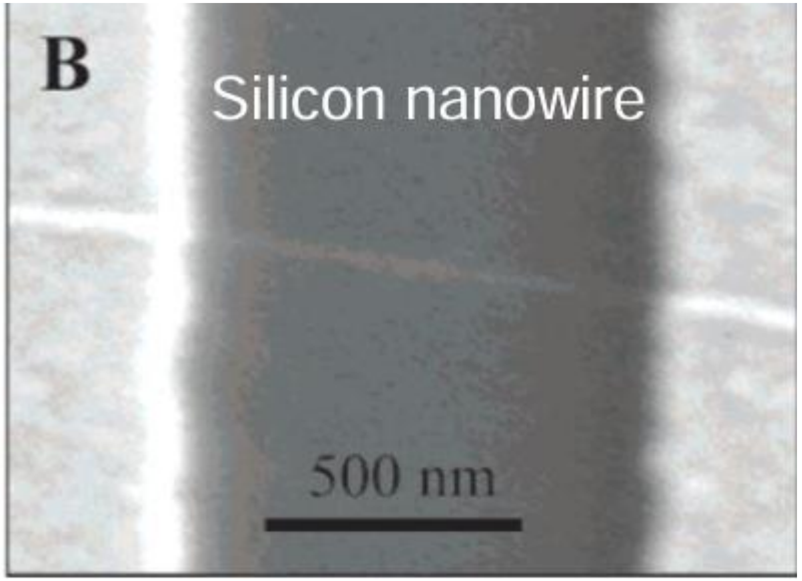
第四代半導體 ??

- 第四代半導體通常指的是以超寬能隙材料為基礎的新一代半導體技術，這些材料在電性、熱性和耐高溫性能上對比於第三代半導體都有提升，能夠滿足極端環境下的應用需求
- 第四代半導體在電動車驅動系統、智慧電力系統、5G及次世代通訊技術、航空航天以及其他需要高功率與高效率的領域中具有極大的應用潛力。不過，目前這些技術和材料仍處於研發階段
- 目前關於第四代半導體還沒有特別指明說是甚麼材料，無論是產業界或是學術界都眾說紛紜，以下是最有可能被認為能代表第四代半導體的族群:
  - 氧化物半導體
    - ✓ Ga_2O_3
    - ✓ ZnO
    - ✓ IGZO
    - ✓ In_2O_3
    - ✓ ITO
  - 氮化物半導體
    - ✓ AlN
    - ✓ BN
    - ✓ 過渡金屬氮化物
  - 鑽石

次世代半導體 (1D ? 2D ?)

- 一維半導體（1D Semiconductor）
- **特性：** 電子傳導僅在一個方向上自由進行，橫向的尺寸被量子限制（量子穿隧）
- **優勢**
  - 高的電子遷移率和低的功耗
  - 獨特的量子效應（如量子電導）
  - 可應用於極小尺寸的電子元件，突破摩爾定律極限
- **應用：**
  - **高性能場效應晶體管（FET）**
  - **感測器**
  - **奈米光電元件**
- **挑戰**
  - 材料一致性控制困難
  - 實現大規模製造的技術瓶頸（成本高）

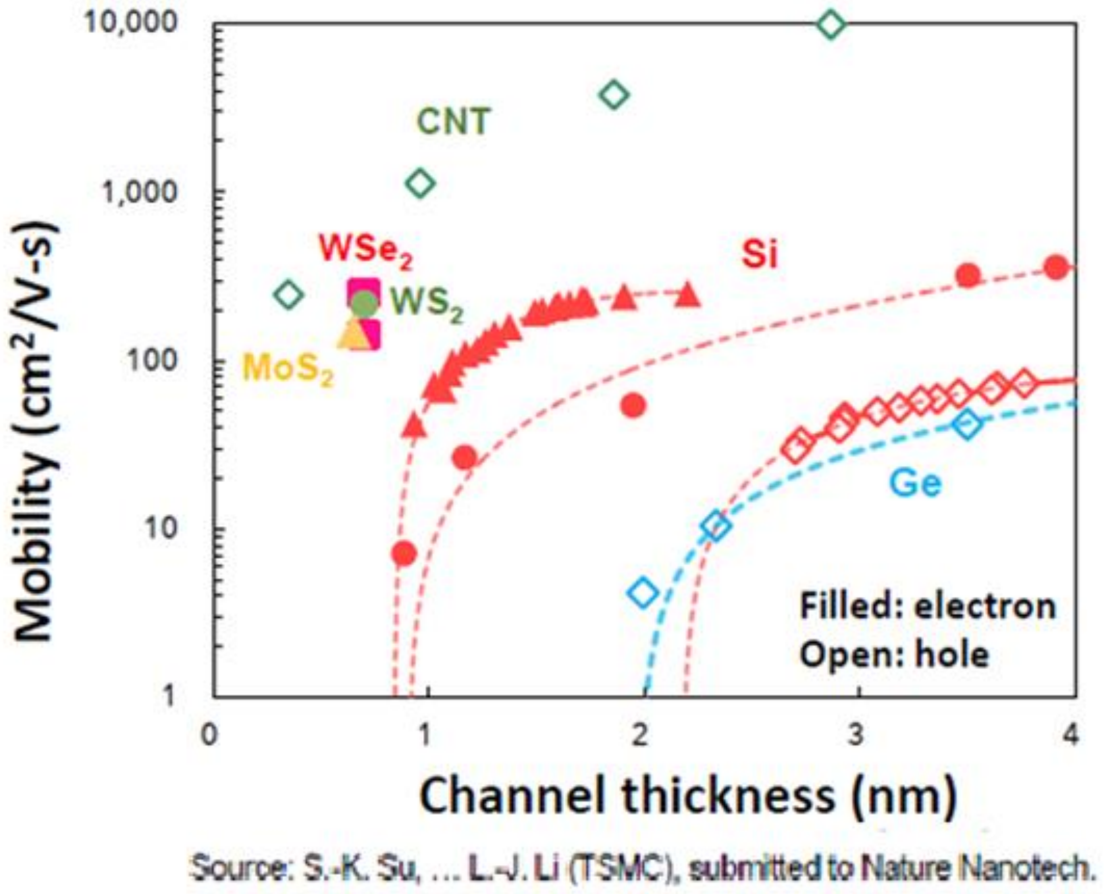




Source: Cui Yi, Nano Letters1999

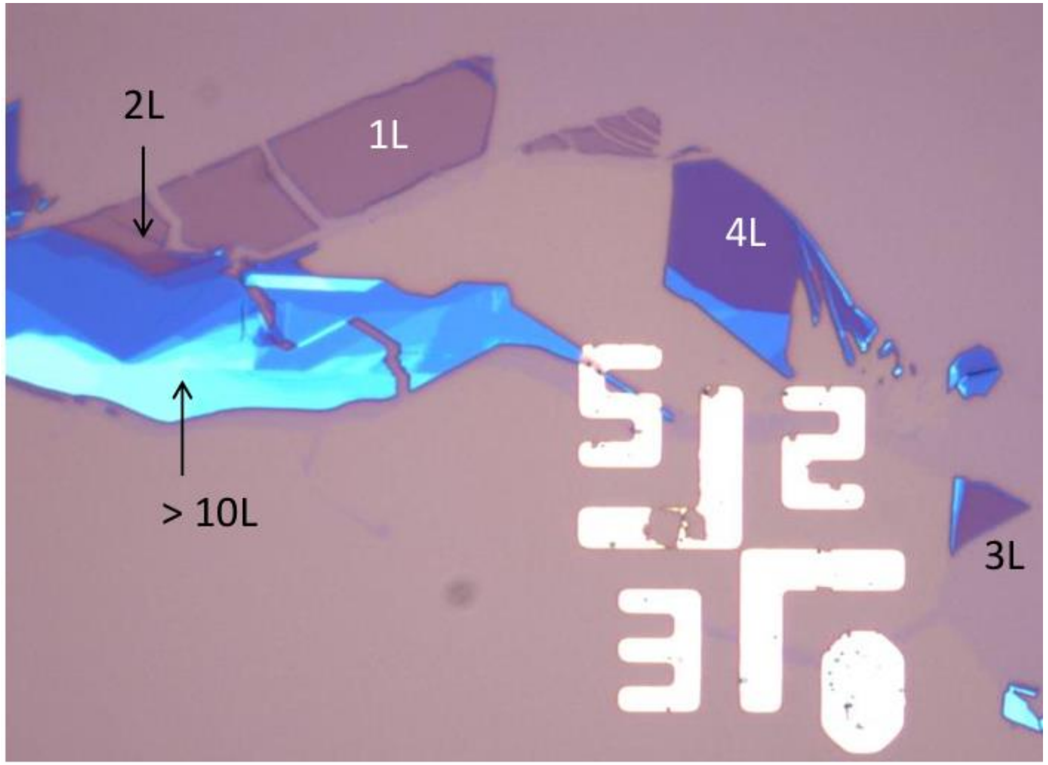
次世代半導體 (1D ? 2D ?)

- **二維半導體（2D Semiconductor）**
- **特性：二維材料**指其厚度僅為單層或少層原子，但橫向尺寸可達數微米到毫米
- **優勢**
  - ➢ 超薄結構使其具有高表面積與極限尺寸
  - ➢ 高電子遷移率可實現透明、柔性電子元件
  - ➢ 凡德瓦力接觸
  - ➢ 表面缺陷少
- **應用**
  - ➢ **柔性電子學**
  - ➢ **高效能電晶體**
  - ➢ **光電子學**
  - ➢ **能源儲存**
  - ➢ **感測器**
- **挑戰**
  - ➢ 材料合成技術
  - ➢ 在元件製造中實現大面積、均勻的轉移技術
  - ➢ 參雜困難



Source: A. Kis, Nature Nanotechnology, 6,147–150 (2011)

次世代半導體 (1D ? 2D ?)



Exfoliated **WSe_2** flakes on SiO_2/Si

Source: A. Kis, Nature Nanotechnology, 6,147–150 (2011)