Chapter 2

Experimental techniques for characterizations
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Table 2.1: Preparation of gases.
2.0 Introduction

In this chapter we present the experimental techniques used to study the structural, optical, surface morphological and microstructural properties of thin films, followed by the experimental set-up used to characterize the thin film gas sensor performances.

The characterization techniques such as X-ray diffraction (XRD), Scanning electron microscopy (SEM), Field emission scanning electron microscopy (FESEM), Atomic force microscopy (AFM), Energy dispersive analysis by X-ray (EDAX), Transmission electron microscopy (TEM), UV-visible spectroscopy and thermoelectric power measurement setup utilized in the present study. It also contains the static gas sensing system to check gases.

2.1 X-ray diffraction (XRD)

![Photograph of X-ray diffractometer.](image)

Fig. 1: Photograph of X-ray diffractometer.

The X-ray diffraction technique is a widely used and accepted tool for characterization of structural properties of materials in thin film/bulk form. In the present study, the structural properties of the films were investigated by using the XRD measurements. In the present work, the crystal structure of the films was determined with a BRUKER D8 ADVANCE X-ray diffractometer (XRD) using a monochromatic Cu-
Kα radiation (λ = 1.5406 Å) with operating voltage of 40 kV and current of 40 mA. The photograph of the X-ray diffractometer is shown in Fig. 2.1. XRD technique can give information regarding the phase composition. In X-ray diffractometry, characteristic radiations from the slit of an X-ray tube fall on the films and are received by a slit at the counter. The two slits and the specimen are located at the circumference of a circle in order that the condition of the parafocusing is met. The pattern is characteristic of the crystal structure; it effectively serves as fingerprint by which material can be identified. Comparing the diffraction peaks with the standard ASTM data, it is possible to identify unknown substances, to determine the grain size, to know the effect of temperature on grain size and crystallinity.

One very important use of XRD when dealing with nanocrystals is to estimate crystal dimensions through the Scherrer relationship:

\[
\text{Crystal diameter} = 0.9 \frac{\lambda}{\beta \cos \theta}
\]

where \(\lambda\) is the X-ray wavelength (1.5418 Å for CuKα, commonly used source), \(\theta\) is the peak position and \(\beta\) is the peak full width at half maximum (FWHM) in radians is the width of the main peak of the phase measured at the half of the height of the peak, as it is shown in Fig. 2.2.

![Fig. 2.2: Full width half maximum (FWHM) measured in a typical peak of phase in a material XRD pattern](image)
**Nature of Sample:**

i) Thin film  
ii) Single crystal  
iii) Powder  

**Uses:**

i) To determine crystal structure and lattice parameter  
ii) To determine particle size  
iii) To determine number of atoms per unit cell  

**Limitations:**

i) Small amount of doping material cannot be detected  
ii) For less amount of material it is not possible to detect all characteristics planes.

*XPowder* is a widely used program to facilitate the analysis of X-ray diffraction patterns. Using *XPowder* software grain size determination, d-spacing, FWHM measurement was carried out.

### 2.2 Transmission electron microscopy (TEM)

Transmission electron microscopy is a technique related to SEM but the magnification is much higher (2,000-450,000X) which is a great advantage to study the samples down to their atomic level, and to determine the size and shape of the particles. In contrast with SEM, the sample preparation using TEM is destructive, requiring the milling in order to reach a submicron thickness necessary for the transmittance of the electrons through the sample. TEM is a more expensive technique than SEM, requiring both high vacuum and a high voltage electron gun to enable the electrons to penetrate the sample. The photograph of the Transmission electron microscope is shown in Fig. 2.3(a). Fig. 2.3(b) shows a schematic outline of a TEM.

**Instrument Details**

Make : PHILIPS  
Model : CM 200  
Specification : Operating voltages: 20-200 kV Resolution: 2.4 Å
A TEM contains four parts: electron source, electromagnetic lens system, sample holder, and imaging system

**Electron source**

The electron source consists of a cathode and an anode. The cathode is a tungsten filament which emits electrons when being heated. A negative cap confines the electrons into a loosely focused beam (Fig. 2.4). The beam is then accelerated towards the specimen by the positive anode. The electrons at the rim of the beam will fall onto the anode while the others at the center will pass through the small hole of the anode. The electron source works like a cathode ray tube.

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*Fig. 2.3: Photograph and schematic outline of TEM.*

(a) Photograph of TEM.

(b) Schematic diagram of TEM.
**Electromagnetic lens system**

After leaving the electron source, the electron beam is tightly focused using electromagnetic lens and metal apertures. The system only allows electrons within a small energy range to pass through, so the electrons in the electron beam will have a well-defined energy.

a) Magnetic Lens: Circular electro-magnets capable of generating a precise circular magnetic field. The field acts like an optical lens to focus the electrons.

b) Aperture: A thin disk with a small (2-100 micrometers) circular through-hole. It is used to restrict the electron beam and filter out unwanted electrons before hitting the specimen.

**Sample holder**

The sample holder is a platform equipped with a mechanical arm for holding the specimen and controlling its position.

**Imaging system**

The imaging system consists of another electromagnetic lens system and a screen. The electromagnetic lens system contains two lens systems, one for refocusing the electrons after they pass through the specimen, and the other for enlarging the image and
projecting it onto the screen. The screen has a phosphorescent plate which glows when being hit by electrons. Image forms in a way similar to photography.

![Image of a TEM imaging system](image)

**Fig. 2.5:** The imaging system of a TEM.

**Working principle**

TEM works like a slide projector. A projector shines a beam of light which transmits through the slide. The patterns painted on the slide only allow certain parts of the light beam to pass through. Thus the transmitted beam replicates the patterns on the slide, forming an enlarged image of the slide when falling on the screen.

TEMs work the same way except that they shine a beam of electrons (like the light in a slide projector) through the specimen (like the slide). However, in TEM, the transmission of electron beam is highly dependent on the properties of material being examined. Such properties include density, composition, etc. For example, porous material will allow more electrons to pass through while dense material will allow less. As a result, a specimen with a non-uniform density can be examined by this technique. Whatever part is transmitted is projected onto a phosphor screen for the user to see.

**Nature of Sample:**

i) Powder

ii) Thin film
Uses:  
   i) To study microstructure, grain size.  
   ii) High resolution of magnification.  
   iii) To study electron diffraction pattern.  

Limitations:  
   i) It is difficult to study the microstructure of thin film having thickness greater than 10 Å.

Sample and grid preparation

In comparison with other materials, powder samples are the easiest to prepare. The greatest advantage is that grain size is normally thin enough to let the electrons pass through material, and no thinning is needed. There are two important parameters that we should improve in order to obtain good images of our nanoparticles. On one hand, we will have to assure a good dispersion of the nanopowders, avoiding their agglomeration. And on the other hand, it will be interesting to obtain grid membranes as thin as possible to improve TEM image.

Fig. 2.6: a) A drop containing the mixture of ethanol and powder sample is deposited on a Cu mesh grid. b) After ethanol evaporation, material remains in the FORMVAR membrane with holes. c) Magnified detail of the membrane d) Nanopowder suspended on a hole will display good contrast TEM images.
Good dispersion results of nanograins were obtained as follows:

- Mixing of approximately 1 part of powder with 100-500 parts of high purity ethanol. No influence of ethanol over structural and morphological characteristics of the samples has been observed.
- Ultrasonic dispersion of the mixture. This process let a dispersion of agglomerated material.
- Deposition of a single drop of the dispersed material mixture on a FORMVAR carbonated film with holes placed on a ~ 400 mesh grid.
- Evaporation of ethanol from the grid in a dry environment.

**Selected area electron diffraction (SAED)**

This technique basically consists in performing a diffraction pattern of a specified region of the sample. Diffraction patterns can be easily interpreted. We will obtain a set of spots, which corresponds to those families of planes that satisfy the Bragg’s law in real space. These spots can be related to the distance between atomic material planes. After indexing SAED pattern, we will obtain useful information about the structural composition of material.

If the specimen studied is polycrystalline, the random orientation of individual grains will create a set of concentric rings in SAED pattern composed of fine spots.

**2.3 Field emission scanning electron microscopy (FESEM)**

A field-emission cathode in the electron gun of a scanning electron microscope provides narrower probing beams at low as well as high electron energy, resulting in both improved spatial resolution and minimized sample charging and damage. For applications which demand the highest magnification. The FESEM (HITACHI-S-4800 (II)) as shown in Fig. 2.7 is used in the present investigations.
The word FESEM means 'Field-Emission Scanning Electron Microscope'. With this microscope tiny structures as small as 1 nanometer (1 nm = one millionth of a millimeter = 10^{-9} m) can be visualize in small objects. Like the name FESEM already indicates, this microscope does not work with light (photons) but with electrons. Electrons are generated in a 'source' (Emission) and accelerated under influence of a strong electrical voltage gradient (Field). With electromagnetic coils an electron beam is formed that scans the object (Scan) and secondary electrons are produced by interaction with the atoms at the surface of the sample. These electrons contain valuable information that is employed to reconstruct a very detailed image of the topography of the surface of the specimen.

**Nature of Sample:**

i) Powder  
ii) Thin film.

**Uses:**

i) To study surface morphology, particle size  
ii) High resolution of magnification

**Limitations:**

i) One cannot study the interior of the sample
2.4 Scanning electron microscopy (SEM)

![Image of SEM]

**Fig. 2.8**: Photograph of SEM.

The photograph of the SEM coupled with EDAX is shown in Fig. 2.8. SEM is a surface analytical technique, in which a finely focused electron beam impinges on the sample surface. The secondary electrons, which are generated by the electron beam strongly depend on the surface topology and therefore are used for image formation. The grain size and its distribution can be determined from the SEM images. Besides this, the morphological characterization such as surface structure, porosity, and shape of the particle can be determined from SEM. However, one major drawback of SEM is that grains with size less than 20 nm cannot be detected with this technique due to inadequate resolution. Electron gun, magnetostatic lenses functioning as condenser, objective and projector, a fluorescence screen and optical camera unit are the major part of an electron microscope in addition to the built in high voltage stabilized power supply.

The SEM is an instrument provided with a facility to scan the selected region on the specimen using electron beam emerging from condensing lens. The image formed by the objective lens is further magnified by an intermediate lens and finally projected on a fluorescence screen. Emissive, reflective, adsorptive, transmission, X-ray, cathode luminescence and beam induced conductivity models are generally employed. JEOL-JSM-2300 model was employed in the present investigation.
Nature of Sample:  
i) Thin film  
ii) Powder  

Uses:  
i) To study microstructure, grain size, surface morphology  
ii) Resolution of magnification is comparable.  

Limitations:  
i) One cannot study the interior of the sample  
ii) It is difficult to study the microstructure of non-conducting compounds  

2.5 Energy-dispersive analysis by X-rays (EDAX)  

Energy-dispersive analysis by X-rays (EDAX) is an analytical technique used for the elemental analysis or chemical characterization of a sample. This unit is attached to the scanning electron microscope (SEM). It relies on the investigation of an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray spectrum. To stimulate the emission of characteristic X-rays from a specimen, a high-energy beam of charged particles such as electrons or protons, or a beam of X-rays, is focused into the sample being studied. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. As the energy of the X-rays are characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured. Lithium drifted Si-diode, held at liquid nitrogen temperature is used as a detector of the X-rays. JEOL- JSM-2300 model was employed in the present investigation.
Nature of Sample:  
i) Thin film  
ii) Powder  

Uses:  
i) Elemental analysis  

Limitations:  
ii) One cannot get accurate measurement of light elements (small atomic number).  

2.6 Atomic force microscopy (AFM)

Fig. 2.9: Photograph of AFM.

The photograph of the AFM is shown in Fig. 2.9. To solve processing and materials problems, the AFM is being used in a wide range of semiconductors. AFM images show critical information about surface features with unprecedented clarity. The AFM can examine any rigid surface, either in air or with the specimen immersed in liquid. Minor or major differences between smooth surfaces are shown dramatically. The AFM can resolve any tiny features, even single atoms, those were previously unseen. The AFM can examine a field of view larger than 125 microns, so that one can make comparison with other information, e.g. features seen in the light microscope seen by eye. The AFM can also examine rough surfaces, since its vertical range is more than 5 microns. In conventional contact mode AFM, the probe tip is simply dragged across the surface and the resulting image is a topographical map of the surface of the sample and in taping
mode, imaging is implemented in ambient air by oscillating the cantilever assembly at or near the cantilevers resonant frequency using a piezoelectric crystal.

In the present investigation an AFM Nanoscope (Model-NSE, Serial no. 245) digital instrument with a silicon nitride cantilever was used to probe different portions of the film surface in contact mode AFM.

**Nature of Sample:**
1) Thin film
2) Powder

**Uses:**
1) To study surface morphology.
2) To determine surface roughness of the film material.

**Limitations:**
Can cause substantial damage to sample or tearing of surface in contact mode of AFM.

### 2.7 UV–visible spectrophotometer

**Fig. 2.10:** Photograph of UV-visible spectrophotometer.

Optical spectroscopy is often carried out on thin films to verify that the films have a band gap expected from the deposited semiconductor. Since thin films are often nanocrystalline and the most apparent effect of very small crystal size is the increasing the bandgap due to size quantization, absorption (or transmission), optical spectroscopy is
clearly a fast and simple pointer to crystal size, since band gap size correlations have
been made for a number of semiconductor colloids and films.

A spectrophotometer measures transmission but not absorption. Absorption is
usually measured as absorbance, \( A \), which is defined as:

\[
A = \log_{10} \frac{I_0}{I}
\]

where, \( I \) is the intensity of the transmitted light and \( I_0 \) that of the incident light.

The transmission \( T \) is \( T = \frac{I}{I_0} \)

The spectrophotometer measures the transmission, and an absorption measurement is
carried out by converting the transmission into absorbance using these equations. The
optical absorption studies of the films were carried out using Shimadzu-2450
spectrophotometer. The photograph of the UV-spectrophotometer is shown in Fig.2.10.

**Nature of Sample:**

i) Thin film

ii) Powder

iii) Liquid

**Uses:**

i) To determine optical band gap of material

ii) To find out nature of transition (direct or indirect)

iii) To study the transmission

**Limitations:**

i) Reflectance, \( R \) is assumed to be zero

ii) It is difficult to study the microstructure of non-conducting compounds

2.9 Thermoelectric power (TEP) measurement setup

A temperature difference between the two ends of a semiconductor gives rise to an
thermo electromotive force (\( V_S \)). It is found that the generated thermo e.m.f. is
proportional to the temperature difference (\( \Delta T \)) and is given by the relation:

\[
V_S = \frac{S}{\Delta T}
\]

where, \( S \) is the Seeback coefficient also often known as the thermo electric power. The
measurement of thermo e.m.f. is simple and its sign gives vital information about the type
of conduction in semiconductors, whether it is p-type or n-type. Another important
significance of thermo e. m. f. is that, it enables one to calculate the values of Fermi-
energy and carrier concentration. A knowledge of Fermi-energy helps in the determination of various regions viz., impurity conduction, impurity exhaustion and intrinsic conduction regions of a semiconductor.

The photograph of experimental set up to determine thermo e.m.f. is shown in Fig. 2.11. It consists of two contact probes, which acts as a hot junction and cold junction. Between the two junctions a sample is kept. The temperature of the hot surface is raised to a maximum of around 150 °C with help of electric heater. In the case of an n-type semiconducting material, the hot surface becomes positively charged, as it loses some of its electrons. The cold surface becomes negatively charged due to the diffusion of free electrons from the hot portion. Conversely, in a p-type semiconducting material, the hot surface becomes negative, and the cold one positive.

![Fig. 2.11: Photograph of thermo e. m. f. measurement set up.](image)

Thus the type of conduction in a given semiconducting material can be readily being determined from the sign of the thermo e.m.f. The values of thermo e.m.f. have been noted while cooling, because the samples will attain sufficient thermal stability while cooling rather than while heating. The temperatures of the two surfaces have been measured with the help of a thermocouple.

**Nature of Sample**: Thin film  
**Uses**:  
1) To determine type of conductivity.  
2) To find out carrier concentration.
2.10 Gas Sensing System

![Photograph and schematic representation of the gas sensing system.](image)

**Fig. 2.12:** Photograph and schematic representation of the gas sensing system.

The gas sensing system and schematic representation of the gas sensor experimental set up as shown in Fig. 2.12, for testing the sensing performance of the sensors was used in the present study. There are electrical feeds through the base plate. Heater is fixed on the base plate. A sample under test can be mounted on the heater. The Cr–Al thermocouple is mounted to measure the operating temperature. The output of the
A thermocouple is connected to a temperature indicator. A gas inlet valve is fitted at one of the ports of the base plate. The gas concentration inside the static system is achieved by injecting a known volume of a test gas with a gas-injecting syringe. Constant voltage is applied to the sensor and the current is measured by a picoammeter.

**Nature of Sample:**

i) Thin film  
ii) Thick film  
iii) Pellet

**Uses:**

i) I-V Characteristics  
ii) Electrical conductivity  
iii) Sensor characteristics

### 2.11 Preparation of gases

For testing thin films towards various gases, the treatment required to prepare the gases as shown in Table 2.1.

**Table 2.1:** Preparation of gases.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Treatment</th>
<th>By products</th>
<th>Prepared gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen sulphide</td>
<td>FeS + HCl</td>
<td>---</td>
<td>H₂S</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>HCOOH + H₂SO₄ (conc.)</td>
<td>---</td>
<td>CO</td>
</tr>
<tr>
<td>Ammonia</td>
<td>Heat liquor ammonia</td>
<td>---</td>
<td>ammonia vapor</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>CaCO₃ + HCl</td>
<td>CaCl₂</td>
<td>CO₂</td>
</tr>
<tr>
<td>Ethanol</td>
<td>Heat ethyl alcohol</td>
<td>---</td>
<td>ethanol vapor</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>Zn (dust) + 2HCl(dil.)</td>
<td>ZnCl₂</td>
<td>H₂</td>
</tr>
<tr>
<td>Chlorine</td>
<td>KMnO₄ + 2HCl (dil.)</td>
<td>MnO₂, KCl</td>
<td>Cl₂</td>
</tr>
<tr>
<td>LPG</td>
<td>---</td>
<td>---</td>
<td>LPG</td>
</tr>
<tr>
<td>Oxygen</td>
<td>---</td>
<td>---</td>
<td>O₂</td>
</tr>
</tbody>
</table>

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