Behaviour of Electron in Materials and Emerging properties for multifunctional applications

Chapter-3

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Concept of Formation of band in Materials

Formation of band in materials involved through chemical bonding of electrons. We take an example of Si atoms, which is most abundant element in the earth crust. These materials are being used in various applications in Electronics, Medical science, cement industry etc. [1-2]. The Si atom has 14 electrons, which distribute themselves in the various atomic energy levels (Fig. 3.1). The inner shells, n=1and n=2 are full and therefore “closed”. Since these shells are near the nucleus, when Si atoms come together to form the solid, they are not much affected and they stay around the parent Si atoms. Therefore, be excluded from further discussion. The 3s and

3p subshells are further away from the nucleus. When two Si atoms approach, these electrons strongly interact with each other. Hence, in studying the formation of bands in the Si solid, we will only consider the 3s and 3p levels.

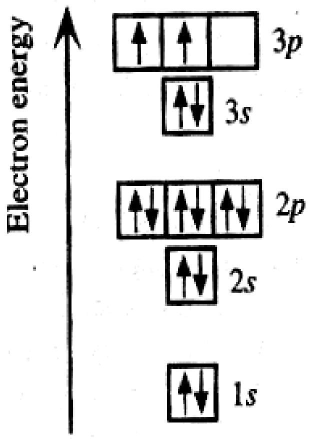
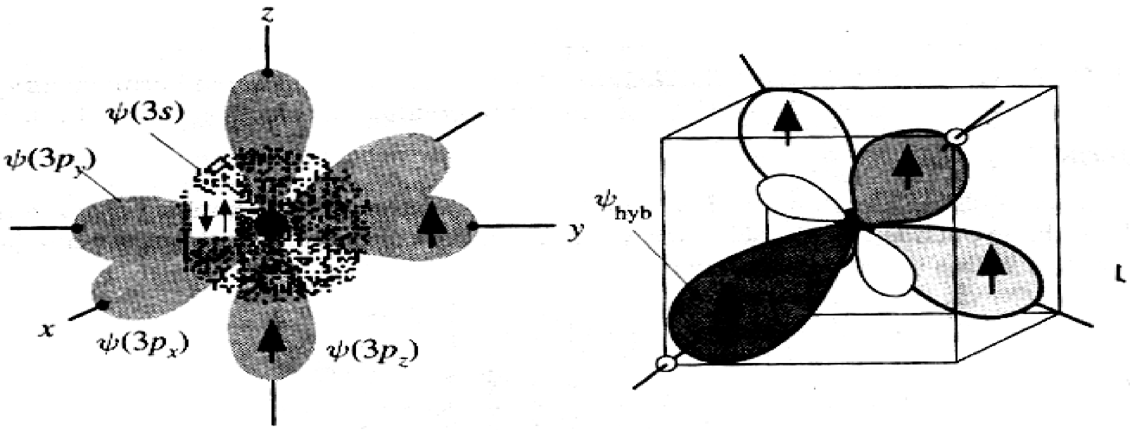


Figure 3.1 The electronic structure of Si.

Why Si actually bonds with four neighbors, since the 3s orbital is full and there are only two electrons in the 3p orbitals. The full 3s orbital should not overlap a neighbor and involved in bonding. Since only two 3p orbitals are half full, bonds should be formed with two neighboring Si atoms. In reality, the 3s and 3p energy levels are quite close and when five Si atoms approach each other, the interaction results in the four orbital is $\psi(3s), \psi(3p_x), \psi(3p_y), \psi(3p_z)$ mixing together to form four new **hybrid orbitals**, which are directed in tetrahedral directions; that is, each one is aimed as far away from the others as possible, (Fig. 3.2).



(a) Isolated Si **(b) Si preparing to bond**

Figure 3.2
(a) Si is in Group IV in the Periodic Table. An isolated Si atom has two electrons in the 3*s* and two electrons in the 3*p* orbitals.
(b) When Si is about to bond, the one 3*s* orbital and the three 3*p* orbitals become perturbed and mixed to form four hybridized orbitals, ψ_{hyb}, called sp^3 orbitals, which are directed toward the corners of a tetrahedron. The ψ_{hyb} orbital has a large major lobe and a small back lobe. Each ψ_{hyb} orbital takes one of the four valence electrons.

We call this process sp^3 **hybridization**, since one s orbital and three p orbitals are mixed. (The superscript 3 on *p* refers to the number of p orbitals used in the hybridization).The four hybrid orbitals, , have one electron, each so they are half occupied. This means that four Si atoms can have their orbitals. Overlap to form bonds with one Si atom, which is what actually happens; thus, one Si atom, bonds with four other Si atoms in tetrahedral directions. In the same way, one Si atom bonds with four H atoms to form $Si\,H_4$ - an important gas known as silane which is widely used in Materials technology to fabricate Si based devices. In $Si\,H_4$, four hybridized orbitals of the Si atom overlap with the 1s orbitals of four H atoms. In exactly the same way, one carbon atom bonds with four H atoms to form methane, CH_4.There are two ways in which the hybrid orbital Ψ_{hyb} can overlap with that of the neighboring Si atom to form two molecular orbitals. They can add in phase (both positive and both negative) or out of phase (one positive and the other negative) to produce a bonding or an antibonding molecular orbital Ψ_B and Ψ_A, respectively, with energies E_B and E_A. Each $Si-Si$ bond thus corresponds to two paired electrons in a bonding molecular orbital. In the solid, there are $N\ (\sim 5\times 10^{22}\ \mathrm{cm}^{-3})$ Si atoms, and there are nearly as many such bonds. **The interactions between the orbital (i.e. the bonds) lead to the splitting of the E_B energy levels to N levels, thereby forming an energy band labelled the valence band (VB) by virtue of the valence electrons it contains. Since the energy level is full, so is the valence band.** Fig. (3.3) illustrates the formation of the VB from E_B .

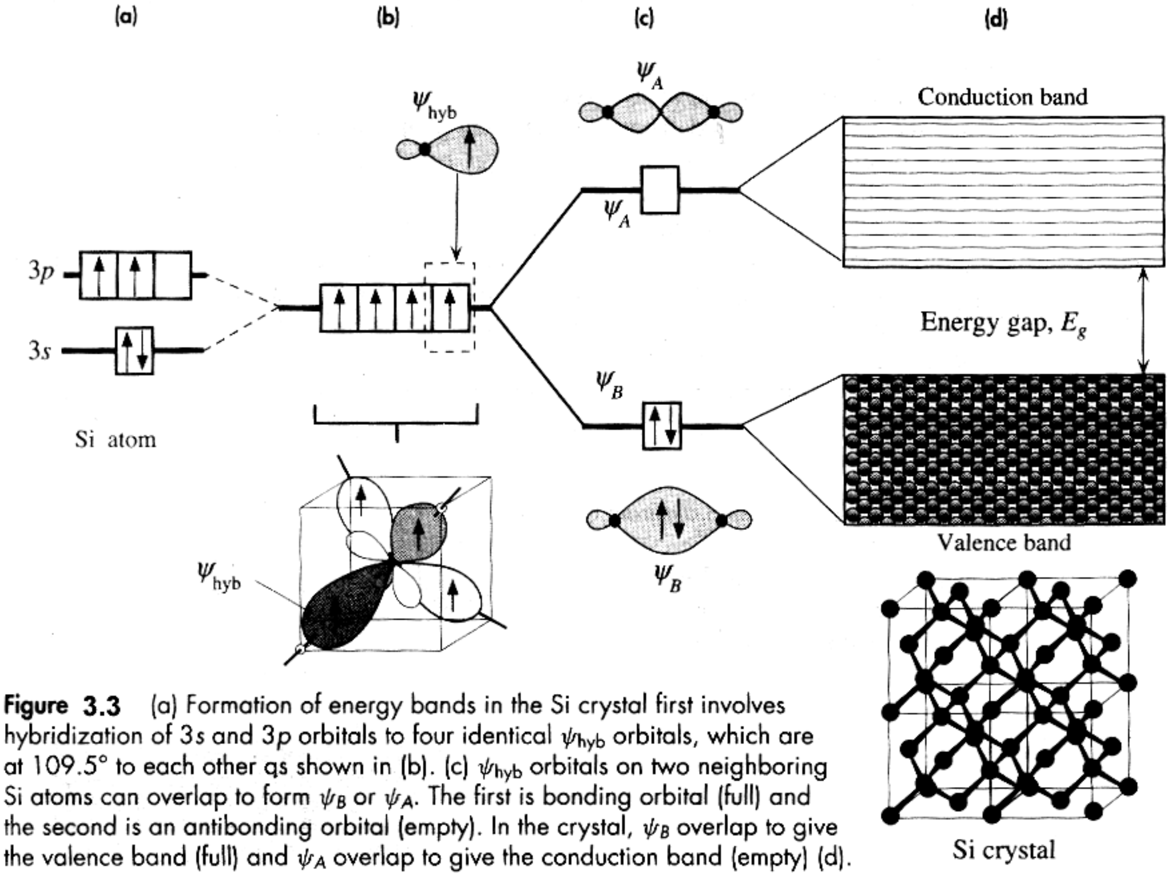
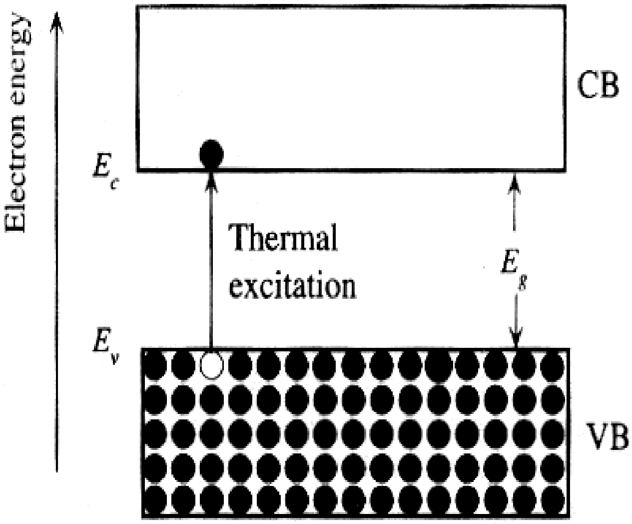


Figure 3.3 (a) Formation of energy bands in the Si crystal first involves hybridization of 3*s* and 3*p* orbitals to four identical ψ_{hyb} orbitals, which are at 109.5° to each other as shown in (b). (c) ψ_{hyb} orbitals on two neighboring Si atoms can overlap to form ψ_B or ψ_A. The first is bonding orbital (full) and the second is an antibonding orbital (empty). In the crystal, ψ_B overlap to give the valence band (full) and ψ_A overlap to give the conduction band (empty) (d).

In the solid, the interactions between the N number of ψ_A orbitals result in the splitting of the energy level E_A to N levels and the formation of an energy band that is completely empty and separated from the full valence band by a define energy gap E_g . In the gap region, there are no states; therefore, the electron cannot have energy with a value within E_g . The energy band formed from orbitals is a **conduction band** (CB)[Fig. 3.3]. The electronic states in the VB (and also in the CB) extend throughout the whole solid, because they result from N ψ_B orbitals interfering and overlapping each other. N ψ_B orbitals can overlap in N different ways to produce N distinct wavefunctions ψ_{vb} that extend throughout the solid. We cannot relate a particular electron to a particular bond or site because the wavefunctions ψ_{vb} corresponding to the VB energies are not concentrated at a single location. **The electrical properties of solid materials are based on the fact that in solids, such as semicondcutors and insulators there are certain bands of allowed energies for the electrons, and these bands are separated by energy gaps, that is, band gaps.** At temperatures above absolute zero, the atoms in a solid vibrate due to their thermal energy. Some of the atoms can acquire a sufficiently high energy from thermal fluctuation to strain and rupture their bonds. Physically, there is a possibility that the atomic vibrations will impart sufficient energy to the electron for it to surmount the bonding energy and leave the bond. The electron then must enter the higher energy state. In the case of Si, this means entering a state in the CB (Fig. 3.4).

Figure 3.4 Energy band diagram of a semiconductor.
CB is the conduction band and VB is the valence band. At 0 K, the VB is full with all the valence electrons.



If there is an applied electric field E_x in the $+x$ direction, then the excited electron will be acted on by a force $-eE_x$ and it will try to move in the $-x$ direction. For it to do so, there must be empty higher energy levels, so that as the electron accelerates and gains energy, it moves up the band. When an electron collides with a lattice vibration, it loses the energy acquired from the field and drops down within the CB. Again, it would be emphasized that states in any energy band are extended; that is, the electron is not localized to any one atom. Note that the thermal generation of an electron from the VB to the CB leaves behind a VB state with a missing electron. This unoccupied electron state has an apparent positive charge, because the crystal region was neutral prior to the removal of the electron. **The VB state with the missing electron is called a hole and is denoted h^+ . The hole can "move" in the direction of the field by exchanging places with a neighbouring valence electron and hence it contributes to conduction.**

Energy (E) Wave Vector (K) Diagram

When the electron is within a potential well of size *l*, its energy is quantized and given by

$$E_n = (\hbar k_n)^2 / 2m$$

where the wave vector is essentially a quantum number determined by

$$k_n = n\pi / l$$

Where $n = 1, 2, 3$, The energy increases parabolically with the wave vector k_n . We also know that the electron momentum is given by $\hbar k_n$. This description can be used to represent the behavior of electrons in a metal within which their average potential energy can be taken to be roughly zero. In other words, we take within the metal crystal and $V(x)$ to be large [e.g.] $V(x) = V_0$ outside so that the electron is contained within the metal. The potential energy of the electron depends on its location within the crystal and is periodic due to the regular arrangement of atoms. To find the energy of the electron in a crystal, we need to solve Schrodinger equation for a periodic potential energy function in three dimensions. We first consider the hypothetical one-dimensional crystal (Fig. 3.5).

The electron potential energy functions for each atom add to give an overall potential energy function $V(x)$, which is clearly periodic in *x* with the periodicity of the crystal *a*. Thus,

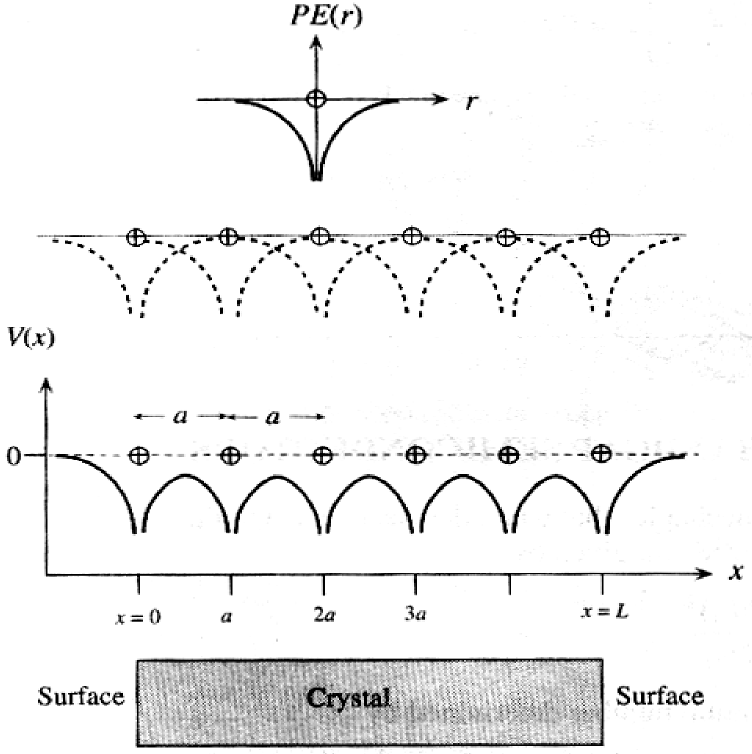
$$V(x) = V(x + a) = V(x + 2a) = \dots$$

and so on. We want to solve the Schrodinger equation

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\,[E - V(x)]\,\psi = 0 \qquad (3.1)$$

subject to the condition that the potential energy is periodic in *a*, that is

$$V(x) = V(x + ma)\; m = 1, 2, 3, \ldots \qquad (3.2)$$



PE of the electron around an isolated atom.

When N atoms are arranged to form the crystal then there is an overlap of individual electron PE functions.

PE of the electron, V(x), inside the crystal is periodic with a period a.

Figure 3.5 The electron potential energy (*PE*), *V*(*x*), inside the crystal is periodic with the same periodicity *a* as that of the crystal. Far away outside the crystal, by choice, *V* = 0 (the electron is free and *PE* = 0).

The solution of equation (3.1) will give the electron wave-function in the crystal and hence the electron energy. Since $V(x)$ is periodic, we expect the solution to be periodic. The solutions to equation (3.1) are called the **Bloch wavefunctions** and are of the for

$$\psi_k(x) = u_k(x) \exp(jkx) \qquad (3.3)$$

when $u_k(x)$ is a periodic function that depends on $V(x)$ and has the same periodicity *a*as $V(x)$. The term $\exp(jkx)$ represents a travelling wave. We have to multiply this by $\exp(-jEt/\hbar)$, where E is the energy, to get the overall wavefunction $\psi(x,t)$. Thus the electron wavefunction in the crystal is a travelling wave that is modulated by $u_k(x)$.

There are many such Bloch wavefunction solutions to the one-dimensional S.E, each identified with a particular k value, (say) , which acts as a kind of quantum number. Each $\psi_k(x)$ solution corresponds to a particular k_n and represents a state with an energy. The dependence of the energy E_k on the wavevector k is called the **diagram.** Fig. (3.6) shows a typical $E - k$ diagram for the hypothetical one-dimensional solid for *k* values in the range $-\pi/a$ to $+\pi/a$ $\hbar k$ for the Bloch electron is the momentum involved in its interaction with external fields. The rate of change of is the externally applied force on the electron such that due to an electric field Thus, for the electron within the crystal,

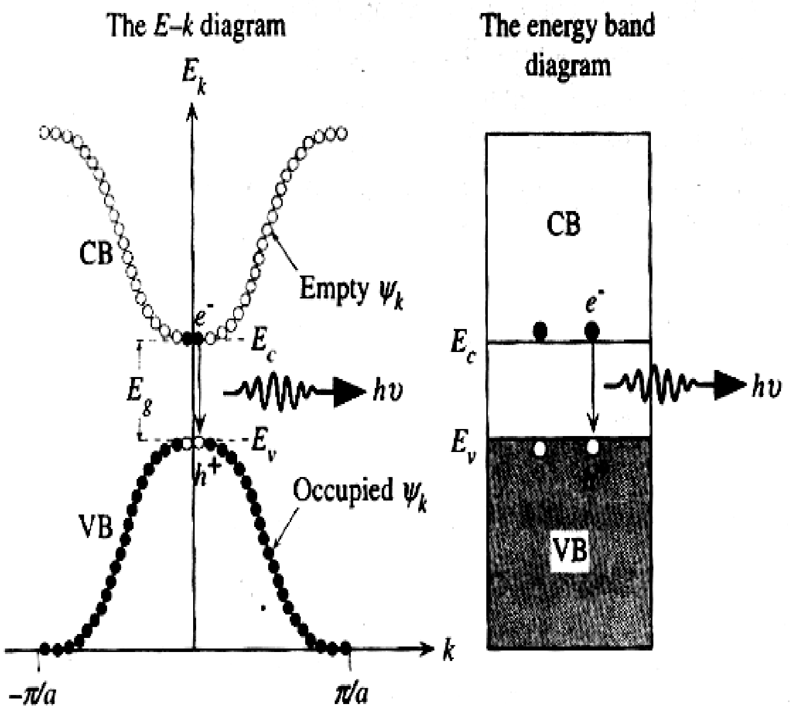


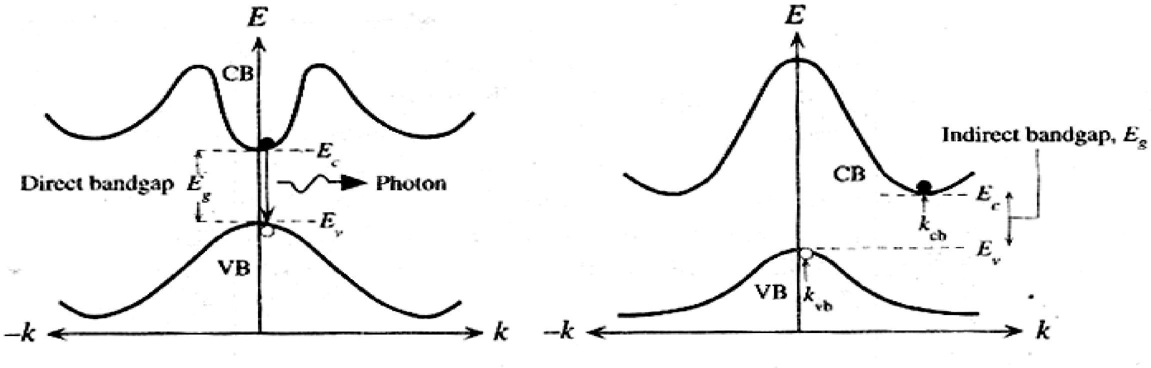
Figure 3.6 The *E–k* diagram of a direct bandgap semiconductor such as GaAs.
The *E–k* curve consists of many discrete points, each corresponding to a possible state, wavefunction $\psi_k(x)$, that is allowed to exist in the crystal. The points are so close that we normally draw the *E–k* relationship as a continuous curve. In the energy range E_v to E_c, there are no points [$\psi_k(x)$ solutions].

$$\frac{d(\hbar k)}{dt} = F_{ext}$$

and consequently we call the crystal momentum of the electron.The $E - k$ diagram is an **energy versus crystal momentum plot.** The states $\psi_k(x)$ in the lower curve constitute the wavefunctions for the valence electrons and thus correponds to the states in the VB. Those in the upper curve, on the other hand, correspond to the states in the conduction band (CB), since they have higher energies. All the valence electrons at the absolute zero of temperature therefore fill the states, particular k_n values, in the lower $E - k$ diagram. It should we emphasized that an $E - k$ curve consists of many discrete points, each corresponding to a possible state, wavefunction $\psi_k(x)$, that is allowed to exist in the crystal. The points are so close that we draw the $E - k$ relationship as a continuous curve. It is clear from the $E - k$ diagram that there is a range of energies, from E_v to E_c, for which there are no solutions to the S.E. and hence there are no $\psi_k(x)$ with energies in E_v to E_c. The $E - k$ behavior is not a simple parabolic relationship except near the bottom of the CB and the top of the VB.

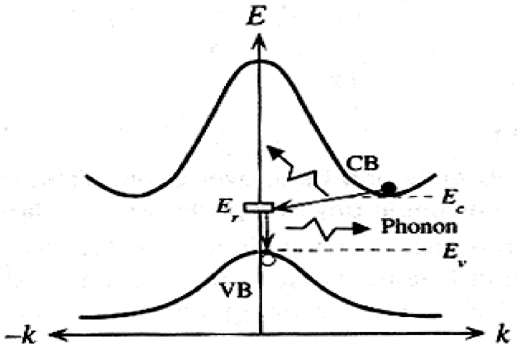
Direct Bandgap Semiconductor

Above absolute zero of temperature, due to thermal excitation, however, some of the electrons from the top of the valence band will be excited to the bottom of the conduction band. According to the diagram (Fig. 3.6), when an electron and hole recombine, the electron simply drops from the bottom of the CB to the top of the VB without any change in its *k* value, so this transition is quite acceptable is terms of momentum conservation. The momentum of the emitted photon is negligible compared with the momentum of the electron. The $E - k$ diagram in Fig. 3.6 is therefore for a **direct band gap semiconductor.** The simple $E - k$ diagram sketched in Fig. 3.6 is for the hypothetical one-dimensional crystal in which each atom simply bonds with two neighbors. In real crystals, we have a three-dimensional arrangement of atoms with $V(x, y, z)$ showing periodicity in more than one direction. The $E - k$ curves are then not as simple as that in Fig. 3.6 and often show unusual features. The $E - k$ diagram for GaAs (Fig. 3.7a) has main features that are quite similar to that sketched in (Fig. 3.6). GaAs is therefore a direct bandgap semiconductor in which electron-hole pairs can combine directly and emit a photon. It is quite apparent that the light emitting devices use direct bandgap semiconductors to make use of direct recombination.



(a) GaAs

(b) Si



(c) Si with a recombination center

Figure 3.7
(a) In GaAs the minimum of the CB is directly above the maximum of the VB. GaAs is therefore a direct bandgap semiconductor.
(b) In Si, the minimum of the CB is displaced from the maximum of the VB and Si is an indirect bandgap semiconductor.
(c) Recombination of an electron and a hole in Si involves a recombination center.

Indirect Bandgap Semiconductor

In the case of Si, the diamond crystal structure leads to an $E - k$ diagram that has the essential features depicted in Fig. 3.7b. We notice that the minimum of the CB is not directly over the maximum of the VB. An electron at the bottom of the CB therefore cannot recombine directly with a hole at the top of the VB because, for the electron to fall down to the top of the VB its momentum must change from k_{cb} to k_{vb} , which is not allowed **by the law of conservation of momentum.** Thus direct electron-hole recombination does not take place in Si and Ge. The recombination process in these elemental semiconductors occurs via a recombination centre at an energy level E_r . The electron is captured by the defect at E_r ,from where it can fall down into the top of the VB. The indirect recombination process is illustrated in Fig. 3.7c. The energy of the electron is lost by the emission of phonons, that is, lattice vibration. The $E - k$ diagram in Fig. 3.7b for Si is an example of an **indirect bandgap semiconductor.**

In some indirect bandgap semiconductor (GaP), the recombination of the electron with a hole at certain recombination centers results in photon emission. The $E-k$ diagram is similar to that shown in Fig. 3.7c except that the recombination centers at E_r are generated by the purposeful addition of nitrogen impurities to GaP. The electron transition from E_r to E_v involve photon emission.

Band gap in Li-Mg-Ferrite Nanomaterials using Tauc plot

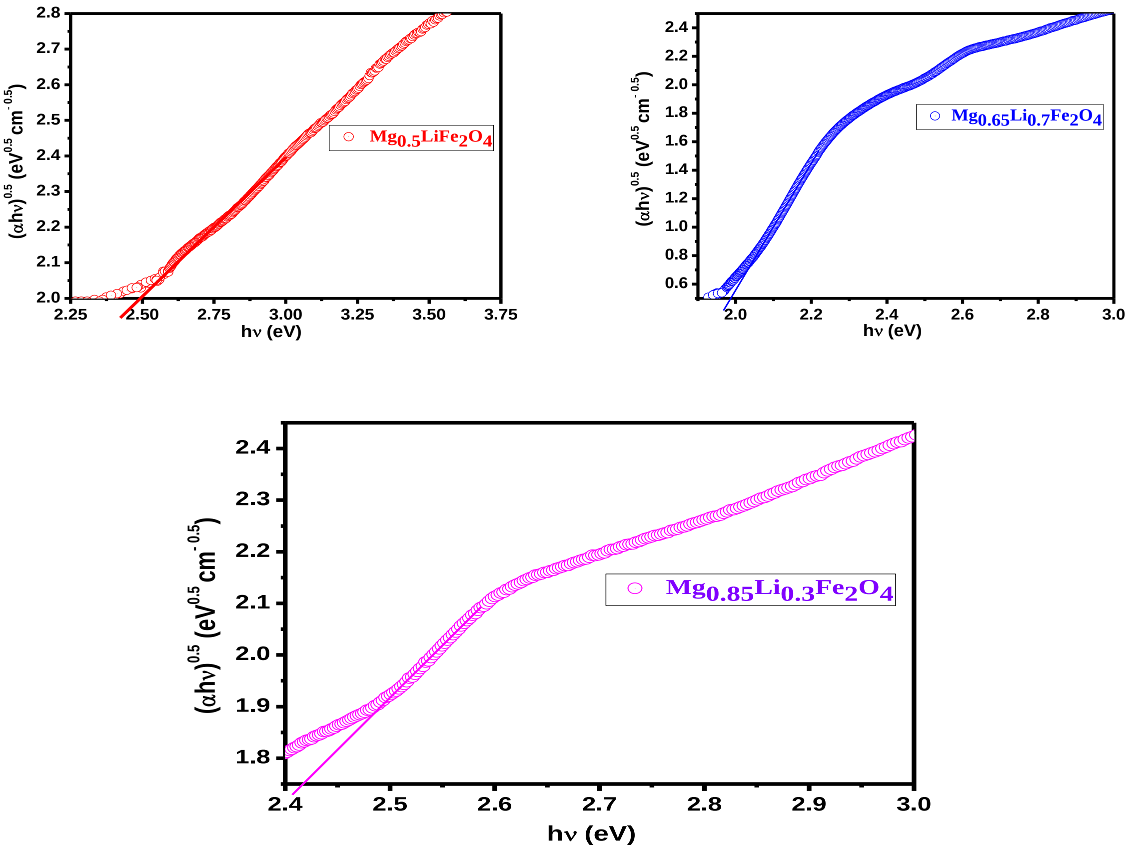


Fig.1.8. Tauc plot of $Mg_{0.5+x}Li_{1-2x}Fe_2O_4$different concentration having $0 \leq x \leq 0.35$.

Band gap order- (2.5 eV), (1.98 eV) and (2.41eV)

Ref- Nishant Kr and Rakesh Kr Singh et al, J. Materials : Materials in Electronics- in press

Motion of an Electron in crystal and its Effective Mass

The response of a conduction band electron to an applied field can be understood by examining the $E - k$ diagram. We consider one-dimensional crystal. The electron is wandering around the crystal quite randomly due to scattering from lattice vibrations. Thus the electron moves with a certain *k* value in the $+ x$ direction, say k_+ (Fig. 3.8a). When it is scattered by a lattice vibration, its *k* value changes to k_- (Fig. 3.8a). This process of *k* changing randomly from one scattering to another scattering process continues all the time, so over a long time the average value of k is zero; that is, average is the same as average .

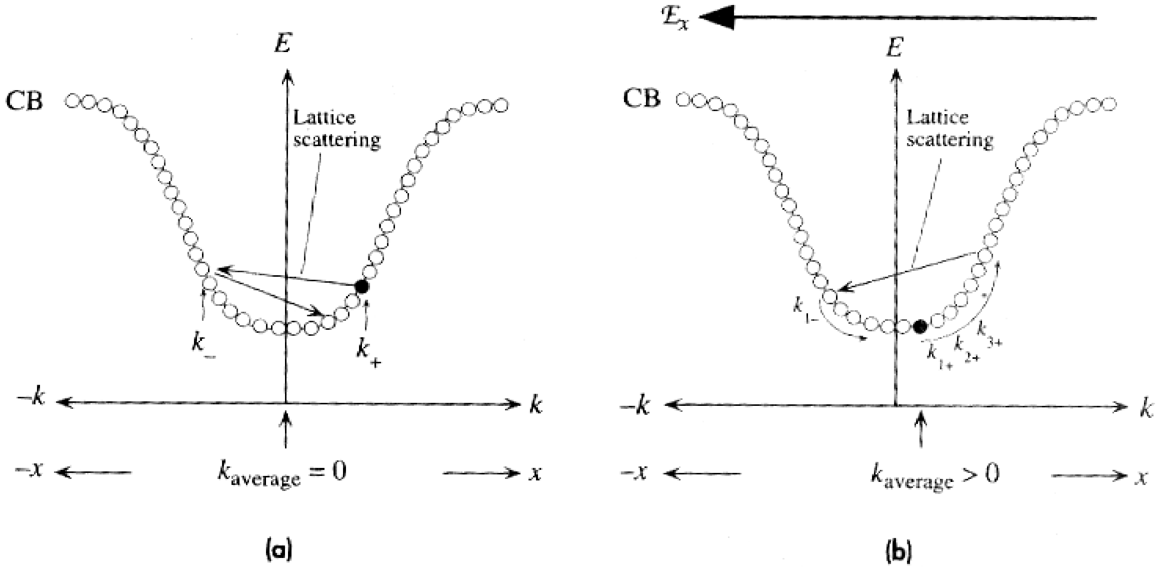


Figure 3.8
(a) In the absence of a field, over a long time, the average of all *k* values is zero; there is no net momentum in any one particular direction.
(b) In the presence of a field in the $-x$ direction, the electron accelerates in the $+x$ direction increasing its *k* value along *x* until it is scattered to a random *k* value. Over a long time, the average of all *k* values is along the $+x$ direction. Thus the electron drifts along $+x$.

When an electric field is applied in the $- x$ direction the electron gains momentum in the $+ x$ direction from (eE_x) the force of the field. With time, while the electron is not scattered, it moves up in the $E - k$ diagram from k_{1+} to k_{2+} to k_{3+} and so on until a lattice vibration randomly scatters the electron to k_{1-} (Fig. 3.8b). Over a long time, the average of all k_{-} is no longer equal to the average of all and there is a net momentum in the $+x$ direction, which is tantamount to a drift in the same direction.

Effective Mass of an Electron

The inertial mass of a particle is defined by mass = force/acceleration. We will evaluate the velocity and acceleration of the electron in the CB in response to an electric field E_x along $-x$ that imposes an external force $F_{ext} = eE_x$ in the direction (Fig. 3.8b).Since we are treating the electron as a wave, we have to evaluate the group velocity, which, by definition, is

$$v_g = d\omega / dk$$

The time dependence of the wave function is $\exp(-jEt/\hbar)$ where the energy

$$E = \hbar\omega$$

ω is the an angular frequency associated with the wave motion of the electron. Both E and depend on *k*. Thus the group velocity is

$$v_g = \frac{1}{\hbar}\frac{dE}{dk} \tag{3.4}$$

Thus the group velocity is determined by the gradient of the $E-k$ curve. In the presence of an electric field, the electron experiences a force $F_{ext} = eE_x$ from which it gains energy and moves up in the $E-k$ diagram until, later on, it collides with a lattice vibration (Fig. 3.8b). During a small time interval δt between collisions, the electron moves a distance $v_g\delta t$ and hence gains energy δE , which is

$$\delta E = F_{ext} v_g \delta t \tag{3.5}$$

$$F_{ext} = \frac{1}{v_g}\frac{dE}{dt} = \hbar\frac{dk}{dt} \tag{3.6}$$

The acceleration *a* is defined dv_g / dt as .

$$a = \frac{dv_g}{dt} = \frac{d\left(\frac{1}{\hbar}\frac{dE}{dk}\right)}{dt} = \frac{1}{\hbar}\frac{d_2E}{dk^2}\frac{dk}{dt} \qquad (3.7)$$

From equation (3.7), we can substitute for dk/dt in equation (3.6) to obtain

$$F_{ext} = \frac{\hbar^2}{\left[\frac{d^2E}{dk^2}\right]} a \qquad (3.8)$$

We know that $F_{ext} = ma$ where m is the electron mass in vacuum. Therefore the effective mass of the electron in the crystal is

$$m^* = \hbar^2 \left[\frac{d^2E}{dk^2}\right]^{-1} \qquad (3.9)$$

The effective mass depends on the $E-k$ relationship, which in turn depends on the crystal symmetry and the nature of bonding between the atoms. The value is different for electrons in the CB and for those in the VB, and moreover, it depends on the energy of the electron since it is related to the curvature of the $E-k$ behavior (d^2E/dk^2) . The effective mass is a quantum mechanical quantity in as much as the behavior is a direct consequence of the application of the S.E. to the electron in the crystal. When the $E-k$ curve is a downward concave as at the top of a band (Fig. 3.6), the effective mass of an electron at these energies in a band is negative. When the electron moves up on the $E-k$ curve by gaining energy from the field, it actually decelerates, that is, moves very slowly. Its acceleration is therefore in the opposite direction to an electron at the bottom of the band

Model Questions

1. What is Effective mass of an electron? Differentiate the direct and indirect gap semiconductors.

2. Explain, motion of an electron in nanocrystaline solid materials?

References

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