Chapter Three

3.0 Thin films

3.1 Optical thin film material*s:*

Today virtually no optical component of practical relevance is purely based on bulk optical material. Optical thin film system are indispensable parts of optical systems and in many cases not only improve the performance of bulk components, e.g. antireflection(AR) coating avoiding stray light in optical lens systems. The materials incorporated in thin film systems are mostly the same oxides and fluorides, the behavior of thin films and systems, strongly differ from the bulk systems as a result of coating preparation and design [17, 19].

3.2 Thin semiconducting films:

A thin semiconducting film has a higher resistivity than a bulk semiconductor which contains the same number of current carriers (holes or electrons) per unit volume, we except the resistivity to depend also upon the amount of added impurity, since that determines the number of current carriers which the semiconductor contains. A thin film normally contains many defects, which may also act as a source of current carriers; some of them might be expected to produce electrons and others, holes. If there were equal numbers of them, and neither were too numerous, the extra electrons would just combine with the holes and the thin film would behave like an intrinsic semiconductor. But usually the numbers are large and unequal; all the films are evaporated one on top of another on the insulating substrate which is usually made of glass or something with similarly smooth surface[27].

3.3 Film thickness:

The growth of the importance of thin films has been attended by considerable development of methods for determining film thickness and optical constant. The method devised are many varied and depend on such features as the nature of the film, whether transparent or absorbing, the thickness ranged which its desired to cover and whether or not its required to study changing thickness with time. a thickness of an evaporated film at any point on the start dependence on the emissive characteristics of the source.

The geometry and arrangement of the substrate to the source and amount of material vaporized [18,22].

3.4 Optical properties of thin films:

The most commonly used instrument for the measurement of the optical performance of thin film coating is the spectrophotometer. The wave length dispersion of commercial instruments for 0.185-to8.00µm spectral range is usually provided by prisms or by ruled or holographic gratings. Grazing incidence gratings, crystal, or multilayer coatings are used in the soft x-ray and extreme ultraviolet (XUV) spectral regions. Fourier transforms spectrometers are capable of measurements from about 2 to 500µm. A variety of attachment is available for the measurements of specular and diffuse reflectance. Absolute measurements of T and R that are accurate within±o.1percent are difficult even in the visible part of the electromagnetic spectrum. Very small absorption of single layers is normally measured with calorimeters. The losses of high- performance laser reflectors are obtained from measurement of the decay times of Fabry-Perot interferometer cavities formed form these mirrors.

The transmittance, reflectance, and absorbance of some optical coatings are affected by exposure to atomic oxygen and by electron, proton, and ultraviolet irradiation. They also depend critically on the cleanliness of the components measured. In space, contamination of optical components can also take place [19, 24].

3.5 Mechanical properties of thin films:

Optical multilayer coatings are frequently required to operate under severe mechanical and environmental conditions. A number of standards deal with the substrate and coating quality, the adhesion of coatings, their abrasion resistance, hardness, and resistance to humidity, salt solution, and salt spray. Depending on the application, multilayer coatings may be required to meet one more of these standards. An overview of the subject of stresses and hardness of thin films on a substrate has been recently published by Baker and Nix [19,28].

3.6 Characterization of thin films:

The features of thin films are in the following table:

Table 3.1 Features of thin films

Features	Extra ordinary phenomena	Application
Electron transportation	Increase of resistivity Decrease of temperature coefficient.	Thin film resistors
Magnetism	Amplitude and maximal of electromagnetic characteristics.	Magnetic memory
Super conductivity	Tunnel effect	Josephson device
Optics	Dependence of reflection and absorption rate to wavelength.	Anti-reflection coating.

3.7 Some applications of thin films:

Thin film has many usually it use for example in coating the glass and lens, and it also improve the property of material. And also use for decoration.

The physicist concern with easy thin film formation, it has many application provide, thin film science and technology have shown tremendous industrial applications and potential in the past decade. .Thin film applications requiring electron beam evaporation are continually increasing. Applications are found in the medical, metallurgical, telecommunication, microelectronic, optical coating nanotechnology, and semiconductor industries [18].

3.8 Optical Filter:

In the broadest sense of the term, an optical filter is any device or material which is deliberately used to change the intensity distribution or the state of polarization of the electromagnetic radiation incident upon it. The change in the spectral intensity distribution may or not depend on the wave length. The filter may act in transmission, in reflection, or both. Filter can be based on many physical phenomena's, including absorption, reflection, interference, diffraction, scattering, and polarization.

3.8.1 General theory of filters:

There are many different ways of describing the performance of optical coating and filters. For example, transmission and reflection filter intended for visual application are adequately described by color name alone, or by reference to one the several existing color system. However, the most complete information on the filter is provided by spectral transmittance, reflectance, absorptance, and optical density curves [19].

At wave length (λ) the normal incidence spectral transmittance $T(\lambda)$ of a filter placed between two semi-infinite media is equal to the ratio of the light intensity of that wave length transmitted IT(λ) by the filter to that incidence Io(λ) upon it.

$$T(\lambda) = \frac{I_T(\lambda)}{I_o(\lambda)} \qquad (3.1)$$

At non-normal incidence, the component of the intensity perpendicular to the interface must be used in the preceding equation. The spectral reflectance R(λ) of the filter is defined in a similar way,

$$R(\lambda) = \frac{I_R(\lambda)}{I_o(\lambda)} \qquad (3.2)$$

The relation between the transmittance T(λ) and the density of filter, sometimes also called the absorbance, is given by

$$D(\lambda) = \log \frac{1}{T(\lambda)} \qquad (3.3)$$

3.9 Emission of light

Light is a form of energy. To create light, another form of energy must be supplied. There are two common ways for this to occur, incandescence and luminescence:

3.9.1 Luminescence properties:

Luminescence is defined as the phenomenon in which the electronic state of a substance is excited by some kind of external energy and the excitation energy is given off as light. The word light includes not only electromagnetic waves in the visible region of 400 and 700 nm, but also those in the neighboring region on both ends, i.e. the near-ultraviolet and the near-infrared regions. Luminescence is divided into fluorescence and phosphorescence according to the duration time of the after-glow. As mentioned, the after-glow that can be perceived by the human eye, namely that persists for longer than 0.1 s after cessation of excitation is usually called phosphorescence [30].

3. 9.2: Incandescence

Incandescence is light from heat energy. If something is heated to a high enough temperature it will begin to glow. When the tungsten filament of an ordinary incandescent light bulb is heated it glows brightly. The sun and stars glow by incandescence. Incandescent light is produced by lattice vibrations, called phonons, which emit part of their energy in the form of electromagnetic radiation [31].

Light intensity can be written as:

$$I = I_0 e^{\tau / t} \qquad (3.\ 3)$$

Where: I = Fluorescent light intensity (arbitrary units)
Io= Initial fluorescent light intensity
t = time after excitation
τ = prompt fluorescent decay time Prompt fluorescent decay time is the time it takes for the light intensity to decay to e-1(36.8%) after excitation [32].

Triboluminescence phenomena itself is a time-dependent process, where light intensity I is proportional to the rate of new surface creation. Surface energy increases while propagation of recent fractured surfaces accumulates releasing energy in the form of light. This can be shown by a derivation of this model. As shown in Figure 3.1, let the excitation phase be a population (N) of particles given enough mechanical energy to ascend energy levels. The number of excited particles (n) over time is proportional to the population (N) present given by equation (3.4). The derivation is as follows:

$$\frac{dn}{dt} \alpha - N \qquad (3.\,4)$$

$$\frac{dn}{dt} = KN \qquad (3.\,5)$$

$$\int \frac{dN}{N} = -\int Kdt \qquad (3.\,6)$$

$$N = N_0 \exp^{-kt} \qquad (3.\,7)$$

$$I = I_0\, e^{-kt} \qquad (3.\,8)$$

Finally, light intensity is presented as the accumulation of photons/excited population released as shown in equation (3.7) where I and Io are substituted in as the final and original intensity of the population equation (3.8) [33].

Indeed light intensity also can be time dependent.

Assuming the rise and fall of light intensity, depends on creation and cessation of crack propagation [34].

This is represented in equation (3.8).

$$I \; \alpha \, t^2 e^{-kt} \qquad (3.\,9)$$

Likewise, in a wave form light intensity can be addressed as being proportional to the amplitude squared [49].

A wave form can be observed by measuring its wavelength. See Figure1.1 of Electromagnetic spectrum and wavelength of blue, green and red light [36,37]. .

Measuring the spectrum of light emission in contrast to a specimen's wavelength expresses in detail how the phenomenon was excited [38,39].

3. 9.3 Luminescence:

Luminescence takes place at normal and low temperatures. Light emission is produced by the relaxation of electrons from excited to ground states which produces photons with energies equal to the energy difference between the two transition states. The movement of electrons through the energy levels produces the charge required for illumination as shown in the schematic Figure 3.2

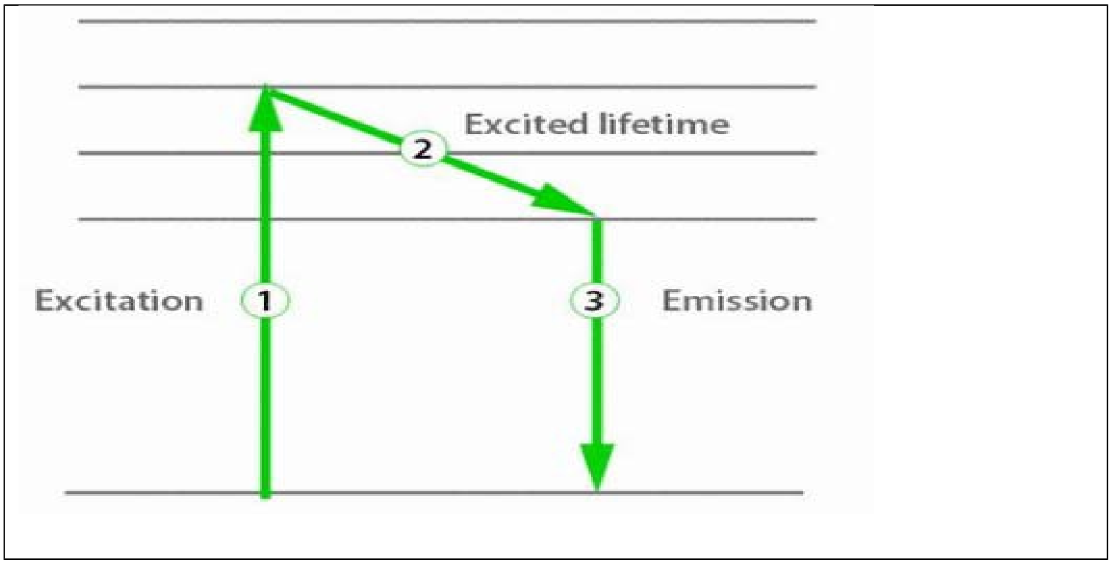

Figure 3.2 Excitation to emission [33].

Emission of light happens when particles lose energy by descending through lower energy levels. Described by Figure 2, electrons are excited (1) to exceed higher energy levels and emit light when falling through the energy levels. Types of Luminescence can be distinguished by examining the excitation source as described in Table 1 below.

Table 3.2 Luminescence types and excitation source

Luminescent Type	Excitation source
Cathodoluminescence	Electrons
Photoluminescence (UV)	Photons
Chemiluminescence's	Chemical reaction energy
Electroluminescence	Electric field
Tribo luminescence	Mechanical energy
Mechano luminescence	Mechanical energy

a. Photoluminescence:

This is luminescence by which electromagnetic radiation, i.e. photons, are used to excite the material, usually done by ultraviolet light.

b. Cathodoluminescence:

This is the process by which a beam of electrons excites the material to luminescence [40].

c. Thermo luminescence:

Thermoluminescence is phosphorescence triggered by temperatures above a certain point. This should not be confused with incandescence, which occurs at higher temperatures; in thermoluminescence, heat is not the primary source of the energy, only the trigger for the release of energy that originally came from another source. It may be that all phosphorescent materials have a minimum temperature; but many have a minimum triggering temperature below normal temperatures and are not normally thought of as thermo luminescent materials [33].

d. Electroluminescence:

This process occurs if a high electric field is applied across the luminescent material. Electron-hole pairs get excited due to the applied field and as they recombine, they emit photons [28, 31, and 41].

Luminescent materials are either electrically semi conducting (band gaps < 3 eV) or insulating (band gaps > 3 eV). The differences in band gap give rise to mechanisms of luminescence; band gap and characteristic luminescence.

3.9.4 Band gap luminescence:

Band gap luminescence is light emission from semiconductors due to different crystal structures. A crystal consists of a periodic arrangement of atoms, which is called a crystal lattice. There are many different kinds of crystal lattices and are classified according to their symmetries. In an isolated state, each atom has electrons that exist in discrete electronic energy levels and the states of these bound electrons are characterized by atomic wave functions. Their discrete energy levels, however, will have finite spectral width in the condensed state because of the overlaps between Electronic wave functions belonging to different atoms. This is because electrons can become itinerant between atoms, until finally they fall into delocalized electronic states called electronic energy bands. The lower energy state, the valence band, gets occupied by electrons originating from bound electrons of atoms. The energy bands having higher energies are not occupied by electrons at 0 K and are called conduction bands. Usually, in materials having crystal symmetries such as zinc-blende structures, there is no electronic state between the top of the valence band (the highest state of occupied bands) and the bottom of the conduction band (the lowest state of unoccupied bands); this region is called the band gap. Unoccupied states are called conduction bands, due to the fact that an electron in a conduction band is almost freely mobile if it is excited from a valence band.

Electrons in valence bands cannot be mobile because of a fundamental property of electrons, i.e. only two electrons (spin up and down) can occupy an electronic state. It is therefore necessary for electrons in the valence band to have empty states in order for them to move freely when an electric field is applied. After an electron is excited to the conduction band, a hole that remains in the valence band behaves as if it were a mobile particle with a positive charge. This particle is called a hole[37].

Excitation occurs due to energy transfer from the incident, high energy, particles to electrons in the valence band. If the energy transferred is high enough the electrons get excited to the higher energy levels. Relaxation (dotted lines) is the release of the extra energy as a photon while it is de-excited back to the lower energy levels, thus luminescence occurs.

A material having the above mentioned energy bands is called a semiconductor and is most commonly used for conduction purposes, other than for luminescence in phosphors. Semiconductors fall on the conduction spectrum between an insulator and a full scale conductor. Empty bands, which contain no electrons, are not expected to contribute to the electrical conductivity of a material. Partially filled bands contain electrons as well as available energy levels at slightly higher energies. These unoccupied energy levels enable carriers to gain energy when moving in an applied electric field. Electrons in a partially filled band therefore contribute to the electrical conductivity of the material.

One of the main reasons that semiconductors are useful in electronics is that their electronic properties can be greatly altered in a controllable way by adding small amounts of impurities. These impurities are called dopants.

The concentration of carriers in an intrinsic semiconductor is strongly dependent on the temperature. At low, the valence band is completely full, making the material an insulator. Increasing the temperature leads to an increase in the number of carriers and a corresponding increase in conductivity. A semiconductor that has been doped with impurities to modify the number and type of free charge carriers present is called an extrinsic semiconductor [27, 28].

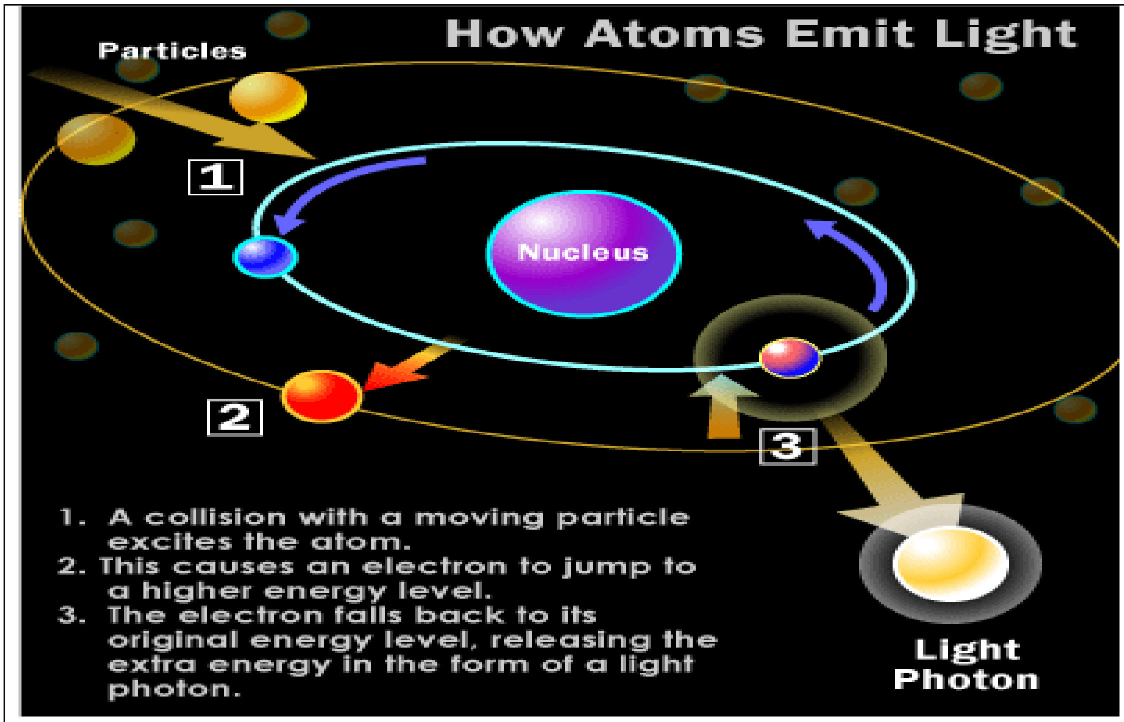

Figure 3.3 Schematic diagram of how atoms emit light [30].

3.9.5 Properties of semiconductors:

Semiconductors are a group of materials having electrical conductivities intermediate between metals and insulators.

The most important property of these materials is that their conductivity can be varied over orders of magnitudes by changes in temperature, optical excitation, and impurity content. This variability of electrical properties makes the semiconductor materials natural choices for electronic device investigations

The term semiconductor implies that, at room temperature, the resistivity of the material lies somewhere between that of a good conductor (e.g. copper, 1o-8 Ω m) and that of an insulator (e.g. glass1o13 Ω m). For example, the resistivity of the semiconductors germanium when highly purified is 0.5 Ω at room temperature.

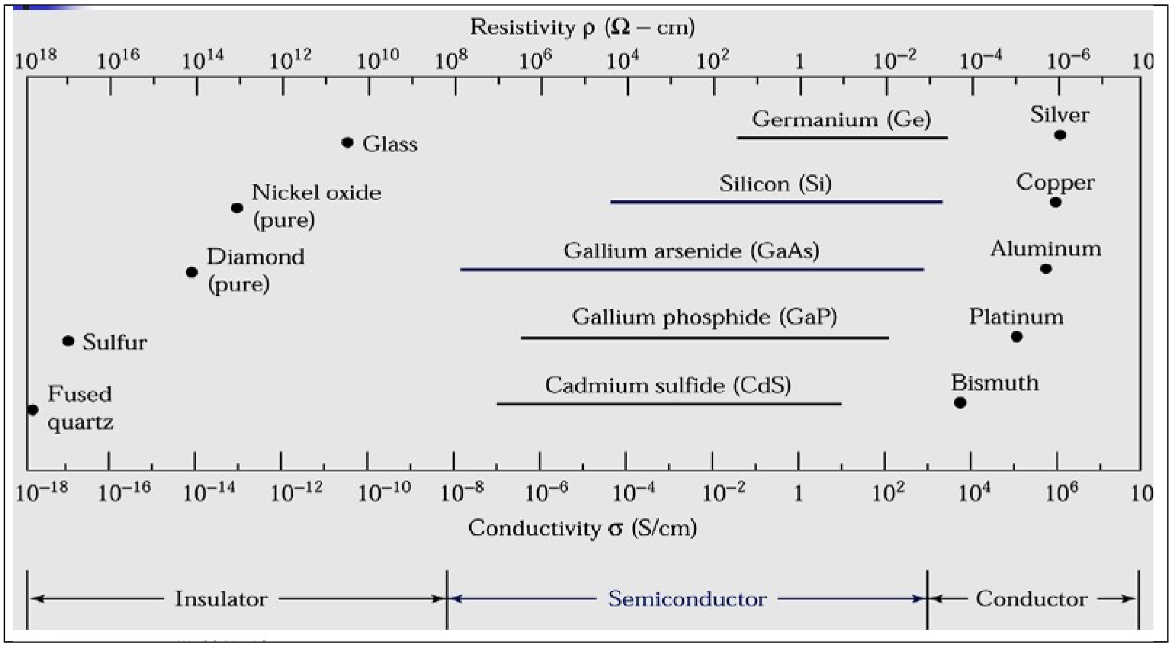

Figure 3.4 Schematic diagrams of Insulators, semiconductors and conductors.

A semiconductor however is more closely related to an insulator than to a metal, for all semiconductors become insulators if the temperature is lowered sufficiently, and if kept in the dark. It is only the presence of a stimulus such heat or light that the material is able to conduct electricity. Thus unlike most good conductors, the resistivity of a semiconductor actually decreases as the temperature rises [28].

This behavior is related to the way in which the outermost electrons of an atom are bound to it. These electrons are called the valence electrons, and they take part in binding the atoms one to another. In an insulator these valence electrons are very tightly held in place, while in a metal they are free to move from atom to atom to conduct an electric current. The valence electrons in a semiconductor are held rather tightly, but not so tightly as in an insulator. We measure the strength with which they are bound by the energy required to release a single electron. These called energy gap, and in diamond, which is an insulator, it is about 6eV as against 1.1eV in silicon and 0.7eV in germanium, both of which are semiconductors. In a metal, there is of course no energy gap. Now, if a semiconductor is held at a very low temperature, the electrons are all held tightly in place. However, warming the solid causes the atoms of which it is made to acquire heat energy, and they begin to vibrate rapidly back and forth in a random fashion.

The energy of this vibration may be partly transferred to some of the electrons, giving them enough energy to break free from the atoms to which they were bound. At low temperatures, it is only very rarely that electrons are free at any one time. In silicon, for instance, only one in 1010 of the valence electrons are free at room temperature, while in diamond, the energy required to free each electron is large enough that the number free at any time is so small that diamond is an insulator [45].

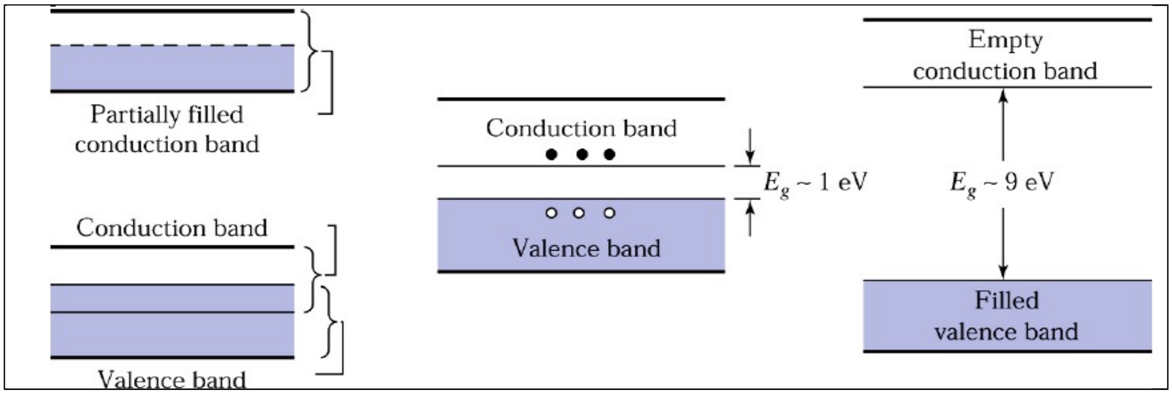

Figure 3.5 schematic energy band a conductor with possibilities partially filled conduction band and shown a semiconductor and insulator.

Since the process of freeing electrons is governed by both the temperature and the energy gap, the number of free electrons at any temperature can be expressed mathematically in terms of these quantities. At ordinary temperatures, theory leads to the approximate equation:

$$\frac{n}{no} = e\,\frac{-E}{2kt} \qquad (3.10)$$

Where n/no is the fraction of electrons freed at an absolute temperature T, in a material with energy gap Eg, and k is Boltzmann’s constant. This exponential relationship between n and T means that the number of free electrons, and hence also the conductivity, rises very rapidly indeed with temperature. There is one most peculiar characteristic about the positions vacated by the freed electrons. These vacant positions are free to move about in the solid and in doing so they behave as if they carried a positive charge of the same magnitude as the negative charge on the electron. The important fact is that, for every electron capable of carrying a current, there is in addition appositively charged particle which can do the same-and this increases the current which can flow, these new particles are called positive holes, and they play a most important role in transistors, among other devices. It is important to note that the equality in the numbers of free electrons and positive holes is not found in all semiconductors, as might be expected; it is not only heat energy which can cause electrons and holes to be freed for conduction. Light or X-ray may also be used to increase the conductivity of a piece of silicon or germanium, and it's even possible by applying enough across a crystal to give enough energy to the few electrons which are already free to enable them to free others by collision. All these effects have important applications.

The pure semiconductors have some unique properties, the most important attributes is that conductivity can be modified at tiny quantities of impurities. These must be elements with either more or fewer valence electrons than the host material, and in these way two difference kinds of impurity (or extrinsic) semiconductor can be made.

If each atom of the added element has one more valence electron, then this electron will not be to form bonds with the surrounding atoms and so the extra electron needs only a very small energy to release it, then nearly all the additional electrons are able to carry current. This greatly increases the conductivity, but in this case there is no positive hole left behind which can carry current. If impurity is added, then there are many more electrons than holes. Since most of the current carries are negatively charged (electrons), the material is termed an n-type semiconductor.

On the other hand, the added element has one fewer valence electron per atom, the situation is reserved. There are many positive holes than electrons, and the material is called a p-type semiconductor. There are two kinds of impurity, semiconductor are the basic materials for the construction of transistors and other semiconductor devices. Thus in an n-type semiconductor the majority carriers are electrons and the minority carriers are holes.

3.9.6 The energy band structure:

According to the quantum theory, the energy of an electron in a crystal must fall within well-defined bands. The energies of the valence orbital's, which form bonds between atoms, represent one such band of states and is called the valence band. The next higher band is the conduction band which is separate from the valence band of the energy gap, or band gap.

The band gap is an important property of the material that determines the interaction of light with the material. Photons with energy equal or larger than the band gap are needed to create electron hole pairs.

3.9.7 Intrinsic and extrinsic semiconductors:

A perfect semiconductor crystal with no impurities or lattice defects is called an intrinsic semiconductor. Such a material contains just the right number of electrons to fill the valence band and the conduction band is empty. Intentional introduction of impurities or defects (doping) into an intrinsic semiconductor causes the sample to become either rich in electrons (n-type) or deficient in electrons (p-type). Increasing a given semiconductor's negative carriers (electrons) by doping with an appropriate element (dopant) from the adjacent right column of the periodic table will make it n-type.

The missing electrons in the valence band are called holes and behave as positively charged particles which are mobile and carry current.

A dopant which consumes some of the material’s valence electrons and thus increases the positive carries (holes), makes the semiconductor p-type. Electrons in the n-type are termed majority carriers and likewise for the holes in the p-type.

Doping an intrinsic semiconductor creates additional energy levels within the band gap. Band diagrams and electron and hole distribution for intrinsic, n-type and p-type semiconductors [46].