CHAPTER - 3

OPTICAL AND ELECRTICAL MEASURMENTS

The optical study of solid concerns not only with physical phenomena such as refraction, reflection, transmission, absorption, polarization, interference but also the interaction 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 constant 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 study of refractive index also provides an understanding of the chemical bonding [1,2]. Absorption studies, on the other hand, provide a simpler means for the evaluation of energy band gap and optical transitions, which may be direct or indirect, allowed or forbidden. The energy band is the most useful concept to understand the semiconductor phenomena. In a semi-conductor, the energy gap usually extends over to less than about three electron-volts and the density of electrons in the upper band is usually less than 10^{20} cm^{-3}.

Principally there are a few methods for optical studies, such as Abbe's method, spectroscopic method and critical angle method[3-6]. The most direct and perhaps the simplest method for probing the band structure of semiconductor is to measure the absorption spectrum. The measurments 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.

There are different possible transitions:

- → Between sub bands,
- → Band-to-band,
- → Between impurities and bands,
- → excitonic,
- → Transition by free carrier within a band and also,
- → The resonances due to vibration states of the lattice and of the impurities.

FUNDAMENTAL ABSORPTION

The fundamental absorption refers to band-to-band transition, due 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 estimate of the energy gap from the ' absorption edge' is not a straight forward process even if competing absorption processes can be accounted for. The momentum of a photon, h/λ, is very small compared to the crystal momementum h/a ("a" is the lattice constant, few angstroms), the photon-absorption process should conserve the momentum of the electron. The absorption coefficient for a given photon energy, $h\nu$, 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. The absorption coefficient is then expressed as,

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

The fundamental absorption can be through:

→ Allowed direct transitions

→ Forbidden direct transitions

→ Indirect transitions between indirect valleys

→ Indirect transition between direct valleys

→ Transition between band tails

→ Absorption in the presence of a strong electric field.

In the case of 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 minimum photon energy and take place only at sufficiently short wavelength.

The absorbance is defined as,

$$A=\log (I/I_0)$$

where,

I_0 = Intensity of incident radiation

I = Intensity of transmitted radiation.

The absorption coefficient, α, is defined as the relative rate of decrease in the light intensity $I(h\nu)$ along its propagation path,

$$\alpha = 1/I(h\nu) \times d[I(h\nu)]/dx$$

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,

$$\alpha = \ln(I/I_o)/t \quad \text{or} \quad \alpha = 2.303\,(A/t)$$

where, A is the absorbance.

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

$$\alpha = B[h\nu - E_g]^m / h\nu$$

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 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 theory of direct and indirect transition in semiconductor is given by Barden[8].

GENERAL OPTICAL SPECTROMETRIC EQUIPMENT:

The optical properties of a material vary with wavelength and measurements are usually made with monochromatic radiations. A suitable light source and a monochromator are used to obtain radiation of various wavelengths. For the visible region, an incandescent lamp or one of various types of discharge lamp is used as the light source. Mercury arc lamps serve as high intensity sources for the ultraviolet region. For long wavelength in the infrared, Nernst glowers and glowbars are commonly used. The entire wavelength range of interest may be covered by prism monochromators. With recently developed cesium iodide prism, the infrared region, as far as 50 μ, can be reached [12]. Gratings have to be used for still longer wavelength [13]. In the visible and ultra violet regions, spectrograph can be used when very high resolutions are required, as in the investigation of the sharp exciton absorption bands in insulating crystal. To reduce the noise and to 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 region, highter sensitivities may be obtained with photomultiplier tubes. Photoconductive cells of PbS, PbSe, and PbTe have been developed into hightly sensitive detectors[14]. The sensitivity is increased by cooling and a limiting power of

10^{-12} watts can be detected. In far infrared work where high sensitivity is needed, the Golay pneumatic detector [15] may be profitably used in place of the thermocouple. The limit of the detector is about 10^{-10} watts.

Now a days in computerized IR Spectroscopy, particularly Fourier transform infrared (FTIR) spectroscopy, has made it possible to obtain infrared spectra of solid, liquid, and gaseous sample, within short time and good precision.

PREPARATION OF THE SAMPLE:

There are various sampling techniques used to obtain infrared spectra of solid as given below,

- Self supporting sample
- Solution
- Films
- Milling in mineral oil and oil emulsion
- Pellets

The author has used the films and pellets method.

Films:

Liquid, emulsion, 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 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 quantitive analysis. The transparent window will reflect and weaken band structure. The spectra, if any, 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.The materials under study, when in thin film form, was coated on KBr crystal substrate for obtaining the IR spectra since KBr is transparent to IR in the range of interest.

Pellet:

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 . 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 effect. The matrix material must be pure and dry. The pellet is then supported in a pellet holder at the focus of the instrument. Pellet sample should be referenced to pure KBr of the same size. The KBr pellet method proves to be quite satisfactory, 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.

ELECTRICAL PROPERTIES:

The following properties of $Bi_{1-x}Sb_x$ have been studied by the author.

→ Electrical conductivity

→ Hall coefficient measurement

→ Thermopower

Electrical conductivity:

The electrical conductivity of crystal can be carried out using one of the following techniques:

→ Van der Pauw method

→ Two Probe Method

→ Four Probe Method

Van der Pauw method :

The room temperature electrical conductivity measurement can be easily carried out using Van der Pauw method[16]. This method is convenient when the crystal size is greater than 5 X 5 X 0.3 mm^3. The basic requirements of the method are as follows : The contant should be at the circumference of the sample, the size of the contants should be negligibly small as compared to that of the sample, the contant should be ohmic, the sample should be very thin as compared to its area, the surface of the sample should be singly connected, The sample should be free from the step and discontinuities, the sample should be flat so that the sample surface and contacts lie in the same plane and the applied field should be low so that breakdown does not occur.

Two Probe Method:

We can use two probe method when the single crystal is very thin. In this method, voltage and current are measured between the same contacts where the voltage is applied. With an accurate measurement of the dimensions of the sample, the conductivity can be determined as $\sigma = IL/VA$, where I is current, V is the voltage drop, L and A are the length area of cross-section of the sample, respectively. The above equation holds true only if the number of carriers is sufficiently large so that the thermal variation in the carrier density is negligible.

Four probe method

Particularly for semiconductor, we normally use four point probe method[17]. In this method, all the current and potential probes are point-contacts, usually mounted on a special holder. This arrangement permits a rapid testing of resistivity or conductivity by simple application of the four points to a specimen and, with limits, the results are independent of the size or shape of the specimen. The simplest case is to have distance between successive points of contact equal. The four probe geometry is schematically shown below :

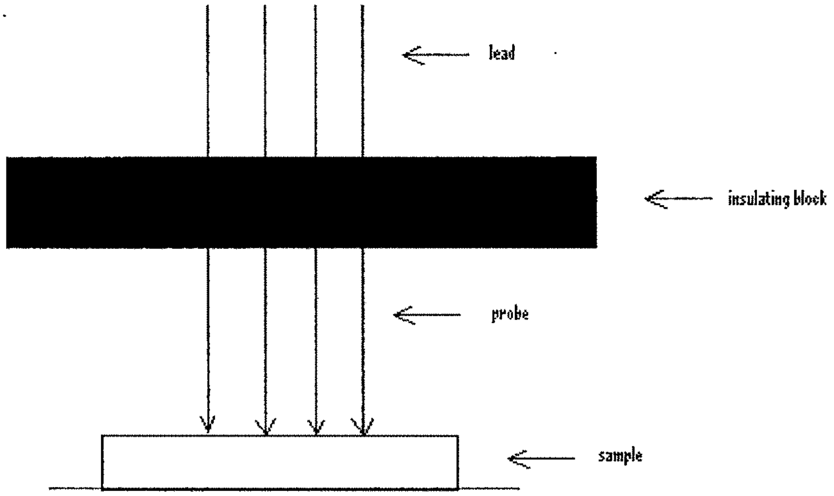

Figure -1

The conductivity is given

$$\sigma = I/2\pi Vs$$

where,

I = the current through the current leads

s= the separation between successive point.

If the probe separation is not the same for each successive pair of contacts, it can be replaced with s given as

$$1/s = 1/s_1 + 1/s_3 - 1/s_{1+}s_2 - 1/s_{2+}s_3$$

where s_1, s_2, s_3 are corresponding probe separations. Then,

$$\sigma = \frac{I\,(1/s_1 + 1/s_3 - 1/s_{1+}s_2 - 1/s_{2+}s_3)}{2\pi V}$$

The method assumes the distance between probes to be small compared to the smallest dimension of the sample and none of the probe is too close to any edge of the sample.

HALL EFFECT:

For Hall measurement, linear four probe geometry is used. Charge carriers contributing the current caused by an applied electric field are deflected by a magnetic field applied perpendicular to the current. The resulting Hall voltage normal both to the current and the field can be measured. The sample is kept between the two poles of a strong electromagnet capable of magnetic field of the order 20 kilo gauss. A sensitive current meter is connected in series with a stabilized Dc power supply and the sample.

THERMOPOWER:

The measurement of the thermoelectric power requires the establishment of a temperature difference ΔT which may be accomplished by holding different the junction temperatures T_1 and T_2. The voltage ΔV developed between the two junctions is measured. The thermoelectric power S is given by the ratio ΔV/ ΔT for ΔT → 0. In practice, S is found as a function of temperature by using ΔT – value as small as the over all accuracy the measurement allows. The temperature difference should, however, never be more than a few percent of the ambient temperature of the sample. There are two alternative methods used to measure the thermoelectric power (i) the integral method and (ii) the differential method. If we keep the temperature of one end of the sample constant and vary that of the other end continuously and measure the developed thermal emf as a function of temperature difference between the constant temperature of the cold end and the varying temperature of the hot end, then the method is termed as the integral method. The thermoelectric power at a given temperature is measured as the slope of the thermal emf Vs temperature plot at the corresponding hot-end temperature. In the differential method, the difference between the hot end and the cold end temperatures is kept constant and small and the temperature of the sample as a whole is varied and the developed thermal emf at different average specimen temperatures is measured. The slope of the thermal emf plot against the average temperature at the temperature of interest gives the thermoelectric power at that temperature.

The IR spectrometric, conductivity, Hall and thermopower measurements carried by the author on the material under study are described in chapter- 8,9.

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