

## 6.3 Extrinsic (or Impure) Semiconductors

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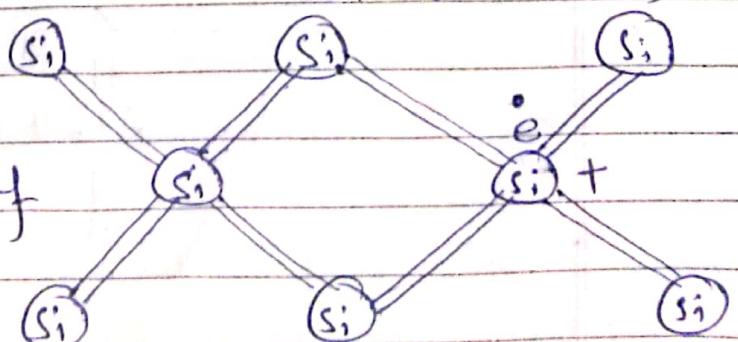
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When some pentavalent atoms of group V (phosphorus, arsenic, antimony,..) and trivalent elements of group III (Aluminum, Boron, Gallium,..) are added in a small extent to an intrinsic semiconductors, the electrical conductivity goes to increase drastically.

The addition of the former type of impurities results to an n-type extrinsic semiconductors while that of the later type results to a p-type extrinsic semiconductors.

### 6.3.9 Donor and Acceptor Energy Levels:

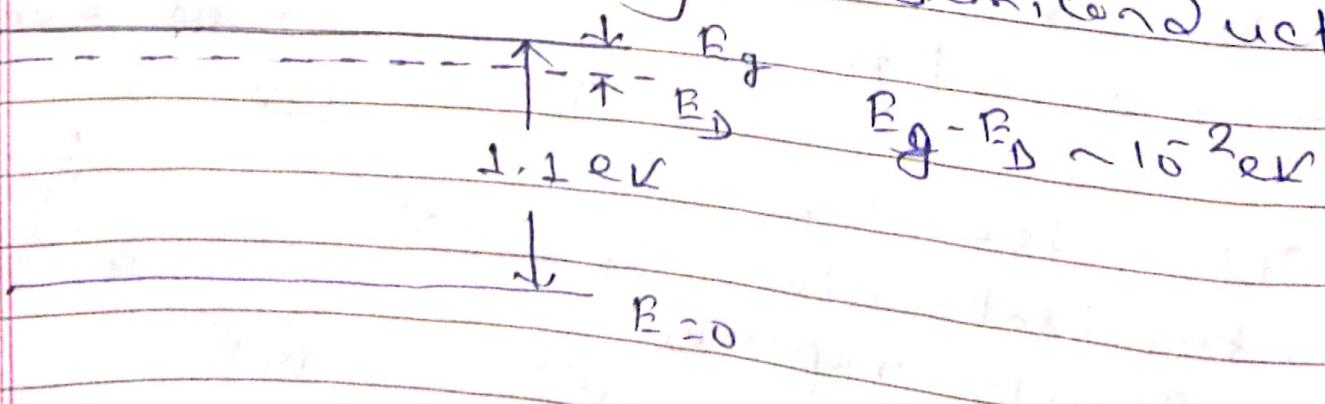
The small amount of impurity atoms added enters the crystal lattice of the semiconductors substitutionally as confirmed by the x-ray studies. The detailed substitution has been outlined in the fig.



Let's see how a pentavalent atom of phosphorus replaces a Si atom in the lattice structure. Among the five electrons in the valence

shell, only four electrons go to the covalent bonding with the neighbouring four Si atoms. The remaining one electron as a loosely bound electron ( $\sim 10^{-2}$  eV) can easily be ionised and is free to move throughout the crystal lattice.

In terms of band theory, this extra electron occupies an energy level,  $E_D$ , called the donor energy level that lies  $\sim 10^{-2}$  eV below the conduction band at  $T = 0K$ . On increasing the temp<sup>r</sup>, the electron gains  $10^{-2}$  eV energy and is excited to the conduction band or ionising the impurity atom, but without creating hole in the valence band. The semiconductor hence with an excessive of an electron (-ve charge) is called N-type semiconductor.



A similar situation arises on adding group II element say Al. It replaces a Si atom, the three valence electrons of it combine with the three Si atoms and fails to complete a tetravalent bond scheme due to shortage of one electron. This shortage of one electron creates a vacancy that acts as a strong centre of attraction for a negative charge. At  $T=0K$ , the vacancy remains localized around the Al atom. When the temp<sup>r</sup> is increased, the electron from the adjacent of Si atom jumps to the empty site leaving behind the vacancy on the Si atom. Hence is doing so, the vacancy seems to migrate in a direction throughout the lattice while electrons migrate to the opposite direction of the vacancy (or hole).

In terms of the band theory terminology, there is an energy level  $E_A$ , called the acceptor level nearly above the valence band that is empty at  $T=0K$ . As the temp<sup>r</sup> increases, electrons from the valence band jumps to this energy level leaving behind the hole in the valence band.  $E_A$  lies very much

close to the valence band ( $0.01\text{eV}$  for Ge and  $0.04\text{eV}$  to  $0.1\text{eV}$  ins) the impurity atoms added here accept the electrons from the valence band leaving behind the holes (excess of +ve charges) in the valence band. Hence the semiconductors of this type are called as p-type extrinsic semiconductors.

C.B

$E = E_g$

Hence donor

level is the energy level made by the excess of

electrons from the donor atoms

$E_A \approx 10^2\text{eV}$

of group V that is below the conduction band by an amount  $\approx 10^2\text{eV}$  while acceptor level is the energy level made by the acceptors that are filled by the electrons from the valence band and are slightly above the valence band by the equal amount.

## 6.3. b. Carrier Density and Fermi Level in Impurity Semiconductors

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The addition of impurity atoms significantly alters the no. of electrons in the conduction band or holes in the valence band thereby changing the position of the Fermi level.

While deriving the expressions for  $N_e$  and  $N_h$  in intrinsic semiconductors, neither the value of  $g(\epsilon)$  nor  $F(\epsilon)$  are changed and the expressions are same as in the intrinsic semiconductors differing numerically. Such difference in the numerical value is due to the change in position of the Fermi level.

The determination of Fermi level in intrinsic semiconductor is by equating  $N_e$  and  $N_h$  as the no. of electrons in the conduction band are equal to the no. of electrons in the valence band.

But the situation differs in the extrinsic semiconductors. In N-type semiconductors, the electrons are excited into the conduction band from both the donor levels and the valence band.

More explicitly to say,  $N_e$  is equal to the no. of holes in the valence band plus the no. of donor impurity atoms per unit volume that have been ionised,  $N_d$ .

Hence one writes,

$$N_e = N_h + N_D^+ \quad \text{--- (6.8)}$$

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$N_D^+$  is the neutrality eq?

Let  $N_D$  be the no. of Donor atoms and hence there are  $N_D$  electrons at donor level,  $E_D$ .

The no. of ionised atoms is found by multiplying  $N_D$  with the probability that an electron not be at  $E_D$ .

$$\text{i.e., } N_D^+ = N_D [1 - P(E_D)] \quad \text{--- (6.9)}$$

[ $P(E_D) \rightarrow$  probability that an electron be at  $E_D$ .]

,  $1 - P(E_D) \rightarrow$  probability that an electron not be at  $E_D$ .]

Therefore, eq (6.8) now is written as

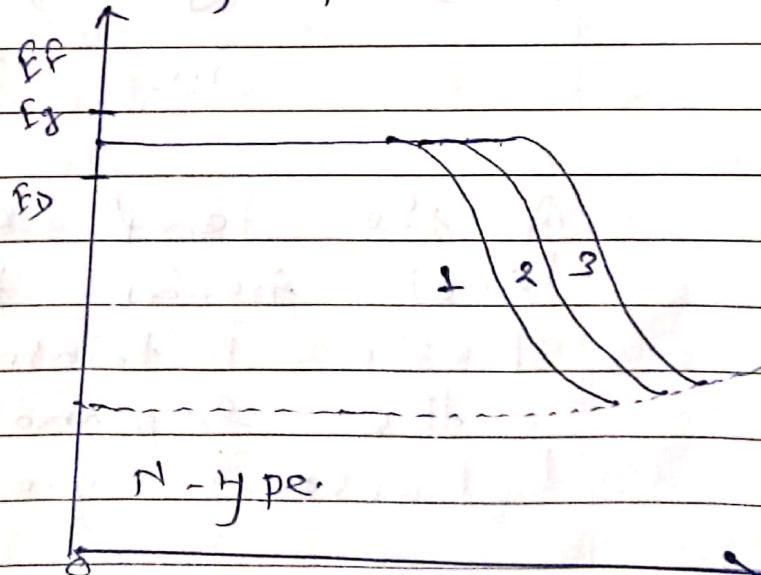
$$N_e = N_h + N_D [1 - P(E_D)]$$

$$N_e e^{-\frac{E_g - E_F}{k_B T}} = N_v e^{-\frac{E_g}{k_B T}} + N_D \left[ 1 - \frac{1}{e^{\frac{E_D - E_F}{k_B T}}} \right] \quad \text{--- (6.10)}$$

$$\text{Where } N_c = \alpha \left( \frac{2\pi m_h^* k_B T}{h^2} \right)^{3/2}$$

$$N_v = \alpha \left( \frac{2\pi m_e^* k_B T}{h^2} \right)^{3/2}$$

Clearly eq (6.20) can't be solved analytically. Hence  $E_F$  can't be found in terms of  $T$  and other parameters of semiconductor. A numerical solution to the eq yields the result as in the fig below showing the variation of  $E_F$  with the temp.



The curves ①, ②, ③ corresponds to the increasing value of donor impurities,  $N_d$

The dashed line represents the value of  $E_F$  for the intrinsic semiconductor with  $T \rightarrow \infty$  the assumption that  $m_h^* > m_e^*$

$$\text{From } E_F = \frac{E_g}{2} + \frac{3}{4} k_B T \ln \frac{m_h^*}{m_e^*},$$

$E_F = \frac{E_g}{2}$ , for intrinsic semiconductor at low temp i.e. the behaviour

is similar to that of intrinsic semiconductor.

At a high temp, the  $E_F$  term becomes significant and  $E_F$  begins to increase with upwards curvature.

Hence followings are the characteristic features:

\* At a low temp, the Fermi level for the extrinsic semiconductor lies half way of  $E_D$  and  $E_g$

$$\text{i.e., } E_{gF} = \frac{E_D + E_g}{2}$$

As the temp increases, the Fermi level tends to approach the value of the intrinsic semiconductor.

The explanation of the graphical behaviour goes like this.

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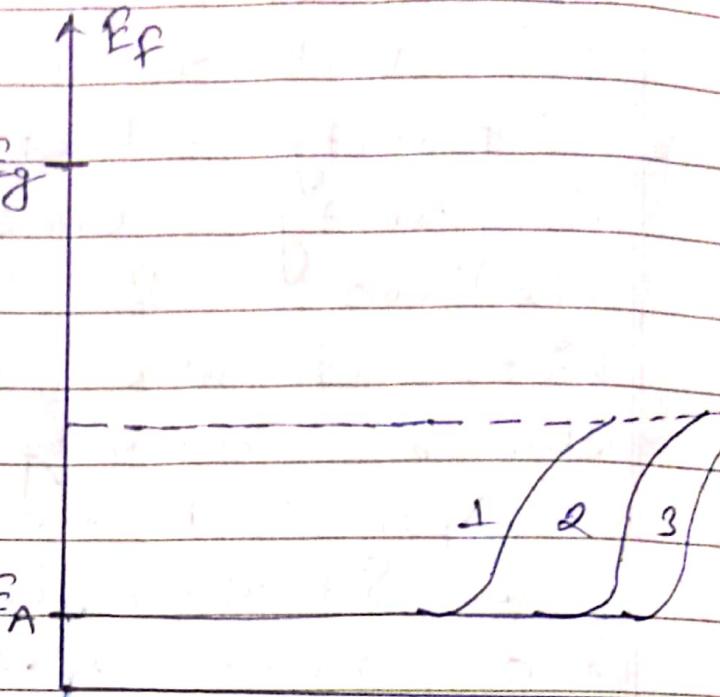
At a room temp and below it, only the electrons at donor level reach to the conduction band, no valence electrons. Hence the Fermi level comes to lie between  $E_D$  and  $E_g$  at mid way i.e.  $E_F = \frac{E_D + E_g}{2}$

But at high temp<sup>r</sup>, a large no. of valence electrons jump to the conduction band and become dominant over the contribution from donor atom electrons to  $10^{28}$  valence electrons/m<sup>3</sup> with  $\sim 10^{22}$  impurity electrons/m<sup>3</sup>, assuming an impurity concentration of one part per million. In other words, the contribution to the conduction band by the donor impurity electrons is negligible as compared to the valence band electrons. The situation hence is similar to that of the real intrinsic semiconductors. Hence at high temp<sup>r</sup>, the Fermi level shifts downwards to resemble with the intrinsic semiconductors.

Clearly the higher the impurity concentration, the more the temp<sup>r</sup> at which the contribution from the electrons excited from the valence band becomes more significant than that of the impurity electrons and hence curves 1, 1, 3 shift rightwards respectively.

[Note: The probability for the electrons to shift to the conduction band from the impurity levels,  $P_n \propto e^{-\frac{E_g - E_D}{k_B T}}$  and from the valence band,  $P_n \propto e^{-\frac{E_g}{k_B T}}$ ]

In case of p-type Eg of semiconductors the Fermi energy level with temperature has been outlined in the fig.



The dashed line indicates the Fermi level for intrinsic semiconductor (that lies half way of the top of the valence band and the conduction band)

i.e.,  $E_F = \frac{E_g}{2}$  as per

The description of the eq?

$$E_F = \frac{E_g}{2} + \frac{3}{4} k_B T \ln \frac{m_h^*}{m_e^*} \text{ and}$$

Curves upwards at high temp as described earlier

The thick line indicates the Fermi level for the intrinsic p-type

Semiconductor. For this, at low temp<sup>r</sup>, transition of the electron from the valence band to the conduction band is the dominant factor. Hence the Fermi level is expected to lie mid-way of the top of the valence band and the E<sub>F</sub>. At high temp<sup>r</sup>, the acceptor level is filled by the valence electrons that act as the source of electrons to the conduction band. The material hence behaves like an intrinsic semiconductors and hence the Fermi level shifts upwards to resemble with the intrinsic Fermi level.

One thing to be noted here is that in N-type Semiconductor, there are more electrons in the conduction band due to the contribution from both impurity levels and the valence band than the holes in the valence band.

Hence electrons are much more abundant than the holes and the electrons are called majority charge carriers while the holes are the minority charge carriers. A similar reversed case arises in P-type semi-conductor.

## 6.9 Electrical Conductivity of Semiconductors

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The current density due to the electronic charge,

$$J = N e V_d, \text{ where } N \rightarrow \text{No. of charge carriers}$$

$V_d \rightarrow$  drift velocity.

$$\& \sigma E = N e V_d E \quad \therefore V_d E = V = \text{Voltage}$$

$$\& \sigma = N e \cdot \frac{e T}{m} \quad \therefore t = \frac{e T}{m}$$

$$\therefore \sigma = \frac{N e^2 T}{m} \quad \& T \rightarrow \text{Collision time with ions.}$$

$m \rightarrow$  mass of the carrier.

In case of semiconductor, there are two types of charge carriers, electrons and holes contributing the current.

Hence the conductivity,

$$\sigma = 1e1^2 \left[ \frac{N_e T_e}{m_e^*} + \frac{N_h T_h}{m_h^*} \right] - (6.11)$$

For the intrinsic semiconductor,

$$N_e = N_h \Rightarrow \sigma = 1e1^2 N_e \left[ \frac{T_e}{m_e^*} + \frac{T_h}{m_h^*} \right] - (6.12)$$

In Semiconductors, both  $\sigma$  and  $T$  depend on temper and for Si and Ge,

$$\tau \propto T^{-3/2}$$

Now

$$\sigma = 2e^2 L \left( \frac{2\pi k_B T}{h^2} \right)^{3/2} \left( m_e^* m_h^* \right)^{3/4} e^{-E_g/2k_B T} \left[ \frac{C_e}{m_e^*} + \frac{C_L}{m_h^*} \right]$$

$$\text{And } \Rightarrow \sigma \propto T^{3/2} e^{-E_g/2k_B T} \left[ \frac{C_e}{m_e^*} + \frac{C_L}{m_h^*} \right]$$

$$\therefore \sigma = \text{const. } T^{3/2} e^{-E_g/2k_B T} \left[ \frac{C_e}{m_e^*} + \frac{C_L}{m_h^*} \right] \quad \rightarrow (6.13)$$

$$\text{As } \tau \propto T^{-3/2} \left( C_e \propto T^{-3/2}, C_L \propto T^{-3/2} \right)$$

$$\Rightarrow \sigma = \text{const. } e^{-E_g/2k_B T} \quad (6.14) \quad \because m_e^*, m_h^* \rightarrow \text{const.}$$

$$\text{Now, } \ln \sigma = -\left(\frac{E_g}{2k_B}\right) \cdot \frac{1}{T} + c \quad (6.15)$$

$$\text{Comparing to } y = mx + c \Rightarrow m = -\frac{E_g}{2k_B}$$

and hence the eq<sup>n</sup> line with -ve slope. The situation is confirmed experimentally.

Let us take the case for N-type semiconductor.

At a high temp<sup>r</sup>, the electrons ionised from the donor impurities become negligible as compared to the electrons excited from the valence band. Hence the nature of the semiconductor becomes intrinsic and thus  $\ln n$  against  $T^{-1}$  is similar as in the above case with the slope =  $\frac{E_g}{2k_B}$

At a low temp<sup>r</sup>, the situation is quite different. The electrons available in the conduction band are only from the donor impurities that leads to conclude  $N_d > N_i$ . Hence on ignoring the hole effect, eq<sup>n</sup> (6.11) reduces to

$$n = 1e1^2 N_d \frac{m_e}{m_h^*}$$

The eq<sup>n</sup> (6.3) is

$$N_e = d \left( \frac{e \pi m_e^* k_B T}{h^2} \right)^{3/2} e^{E_F - E_g / k_B T}$$

and  $\tau \propto T^{-3/4}$  that together imply to write  $\sigma$  as

$$\sigma \propto d^2 10^2 \left( \frac{e \pi m_e^* k_B T}{h^2} \right)^{3/2} e^{E_F - E_g / k_B T} \cdot \frac{T^{-3/4}}{m_e^*}$$

And finally,

$$\sigma = \text{const. } e^{-\left(\frac{E_g - E_D}{2k_B T}\right)}$$

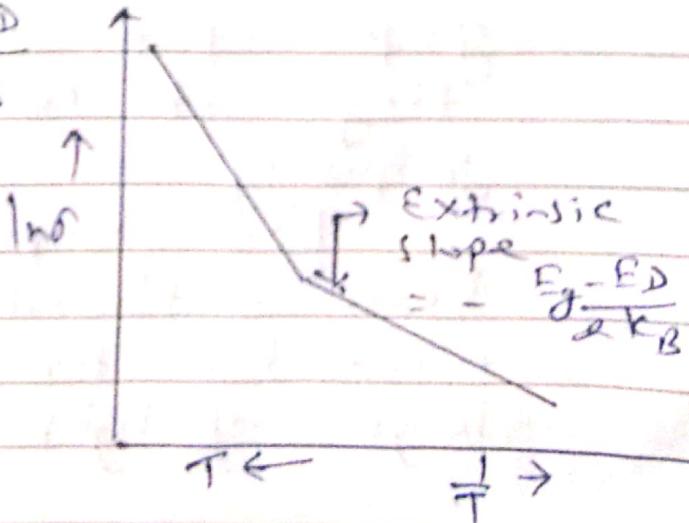
$$\text{But here } E_F = \frac{E_g + E_D}{2}$$

$$\therefore \sigma = \text{const. } e^{-\left(\frac{E_g - E_D}{2k_B T}\right)}$$

$$\ln \sigma = \ln \text{const.} - \left( \frac{E_g - E_D}{2k_B} \right) \cdot \frac{1}{T} + C \quad (6.16)$$

On comparing to  $y = mx + c$ , above eqn is a st. line with a -ve

$$\text{slope} = -\frac{E_g - E_D}{2k_B}$$



## Photoconductivity

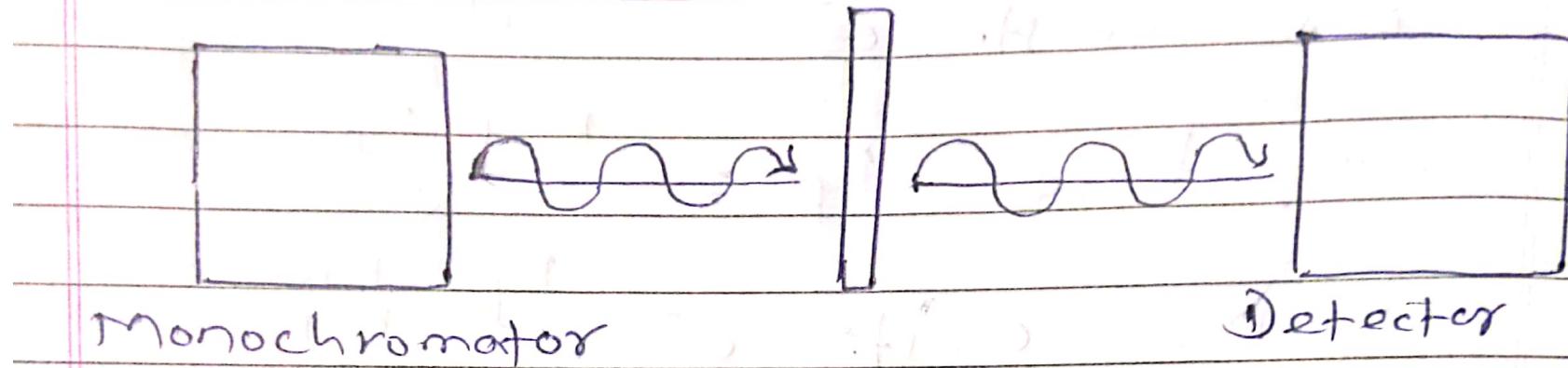


Fig: Absorption of electromagnetic radiation by a semiconductor.

The photoconductivity is the technique to measure the energy gap of a semiconductor by illuminating it with photons of suitable frequency.

The experimental set up has been outlined in the fig. The monochromator selects a given wavelength of light that strikes a thin

slab of the semiconductor and the transmitted part through it is measured using a light meter.

The absorbed amount is measured by subtracting the transmitted part from the incident part. The experiment is repeated over several wavelengths.

At longer wavelength, there is a negligible and a sharp edge, called the absorption edge at which an abrupt change in the absorption is seen.

For Si,  $\lambda_c = 1.1 \times 10^{-6} \text{ m}$ .

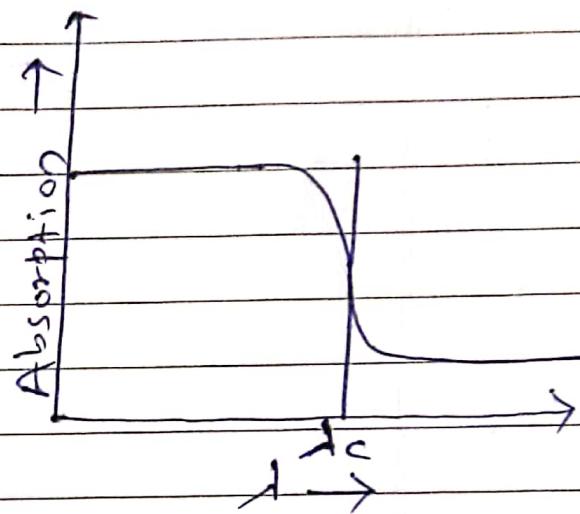


Fig:

Absorption of wavelength.

It can be concluded that for the incident photons of energy  $h\nu$  less than the energy gap  $E_g$  of the semiconductor, it can't excite the electrons to the conduction band and the wavelength gets transmitted. Hence the semiconductor becomes transparent to the incident wavelength.

If the incident wavelength  $\lambda$  is greater than  $E_g$  ( $h\nu > E_g$ ), it excites the electrons to the conduction band, wavelength is opaque, and the semiconductor becomes opaque.