## A DESCRIPTIVE STUDY ON CHARACTERIZATION TECHNIQUES

**Poonam**
Research Scholar, Calorx Teachers' University
Ahmedabad (Gujarat)

**ABSTRACT**

The conduction and valence band are the regular features of all the solids. Only difference is upto which they are occupied and vertical separation between them i.e. energy band gap. Thus energy band may be defined as the gap or region between the valence and conduction the measurement of absorption spectra is the direct method for probing the band structure of semiconductors band. The band gap may be classified as direct and indirect band gap depending upon the electron transition.

**KEYWORDS:** Forbidden direct transition, Optical properties, Structural properties, Electrical properties, Topography.

### INTRODUCTION

It is very important to thoroughly characterize the films, for making them useful in device fabrication. There are following techniques for the characterization of the film:
1. Optical properties
2. Structural properties
3. Electrical properties

### OPTICAL CHARACTERIZATION OF THIN FILMS

The optical behaviour of the thin films deals with optical reflection, transmission and absorption properties and their relation to optical constant of films.

### OPTICAL ABSORPTION

In the absorption process a photon of known energy excites an electron from a lower to a higher energy state. In other manner we can say that absorption is also resulted from interaction between atoms and electromagnetic radiations.
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### DIRECT AND INDIRECT BAD GAP
As the photon of incident light is absorbed by the material, an electron is excited from lower to upper energy state. This transition of electron can be direct or indirect. In a direct transition an electron in the conduction band can fall to an empty state in the valence band giving off the

energy difference $E_g$ as photon of light. On the other hand, if an electron in the conduction band cannot fall directly to the valence band but must undergo a momentum change as well as changing its energy.

The difference between direct and indirect band structure is very important for deciding that which semiconductor can be used in device requiring light output.

Determination of energy band gap ($E_g$):

The absorption spectrum of the material is an important technique which is used for this method is that it is applicable for any range that is narrow or wide band gap material. In this experiment photons of selected wavelength are incident on the sample and the relative transmission of the various photons is observed.

Let a photon beam of intensity $I_o$ (photons/cm$^2$ sec) is incident at the sample of thickness t and the intensity of light transmitted is $I_t$ then,

$$I_t = I_o e^{-\alpha t} \qquad \text{.........................(1)}$$

Where $\alpha$ is the absorption coefficient and has unit cm$^{-1}$. The coefficient varies with photon wavelength and also with the materials. The difference between direct and indirect transition is possible on the basis of the dependence of absorption coefficient on the photon energy.

To determine the energy band gap from absorption spectra the Tauc relation is used [1].

$$A\, hv = A\, (hv-E_g)^n \qquad \text{........................(2)}$$

Where,

hv = photon energy

$E_g$ = band gap

$\alpha$ = Absorption coefficient

n = ½, 2, 3/2, 3

A = Constant

n = ½, Allowed direct transition

n = 3/2, Forbidden direct transition

n = 2, Allowed indirect transition

n = 3, Forbidden indirect transition

In case of direct band gap the allowed transition are giving by using the equation (2) as,

$$\alpha\, hv = A(hv-E_g)^{1/2} \qquad \text{.................(3)}$$

A plot of $(\alpha\, hv)^2$ versus photon energy (hv) when extrapolated to zero absorption gives the value of energy band gap($E_g$).

While In case of indirect band gap the allowed transitions are given by using equation (3.2) as,

$$\alpha\, hv = A(hv-E_g)^2 \qquad \text{..................(4)}$$

A plot of $(\alpha\, hv)^{1/2}$ versus photon energy (hv) when extrapolated to zero absorption gives the value of energy band gap ($E_g$) of indirect band gap materials.

**OPTIC TRANSMISSION**

Let a light beam of intensity 10 be made incident on a surface and I be intensity of transmitted beam then the ratio of transmitted to incident intensity I/ 10 is termed as the transmission coefficient. If $\alpha$ is the absorption coefficient, t is the thickness and R is the reflectivity then the radiation traversing the first interface is (1-R) 10. The radiation reaching the second interface is (1-R) 10 exp (-$\alpha$t). The resultant i.e. the overall transmission is given by

$T = (1-R)^2 \exp(-\alpha t)$

$1 - R^2 \exp(-2(-\alpha t)$

If product at is large then we can write

$T = (1-R)^2 \exp(-\gamma t)$.

Determination of optical constants: the optical behaviour of a material is generally used to determine the optical constants

n ( refractive index)

k ( extinction coefficient)

ε ( dielectric constant)

t (thickness)

Transmission method for determination of n, k & t [2-4]:

If we assume that the film is weakly absorbing and substrate is completely transparent, then using manifacier envelope method [2] the refractive index (n) and extinction coefficient (k) of the film on a transparent substrate can be evaluated from the transmission spectra.

For normal incidence the refractive index of the material is given by,

$$n = [N + (N^2 - n_o^2 n_1^2)^{1/2}]^{1/2}$$

Where

$$N = \{(n_0^2 + n_1^2)/2\} + 2n_o n_1 [(T_{max} - T_{min})/(T_{max} . T_{min})]$$

The boundary of envelope gives the value $T_{max}$ & $T_{min.}$

We have different value of λ at different N. Thus refractive index n is the function of λ.

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Thus the thickness of the thin film can be calculated as,

**t = (M λ₁λ₂)/ 2 [n (λ₁) λ₂ - n (λ₂) λ₁]**

Where M is the no. of oscillations b/w two extrema (M =1 b/w two consecutive maxima or minima). $\Lambda_{1, n}$ (λ₁), λ₂, n (λ₂) are the corresponding wavelength & indices of refraction.

Knowing t we can calculate the extinction coefficient K from

**K = -λ/4πt [ln P]**

Where

**P = exp (-αt) or exp [-4πKt/ λ]**

Where α is the absorption coefficient.

Also **P=C₁/ C₂ [ {1- (T_{max}/ T_{min})}/ {1+ ( T_{max}/T_{min})} ]**

Where **C₁ = (n₀ + n) (n₁ + n)**

**C₂ = (n - n₀) (n₁ – n)**

Where $n_0$ = the refractive index of the air.

$n_{1 =}$ the refractive index of the substrate (glass)

n = the refractive index of material

α = is the absorption coefficient.

Crystals cause broadening (a small angular divergence) of the diffracted beam i.e. diffraction (scattering) at angles near to, but not equal to, the exact Bragg angle. We must therefore consider the scattering of ray's incident on the crystal planes at angles deviating slightly from the exact Bragg angle.

When we consider incident rays that make Bragg angles only slightly different from $\theta_B$, we find that destructive interference is not complete. Ray B, for example, makes a slightly large angle $\theta_1$, such that ray L from the mth plane below the surface is (m+1) wavelengths out of phase with B, the ray from the surface plane. This means that midway in the crystal there is a plane scattering a ray which is one-half (actually, an integer plus one-half) wavelength out of face with ray B from the surface plane. These rays cancel one another, and so do the other rays from similar pairs of planes throughout the crystal the net effect being that rays scattered by the top half of the crystal annual those scattered by the bottom half. The intensity of the beam diffracted at an angle $2\theta_1$ is therefore zero. It is also zero at an angle $2\theta_2$ where $\theta_2$ is such that ray N from the mth plane below the surface is (m-1) wavelengths out of phase with ray C from the surface plane. We have therefore found two limiting angles, $2\theta_1$ and $2\theta_2$, at which the diffracted must drop to zero. It follows that the diffracted intensity at angles near $2\theta_B$, but not greater than $2\theta_1$ or less tan $2\theta_2$, is not zero but has a value intermediate between zero and the maximum intensity of the beam diffracted at an angle $2\theta_B$.

the width B is usually measured, in radians, at an intensity equal to half the maximum intensity (Note that b is an angular width, in terms of 2θ (notθ), and not a linear width) As a rough measure of B, we can take half the difference between the two extreme angles at which the intensity is

zero, which amounts to assuming that the diffraction line is triangular in shape. Therefore, Effect of fine particle size on diffraction curves (schematic)

$B = 1/2 (2\theta_1 - 2\theta_2)$

$= (\theta_1 - \theta_2)$

We now write path-difference equation for these two angles, similar to the equation $2d\sin\theta = n\lambda$, but related to the entire thickness of the crystal rather than to the distance between adjacent planes:

$2t\sin\theta_1 = (m+1)\lambda$,

$2t \sin\theta_2 = (m-1)\lambda$,

By subtraction we find

$t (\sin\theta_1 - \sin\theta_2) = \lambda$,

$2t\cos (\theta_1 + \theta_2)/ 2 \sin (\theta_1 - \theta_2)/2 = \lambda$

But $\theta_1$ and $\theta_2$ are both very nearly equal to $\theta_B$, so that

$$\theta_1 + \theta_2 = 2\theta_B \text{ (approx.)}$$

And

$$\sin (\theta_1 - \theta_2)/2 = (\theta_1 - \theta_2) /2 \text{ (approx.)}$$

Therefore

$$2t (\theta_1 - \theta_2)/2 \cos\theta_B = \lambda\theta$$
$$t = \lambda / B \cos \theta_B$$

A more exact treatment of the problem gives.

$$t = 0.9 \lambda / B \cos \theta_B$$

Which is known as the Scherrer formula? It is used to estimate the particle size of very small crystals from the measured width of their diffraction curves.

For example, suppose $\lambda = 1.5 A^0$, $d = 1.0 A^0$, and $\theta = 49^0$. Then for a crystal 1mm in diameter the breadth B, due to the small crystal effect alone, would be about $2\times 10^{-7}$ radian ($10^{-5}$ degree), or too small to be observable.

Such a crystal would contain some $10^7$ parallel lattice planes of the spacing assumed above.

However, if the crystal were only $500 A^0$ thick, it would contain only 500 planes, and the diffraction curve would be relatively broad, namely about $4\times 10^{-3}$ radian ($.2^0$), which is easily measurable.

Nonparallel incident rays, such as B and C in fig actually exist in any real diffraction experiment.

## SCANNING ELECTRON MICROSCOPY (SEM)

The first SEM image was obtained by Max Knoll, who in 1935 obtained an imageof silicon steel showing electron channeling contrast.

Further pioneering work on the physical principals of the SEM and beam specimen interactions was performed by Manfred von Ardenne in 1937, which produced a British patent but never made a practical instrument.

The SEM was further developed by Professor Sir Charles Oatley and his postgraduate student Gary Stewart and first marketed in 1965 by the Cambridge Instrument Company as the "Stereoscan". The first instrument was delivered to DuPont.

The **scanning electron microscope (SEM)** is a type of electron microscope that images the sample surface by scanning it with a high- energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity.

The types of signals produced by an SEM include secondary electrons, back-scattered electrons (BSE), characteristic X – rays, light (cathodoluminescence), and specimen current and transmitted electrons.

Secondary electron detectors are common in all SEMs, but it is rare that a single machine would have detectors for all possible signals. The signals result from interaction of the electron beam

with atoms at or near the surface of the sample. In the most common or standard detection mode, secondary electron imaging or SEI, the SEM can produce very high- resolution images of a sample surface, revealing details about less than 1 to 5 nm in size. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample.

This is exemplified by the micrograph of pollen shown to the right. A wide range of magnifications is possible, from about 10 times (about equivalent to that of a powerful hand-lens) to more than 500,00 times, about 250 times the magnification limit of the best light microscopes. Back-scattered electrons (BSE) are beam electrons that are reflected from the sample by elastic scattering.

BSE are often used in analytical SEM along with the spectra made from the characteristic X-rays. Because the intensity of the BSE signal is strongly related to the atomic number (Z) of the specimen, BSE images can provide information about the distribution of different elements in the sample.

For the same reason, BSE imaging can image colloidal gold immune-labels of 5 or 10 nm diameter which would otherwise be difficult or impossible to detect in secondary electron image in biological specimens. Characteristic X –rays are emitted when the electron beam removes an inner shell electron from the sample, causing a higher energy electron to fill the shell and release energy. These characteristic X-ray are used to identify the composition and measure the abundance of element in the sample.

The SEM utilizes the principle of electron beam scanning to form an image on a television or oscilloscope monitor.

The characteristic information we get from SEM are

1. Topography
2. Morphology
3. Compositional
4. Crystallographic information

The surface morphology of the materials helps in the study of grain growth, orientation of the graine, compositional and topographical features present on the surface of the material. It is well known that different phases formed during sintering show different morphology when examined with scanning electron microscope. From scanning electron microscope it is possible to determine the compactness of the material, the particle size and shape etc.

In SEM abeam of electron from an electron gun is focused by a set of electron lenses. Between the electron lenses the beam is periodically deflected by the system of deflection coils or, so that it runs over the surface under examination.

A cathode ray display tube is scanned synchronously with the electrons beam when the electron beam impinges on the surface, secondary electrons are emitted, which are extracted by the electric field to the collector and used as constant single.

**SCANNING PROBE MICROSCOPY**

Scanning probe microscopy (SPM) is a technique that is used to study the properties of surfaces at the atomic level. A Scanning Probe Microscope scans an atomically sharp probe over a surface, typically at a distance of a few angstroms or nanometres. The interaction between the sharp probe and surface provides 3-D topographic image of surface at the atomic scale.

**(a)** Scanning Tunneling Microscopy (STM)
**(b)** Atomic Force Microscopy (AFM)

**ATOMIC FORCE MICROSCOPE (AFM)**

The atomic force microscope (AFM) or scanning force microscope (SFM) was invented in 1986 by Binning, Quate and Gerber. The AFM utilizes a sharp probe moving over the surface of a sample in

a raster scan. In AFM, the probe is a tip on the end of a cantilever which bends in response to the force between the tip on the end the sample. The first AFM used a scanning tunnelling microscope at the end of the cantilever to detect the bending of the lever, but now most AFMs employ an optical lever technique.

The diagram illustrates how this works; as the cantilever flexes, the light from the laser is reflected onto the split photo-diode. By measuring the difference signal changes in the bending of the cantilever can be measured.

Since the cantilever obeys Hooke's Law for small displacement, the interaction force between the tip and the sample can be found. The movement of the tip or sample is performed by an extremely precise positioning device made from piezo-electric ceramics, most often in the form of a tube scanner. The scanner is capable of sub-angstrom resolution in x-, y- and z- directions. The z-axis is conventionally perpendicular to the sample.

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