Research Paper

Basics of Optical Absorption Characterization of Semiconductors – Photonic Materials

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Abstract
This review describes interaction between matter and photon. The study of optical properties of these semiconductors gives a good understanding of their electronic properties and band structures. The optical band gaps of semiconducting materials play an important role in deciding the photoelectric properties of the optoelectronic devices. Thus, it is always interesting to investigate the nature of transport of carriers in a semiconducting material. Working of UV VIS NIR Spectrophotometer with diagram is described. Basic formulae regarding direct and indirect transitions are mentioned and explained with proper way. For determination of band gap for semiconducting materials, absorption of incident photon by semiconducting material is an important technique.
Key words: Optical absorption, Spectrophotometer and Direct & indirect band gap semiconductors.

I. INTRODUCTION

Garmenium, Tin and Iron and mixed compound of these three possess interesting optical and photo-absorption properties [1-3]. These semiconducting materials belong to chalcogen group and are found to possess layered structure. Several studies, mainly on the optical properties, have been carried out in the past few years, [4-10]. Bassani and Parravicini [11] treated some of the layered compounds as two-dimensional lattice Fivaz and Mooser [12-14] discussed how pronounced anisotropic properties might affect the motion of free carriers in layered semiconductors. It was shown that in these structures, the free carriers might be localized within individual layers, behaving as if moving through a stack of individual layers, "independent layer approximations".

Photonic materials are gaining more and more attention of researchers in the last few decades. These materials in various forms e.g. bulk crystalline solids, nano crystals, multilayers, quantum dots etc. are increasingly impacting next generation electronics industry in fields like communication, data manipulation and storage, aviation, defence, food processing and packaging, advertising, entertainment etc.

To understand the nature of semiconductors one must consider what happens when similar atoms are brought together to form a solid such as a crystal. As two similar atoms approach each other the wave functions of their electrons begin to overlap. The energy distribution of the states depends strongly on the interatomic distance. It is the extent of the energy gap and the relative availability of electrons that determine whether a solid is a metal, a semiconductor, or an insulator. In a semiconductor the energy gap usually extends over less than about 3 eV and the density of electrons in the upper band is usually less than 10^{20} cm^{-3}.

Since the interatomic distance in a crystal is not isotropic but rather varies with the crystallographic direction, one would expect this directional variation to affect the banding of states. Thus, although the energy gap, which characterizes a semiconductor, has the same minimum value in each unit cell, its topography within each unit cell can be extremely complex. In compound semiconductors a deviation from stoichiometry generates donors or acceptors depending on whether it is the cation or anion, which is excess. However, it has been shown that it is not the excess ion but rather the vacancy, which determines whether the material is n-type or p-type in nature [15].

METHODS FOR OPTICAL ABSORPTION OF SEMICONDUTORS

The optical band gap of a semiconducting material play an important role in determining the photo conversion efficiency of a solar cell fabricated with it and the optical band gap (direct as well as indirect) can be determined by the following methods :

1. Optical absorption
2. Photo electrochemical methods
(a) Quantum yield η versus ħν plot
(b) Action spectrum
(c) Capacitance measurements
3. Intrinsic conduction measurement at high temperature
4. Photoemission and
5. Band structure calculations.

The optical absorption technique is an important technique for finding out the nature of transitions of carriers and band gap of a material by investigating measurement of the absorption edge of the material. In this technique, photons of selected wavelengths are directed at normal incidence on the sample and their relative transmission is observed. Since the photons with energies less than the band gap energy are absorbed while photons with energies greater than band gap are transmitted. The technique provides an accurate measurement of the energy band gap. The absorption of light from the ultraviolet-visible region of the spectrum sets valence electrons into oscillation and produces an excitation of the molecule from the ground electronic state to the excited electronic state. On the other hand, the absorption of energy from the far infrared region of the spectrum produces molecular rotations and absorption of near infrared radiation produces the rotations plus atomic vibrations. Thus, the light absorption produces changes in the internal energy of molecules from which much can be learnt about molecular structure and intermolecular forces.

UV-VIS-NIR SPECTROPHOTOMETER

The UV-VIS-NIR Spectrophotometer is shown in Figure 3. Which is used for the analysis of various semiconductors to find out the absorbance value and wavelength maxima in UV-VIS-NIR region. This is also used in the research and development of new compounds, chemicals, dyes, optical properties of thin films, thickness and various types of filters etc. The accessory "Integrating Sphere" with Lambda-19 spectrometer helps to analyse samples in reflectance mode. This accessory helps to analyse samples like cloth, lather, films, dye-products and colour-products etc. The instrument is also useful to study kinetic behaviour of chemical reaction with respect to time. It can also be used for various biological samples and reaction studies. The instrument consists of double-beam double monochromator with ratio recording of UV-VIS spectrometer with microcomputer electronics, controlled by personal computer. For obtaining the absorption spectra using UV-VIS-NIR spectrophotometer from single crystal specimens, thin flakes of as grown crystals are used. These flakes are pasted on a thick black paper with a cut exposing the crystal flake to the incident light. The reference used is a replica of the black paper, having the cut at exactly the same position as the crystal flake. This arrangement is necessary because the crystal size is smaller than that of the sample compartment. Blank glass slides can also be used as replica. For reflectance measurement standard aluminum coated mirror can be used as reference.

Figure 1: UV-VIS-NIR Spectrophotometer.

❖ **Specifications**

Facility :Double Beam, Double Monochromator, Ratio Recording
Lamp :Deuterium(UV),Tungsten-Halogen(VIS/NIR)
Detectors : Photomultiplier tube for UV/V, Lead-
Sulphide cell
 (PbS) for NIR
Wavelength Range : 185-3200 *nm*
Scan speed : 0.3 to 1200 *nm/min*
Wavelength Accuracy : ±0.15 *nm* for UV/VIS & ±0.6 *nm* for NIR
Base line flatness : ± 0.001 *Å*, 4 *nm* slit
Ordinate Mode :Scan,Time Drive,Wavelength Programming, Concentration
Photometric Accuracy : ± 0.003 *Å* or ± 0.08 %*T*
Software used :PECOL Software for quantitative description of color

Figure 1 shows the path followed by a single ray within the radiation beam. The beam is reflected from the condensing mirror (A) to the slit entrance mirror (B), which directs the beam to the chopper (C). The chopped beam passes through the adjustable entrance slit (D) and into the monochromator. The beam is reflected from the collimating mirror (E) in parallel rays through a reflecting quartz prism (F), which disperses the beam into its spectrum of successive wavelengths. The back surface of the prism is aluminized so that the beam is reflected back through the prism and further dispersed as it emerges. Rotation of the prism relative to collimating mirror changes the angle of incidence and enables selection of a particular group of wavelengths that comprise a spectral band. This band of radiation is directed back to the collimating mirror, which focuses the entrance slit image on the exit slit (G). Upon passing from the monochromator, the radiant energy is directed by lens (H) into the double beam optical system in the sample compartment.

The Beckman model DK-A instrument is double beam ratio recording spectrophotometer, i.e. radiant energies transmitted by the reference and sample beams (J and M) are compared, and the ratio of the sample energy to the reference energy is recorded as a percent transmission. The double beam optical system consists of two synchronized semi-circular rotating mirrors (I and N), and two stationary mirrors (L and K) in the sample compartment. The rotating mirrors consequently deflect and pass the radiant energy so that it is directed alternatively into sample and reference cells fifteen (or 12.5) times per second. Energy transmitted by the sample and reference cells is focused by the detector selector mirror (O) onto to the detector.
Detection of transmitted radiant energy requires two detectors to cover the entire wavelength range of the instrument. One - the lead sulphide cell (P) - responds in the region between 400 to 3500 nm. For measurements in the wavelength range extending below 700 nm, a photomultiplier tube (Q) is used.
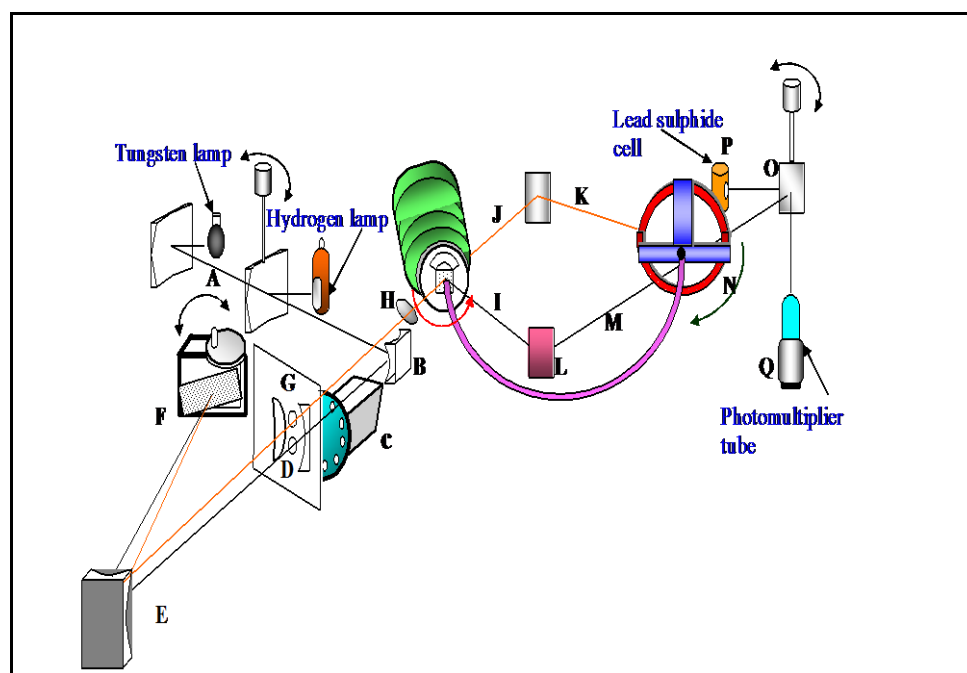

Figure 2: Optical diagram of Spectrophotometer.

OPTICAL ABSORPTION

The most direct and the simplest method for probing the band structure of semiconductors are to measure the absorption spectrum. In the absorption process, a photon of a known energy excites an electron from a lower to a higher energy state. Thus by inserting a slab of semiconductor at the output of a monochromator and studying the changes in the transmitted radiation, one can discover all the possible transitions an electron can make and learn much about the distribution of states. Absorption is expressed in terms of coefficient $\alpha(h\upsilon)$, which is defined as the relative rate of decrease in light intensity $L(h\upsilon)$ along its propagation path:

$$\alpha = \frac{1}{L(h\upsilon)}\frac{d[L(h\upsilon)]}{dx} \tag{1}$$

The optical absorption is known to arise through the interaction of the excited electrons with the lattice perturbed by vibrations or imperfections. In fact, the absorption phenomenon can be considered quantum mechanically [8] as a two – step process in which the electron absorbs a photon and is excited to an intermediate state, where it interacts with the lattice vibrations or impurities and reaches a final state, the net result being the absorption of a photon.

The fundamental absorption refers to band-to-band or to exactions transition, *i.e.*, to the excitation of an electron from the valence band to the conduction band. The fundamental absorption, which manifests itself by a rapid rise in absorption, can be used to determine the energy gap of the semiconductor. However, because the transition are subject to certain selection rules, the estimation of the energy gap from the "absorption edge" is not a straight forward process-even if competing absorption process can be accounted for.

Because the momentum of a photon, h/λ, (λ is the wavelength of light), is very small compared to the crystal momentum h/a (a is the lattice constant), the photon-absorption process should conserve the momentum of the electron. The absorption coefficient $\alpha(h\upsilon)$ for a given photon energy $h\upsilon$ is proportional to the probability P_{if} for the transition from the initial state, n_i, and also to the density of available (empty) final state, n_f, and this process must be assumed for all possible transitions between states separated by an energy difference equal to $h\upsilon$:

$$\alpha(h\upsilon) = A\sum p_{if}n_in_f \tag{2}$$

Here, for simplicity we shall assume that all the lower states are filled and that all the upper states are empty, a condition which is true for undoped semiconductor at 0 *K*.

DIRECT AND INDIRECT TRANSITIONS

The absorption process-taking place in a semiconductor can be described as an example of electronic transition processes, which are fully quantum mechanical in nature. These electronic transition processes give rise to interband absorption in solids, which are of two types, known as direct and indirect (interband) transitions.

DIRECT ALLOWED TRANSITIONS

Let us consider absorption transition between two direct valleys where all the momentum-conserving transition are allowed as shown in Figure 1. Every initial state at E_i is associated with a final state at E_f such that
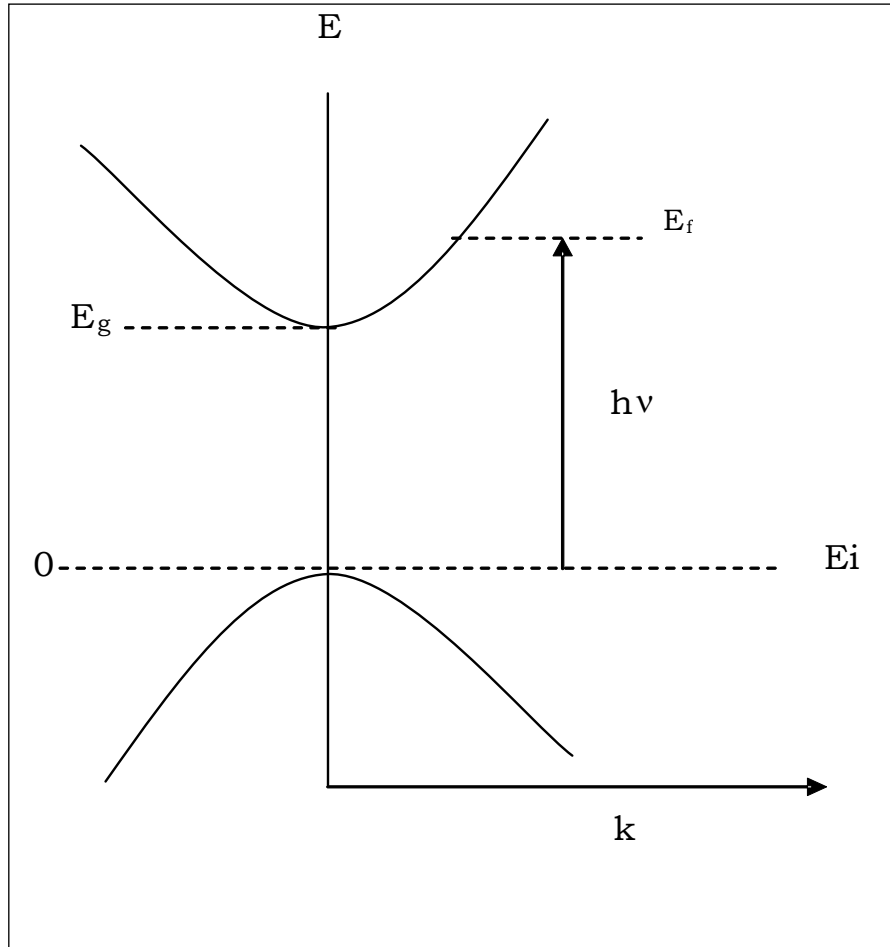
$$E_f = h\upsilon - |E_i| \tag{3}$$

Figure 3: Schematic diagram showing direct transitions.

But in parabolic bands,

$$E_f - E_g = \frac{h^2 k^2}{2m_e^*} \qquad (4)$$

and

$$E_i = \frac{h^2 k^2}{2m_h^*} \qquad (5)$$

therefore

$$h\upsilon - E_g = \frac{h^2 k^2}{2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) \qquad (6)$$

The density of directly associated states is

$$N(h\upsilon)d(h\upsilon) = \frac{8\pi k^2 dk}{(2\pi)^3} \qquad (7)$$

$$N(h\upsilon)d(h\upsilon) = \frac{(2m_r)^{3/2}}{2\pi^2\hbar^3}(h\upsilon - E_g)^{1/2}d(h\upsilon) \qquad (8)$$

where m_r is the reduced mass given by $\dfrac{1}{m_r} = \dfrac{1}{m_e^*} + \dfrac{1}{m_h^*}$. Hence the absorption coefficient is

$$\alpha(h\upsilon) = A^*(h\upsilon - E_g)^{1/2} \qquad (9)$$

where A^* given by Bardeen [16]

$$A^* \approx \frac{q^2 \left(2 \dfrac{m_h^* m_e^*}{m_h^* + m_e^*} \right)^{3/2}}{nch^2 m_e^*} \tag{10}$$

for an index of refraction $n=4$ and assuming the hole and electron effective masses equal the free electron mass($m_h^* = m_e^*$ =m), one gets,

$$\alpha(h\upsilon) \approx 2 \times 10^4 (h\upsilon - E_g)^{1/2} \text{ cm}^{-1} \tag{11}$$

DIRECT FORBIDDEN TRANSITIONS

In some materials, quantum rules forbid direct transitions at k = 0 but allow them at $k \neq 0$, with the transition probability increasing with k^2. In the model of Figure 1 this means that the transition probability increases proportionally to (hv-E_g). Since the density of states linked in direct transitions is proportional to (hv-E_g)$^{1/2}$, the absorption coefficient has the following spectral dependence

$$\alpha\left(h\nu\right) = A^{'} \left(h\nu - E_g\right)^{\frac{3}{2}} \tag{12}$$

Where A' is given by [17]

$$A^{'} \approx \frac{4}{3} \frac{q^2 \left(\dfrac{m_h^* m_e^*}{m_h^* + m_e^*} \right)^{\frac{5}{2}}}{nch^2 m_e^* m_h^* h\upsilon} \tag{13}$$

Again, for n = 4 and $m_h^* = m_e^*$ =m

$$\alpha(h\nu) = 1.3 \times 10^4 \frac{(h\nu - E_g)^{\frac{1}{2}}}{h\nu} cm^{-1} \tag{14}$$

In general, however, at high temperature, phonons are present and can participate in the absorption process. The optical transition is accordingly said to be non-vertical or indirect. Such indirect transitions are great importance in semiconductors and provide a means of determining the energy band gap separating the top of the valence band and the bottom of the conduction band when these band extrema occur at different values of the *k* vector.

For determination of band gap for semiconducting materials, absorption of incident photon by semiconducting material is an important technique. In this technique, photons of selected wavelengths are bombarded on the sample and their relative transmission is observed. Since the photons with energies less than the band gap are absorbed while photons with energies greater than band gap are transmitted, the technique provides an accurate measurement of the energy band gap. The ratio of transmitted to incident radiation intensities is expected to depend on photon wavelength and the thickness of the sample.

When a photon beam of intensity I_o (photon/cm^{2}sec) transmits through a slab of a medium of thickness *x*, the beam of photons attenuates in accordance with the exponential law

$$I = I_0 e^{(-\alpha x)} \tag{15}$$

where, 'α' is called as the absorption coefficient and has units of cm^{-1}. This coefficient α can be obtained simply by measuring I_0/I of the intensities impinging and emerging from the samples respectively.

II. CONCLUSION

For device fabrication, optical band gaps of semiconducting materials play an important role in deciding the photoelectric properties of the optoelectronic devices. In order to tailor the optical properties it is always interesting to investigate the nature of transport of carriers in a semiconducting material. Mechanism of UV VIS NIR Spectrophotometer with diagram is described. Basic formulae regarding direct and indirect transitions are explained with references.

ACKNOWLEDGEMENT

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