

Classification of solids (types of bonding)

- ▶ There are three broadly recognisable kinds of electrically insulating solid with clearly distinguishable types of spatial electronic distributions:

Types of bonding:

- 1. Ionic** – transfer of electron(s) from one atom to another
- 2. Covalent** – electron shared between two atoms
- 3. Van der Waals** – weak forces between dipoles

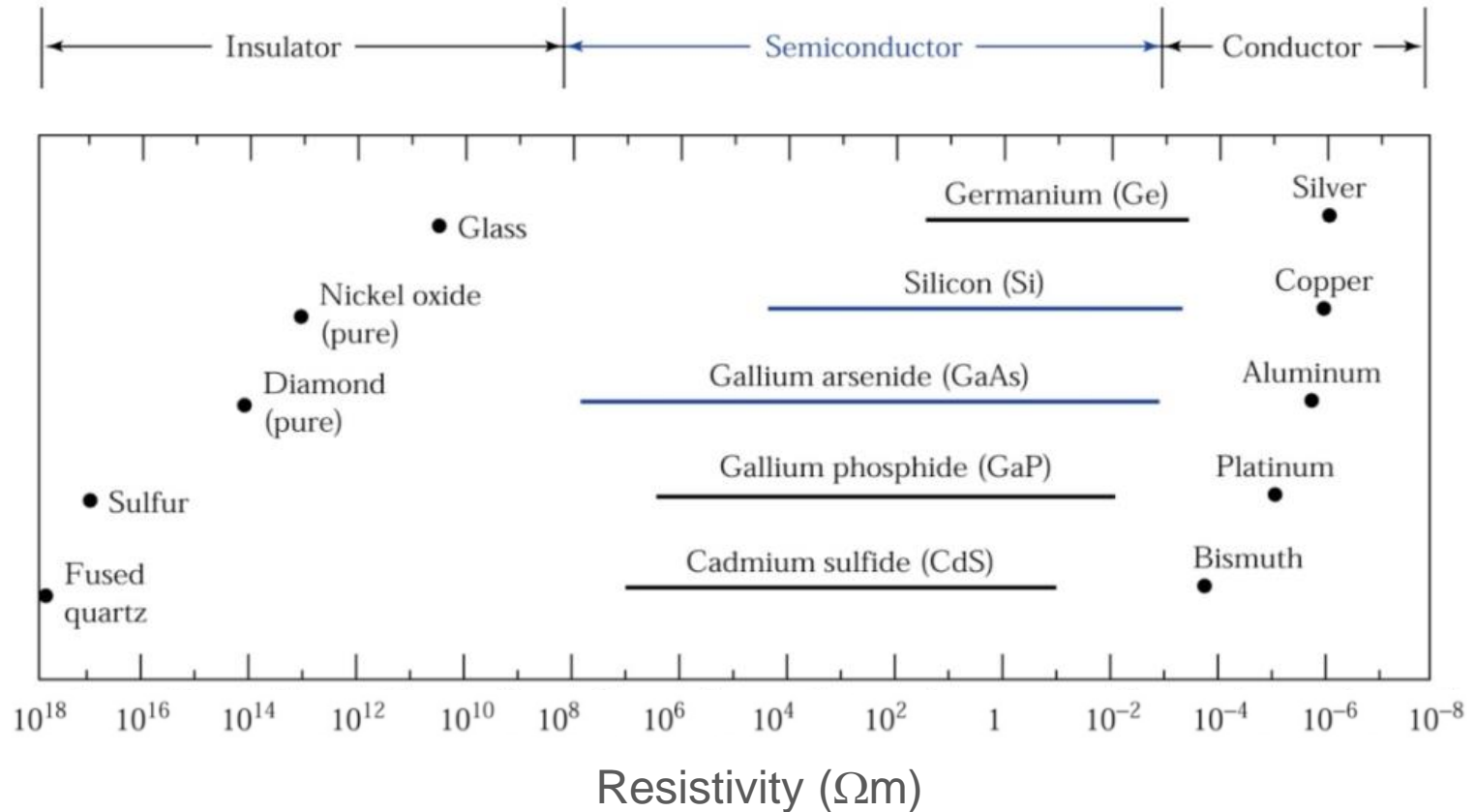
- ▶ Note that the broader distinction between **insulators** and **metals** is based on how electrons are distributed among energy levels in the solid but we can also obtain some insight from the spatial distribution of electrons

Learning outcomes: electrical transport and energy band theory

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- ▶ Describe characteristics and properties of 'metallic' bonding
- ▶ Describe assumptions of classical theory of metallic conduction
- ▶ Microscopic analysis of current flow in materials, know derivations of: drift velocity, Ohm's Law and expression for electrical conductivity
- ▶ Explanations of origin and differences between metals, insulators and semiconductors using energy band picture and how these account for observed electrical behaviour
- ▶ Behaviour of electrons and holes under applied fields and idea of carrier mobility
- ▶ Influence of semiconductor doping on electrical transport

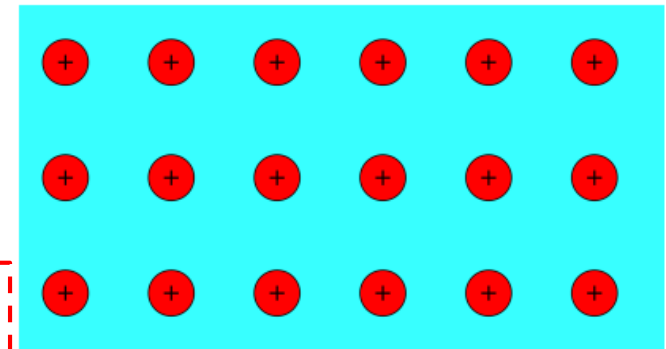
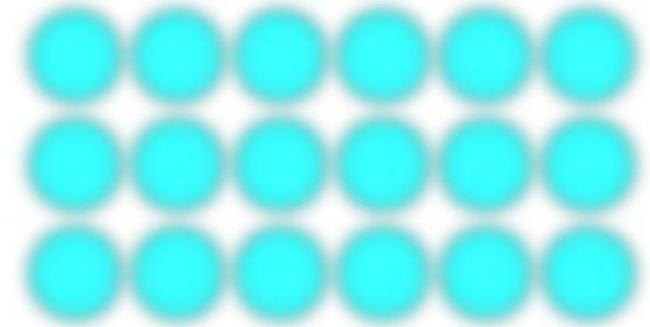
Electrical conductivity in solids



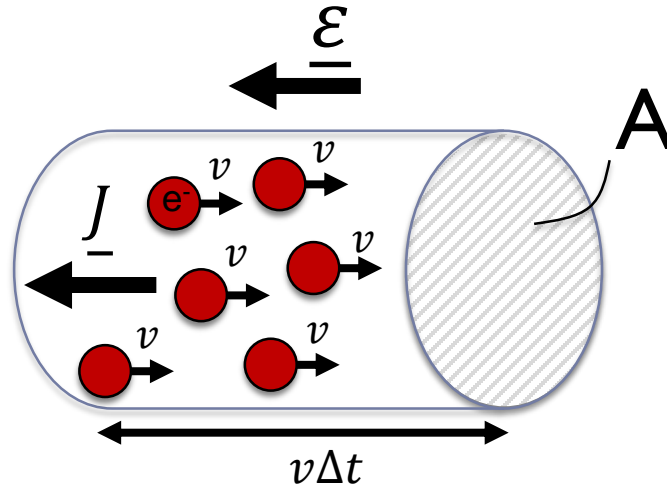
- ▶ Electrical resistivity in solids spans 24 orders of magnitude – one of the broadest ranges for a physical property that can be measured in the lab
- ▶ Note that semiconducting materials can be ‘tuned’ to span many orders of magnitude

Metallic bonding

- ▶ In terms of spatial distribution of electrons, this is the limiting case of covalent bonding where *all* electrons are shared by *all* ions in the crystal i.e. $N \sim 10^{28} \text{ atoms/m}^3$ share N electrons
 - ▶ Covalent bonds: 2 atoms \rightarrow 2 molecular orbitals
 - ▶ In metals: N atoms $\rightarrow N$ molecular orbitals
- ▶ Idealised picture: fixed array of ion cores surrounded by a uniform charge density, a 'sea' of free electrons
- ▶ The electrons are delocalized (not confined to local regions of high electron density between atoms, c.f. in covalent bonds)
- ▶ Properties:
 1. High electrical conductivity
 2. High thermal conductivity
 3. Malleable and ductile; do not cleave



Microscopic picture of charge transport



- Consider n electrons per unit volume all moving with some velocity v . Over a time interval Δt the total charge ΔQ that passes A is:

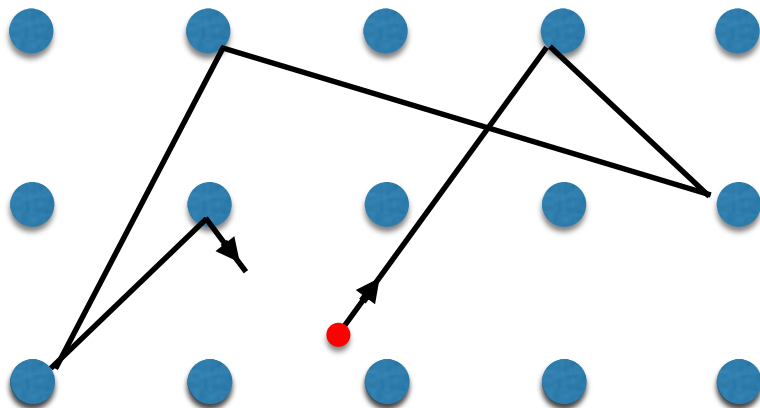
$$\Delta Q = \frac{\text{charge}}{\text{volume}} \cdot \text{volume} = (nq)(Av\Delta t)$$

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

- The magnitude of the current per unit cross sectional area $J = I/A$
- $\therefore \underline{J} = nq\underline{v}$ where the direction of \underline{J} depends on the velocity direction and sign of charge (q)

Classical free-electron picture of metallic conduction

- ▶ Outer electrons become completely detached from host atom and are free to move under applied fields
- ▶ Density of free electrons contributed per atom depends on the material considered
- ▶ Free electrons form a 'gas' of independent particles with some temperature T . Electrons move randomly between collisions with ions so no net current flows when $\underline{\varepsilon} = 0$



Electron scattering is pictured as the physical origin for electrical resistance

Classical free-electron picture of metallic conduction

- ▶ When an electric field is applied, electrons are **accelerated along the field axis** in between randomising collisions with ions. This electron scattering is pictured as the physical origin for electrical resistance.
- ▶ The on-average charge movement along the applied field axis forms the current
- ▶ Classical mechanics picture: Newton's 2nd law applies

$$F = m_e a = q\varepsilon$$

$$a = -\frac{e\varepsilon}{m_e}$$

$$\Delta v = \int_0^t a dt = -\frac{e\varepsilon \Delta t}{m_e}$$

ε is the applied electric field

m_e is electron mass,

$q = -e$ is electron charge

Δt is the time elapsed since the electrons previous collision with an ion

Classical free-electron picture of metallic conduction

- ▶ Let τ be the **average time between electron-ion collisions**
- ▶ Hence, the average velocity $\langle \Delta v \rangle$ in the field direction is:

$$v_d = \langle \Delta v \rangle = -\frac{e\tau}{m_e} \varepsilon$$

$$\left[v_d = \frac{q\tau}{m} \varepsilon \text{ in general} \right]$$

- ▶ We denote this as the '**drift velocity**' v_d and is a measure of the average field-induced velocity associated with the moving charge carriers
- ▶ This is often written as: $v_d = \mu \varepsilon$
- ▶ where the '**mobility**' μ is defined as: $\mu = \frac{v_d}{\varepsilon} = \frac{q\tau}{m}$
- ▶ The larger the value μ , the higher the drift velocity v_d produced under a given applied field ε .

Derivation of Ohm's Law

- Recall the definition for current density from previous, where the velocity term is now the 'drift velocity':

$$\underline{J} = nq\underline{v}_d \text{ and know } q = -e \text{ and } v_d = -\frac{e\tau}{m_e} \underline{\varepsilon} :$$

$$\underline{J} = n(-e) \left[\frac{-e\tau}{m_e} \underline{\varepsilon} \right]$$

$$\underline{J} = \left[\frac{ne^2\tau}{m_e} \right] \underline{\varepsilon} = \sigma \underline{\varepsilon}$$

“conductivity” $\sigma = \left[\frac{ne^2\tau}{m_e} \right]$

“resistivity” $\rho = \frac{1}{\sigma} = \left[\frac{m_e}{ne^2\tau} \right]$

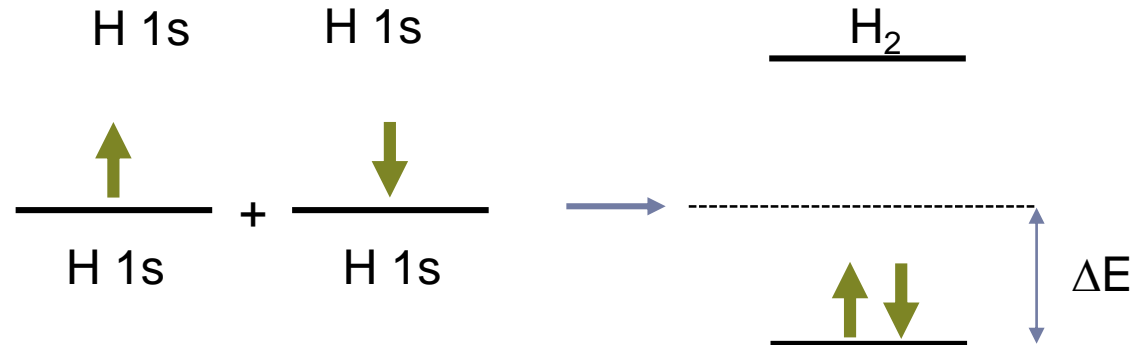
- The result $\underline{J} = \sigma \underline{\varepsilon}$ is a restatement of Ohm's Law and is the main success of the classical treatment since it provides a microscopic picture that accounts for the existence of resistance

Example: estimating conductivity σ for Al

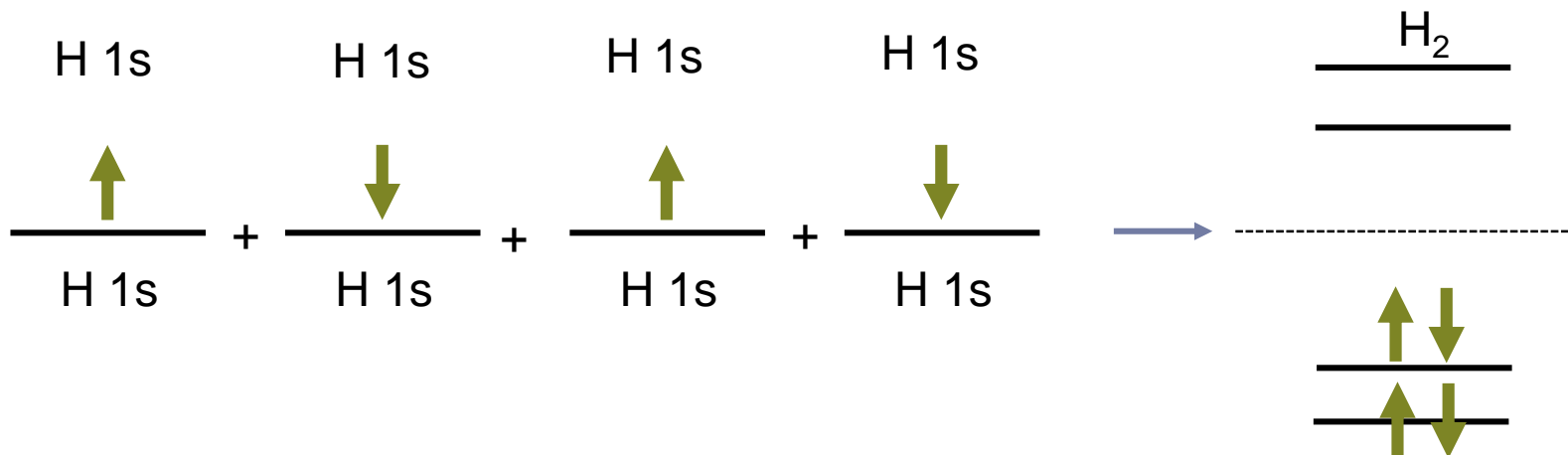
Q. Determine the electrical conductivity of Aluminium, which has 3 outer electrons per atom. Aluminium has an atomic density of $6 \times 10^{28} \text{ m}^{-3}$ and assume that the average time between electron-ion collisions is 8.5 fs.

Recap: energy picture for covalent bonding

- For 2 atoms involved in covalent bonding, spatial overlap of charge distribution associated with outer electrons leads to 2 molecular orbitals



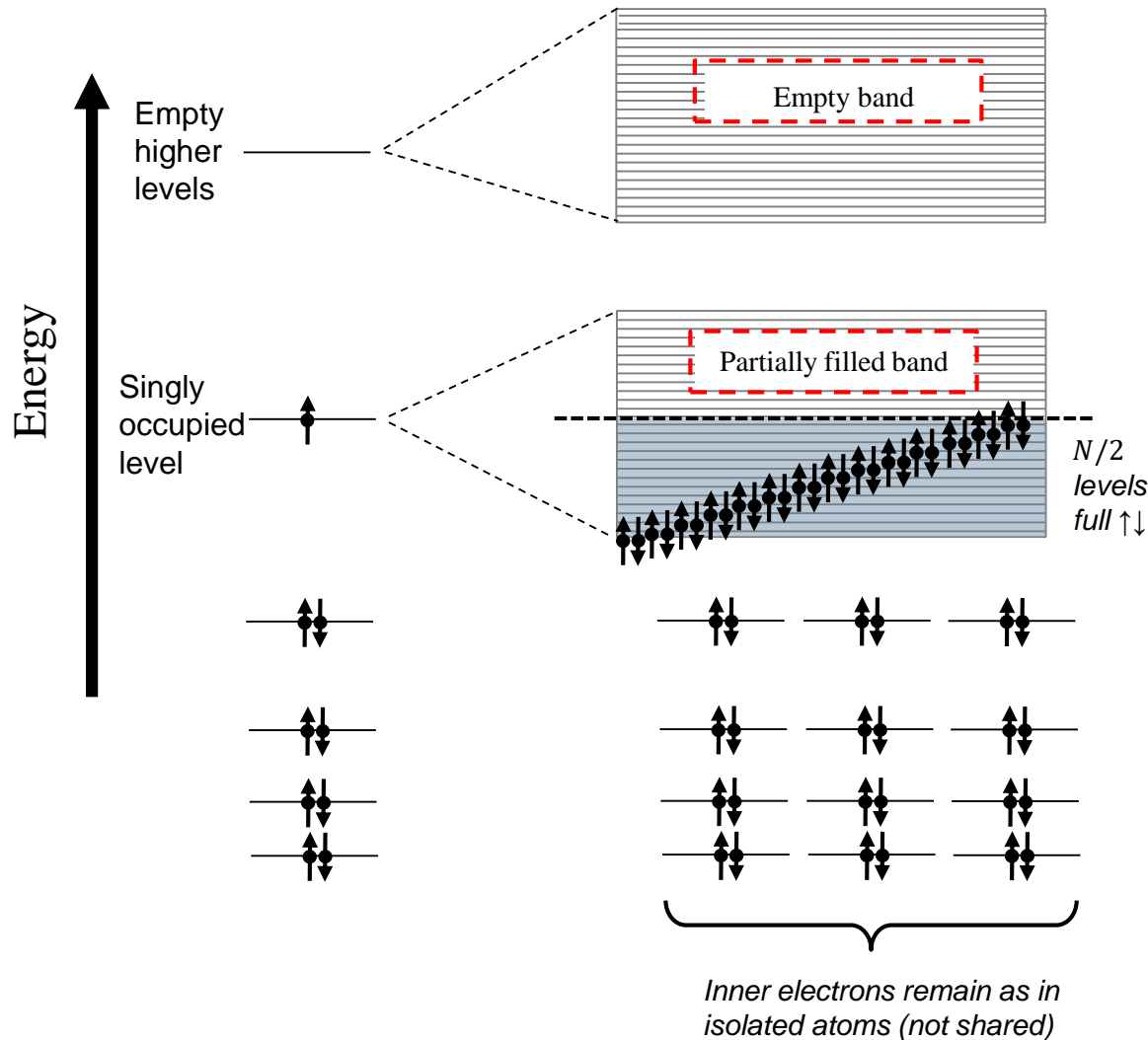
- For 4 atoms involved in covalent bonding, spatial overlap of charge distribution associated with outer electrons leads to 4 molecular orbitals...



Energy bands in metals (e.g sodium)

N isolated atoms:

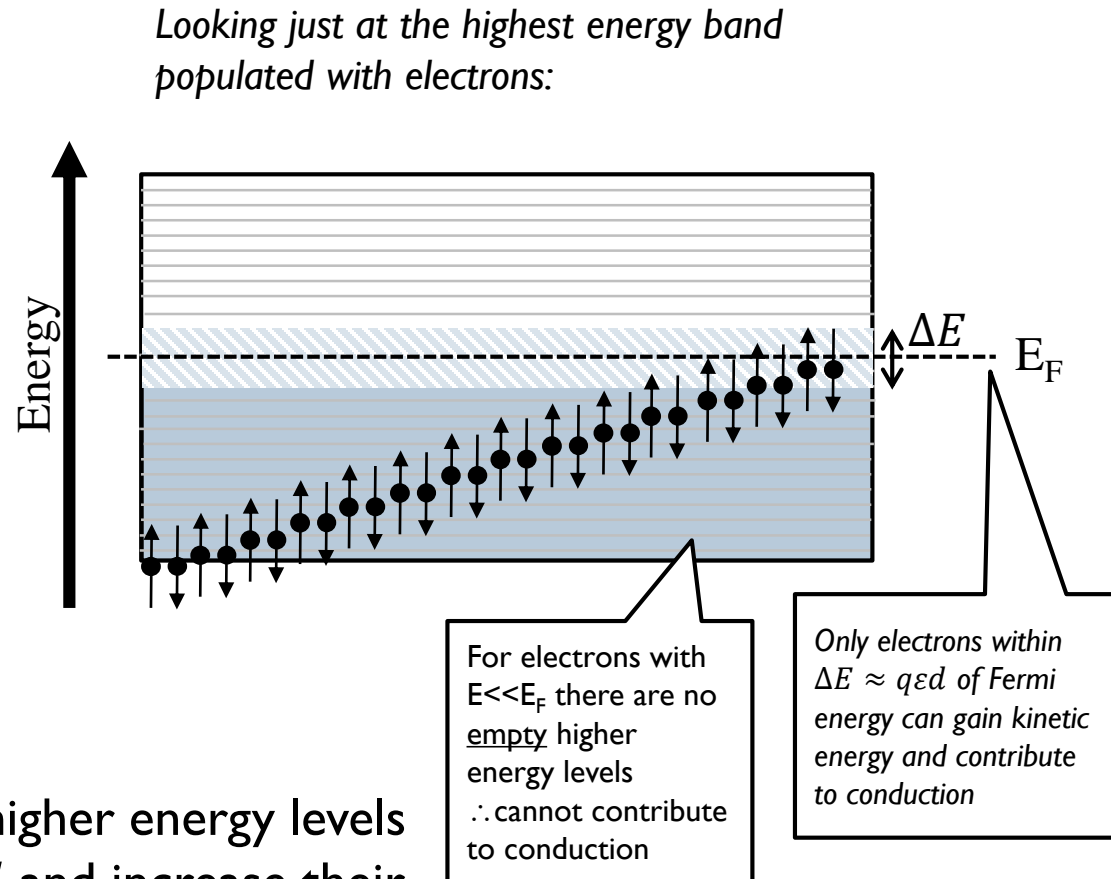
Energy “bands” in solid



- ▶ Consider sodium which has one outer s-orbital electron
- ▶ For outer valence electrons in N sodium atoms, spatial overlap of charge distributions associated with N atoms leads to N distinct energy levels that can be occupied
- ▶ N levels very closely spaced together in energy – an almost continuous “**energy band**”
- ▶ At $T = 0\text{ K}$ all electrons occupy lowest energy discrete levels
- ▶ N electrons can occupy $N/2$ lowest energy levels due to opposite spin pairing $\uparrow\downarrow$ (i.e. 2 electrons per energy level)

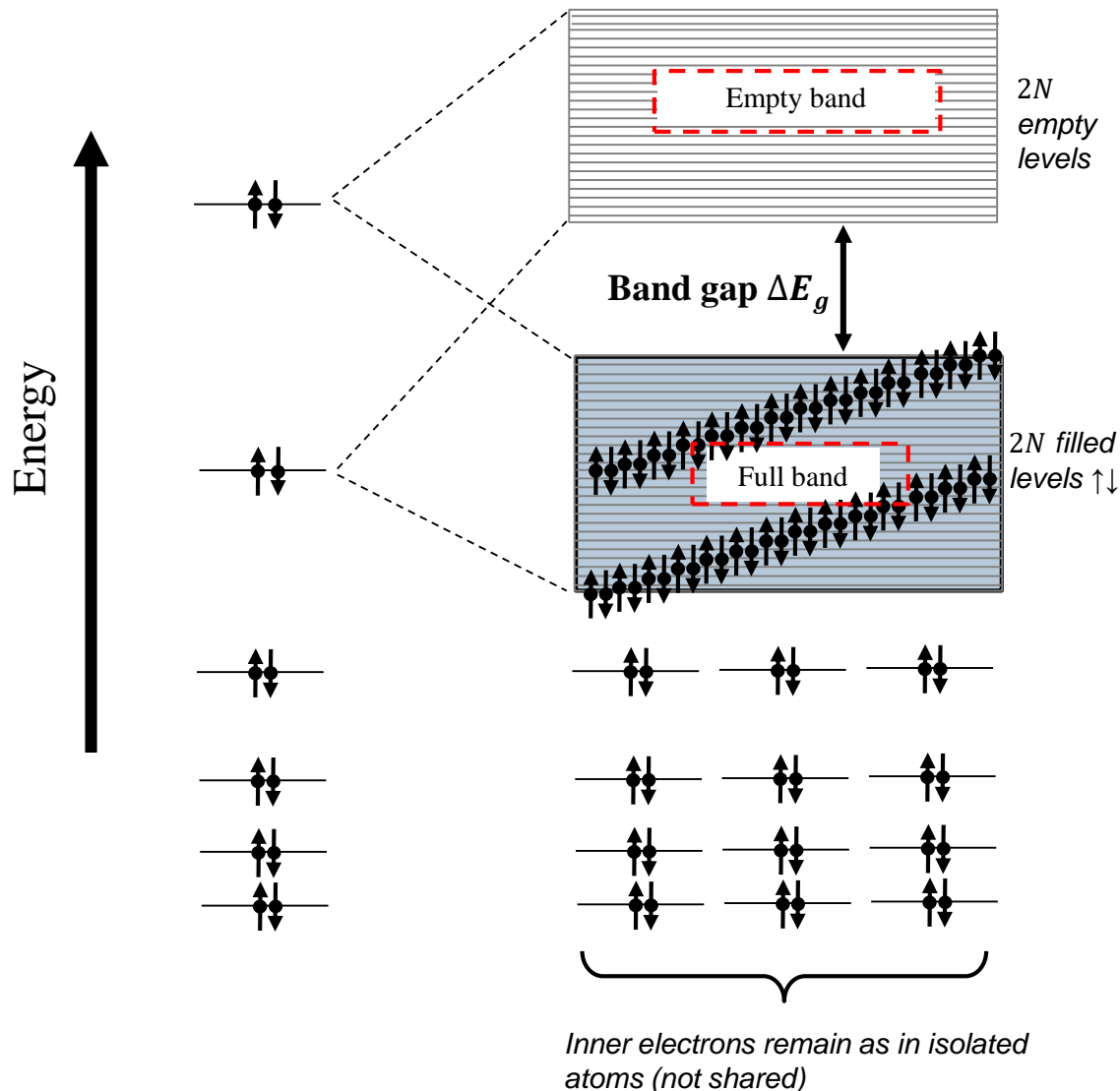
Electrical conduction in metals (energy band picture)

- ▶ Acceleration of an electron in real-space by an electric field ε (giving current flow) is pictured as a shift of the electron into higher-energy vacant levels within the energy band
- ▶ Only possible if empty higher energy levels are available
- ▶ True only for electrons close to highest-energy filled level, called the “Fermi level”
- ▶ These electrons can move into higher energy levels within a small interval $\Delta E \approx q\varepsilon d$ and increase their kinetic energy
(d = average distance electron travels before being scattered by an ion)



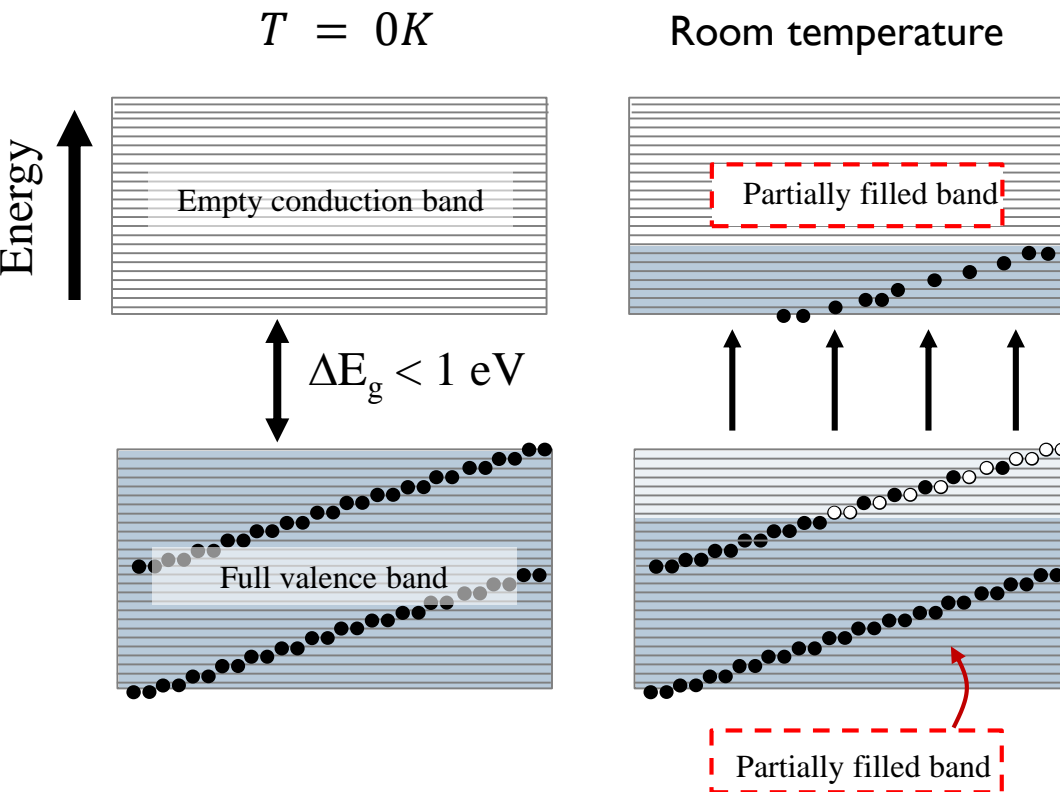
Energy bands in covalently bonded insulators (e.g. diamond)

N isolated C atoms: Energy “bands” in diamond



- ▶ Carbon atoms (e.g. covalently bonded in a diamond crystal) have 2 outer s-electrons and 2 outer p-orbitals
- ▶ The valence band is **full**: for N atoms, $4N$ outer electrons fill $2N$ energy levels (2 electrons per level) in one band
- ▶ No empty higher-energy levels exist within the same band for electrons to move into
- ▶ If the energy “band gap” to the next higher-energy band is large $E_g > 2\text{ eV}$ electrons cannot be promoted by an electric-field
- ▶ No acceleration of electrons occurs \therefore **electrical insulator**
- ▶ Example:
Diamond ($E_g = 5.5\text{ eV}$)

Energy bands in semiconductors (e.g. silicon)

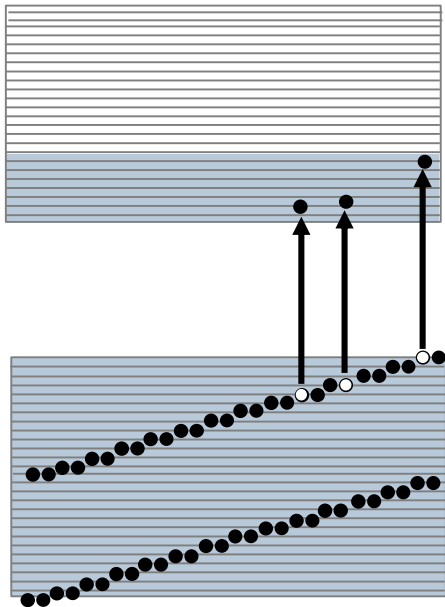


- ▶ Semiconductors, e.g. Si and Ge have similar outer electron configuration and bonding to diamond i.e. full valence band
- ▶ Key difference is semiconductors have smaller band gap ($\sim 1 \text{ eV}$)
 - ▶ Si $E_g = 1.1 \text{ eV}$
 - ▶ Ge $E_g = 0.7 \text{ eV}$
- ▶ At low temperatures $T \sim 0K$ insulating behavior observed
- ▶ As temperature is increased electrons can be **thermally** excited above the band gap into levels in the next band (called conduction band)
- ▶ Number of electrons per unit volume $n(T)$, and hence conductivity $\sigma(T)$, **increase** strongly with temperature
 - ▶ $n(T) \propto e^{-E_g/2k_B T}$

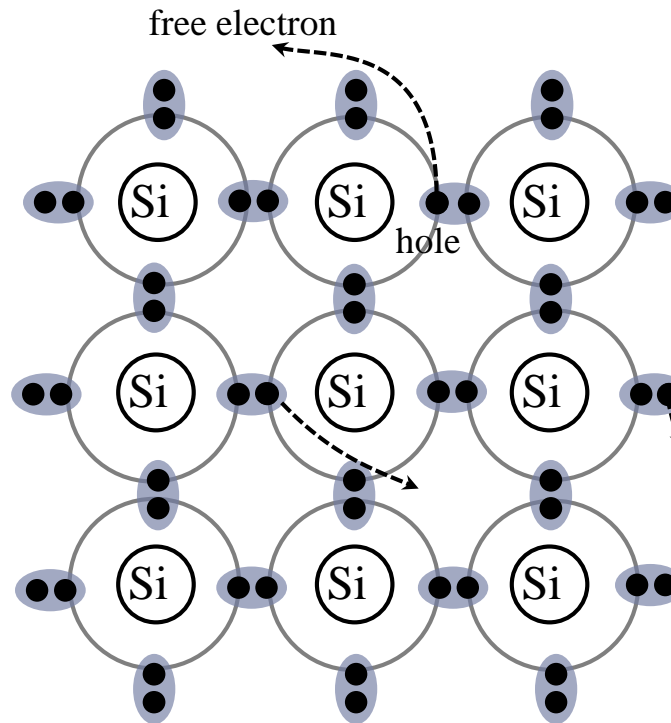
- ▶ For $T > 0K$, electrons thermally excited into the conduction band can be moved into vacant higher energy states by an electric field and contribute to current flow

Semiconductors: thermal generation of electron-hole pairs

Energy band picture



Spatial picture

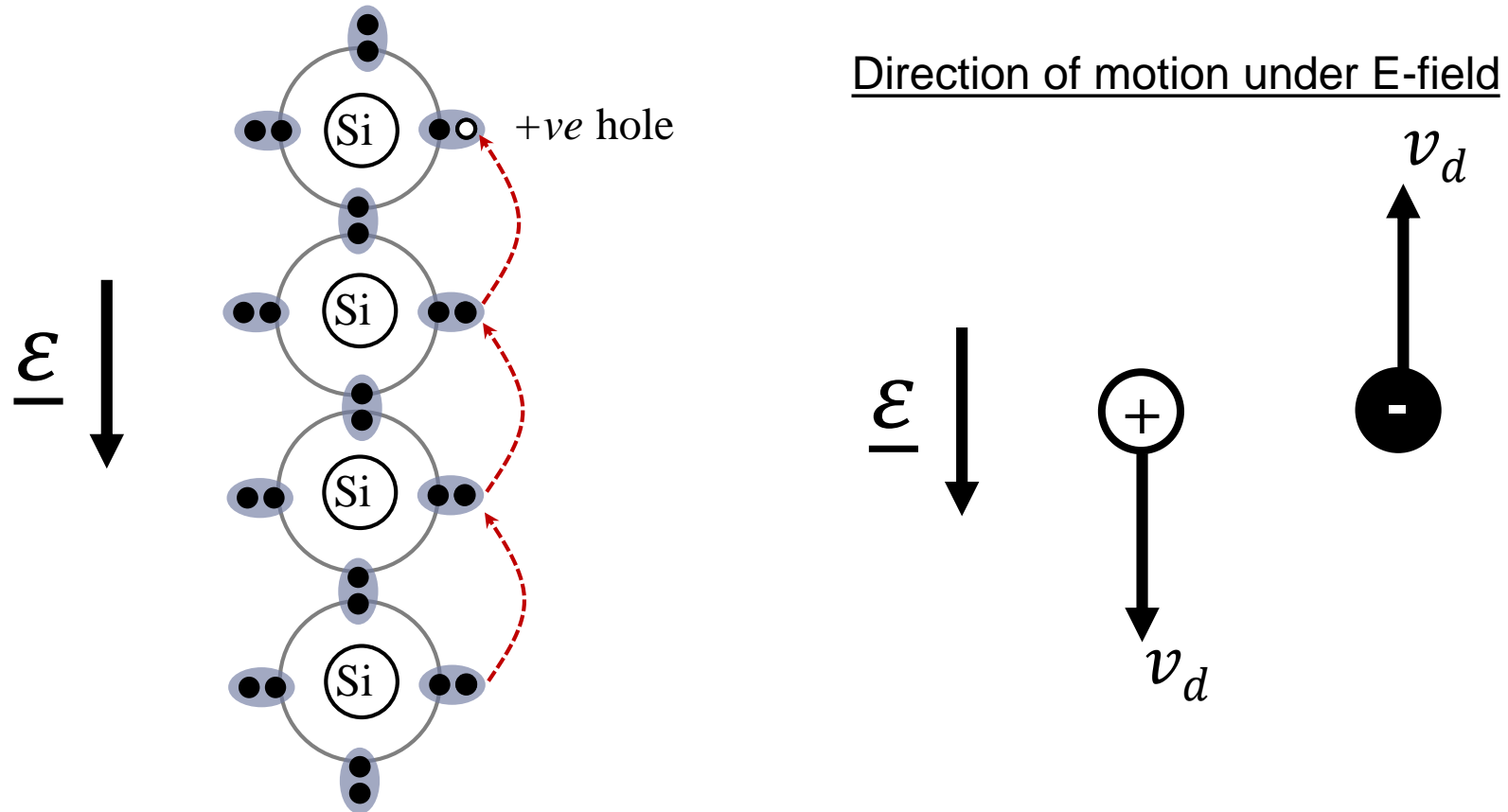


Intrinsic semiconductor
no. electrons in conduction band
= no. of holes in valence band

Thermal generation of electron/hole pairs:

- ▶ Each time an electron is thermally promoted to the conduction band a vacancy is left behind in the valence band
- ▶ In real-space this corresponds to a gap in the bonding structure which moves under electric fields in the same way as a positively charged particle would. The vacancy is known as a positively charged electron “hole”

Semiconductors: electron/hole currents



- ▶ Conduction electrons and valence holes move in opposite directions by applied electric fields and both **independently** contribute to the current
- ▶ Electrons are called “**n-type**” carriers and holes are called “**p-type**”

Current flow in semiconductors

- ▶ How do we account for the hole-current in our previous description for the expected current density?
- ▶ We now acknowledge that there is also a hole carrier density (n_h) as well as free electron density (n_e) in calculations. Total current density \underline{J} is the sum of both contributions:

$$\underline{J} = (nq\underline{v}_d)_{electrons} + (nq\underline{v}_d)_{holes} \qquad \begin{array}{ll} q_e = -e & v_e = -|\underline{v}_e| \\ q_h = +e & v_h = +|\underline{v}_h| \end{array}$$

$$J = n_e e v_e + n_h e v_h$$

Note: electrons and holes travel in opposite directions under an applied ε -field but their current contributions combine additively

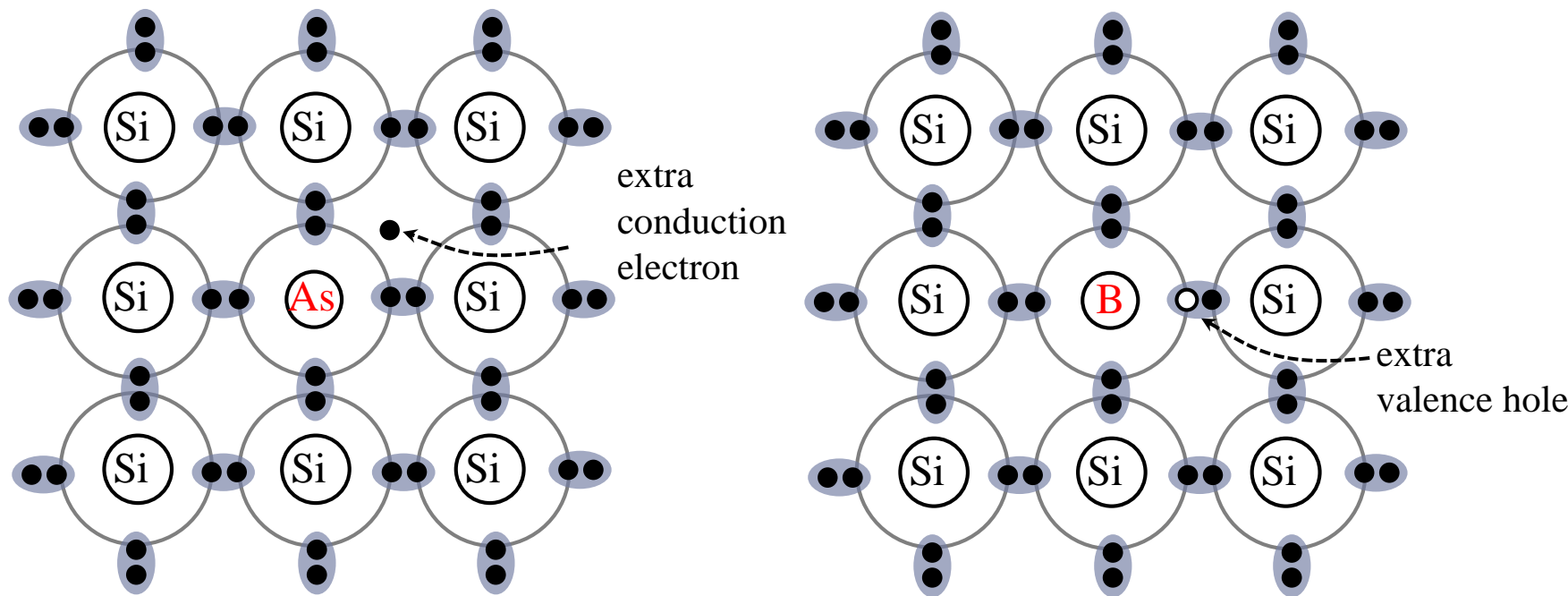
- ▶ Holes and electrons in the same material do not necessarily move with the same speeds (i.e. v_e and v_h are different) under an applied field. This is captured in the different material-dependent mobility values for electrons (μ_e) and holes (μ_h)

$$v_d = \mu \varepsilon$$

$$J = (n_e e \mu_e + n_h e \mu_h) \varepsilon$$

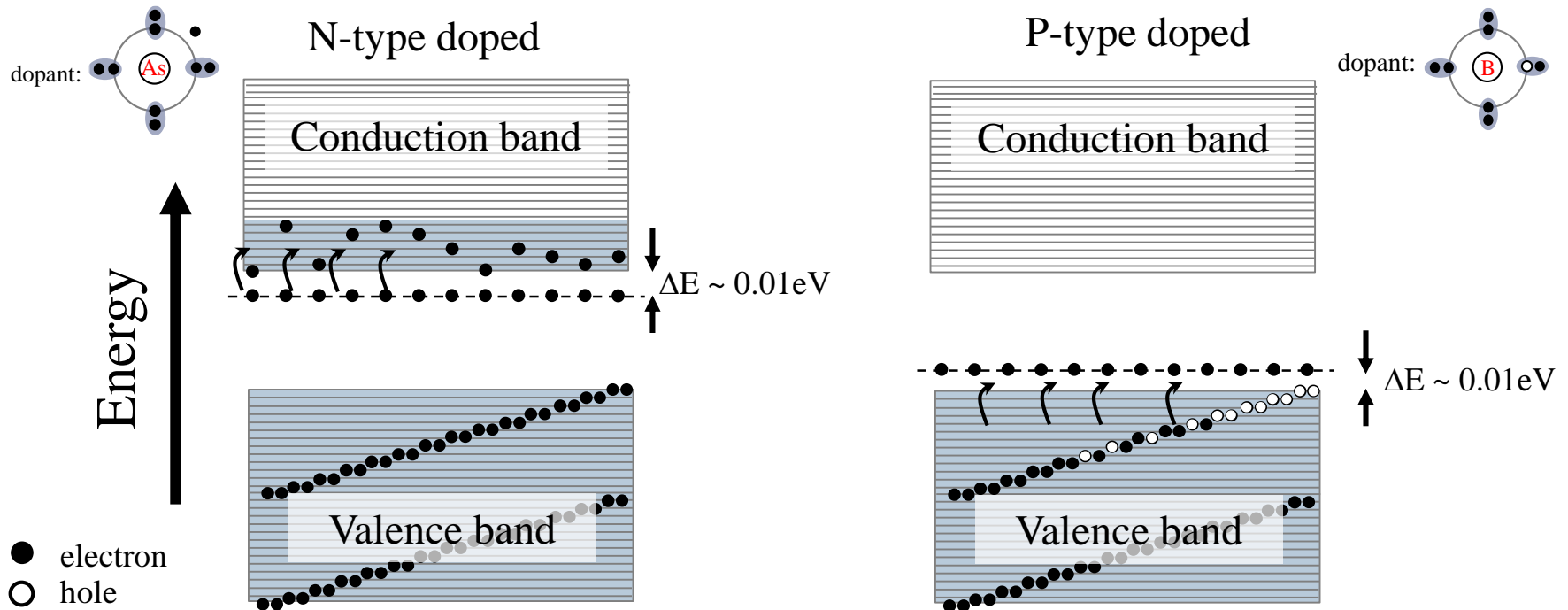
Semiconductor doping: spatial picture

- ▶ Semiconducting materials are extremely useful because the type of conductivity (p-type or n-type) and magnitude can be precisely tuned by adding a very small amount of an impurity species – “**doping**” - to highly pure Si or Ge



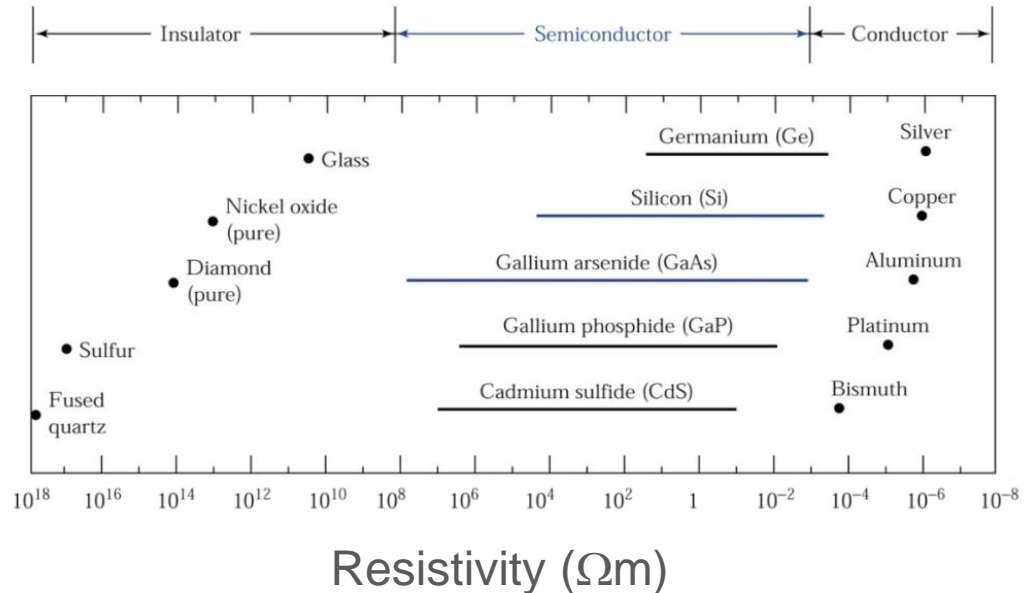
- ▶ **N-type doping:** dopant atoms have more valence electrons than host (e.g. As, Sb, P). Each substitute impurity atom introduces an extra electron for conduction
- ▶ **P-type doping:** dopant atoms have fewer valence electrons than host (e.g. Al, B). Each substituted impurity atom introduces an extra hole into the bonding structure

Semiconductor doping: energy band picture



- ▶ **N-type doping:** Loosely-bound dopant electrons occupy an energy level in band gap region just below Si conduction band. Effectively all dopant electrons are thermally excited into conduction band at room temperature. These electrons can change energy state and are primarily responsible for the net current flow under applied field
- ▶ **P-type doping:** Dopant holes occupy energy levels just above valence band edge, at room temperature all holes are occupied by electrons from Si valence band. The holes can then move through the valence band under applied fields and generate a net current equivalent to that associated with positive charge movement

	Sb	P	As	Ti		C	Pt	Au	O
Si	0.039	0.045	0.054	0.21		0.25	0.25		0.16
									0.38
								0.54	0.51
								A	0.41
				0.34		0.35	0.36		
					D		0.3		
				0.16				0.29	
								D	
	B	Al	Ga	In	Pd				



- ▶ In a doped semiconductor the number of electrons \neq the number of holes, called an “**extrinsic semiconductor**”
- ▶ As little as 1 part in 10^{10} impurity atoms determines current flow at room temperature to be almost completely due to dopant carriers rather than thermally generated electron/hole pairs