Chapter 3
Characterization Techniques
3.1 ABSTRACT:

This chapter provides with some theoretical background to the various phenomena and a brief description of the various techniques employed in the course of this study.

3.2 CHARACTERIZATION TECHNIQUES:

The semiconducting oxides like BaSnO$_3$, ZnGa$_2$O$_4$, WO$_3$, etc have been characterized by various characterization techniques. These include among other X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), Differential Thermal Analysis (DTA), Scanning Electron Microscopy (SEM), for structural and morphological studies and also surface science technique such as X-ray Photoelectron Spectroscopy (XPS) and Temperature Programmed Reduction (TPR) and Temperature Programmed Desorption (TPD).

In the present investigation we have characterized the materials by using the following techniques:

- X-Ray Diffraction (XRD)
- Fourier Transform Infrared Spectroscopy (FTIR)
- X-Ray Photoelectron Spectroscopy (XPS/ESCA)
- Scanning Electron Microscopy (SEM)
3.2(a) **X-RAY DIFFRACTION**

X-rays have often been used in catalytic work in relation to the estimation of crystallite size and to obtain information on the bulk crystallographic structure of catalytic materials. A straightforward application of XRD is the use of the XRD patterns to identify the various phases existing in a material.

X-rays are electromagnetic radiation with wavelengths in the angstrom range. Consequently, they can penetrate matter and therefore are especially well suited to probe the structure of solids. Bombarding a solid (target) with high-energy electrons to create inner-shell electron vacancies commonly generates X-rays. Two types of X-rays are thus generated; (a) a continuous spectrum, and (b) a characteristic line spectrum. The continuous spectrum arises from the deceleration of the incoming high-speed electrons by the target. Line spectra occur when an electron from a high-energy orbital fills a low-energy vacancy in the inner electron orbitals. The line spectrum is characteristic of the emitting material and used for X-ray spectroscopy. The peaks of the line spectra are designated by the orbital (shell) into which the electrons fall (K, L, M, N) and a Greek letter indicating the original orbital (α, β, etc.). Due to the characteristic well-defined energy, the X-ray lines are used as a quasi-monochromatic x-ray source in diffraction equipment.
Diffraction occurs when a wave interferes with an array of scattering centers causing the outgoing waves to reinforce each other (constructive interference) or to be out of phase and cancel each other (destructive interference). X-rays are scattered by the electrons of the irradiated matter. Elastically scattered X-rays have the same frequency as the incoming X-rays (coherent scattering) the opposite is true for inelastic scattering (incoherent scattering). Elastically scattered X-rays, which are important in diffraction, can be depicted as reflected by the scattering atom.

Bragg used the reflection analogy to explain X-rays diffraction. Fig. 1 shows a monochromatic X-ray beam of wavelength \( \lambda \) directed on two successive planes of a crystal. The reflected beam (i.e., scattered) and associated wavelengths are also shown.

Fig. 1 Monochromatic X-ray beam
If the reflected rays are to be in phase, the path difference of the two successive incoming rays, \( CB + BD = 2d \sin \theta \), must be equal to an integral number of wavelengths, that is,

\[
2d \sin \theta = N\lambda
\]

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The equation above, known as Bragg's law, related the \( d \) spacing of the crystal with the angle of incidence and wavelength of the incoming X-rays. \( N \) is known as the order of the reflection. Equation (1) indicates that measuring the intensity of the diffracted beam as a function of the incident angle gives a diffraction pattern which is characteristic of the crystallographic structure of the irradiated sample. Such measurements, which constitute one of the many methods of XRD analysis, are most easily attained with a X-ray diffractometer. A X-ray diffractometer consists of a circular table with a stationary X-ray source and a moving detector located in the circumference of the table with the sample set at the center. The moving detector, usually a proportional counter, records the intensity of the reflected beam as a function of the reflected angle \( 2\theta \).

X-ray diffraction lines broaden when the crystallite size falls below about 100 nm. This technique is applicable to metal oxide (metal) crystallites of 3.5-6.0 nm size. Below 3.5 nm the line broadening is very broad and diffuse or even absent, while above 6.0 nm the change in line shape is too small. X-ray line broadening gives rapid information about dispersion, degree of metal oxide
present at the surface of the support or even embedded in it. Thus the method has an important place in materials technology.

X-ray diffraction analysis of all materials are carried out by using a Siemens/D. 5000 X-ray diffractometer (Cu Kα radiation \( \lambda = 1.5406 \text{ Å} \)).

3.2(b) CRYS TALLITE SIZE DETERMINATIONS FROM XRD

LINE BROADENING (SCHERRER EQUATION):

Diffraction lines should, in principle, be very narrow; however, when the crystallite size of a polycrystalline material falls below 1000 Å, broadening of the diffraction lines is observed. Instrumental limitations and lattice strain can also cause line broadening.

Line broadening due to particle size only arises because of incomplete destructive interference. When the incident beam is slightly off the Bragg angle, the reflected ray, which would nullify it originates from N planes inside the crystal. If the crystal is smaller than about 1000 Å, most planes do not have their destructive counterparts N planes away, so that finite diffracted lines will be observed at the off-Bragg angle setting, causing line broadening. Various measures of the peak broadening are used, the most common being the width at half intensity \( \beta_{1/2} \), and the integrated breadth, \( \beta_1 = \int_{01}^{\frac{\text{0.2}}{\text{1/1 max}}} (1/I_{\text{max}}) \text{ d} \theta \), where I is the observed intensity of the diffracted beam.
The relation between line broadening and crystallite size for a stress free material, known as the Scherrer formula [2], is

$$< L >_{hkl} = \frac{K \lambda}{\beta_{hkl} \cos \theta} \quad \text{(2)}$$

Where $K$ is a constant that depends on the definition of $\beta$ (FWHM value of a particular hkl plane, in degrees [a polar co-ordinate], needs to be converted into radians [Cartesian Co-ordinates], since, crystallite size measures in length units) used and the crystal geometry. The constant $K$ varies from 0.93 to 1.39, but because of experimental uncertainties, the constant is often set equal to 1. When $\beta$ is defined as the integral breadth, $< L >$ is a volume average crystallite size.

In the absence of lattice stress, broadening also occurs due to experimental limitations such as nonparallel and non-monochromatic irradiation. Other experimental factors also contribute to broadening, even if the specimen is of "infinite size" i.e., larger than 1000 Å. Consequently, for the correct estimation of crystallite size using Scherrer's formula, the experimental contribution to line broadening must be separated to obtain the pure diffraction broadening.
3.2(c) FOURIER TRANSFORM INFRARED SPECTROSCOPY

(FTIR):

IR spectroscopy gives qualitative information about the way adsorbed molecules are bonded to surfaces as well as structural information of solids. It can also be used to measure the amount of materials measured adsorbed and in some cases it can be used to study the rate at which certain surface processes occur. Infrared region of the electromagnetic spectrum includes radiations with wave number from 1400 cm$^{-1}$ to 20 cm$^{-1}$. The spectral range of greatest use is the mid-infrared region which covers the frequency range from 1400 cm$^{-1}$ to 200 cm$^{-1}$. Upon interaction with infrared radiation the atoms in a molecule at particular wavelength absorb a portion of the incident radiation. The multiplicity of vibrations occurring simultaneously produces a highly complex absorption spectrum, which is characteristic of the functional groups comprising the molecule and the overall configurations of the atom as well.

For IR absorption to occur, two major conditions must be fulfilled. First, the energy of the radiation must coincide with the energy difference between the excited and ground state of the molecules. The molecule will then absorb radiant energy, increasing its natural vibrations. Second, the vibration must entail a change in the electrical dipole moment, a restriction that distinguishes IR from Raman spectroscopy. The intensity of an IR absorption band is proportional to
the square of the rate of change of dipole moment with respect to the displacement of the atoms in molecule.

In this work, IR spectra of polycrystalline samples were recorded using the pellet technique. This technique involves mixing the finely ground samples with KBr salt and pressing the mixture in an evacuable die at sufficient pressure to produce a transparent disc.

Fourier transform infrared spectra of the samples were recorded on Nicolet 740 FTIR spectrometer at ambient conditions by using KBr as diluent.

3.2(d) SCANNING ELECTRON MICROSCOPY (SEM):

The most common use of an electron microscopy (EM) in Materials Science is to measure the distribution of crystallite sizes as well as the morphology of supported or unsupported active materials. An electron microscope differs from an optical microscope in that the electron beam replaces the light beam and electromagnetic lenses replace the optical lenses. The use of an electron beam improves the resolution of the microscope, which is proportional to the wavelength \( \lambda \) of the incident beam, in accordance with \[3\]

\[
X = 0.6 \ C_s \ ^{1/4} \ \lambda \ ^{3/4}
\]

Where \( X \) is the resolution (i.e. the minimum size that can be distinguished in the microscope) and \( C_s \) is the spherical aberration of the incident beam.
Equation (3) illustrates the advantage of using an electron beam ($\lambda=0.5$ to $10\ A^0$) instead of light ($\lambda = 4000$ to $7000\ A^0$).

In SEM, images are produced from secondary electrons generated by the electron beam. The sample need not be transparent to electron transmission. Electron impact creates a volume of primary excitation from which elastically scattered and inelastically scattered electrons or secondary electrons are emitted. Secondary electrons have low energy and therefore only those electrons near the surface can be emitted outward in all directions. An electron detector system is used to collect both types of emitted electrons and produce a signal proportional to their intensity. The detection of secondary electrons depends on the sample topography. Electrons emitted from the specimen surfaces facing the detector will show a bright face, whereas those emitted from surfaces away from the detector will not be detected creating a shadowing effect. Furthermore, as the name indicates, a SEM is equipped with deflecting coils, which permit scanning the electron beam over the sample in raster mode. The raster pattern of the primary electron beam is synchronized with the scanning pattern of a cathode ray tube (CRT) used to display the detector signal so that a two-dimensional image of the scanned area is produced. Images are produced in the CRT or a TV, and permanent records can be obtained directly from the CRT using an instant camera or by videotape recording from a TV.

Numerous materials of industrial and scientific importance consist of particles within the colloidal size of fifty angstroms to one micron. The particle
behavior of many of these substances is dependent to a large extent upon the particle size. Therefore, it is entirely appropriate that many applications of the electron microscope have involved measurements of particle size and of size distribution.

Frequently the measure of a few particles on a micrograph with a ruler is adequate. In other instances it is necessary to employ statistical concepts and methods of handling and interpreting the data. With very few, if any exceptions, no particle specimen has exclusively particles of one size, so it is necessary to express size measurement in terms of averages. An average is by definition a measure of central tendency. The arithmetic mean is probably the representation of the average in particle size measurements and it is the one most commonly used. The arithmetic mean is the sum of all measurements divided by the number of measurements. For example if \( x_1, x_2, x_3, \ldots, x_n \) represent the diameters of each of the particle measurements and 'n' particles are measured. The arithmetic mean may be calculated by the equation (4).

\[
a = \frac{x_1 + x_2 + x_3 + \ldots + x_n}{n}
\]

SEMs is used in general for physical characterization of particles such as particle size, shape, surface structure and porosity, make up of aggregates and dispersion of one phase into another. To observe possible morphological changes and also to know the shape of the particles, the sample were mounted on a silver sample holder with the help of an adhesive to make the sample
surfaces conductive, it was coated with gold metal at 10 mm Hg pressure. For 
recording micrograph scanning electron microscope was used at 10 kv as 
accelerating voltage with different magnification.

3.2(e) TRANSMISSION ELECTRON MICROSCOPY:

Electron diffraction is another technique used to identify the structure of 
solids. In the simplest view, electron diffraction from crystalline lattice can be 
described as a kinematic scattering process that meets the wave reinforcement 
and interference conditions given in the Braggs equation. In many applications 
the samples are thinned to thickness of a few thousand angstroms by chemical 
etching or ion milling. The patterns are formed by diffraction on an electron beam 
(typically 50-200 KeV) transmitted through the thin sample.

For cubic crystals with planer Miller indices \( \{hkl\} \) and lattice parameter \( a \), 
the interplanar spacing \( d \) is given by

\[
d_{hkl} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}}
\]

(5)

If the specimen to photographic records plan distance is \( L \), then the radius 
\( R \) of the diffraction rings is related to the interplanar spacing by

\[
\lambda L = R d_{hkl}
\]
where \( \lambda \) wavelength of the electrons and small angle approximation is used. The radius \( R \), are plotted versus \((h^2 + k^2 + l^2)^{1/2}\) and the slope, \( a/ \lambda L \) determines the camera constant. For a given specimen, the interplanar spacing \( d_{hkl} \) can be found from the measured values of the radius and the camera constant. Cross-sectional TEM of sample show planarity of the interface and the structure of the various related layers.

3.3 SPECTROSCOPIC TECHNIQUES

X-RAY PHOTOELECTRON SPECTROSCOPY:

It has been shown that photoelectron spectroscopy can yield values for the binding energies of all the electrons in an atom or molecule. The basic principle involves an absorption process, where the electron is excited by absorption of electromagnetic radiation from a lower to a higher energy level. If the energy of the electromagnetic radiation is greater than the difference between the initial electronic energy level and any higher energy level, the electron will actually leave the atom or molecule and travel in free space with velocity determined by the energy difference between the initial energy level and the energy of the electromagnetic radiation.

If electromagnetic radiation is in the X-ray range, say, the MgK\( \alpha \) or AlK\( \alpha \) radiation is used, all the core orbital electrons as well as the valence orbital electrons could be ejected to give photoelectrons of different energies. This type
of photoelectron spectroscopy is called X-ray photoelectron spectroscopy [XPS] or Electron spectroscopy for chemical analysis [ESCA]. If the photons are in the ultraviolet region, the term "ultraviolet photoelectron spectroscopy (UPS)" is used. The UPS gives the information only valence bands of solids, whereas XPS probes both valence bands and core levels. In UPS one normally employs He I (21.22 eV) or He II (40.8 eV) radiation. In XPS, AlKα (1253.6 eV) or MgKα (14586.6 eV) radiation is generally employed. The escape depth of electrons in UPS is only 5-10 Å where as in XPS it is 20-40 Å. Schematic diagram of ESCA is shown in Fig. 2. Once the kinetic energy of the ejected electrons has been measured in the spectrometer the binding energy can be obtained using the following equation

\[\text{K.E. (ejected electron)} = h \nu B\]  

\[B\] is the energy of the electronic energy level from which the electron was ejected measured as a binding energy.

The recoil energy of the atom or molecule is negligible and hence ignored. In the case of solid materials the attachment of the sample to the holder will give rise to a contact potential equal to the difference in the work function between the sample and the sample holder. This gives

\[\text{K.E.} = h \nu - B + \phi_{cpd} - \phi_{sp}\]
Putting a on scale with respect to the Fermi level, $a'$, rather than with respect to the vacuum level, where

$$B = B' + \phi_{cpd}$$  \hspace{1cm} \text{(8)}

$$K.E. = h\nu - B' - \phi_{sp}$$  \hspace{1cm} \text{(9)}

In addition, the sample charging effect has also to be considered each time. Once the binding energy of a particular electron is obtained. Using the above equation useful chemical information is obtained.

The case of core orbitals is different. If the element exists in its free state it gives a single peak for the photoelectrons ejected. But if this element is bonded to some other species then the binding energy is either less than or greater than the original value depending on whether the species is more electropositive or more electronegative than the element. Thus the binding energies of core electrons give rise to a chemical shift. If both the free element and the bonded species co-exist then, this gives rise to two peaks.

In fact chemical shifts can be observed for the core electrons of all element except hydrogen (whose single electron is involved in all compounds involving hydrogen and is thus always a valence electron). This means that the photoelectron spectroscopy of core electrons is a very powerful technique for investigating the structure and bonding in chemistry. In addition, since the core electron binding energies are characteristic of a particular type of atom, the
Fig – 2: Principles of an electron spectrometer for chemical analysis.
atomic constituent of a compound can be readily determined, and further, the area under the peaks corresponds to the number of atoms present. It is these two features that lead to the name ESCA.

3.3(b) PHOTOLUMINESCENCE (PL)

3.3(b)(1) PRINCIPLES:

One of the characterization techniques, photoluminescence, has been considerably improved in sensitivity and versatility over the years. The PL technique provides a contactless, non-destructive means for analysis of semiconductors. The method gives information about both intrinsic and extrinsic semiconductor properties. For example, the spectral features associated with the intrinsic process like band to band recombination are a measure of the band gap energy which can be used to determine the composition in alloy semiconductors. The shape of PL spectra associated with recombination of free and bound excitation provides a measure of the crystal quality.

Briefly, the PL process involves the excitation of a sample with laser light and the observation of any resulting emission. In general, excitation promotes an electron from the valence band of a semiconductor material into the conduction band. The minimum laser energy of the maximum wavelength capable of producing this excitation is equal to the band-gap energy. When the electron returns to its unexcited state by a radiative transition, PL is observed. The
transition may be directly between the conduction and valence bands providing a measure of the band gap.

3.3(b)(2) EXPERIMENTAL SETUP:

A schematic diagram of the measurement system is shown in Fig. 3. The sample is mounted on a substrate holder. The luminescence from the sample is excited by a laser source. The energy of excitation should be greater than the band gap of the sample. An argon ion laser with main lines at 488 and 514 nm and 10-100 mW power over 1mm diameter spot (or power density = 1-10 W/cm²) is suitable for this purpose. A narrow line laser filter is incorporated in the beam path to select either the 488 or 514 nm line. The luminescence from the sample is collected and focussed on to monochromator input slit. The signal from the detector is fed into the current preamplifier of a lock in amplifier which measures the luminescence signal in phase with the reference signal generated by a chopper.

3.3(c) LASER-RAMAN SPECTROSCOPY:

Raman spectroscopy (RS) is a contactless and non-destructive technique to obtain valuable information about semiconductor surfaces and interfaces. In Laser-Raman analysis, a laser beam is bounced off a sample surface and the energy of the scattered light is measured relative to that of the laser beam. The
Fig - 3: Experimental setup for photoluminescence measurements.
resulting Raman spectrum is a record of the intensity of the scattered light corresponding to specific shifts in energy shifts are related to the molecular and structural characterisations of the scattering medium, which offer a unique source of analytical information. RS can also provide insight into process induced strain, dopant levels, the optimum composition of III-V semiconductor alloys, and the nature of crystalline interface which affect the overall electrical properties of devices.

3.3(d) AN IDEAL METAL - INSULATOR - SEMICONDUCTOR DIODE

The Metal - Insulator - semiconductor (MIS) diode is the most useful device in the study of semiconductor surfaces. Since the reliability and stability of all semiconductor devices are intimately related to their surfaces conditions, an understanding of the surface physics with the help of MIS diodes is of great importance to device operations. The MIS structure is shown in Fig. 4 where d is the insulator thickness and V is the applied voltage on the metal field plate. The energy band diagram of an ideal MIS structure for \( V = 0 \) is shown Fig. 5.

3.3(e) ENERGY BAND DIAGRAM OF AN IDEAL MIS STRUCTURE WITH THE BAND BEINDING OF THE SEMICONDUCTOR (n-TYPE)

Fig. 6 shows the energy band diagram of an ideal MIS structure. There are several studies reported on the interface trapped charge also called interface
Metal - Insulator - n-type semiconductor

Fig. 5
states, fast states or surface states. These exist within the forbidden gap due to
the interruption of the periodic lattice structure at the surface. Measurements on
the clean surface in ultra high vacuum conditions have also confirmed that
this charge is very high of the order of the density of surface atoms
\((10^{15} \text{ atoms/cm}^2)\). This interface trapped charge can be neutralised by different
processes, like in the silicon, growing of a thermal oxide \(\text{SiO}_2\) on the silicon
surface neutralises most of the trapped interface charge. This is also known as
passivation. A surface state is considered a donor if it can become neutral or
positive by donating an electron. An acceptor interface trap can become neutral
or negative by accepting an electron.

When a voltage is applied, the interface trap levels move up or down with
the valence and conduction bands while the Fermi level remains fixed. A change
of charge in the interface trap occurs when it crosses the Fermi level. This
change of charge contributes to the MIS capacitance and alters the ideal MIS
curve.

On exposure to air, semiconductor surface invariably form an oxide on the
surface. In case of silicon, \(\text{SiO}_2\) formed, itself acts as a protective layer and
prevents further oxidation. Air exposed GaAs surfaces in particular always have
a layer containing oxides of gallium and arsenic, free arsenic and arsenic
vacancies. These create states in the gap at particular energy levels. This makes
the Fermi level immobile and results in what is known as 'Pinning of Fermi level'
near midgap. These high density of surface states are responsible for the large
number of recombination centres which degrade the material. If it would be possible to passivate or chemically tie up the dangling bonds and physically protect the GaAs surface it would be possible to depin the Fermi level and improve the intrinsic material properties of this semiconductor.

3.4 ELECTRICAL PROPERTIES OF SURFACE & INTERFACES

3.4(a) CURRENT-VOLTAGE (I-V) CHARACTERISTICS:

Obtaining dc I-V curves appears to be a very routine procedure. It is so when the values of current and voltage are in a certain range. (Current in milli-amperes or micro-amperes and voltage in volts). However when the current is in the range of nano-amperes, the internal resistance of the measuring instrument becomes significant and cannot be ignored. The resistance of the diodes with thicker insulator layers, in Metal-Insulator-Semiconductor (MIS) configuration is as high as and often higher than the internal resistance of the voltmeter. Fig. 7 gives a schematic of the setup used for obtaining the I-V characteristics under these conditions.

There current I is the true value (only limited by the instrument, the ammeter), and the voltage across the diode can be found by V-Ir, where 'V' is the voltmeter reading, 'I' is the ammeter reading and 'r' is the internal resistance of the ammeter. This 'r' can be obtained by closing the switch 'S' and noting the corresponding ammeter reading 'I' and voltmeter reading V (r = V/I').

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Fig - 7

P = DC power supply
V = Voltmeter
D = Diode under test
A = Ammeter
S = Switch

Fig - 8

O = Oscillator
T = Ionisation transform
B = Voltage bias
D = Diode under test
C = Capacitor

Preamplifier
Lock-in-Amplifier
It has observed that the forward current density $J$, of the Schottky barrier junction for $V > 3kT/q$ is approximately given by

$$J = A' T^2 \exp \left( -qV_{bi}/kT \right) \exp \left( qV/nkT \right)$$

(10)

Where $A'$ is the effective Richardson constant

$T$ is the junction temperature in K

$k$ is the Boltzmann constant

$n$ is the ideality factor

$V$ is the applied forward bias voltage.

The current density $J$ is the forward current per unit area of the diode (Amp/cm$^2$).

The extrapolated value of the current density to zero bias voltage gives the saturation current density

$$J_{sat} = A' T^2 \exp \left( -qV_{bi}/kT \right)$$

(11)

The barrier built in voltage is then given by

$$V_{bi} = (kT/q \ln (A' T^2 / J_{sat}))$$

(12)

and the ideality factor of the diode

$$n = (q/kT) \left( \partial V/\partial \ln J \right)$$

(13)

where $\left( \partial V/\partial \ln J \right)$ is the slope of $\ln J$ vs $V$ characteristics.
3.4(b) Capacitance-Voltage (C-V) Characteristics.

The C-V method is used to determine barrier heights and surface state density and high frequency using the Terman method. The barrier height is related to the intercept voltage, \( V_i \), by the equation

\[
\Phi_b = V_i + V_n - \Delta \Phi + kT/q
\]  

(14)

Where \( V_n \) is the distance from the bottom of the conduction band to the Fermi level, \( \Delta \Phi \), the image force lowering of the barrier height at the interface and \( kT/q \) due to the contribution of mobile carriers in the reverse layer. The values can be calculated from the slope of \( I/C^2 \) versus Voltage curve.

The schematic experimental setup used for C-V measurements is shown in Fig. 8. The Schottky barrier height \( \Phi_b \) is estimated from the intercept on the \( X\)-axis of the \( I/C^2 \) versus plot.