CHAPTER 6

OPTICAL PROPERTIES

Optical properties of a solid emanate from its interactions with electromagnetic waves. The optical study of a solid concerns not only with the physical phenomena such as refraction, reflection, transmission, absorption, polarisation, interference but also the interactions of photon energy with matter and the consequent changes in the electronic states. From reflection, transmission and absorption measurements it is possible to evaluate the optical constants such as refractive index (n), absorption index or extinction coefficient (k) and absorption coefficient (α) and in turn also the complex dielectric constant (ε^*) of a solid. The last parameter also provides information about the electrical nature of the individual species constituting the solid. The study of refractive index also provides an understanding of the chemical bonding[1,2], photoemission properties and electronic structure of the material[7]. Absorption studies, on the other hand, provide a simple means for the evaluation of optical energy band gap and optical transitions, which may be direct or indirect, allowed or forbidden.

The assemblage of similar atoms into an array leads to the formation of bands of allowed states separated by an energy gap. 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 to less than about three electron-volt and the density of electrons in the upper band (or of holes in the lower band) is usually less than $10^{20}cm^{-3}$. By contrast, in a metal the upper band is populated with electrons far above the energy gap and the electron concentration is of the order of 10^{23} cm^{-3}. Insulators on the other hand have a large energy gap -usually greater than 3 eV and have a negligible electron concentration in the upper band (and practically no holes in the lower band). Since the interatomic distance in a crystal is not isotropic, one would expect the direction variation to effect 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.

Principally there are several methods to determine the optical constants, such as Abbe's method, spectroscopic method, polarimetric method and critical angle method[3-6]. The spectroscopic method is one of the most widely used technique for optical measurements. In order to determine the two optical constants, n and k, measurements of two independent quantities have to be made. The measurement may be made on light transmitted through a specimen or on light reflected from the surface of the material. Only the latter measurements are practical in the case of highly absorbing materials, if the interest is in the properties of the bulk materials rather than thin films. The most direct and perhaps the simplest method for probing the band structure of semiconductors is to measure the absorption spectrum. They may be made easily and conveniently with good accuracy and results are easy to interpret.

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. There are different possible transitions:

(i) band-to-band,
(ii) excitonic,
(iii) between subbands,
(iv) between impurities and bands,
(v) transition by free carriers within a band and also
(vi) the resonances due to vibrational states of the lattice and of the impurities.

These lead to the appearance of bands or absorption peaks in the absorption spectra. Hence the spectral positions of bands determine the types of transitions occurring during the process. Absorption of light by an insulator takes place broadly by two processes namely

(i) by raising the electrons from the valence band to the conduction band or

(ii) by exciting the lattice vibrations of the material or both by photon energy.

The latter provides information regarding bond lengths in the lattice, the effective charge on the lattice atoms and the characteristic lattice vibration frequency. From the process (i), it is however possible to find the electronic band structure. Thus the optical method provides a very simple way of finding the band gap as compared to the electric method using the thermal excitation which is less reliable because of the fact that the effective mass m^* of electrons and holes also influence most of the electrical parameters. The measurement of m^* is not very reliable since it is coupled with many other parameters. On the other hand the optical method is less ambiguous.

FUNDAMENTAL ABSORPTION

The fundamental absorption refers to band-to-band transition, ie., 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 transitions 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 processes can be accounted for.

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

$\alpha(h\nu) = A\sum P_{if}n_i n_f$

In what follows, for simplicity we shall assume that all the lower states are filled and all the upper states are empty, a condition which is true for undoped semiconductors at 0 K.

Now fundamental absorption can be through

1) Allowed direct transitions
2) Forbidden direct transitions
3) Indirect transitions between indirect valleys
4) Indirect transitions between direct valleys
5) Transitions between band tails
6) Absorption in the presence of a strong electric field

In crystalline solids, electron excitations can be discussed on the basis of electronic energy band structure. The excitations from one energy band to another give rise to strong absorption which usually excludes transmission measurements. Such excitations require a minimum photon energy and take place only at sufficiently short wavelengths. For semiconductors, the threshold is usually in the near infrared, depending on the energy gap between the conduction and the valence bands. Insulators with larger energy gaps have thresholds in the visible or ultraviolet region. In various metals, optical interband transitions may begin somewhere in the region from the near infrared to the ultraviolet. At wavelengths longer than the threshold of interband transitions, there is still absorption produced by conduction due to free carriers and the excitation of electrons of impurity atoms. Insulators usually give good transmission. The absorption in semiconductors varies with the carrier concentration, but it is usually possible to measure transmitted radiation with specimens of practical thickness. In metals, however, the large concentration of conduction electrons produces such high absorption as to exclude transmission measurements for all wavelengths, except when very thin films are used. The absorbance is defined as $A = \log (I / I_o)$ where, I_o = Intensity of incident photons and I = Intensity of transmitted photons. The absorption coefficient, α, is defined as the relative rate of decrease in the light intensity $I (h\nu)$ along its propagation path.

$$\alpha = \frac{1}{I(h\nu)} \times \frac{d[I(h\nu)]}{dx}$$

The solution of the equation is

$$I = I_o \exp (-\alpha x)$$

Hence the intensity of light transmitted through the sample of thickness 't' is $I = I_o \exp (-\alpha t)$ where $\alpha = \ln (I/I_o) / t$ or $\alpha = 2.303 (A / t)$ where A is the absorbance.

The absorption coefficient, α[7-11], has been correlated with the band gap E_g through:

$$\alpha = \frac{B [h\nu - E_g]^m}{h\nu}$$

where B is constant, E_g is the energy gap.

The optical energy gap is the minimum energy required to excite an electron from the valence band to the conduction band by an allowed optical transition. The value of the optical energy gap is usually determined by measuring the optical absorption coefficient as a function of the photon energy. The exponent 'm' determines whether the transition is direct or indirect, and allowed or forbidden.

The basic theory of direct and indirect transitions in semiconductors is formulated by Barden[8]. The direct transitions are generally supposed to be taking place from valence band to conduction band under the selection rule:

$$K - K^* + (2\pi i/\lambda) = 0$$

where K and K^* are wave vectors of electron before and after transition, respectively. λ is the wavelength of the photon and i is the unit vector along the direction in which the photon travelled before it is absorbed. This can be simplified to $K = K^*$, since $2\pi/\lambda$ is small as compared to either K or K^*.

This shows that only vertical transitions are allowed; other transitions, if taking place will be of very small probability. Thus the steep edge in absorption spectrum is attributed to the highly possible direct transitions.

In the indirect transition involving the participation of phonons, the minimum of the conduction band energy surface does not coincide with the maximum of the valence band surface. A phonon is either emitted or absorbed depending on whether the energy of photon is either more or less than the indirect band gap energy. The relation applicable is of general form

$$\alpha h\upsilon = B\,(h\upsilon - E_g)^m$$

where B is a parameter that depends on the transition probability. Values of 'm' for allowed direct and indirect and forbidden direct transition are respectively ½, 2, and 3/2.

Interband Transitions

Photons absorbed by a semiconductor can induce three types of electron transitions involving the bands of the solid:

(i) Direct Transition (Electron transitions from a filled valence band to the conduction band)

(ii) Indirect Transition (Electron transition to or from an adsorbate or an equivalent surface state)

(iii) Forbidden Direct Transition (Electron transitions to or from energy levels in the forbidden energy gap region)

DIRECT AND INDIRECT TRANSITIONS

For a semiconductor in which the minimum of the conduction band and the maximum of the valence band occur at the same value of K, absorption begins at $E_g = h\upsilon$ and the electron is transferred vertically between the two bands without a change in momentum. Such a transition is called a Direct Transition.

The optical absorption coefficient for direct transition is given by,

$$a = B\,(h\upsilon - E_g)^{1/2}$$

By plotting $(ah\upsilon)^2$ vs $h\upsilon$ graph, one obtains a linear curve, which is extrapolated to the $h\upsilon$ axis giving the energy value of the direct transition band gap.

In semiconductors where the conduction band minimum and the valence band maximum occur at different K values, optical transition from the latter to the former require the participation of phonons in order to conserve momentum $(dE = h\upsilon \pm E_{ph})$, because of the change in electron wave vector, phonons are either emitted or absorbed. Here E_{ph} = phonon energy.

The optical absorption coefficient for an indirect transition is given by

$$a = B\,(h\upsilon - E_g)^2$$

By plotting the graph of $(ah\upsilon)^{1/2}$ vs $h\upsilon$ and extrapolating the curve to intercept the $h\upsilon$ axis, the energy value of indirect transition is obtained.

The lower straight line portion disappears at low temperatures. This portion corresponds to phonon absorption and no longer occurs when the population of phonon states of required energy becomes small with decreasing temperature.

The presence of excitons [usually manifested as a series of narrow absorption lines at low energy side of the intrinsic band gap absorption] appears for measurements at low temperatures only, since for most of the materials, the excitons are thermally dissociated at room temperature[12].

A wide range of studies on thin films has been made using the optical measurements by various workers. For example, F. F. Sizov[13] has studied optical properties and electronic structure of IV-VI superlattice based quantum wells and has made comparison with the corresponding properties of bulk semiconductors.

S. Bauer et al[14] have studied the optical properties of thin films with thickness less than the wavelength of the radiation and investigated the skin depth using energy balance for the incident, reflected, transmitted and absorbed energies.

GENERAL OPTICAL SPECTROMETRIC EQUIPMENT

Since the optical properties of a material vary with wavelength, measurements are usually made with monochromatic radiations. A suitable light source and a monochromator are used to obtain radiations of various wavelengths. For the visible region, incandescent lamps or various types of discharge lamps are used as the light source. Mercury arc lamps serve as high intensity sources for the ultraviolet region. For long wavelengths in the infrared, Nernst glowers and globars are commonly used. Practically the entire wavelength range of interest may be covered by prism monochromators. With recently developed cesium iodide prisms the infrared region, as far as 50 μ, can be reached[15]. Gratings have to be used for still longer wavelengths[16]. Usable intensity has been obtained for wavelengths up to 125 μ by using a relatively small grating in the optical system of a commercial monochromator[17]. In the visible and ultraviolet regions, spectrographs can be used when very high resolutions are required, as in the investigation of the sharp exciton absorption bands in insulating crystals. To reduce the noise and increase the sensitivity of detection, the radiation is usually interrupted at a certain frequency by a chopper and the detected ac signal is amplified by an amplifier tuned to the chopping frequency. In the visible and ultraviolet regions, higher sensitivities may be obtianed with photomultiplier tubes. For the infrared region, up to 7 μ, photoconductive cells of PbS, PbSe, and PbTe have been developed[18] into highly sensitive detectors. The sensitivity is increased by cooling, and a limiting power of 10^{-12} watts can be detected. Photomultipliers and photoconductive cells have the common drawback of selective detectors being the sensitivity variation with wavelength. In far infrared work where high sensitivity is needed, the Golay pneumatic detector[19] may be profitably used in place of the thermocouple. The limit of the detector is about 10^{-10} watts.

Recent advances in computerized IR spectroscopy, particularly Fourier transform infrared (FT-IR) spectroscopy, have made it possible to obtain infrared spectra of solid, liquid and gaseous samples. The description of the spectrometer used in the present work for obtaining optical band gap is given in Chapter 11.

SAMPLE PREPARATION

The way you prepare and place your sample is very important for achieving good results. Some commonly used techniques in optical measurements are transmittance, diffuse reflectance, specular reflectance, attenuated total reflectance, photo-acoustic spectroscopy, micro-sampling, FT-Raman etc. for which proper sample preparations are required.

Infrared spectra have traditionally been produced by transmission, that is, transmitting light through the sample, measuring the light intensity at the detector and comparing it with the intensity obtained with no sample in the beam, all as a function of the infrared wavelength. The various sampling techniques used to obtain infrared spectra of solids are given below.

1) Self supporting sample

   Certain solid samples are large enough to be mounted so as to fill the sample focus of the instrument without supporting windows, e.g., crystals, large fibers or plastic samples.

2) Solutions

   The sample is dissolved in a solvent and the solution is introduced in a sample cell with infrared transparent windows. Both the solvent and cell windows will add features to the measured spectrum. The cell thickness and concentration of the solution are chosen to yield a transmission spectrum that maximizes the absorption due to the solute species and minimizes the absorption due to the solvent. "Spectral subtraction" can be used to subtract some partially absorbing solvent bands from the spectrum. Carbon tetrachloride and carbon disulfide solvents are commonly used for dilution.

3) Films

   Liquids, emulsions, soluble polymers and similar samples can be smeared on a transparent plate, squeezed between two plates or cast onto a transparent substrate. The method is suitable when the sample is dissolved in a volatile solvent (which, after evaporation, will leave the solute as a deposit) or when the liquid is sufficiently viscous to remain in place after wiping onto the plate. As the sample thickness is difficult to control, this technique does not lend itself to quantitative analysis. The "transparent" window will reflect and/or absorb some radiation leading to a loss of available infrared intensity. Any weak band structure due to the "transparent" plate can be removed with the "Spectral subtraction" function. Plastic materials can be pressed into thin films by using heated platens if decomposition, oxidation and degradation are not problems. By carefully controlling the thickness of the films, this technique can be suitable for quantitative work.

4) Mulling in mineral oil

For samples that are insoluble in IR-transmitting solvents, it may be possible to prepare a mull consisting of a suspension of powdered sample in a mineral oil (Nujol or Fluorolube: Nujol has absorption bands at short wavelengths and Fluorolube at longer wavelengths). The powder must be ground to particles smaller than the minimum wavelength of light to be used. The mull can be held in a regular liquid sample cell. As with previously described methods, the weak bands of mineral oil can be removed using "Spectral Subtraction" to yield the sample-only spectrum.

5) Pellets (also called solid mulls)

Potassium bromide (KBr) pellets can often be prepared for solid samples that are difficult to melt or dissolve. The sample is dispersed in the KBr matrix and pressed into a transparent pellet. Approximately 0.4 to 1.0 mg of sample is usually ground in 200 to 400 mg of KBr or other infrared-transparent pressing powder. The sample and KBr must be ground so that the particle size is less than the wavelength of light, minimizing the band distortion due to scattering effects. The matrix material must be pure and dry. The pellet is then supported in a pellet holder at the focus of the instrument. Pellet samples should be referenced to pure KBr pellets of the same size.

The most promising method has seemed to be the KBr pellet, for although it is comparatively time consuming it combines wide applicability to sample types with the possibility of accurately knowing the total amount of sample in the beam. Somewhat reluctantly, however, it has been recognized by more and more spectroscopists that the technique tends to be non-reproducible.

The detailed optical band gap evaluation carried out in the present investigation is given in Chapter 11.

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