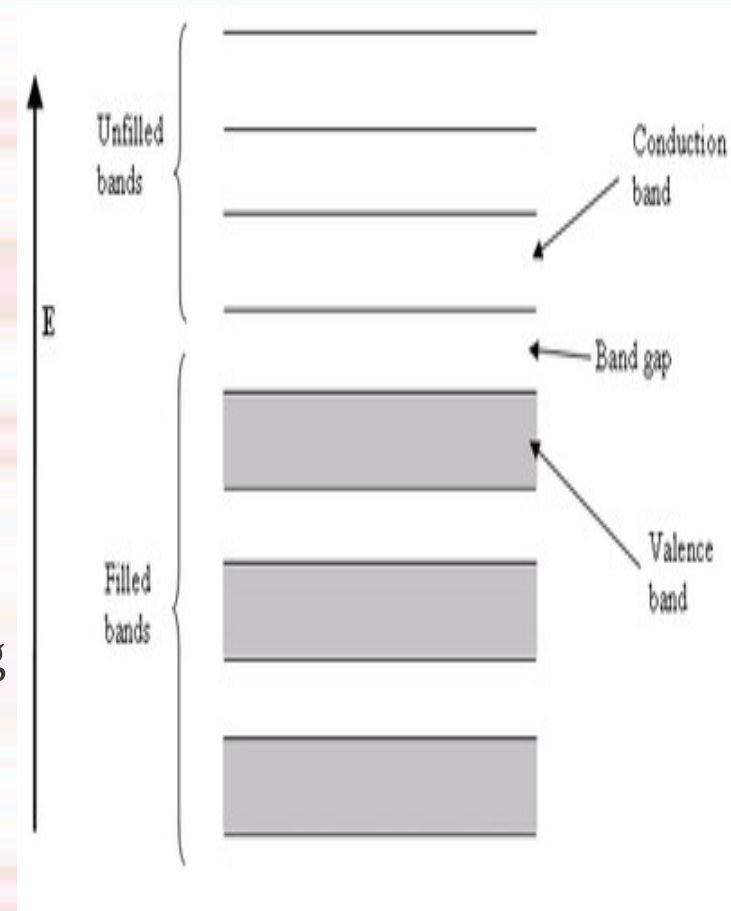


**IN THE NAME OF GOD**

***Calculation of valence band (VB) and  
conduction band (CB)***

■ the valence band is the highest range of **electron energies** in which electrons are normally present at **absolute zero** temperature.

The conduction band quantifies the range of energy required to free an electron from its bond to an **atom**. Once freed from this bond, the electron becomes a 'delocalized electron', moving freely within the **atomic lattice** of the material to which the atom belongs. Various materials may be classified by their **band gap**: this is defined as the difference between the **valence** and conduction bands.



$$E_{\text{CB}} = X - E_{\text{c}} - \frac{1}{2}E_{\text{g}}$$

$$E_{\text{VB}} = E_{\text{CB}} + E_{\text{g}}$$

where  $X$  is the absolute electronegativity (Mulliken) of the atom semiconductor, expressed as the **geometric mean** of the absolute electronegativity of the constituent atoms, which is defined as the **arithmetic mean** of the atomic electron affinity and the first ionization energy;

$$X = \frac{1}{2} (E_{\text{EA}} + E_{\text{ion}})$$

An alternative method for measuring electronegativity was developed by Robert Mulliken (1896–1986; Nobel Prize in Chemistry 1966). Mulliken noticed that elements with large first ionization energies tend to have very negative electron affinities and gain electrons in chemical reactions. Conversely, elements with small first ionization energies tend to have slightly negative (or even positive) electron affinities and lose electrons in chemical reactions. Mulliken recognized that an atom's tendency to gain or lose electrons could therefore be described quantitatively by the average of the values of its first ionization energy and the absolute value of its electron affinity.

# *What is the difference between arithmetic and geometric averages*

We use an **arithmetic average** that each number is an independent event while if the numbers are not independent of each other we require a **geometric average** to represent their mean.

An **arithmetic average** is the sum of a series of numbers divided by the count of that series of numbers.

In **geometric average**, we simply add one to each number, Then, multiply all the numbers together, and raise their product to the power of one divided by the count of the numbers in the series.



1	<div><div><div>≥0 kJ/mol</div><div></div><div>348.6 kJ/mol</div></div></div>																18	
1	<div>H -72.8</div>																<div>He ≥0</div>	
2	<div>Li -59.6</div>	<div>Be ≥0</div>											<div>B 27.0</div>	<div>C 121.8</div>	<div>N ≥0</div>	<div>O -141.0</div>	<div>F -328.2</div>	<div>Ne ≥0</div>
3	<div>Na -52.9</div>	<div>Mg ≥0</div>										<div>Al 41.8</div>	<div>Si 134.1</div>	<div>P 72.0</div>	<div>S 200.4</div>	<div>Cl -348.6</div>	<div>Ar ≥0</div>	
4	<div>K 418.4</div>	<div>Ca 2.1</div>	<div>Sc 18</div>	<div>Ti 8</div>	<div>V 51</div>	<div>Cr 65.2</div>	<div>Mn ≥0</div>	<div>Fe 15</div>	<div>Co 64.0</div>	<div>Ni 111.7</div>	<div>Cu 119.2</div>	<div>Zn ≥0</div>	<div>Ga -40</div>	<div>Ge -118.9</div>	<div>As -76</div>	<div>Se -195.0</div>	<div>Br -327.5</div>	<div>Kr ≥0</div>
5	<div>Rb 46.9</div>	<div>Sr 5.0</div>	<div>Y -30</div>	<div>Zr 41</div>	<div>Nb 86</div>	<div>Mo -72.1</div>	<div>Tc 60</div>	<div>Ru 101.0</div>	<div>Rh 110.3</div>	<div>Pd 54.2</div>	<div>Ag 125.9</div>	<div>Cd ≥0</div>	<div>In -39</div>	<div>Sn -107.3</div>	<div>Sb -101.1</div>	<div>Te -190.2</div>	<div>I -295.2</div>	<div>Xe ≥0</div>
6	<div>Cs -45.5</div>	<div>Ba -14.0</div>	<div>La -45</div>	<div>Hf ≥0</div>	<div>Ta -31</div>	<div>W -79</div>	<div>Re -20</div>	<div>Os -104.0</div>	<div>Ir -150.9</div>	<div>Pt -205.0</div>	<div>Au -222.7</div>	<div>Hg ≥0</div>	<div>Tl -37</div>	<div>Pb -35</div>	<div>Bi -90.9</div>	<div>Po -180</div>	<div>At -270</div>	<div>Rn ≥0</div>
7	<div>Fr</div>	<div>Ra</div>	<div>Ac</div>	<div>Rf</div>	<div>Db</div>	<div>Sg</div>	<div>Bh</div>	<div>Hs</div>	<div>Mt</div>	<div>Ds</div>	<div>Rg</div>	<div>Uub</div>	<div>Uut</div>	<div>Uuq</div>	<div>Uup</div>			
Lanthanides			<div>Ce</div>	<div>Pr</div>	<div>Nd</div>	<div>Pm</div>	<div>Sm</div>	<div>Eu</div>	<div>Gd</div>	<div>Tb</div>	<div>Dy</div>	<div>Ho</div>	<div>Er</div>	<div>Tm</div>	<div>Yb</div>	<div>Lu</div>		
Actinides			<div>Th</div>	<div>Pa</div>	<div>U</div>	<div>Np</div>	<div>Pu</div>	<div>Am</div>	<div>Cm</div>	<div>Bk</div>	<div>Cf</div>	<div>Es</div>	<div>Fm</div>	<div>Md</div>	<div>No</div>	<div>Lr</div>		

Electron Affinities (in kJ/mol) of the Elements

**What is  $E_c$  ?**  $E_c$  is the energy of free electrons of the hydrogen scale (4.5 eV) that is kinetic energy of electrons :  $\frac{1}{2} m v^2$  or  $p^2 / 2m$

$$1\text{eV} = 1.6 \times 10^{-19} \text{ J} = 1.6 \times 10^{-22} \text{ kJ}$$

$$? \text{ kJ / mol} = 1\text{eV} \times 1.6 \times 10^{-22} \text{ kJ / eV} \times 6.022 \times 10^{23} / 1\text{mol} = \mathbf{96.48 \text{ kJ / mol}}$$



## For example ECB and EVB of Ag<sub>3</sub>VO<sub>4</sub>

$$\text{O} \left\{ \begin{array}{l} \text{electro affinity} = 141.1 \text{ kJ/mol} / 96.48 = 1.46 \text{ eV} \\ \text{first ionization energy} = 1313.9 \text{ kJ/mol} / 96.48 = 13.52 \text{ eV} \end{array} \right.$$

$$X_{\text{O}} = \frac{1}{2} (E_{\text{EA}} + E_{\text{ion}}) = \frac{1}{2} (1.46 + 13.52) = 7.49 \text{ eV}$$

$$\text{Ag} \left\{ \begin{array}{l} \text{electro affinity} = 125.7 \text{ kJ/mol} / 96.48 = 1.30 \text{ eV} \\ \text{first ionization energy} = 731 \text{ kJ/mol} / 96.48 = 7.54 \text{ eV} \end{array} \right.$$

$$X_{\text{Ag}} = \frac{1}{2} (E_{\text{EA}} + E_{\text{ion}}) = \frac{1}{2} (1.30 + 7.54) = 4.42 \text{ eV}$$

$$V \left\{ \begin{array}{l} \text{electro affinity} = 50.8 \text{ kJ/mol} / 96.48 = 0.53 \text{ eV} \\ \text{first ionization energy} = 650.9 \text{ kJ/mol} / 96.48 = 6.72 \text{ eV} \end{array} \right.$$

$$X_V = \frac{1}{2} (E_{EA} + E_{ion}) = \frac{1}{2} (0.53 + 6.72) = 3.62 \text{ eV}$$

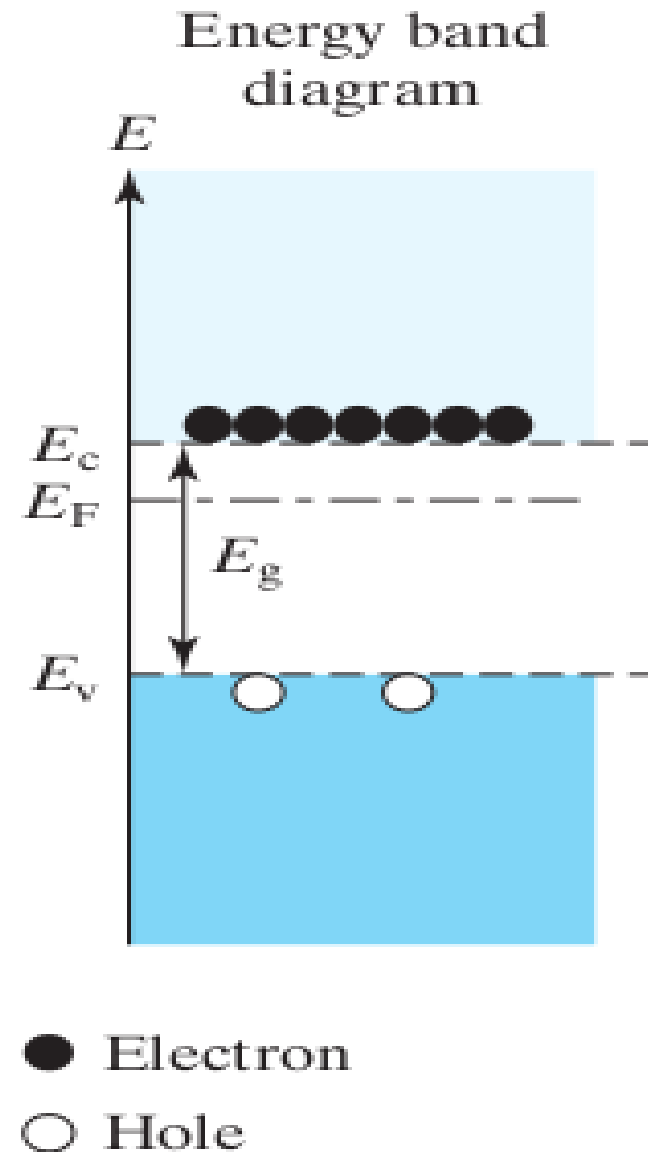
$$X(\text{Ag}_3\text{VO}_4) = (4.42 \times 4.42 \times 4.42 \times 3.72 \times 7.49 \times 7.49 \times 7.49 \times 7.49)^{1/8} = 5.64$$

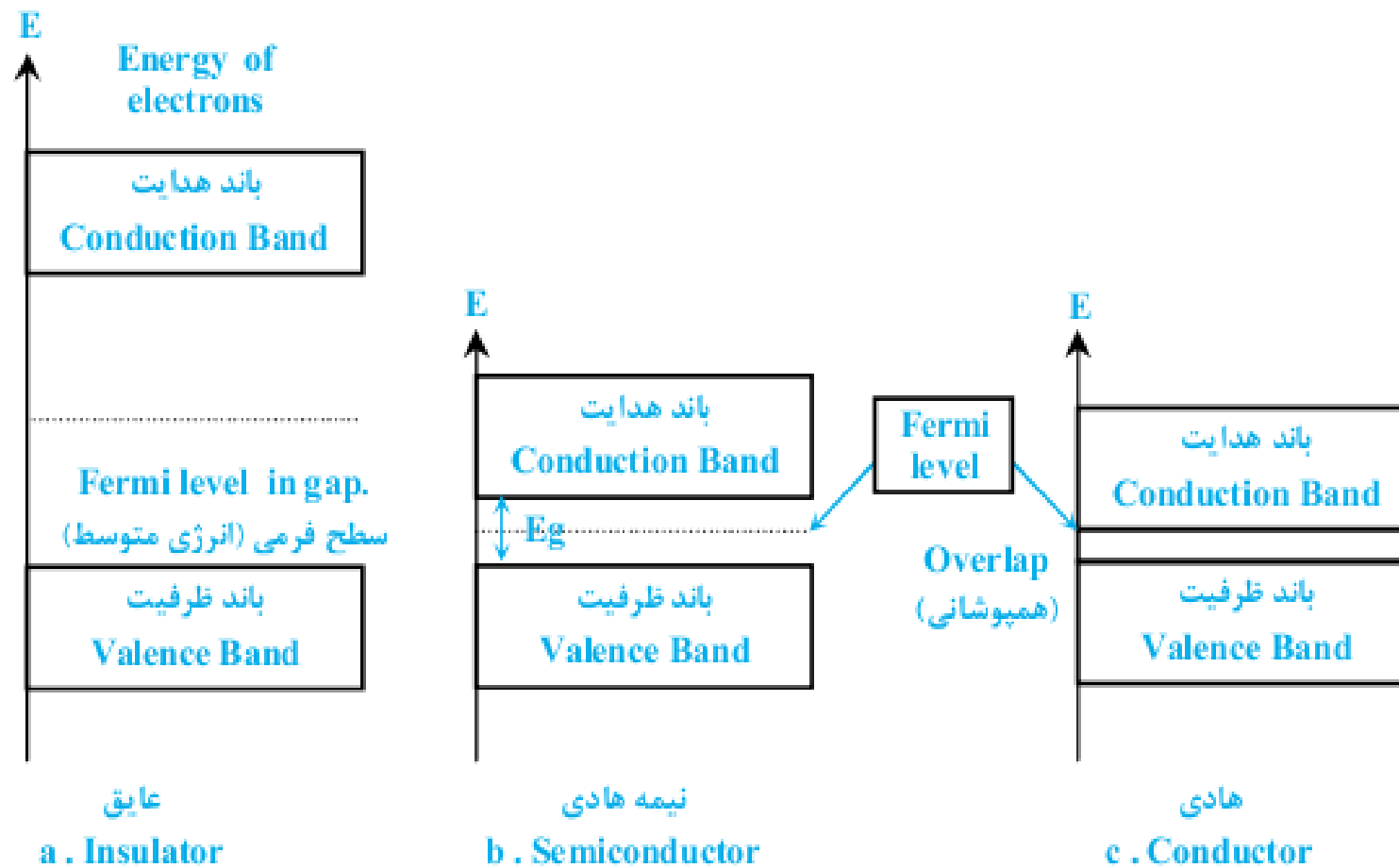
$$E_{CB} = 5.64 - 4.5 - 2.2 / 2 = 0.04 \text{ eV}$$

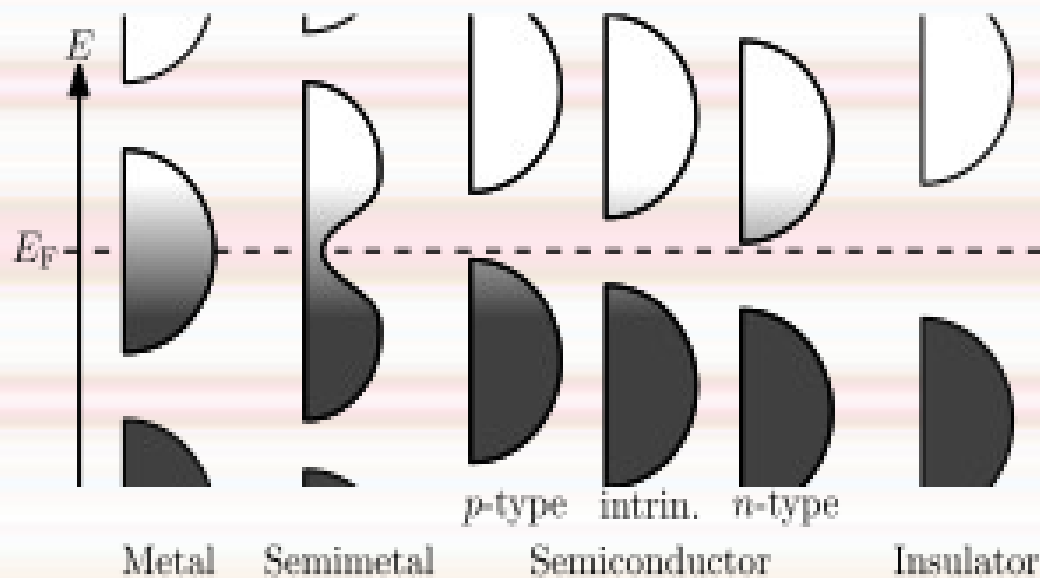
$$E_{VB} = E_{CB} + E_g = 0.04 + 2.2 = 2.24 \text{ eV}$$

# ***Fermi energy***

The Fermi energy is a concept in quantum mechanics usually referring to the energy difference between the highest and lowest occupied single-particle states in a quantum system of non-interacting fermions at absolute zero temperature.







In **metals** and **semimetals** the **Fermi level**  $E_F$  lies inside at least one band.

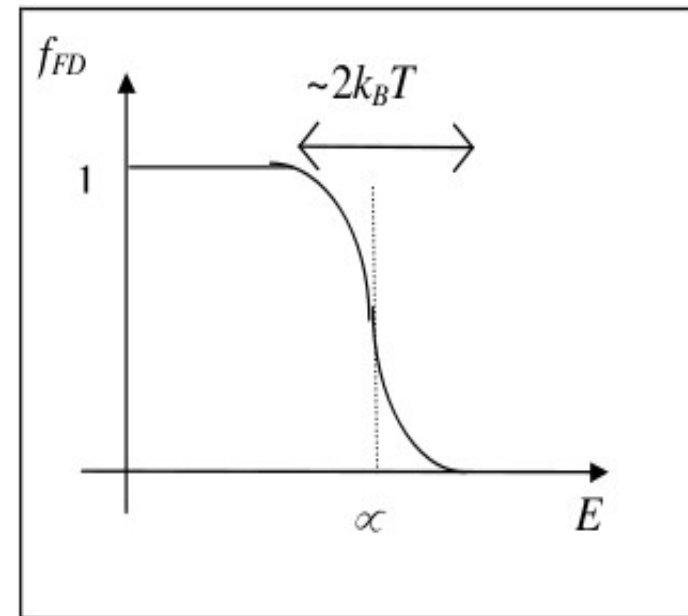
In **insulators** and **semiconductors** the Fermi level is inside a **band gap**;

however, in semiconductors the bands are near enough to the Fermi level to be **thermally populated** with electrons or **holes**.

**Fermi-Dirac function  $f$  (FD) given by :**

$$f_{FD}(E) = \frac{1}{\exp([E - \alpha] / k_B T) + 1}$$

The Fermi–Dirac distribution  $f_{FD}$  gives the probability that an electron will occupy a state having energy  $\epsilon$



where  $\alpha$  is the chemical potential of an electron. If  $E \ll \alpha$ ,  $f_{FD}(E)$  goes to unity. Even if  $E$  is only slightly below  $\alpha$ ,  $f_{FD}(E)$  is still approximately unity at low enough temperature. In the other limit, when  $E \gg \alpha$  or the temperature is high,  $f_{FD}(E)$  goes to zero. If the energy is equal to the chemical potential,  $f_{FD}(E) = 1/2$ .

Confusingly, the term "Fermi energy" is often used to refer to a different but closely related concept, the Fermi level (also called electrochemical potential). There are a few key differences between the Fermi level and Fermi energy, at least as they are used in this article:

- \* The Fermi energy is only defined at absolute zero, while the Fermi level is defined for any temperature.
- \* The Fermi energy is an energy difference (usually corresponding to a kinetic energy), whereas the Fermi level is a total energy level including kinetic energy and potential energy.
- \* The Fermi energy can only be defined for non-interacting fermions, whereas the Fermi level remains well defined even in complex interacting systems, at thermodynamic equilibrium.

As a semiconductor, the Fermi energy level is in the forbidden band between the conduction and valence band.

After doped by other atoms, such as Al doped into ZnO, the Fermi energy level will shift upward into the conduction band.

The basic rule is that:

[A] “As long as the % of the dopant is up to a certain limit, the semiconductor remain a semiconductor”. There may occur some change in its conductivity on doping .

[B] We are simply explaining the n- or p- type conduction on the basis of Fermi Level while keeping in mind that conduction band is analogous to LUMO and the valence band is analogous to HOMO .The Fermi level  $E(F)$  is chemical potential for electrons. It is the energy level at which the probability of electron occupancy is 50%.

[C] there is shifting Fermi Level toward the conduction band in n-type semiconductors, while the Fermi level is shifted towards the valence band while in the p- type semiconductors.

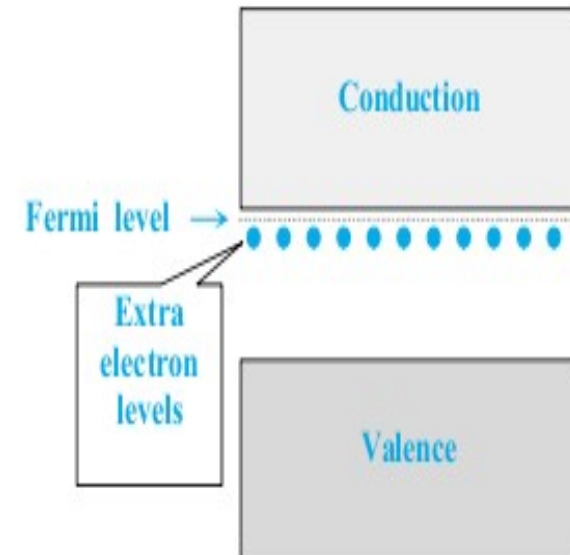
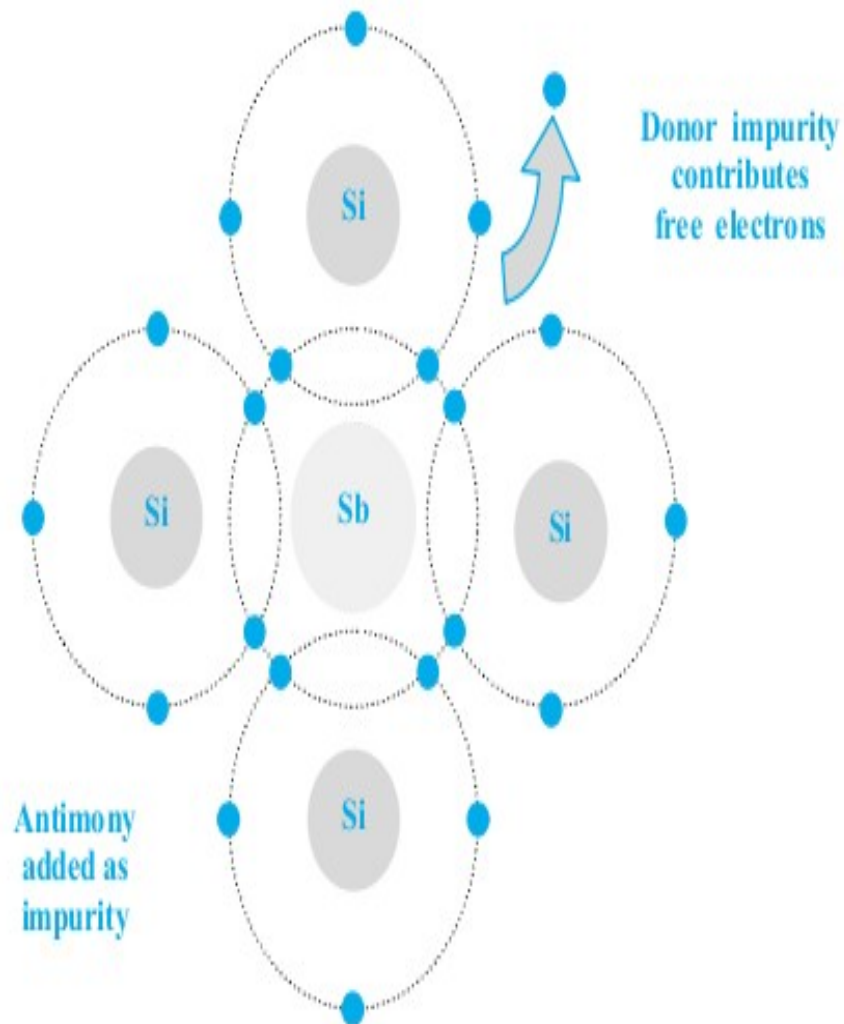


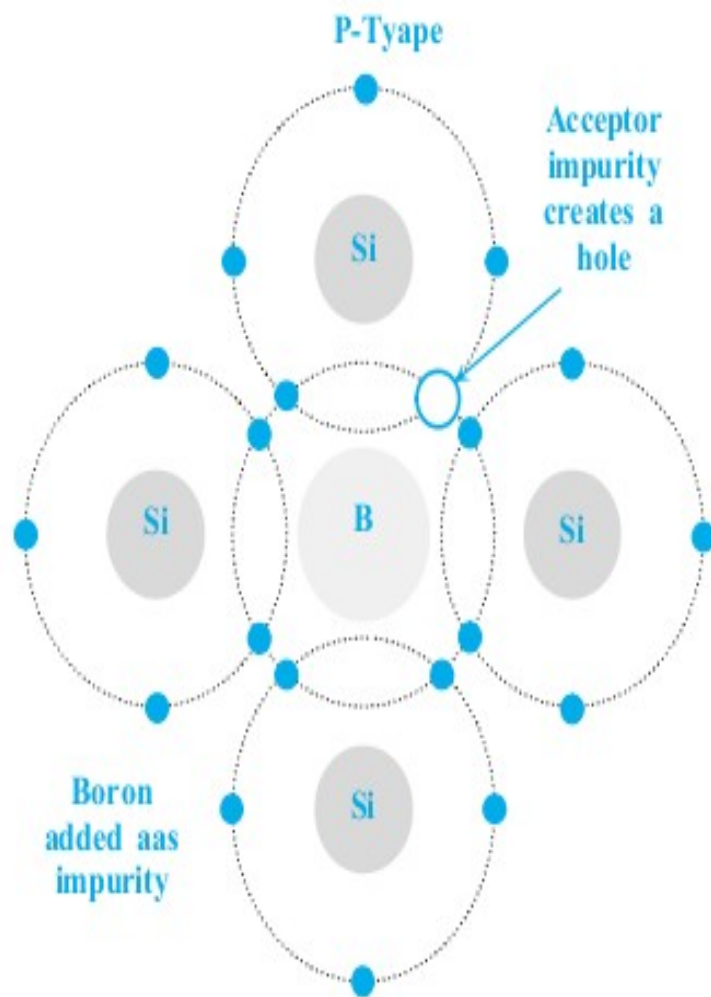
supping we add a dopant to make it n-type semiconductor [ Add P to Si]. It means there is now excess of electrons .i.e.there is more electron density in whole of the bulk of such a n-type conductor.Accordingly, the Fermi Level energy is also is raised in its enegy because now the 50% of this increased electron density will be more. That is why, in n-type semiconductors,the Fermi Level enegy is raised in energy and go closer to the Conduction band of n- type conductor.

Now suppose we add a dopant to make it p-type conductor[ Add B to Si]. It means that now the numbers of electrons are decreased.i.e.there is less electron density in whole of the bulk of such a p-type conductor.Accordingly, the Fermi Level energy is also decreased in its enegy because now the 50% of this decreased electron density will be less. That is why, in p-type semiconductors,the Fermi Level enegy is decreased and go closer to the Valence band of p- type conductor.

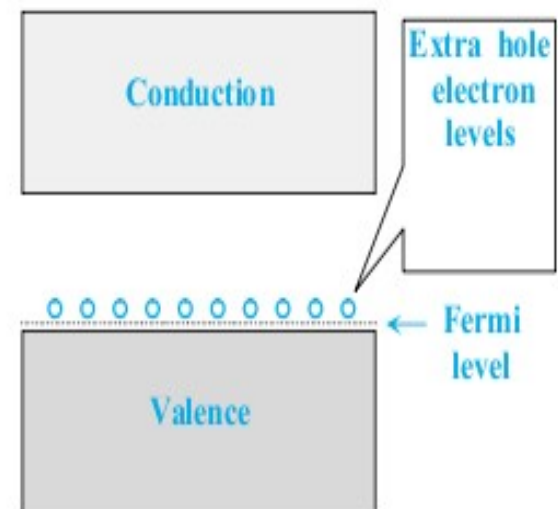
N-Type

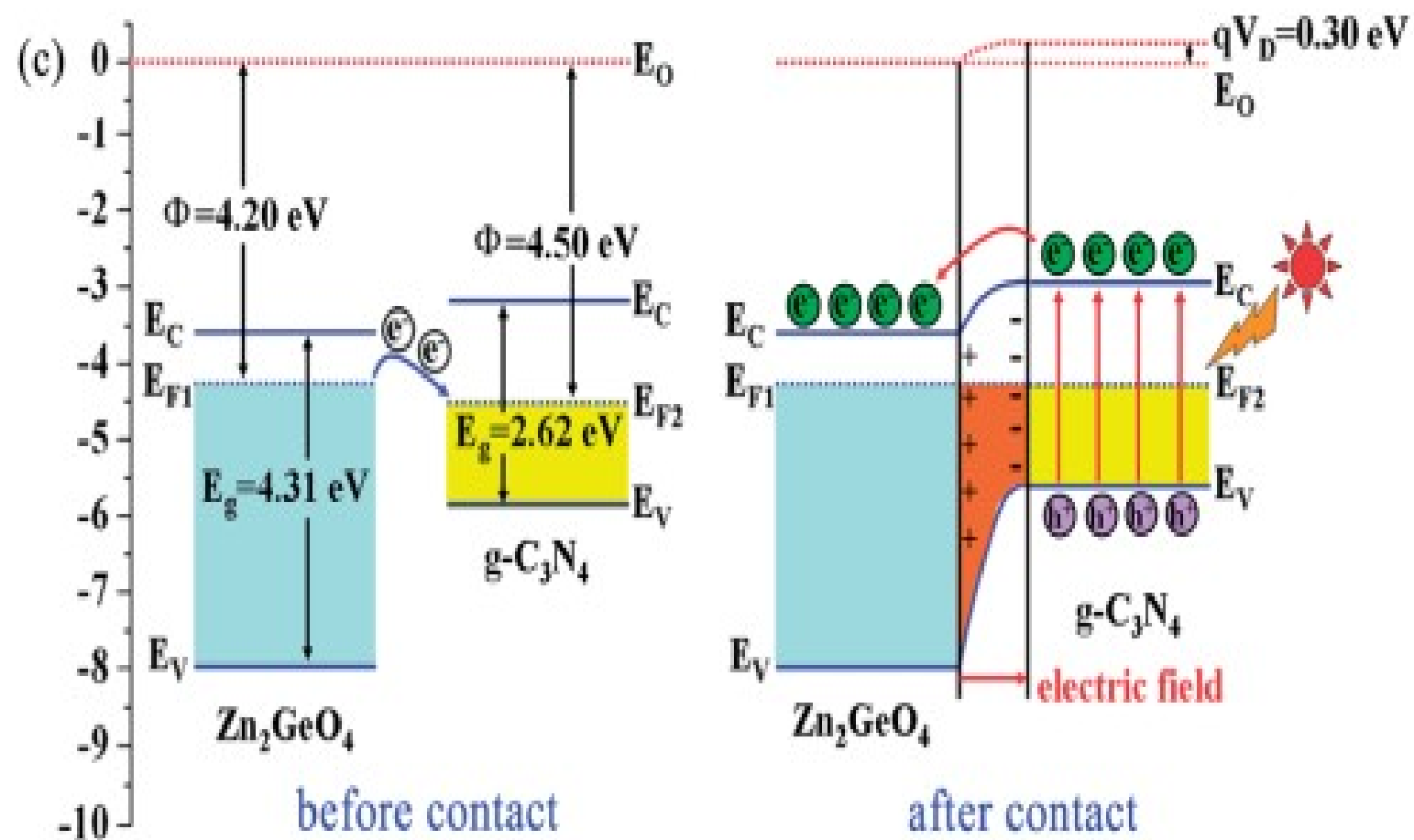
n-Type Semiconductor





## p - Type Semiconductor





When materials with different individual Fermi levels are placed in contact, some electrons flow from the material with the higher Fermi level into the other material. This transfer of electrons raises the lower Fermi level and lowers the higher Fermi level. When the transfer is complete, the Fermi levels of the two materials are equal. This behaviour is important in electronic devices that juxtapose different materials.



Thanks for your attention

