CHAPTER-2

EXPERIMENTAL METHODS

2.1 Introduction

In this chapter we have discussed the methodology used for the synthesis of tungsten trioxide (WO$_3$) and molybdenum trioxide (MoO$_3$) thin films and nanoparticles and the analytical techniques employed for the sample characterization. Thin film samples and nanoparticles were characterized by Grazing Incidence X-ray diffraction (GIXRD), UV-visible optical spectroscopy, electrical characterization, Field Emission Scanning Electron Microscopy (FESEM), Transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM) and Raman spectroscopy. Thin films and nanoparticles were studied for gas sensing applications towards H$_2$S and ethanol vapors. The details of thin film deposition and the preparation of nanoparticles and their characterization studies are discussed in the following sections.

2.2 Deposition of Thin Films by Thermal Evaporation

Thermal evaporation is a well-known technique for thin-film deposition. The source materials are placed in a boat and evaporated in high vacuum. A thermal evaporator uses an electric resistance heater to melt the material and raise its vapor pressure to a useful range. The coating unit consists of rotary pump and diffusion pump. The rotary pump ejects the air particles from inside the chamber. The diffusion pump is used to create high vacuum which is necessary for the deposition of thin films. The high vacuum allows vapor particles to travel directly to the target object (substrate), where they condense back to a solid state without reacting with or scattering against other gas-phase atoms in the chamber. In this way thin film of particular material is deposited on the substrate. The block diagram of thermal evaporation unit is shown in Fig. 2.1.
Fig. 2.1: Block diagram of thermal evaporation coating unit.

2.2.1 **WO\textsubscript{3} Thin Films**

WO\textsubscript{3} powder (99.9\%, Sigma Aldrich, India) was evaporated on fused silica, silicon wafer, microscopy glass slide and hollow alumina tube substrates. Fig. 2.2 is the photograph of the thermal evaporation coating unit in which deposition was carried out. Prior to each deposition, substrates were ultrasonically cleaned in acetone and ethanol. The deposition chamber was first evacuated to a base vacuum of 1.33x10\textsuperscript{-4} Pa with a diffusion pump. The source to substrate distance was ~0.2 m. No deliberate substrate heating was provided during evaporation. The thickness of films was monitored in situ by a gold-coated quartz crystal oscillator. The average deposition rate was: 0.1-0.3 nm s\textsuperscript{-1} and the boat current was in the range: 60-80 A. The final coating thickness was in the range: 373-732 nm in the three runs which were repeated to verify the reproducibility of thin films’ structure and properties. The deposition time during the runs varied from 800 to 2000 s. Thin film samples on silicon, silica substrates, microscopy glass slide and alumina tube were slowly cooled to room temperature and characterized by different techniques.
2.2.2 **MoO$_3$ Thin Films**

Thin films of MoO$_3$ were grown on fused silica, silicon, microscopy glass slide and hollow alumina tube substrates by thermal evaporation. For this, MoO$_3$ powder of 99.9% purity (Thomas Baker, India) was placed in a molybdenum boat. Prior to deposition, substrates were ultrasonically cleaned in acetone and ethanol. The deposition chamber was first evacuated to a base vacuum of 1.33x10$^{-4}$ Pa with a diffusion pump. The source to substrate distance was ~0.2 m. No deliberate substrate heating was provided during evaporation. The thickness of films was monitored *in situ* by a gold-coated quartz crystal oscillator. The deposition rate varied in the range: 0.1-0.3 nms$^{-1}$ and the final coating thickness was in the range: 700-900 nm in three separate runs, which were repeated to check the reproducibility of thin films’ structure and properties. Blue colored films were obtained on all substrates. Thin film samples on silicon, silica substrates, microscopy glass slide and alumina tube were slowly cooled to room temperature. As deposited films were amorphous and crystallized upon annealing at 623 K for 1 h.
2.3 Nanoparticles by Hydrothermal Technique

2.3.1 WO₃ Nanoparticles

Hydrothermal technique was used to prepare the nanoparticles of WO₃. For this 0.2 g of WCl₆ (99.9% Sigma Aldrich, India) was dissolved in ethanol and distilled water mixture (in the ratio 1:3 by volume). Afterwards this solution was heat-treated in an autoclave at 393 K for 6 h. WO₃ nanoparticles were filtered, and washed several times with distilled water and dried in an oven at 373 K for 1 h. This was followed by annealing at 673 K for 7 h. The material was then slowly cooled to room temperature, mixed with ethyl cellulose 4% by weight and its slurry in iso-amyl acetate was painted on an alumina tube for studying the gas response.

2.3.2 MoO₃ Nanoparticles

Hydrothermal technique was used to prepare the nanoparticles of MoO₃. Nanoparticles were prepared using MoCl₅ 99.9 % purity (Sigma Aldrich, India). MoCl₅ was dissolved in ethanol and distilled water mixture. Afterwards this solution was heat treated in a Teflon lined autoclave at 453 K for 24 h. Subsequently the nanoparticles were centrifuged at 1800 rpm for 4 h, the particles precipitated out, and were washed with ethanol several times and dried in an oven at 373 K for 20 min. This was followed by high temperature annealing at 723 K for 1 h. The material was slowly cooled to room temperature, mixed with ethyl cellulose (4% by weight) and it’s slurry in iso-amyl acetate was painted on an alumina tube. The gas response was studied in H₂S and C₂H₅OH air mixtures.

2.4 Grazing Incidence X-ray Diffraction (GIXRD)

X-ray powder diffraction is an analytical technique used for the study of size, structure, orientation and phase identification of a crystalline material and can provide information on unit cell dimensions. X-ray diffraction is based on constructive interference of monochromatic X-rays from a crystalline sample. It is a non-destructive technique. The X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation and directed towards the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray)
when conditions satisfy Bragg's Law (this law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample). X-ray photons are then detected, processed and counted. Bragg’s Law of diffraction is given as:

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

...(2.1)

Where 

\( d = \) inter planar spacing \\
\( \theta = \) incident angle \\
\( \lambda = \) wavelength of incident X-ray \\
\( n = \) order of diffraction

Grazing Incidence X-ray Diffraction (GIXD) is a scattering geometry combining the Bragg condition with the conditions for X-ray total external reflection from crystal surfaces as shown in Fig. 2.3. Its superior characteristics as compared to the other diffraction techniques accomplish the structural characterization of thin films. The major application of GIXRD is to measure strain relaxation in thin layers and multilayers and it also measures lattice relaxation directly.

![Fig. 2.3: GIXRD geometry of XRD [Ricbard Brundle et al. (1992)].](image)

GIXRD measurements were performed on thin film samples on Bruker D8 Focus X-ray diffractometer (Fig. 2.4) in the grazing incidence geometry with Cu-K\(_{\alpha}\) radiation (\( \lambda = 1.54056 \text{ Å} \)). XRD studies were performed on thin film samples by keeping the incidence angle fixed at 2° and scanning the scintillation detector in the 2\( \theta \) range of
The tube was operated at 40 kV and 35 mA. The diffraction patterns were recorded with scanning speed of 1 s per step.

![Photograph of Bruker D8 Focus XRD system with GIXRD attachment.](image)

**Fig. 2.4:** Photograph of Bruker D8 Focus XRD system with GIXRD attachment.

### 2.5 UV-Visible Spectroscopy

Ultraviolet–visible spectroscopy is basically an absorption or reflectance spectroscopy in the ultraviolet-visible region of the electromagnetic spectrum. It consists of the measurement of attenuation of a beam of light after passing it through a sample or after being reflected from a sample. It can be done at a single wavelength or over a wide spectral range. The basic instrumentation of UV-visible spectrophotometer is shown in **Fig. 2.5**. It is used to measure absorbance, reflectance and transmittance of the sample. Band gap of the sample is determined from absorption measurements. The band gap of a semiconductor is of two types, a direct or an indirect band gap. The minimal-energy state in the conduction band and the maximal-energy state in the valence band are each characterized by a certain crystal momentum (k-vector) in the Brillouin zone. If the k-vectors are the same, it is called a direct gap. If they are
different, it is called an indirect gap. The band gap is called direct if the momentum of electrons and holes is the same in both the conduction band and the valence band; an electron can directly emit a photon. In an indirect gap, a photon cannot be emitted because the electron must pass through an intermediate state and transfer momentum to the crystal lattice.

**Fig. 2.5:** Basic diagram of instrumentation of UV-Visible spectrophotometer.

UV-visible specular reflectance and transmittance spectra were measured for both amorphous and crystalline films on Cecil UV-visible Reflectscan system (Model 3055) in the wavelength range: 200-1100 nm (Fig. 2.6). The thicknesses and the refractive index of films were calculated from the position of interference fringes in the reflectance and transmittance spectra.

**Fig. 2.6:** Photograph of UV-Visible spectrophotometer unit.
The interference fringes in the reflectance and the transmittance spectra were used to determine simultaneously the refractive index, \( n \) and thickness, \( d \) of thin film amorphous and crystalline films. The formula of thickness using successive transmittance fringes is given by [Heavens (1965); Manifacier et al. (1976)]:

\[
d = \frac{\lambda_1\lambda_2}{2(\lambda_1-\lambda_2)n} \quad \ldots(2.2)
\]

where \( d \) is the film thickness, \( n \) is the refractive index, \( \lambda_1 \) and \( \lambda_2 \) are the wavelengths of two consecutive maxima. Similarly the formula of the thickness from fringes in the reflectance spectra is given by:

\[
d = \frac{M}{2n^2} \left( \frac{\lambda_3 \lambda_4}{\lambda_3 - \lambda_4} \right) \quad \ldots(2.3)
\]

where \( d \) is the thickness, \( n \) is the refractive index, \( M \) is the number of fringes (\( M=2 \) for two successive fringes), \( \lambda_3 \) and \( \lambda_4 \) are the wavelength positions of two consecutive reflectance maxima.

By combining equations (2.3) and (2.4), the following formula was obtained and used for the measurement of refractive index:

\[
n = \frac{(\lambda_1 - \lambda_2)M}{\lambda_1\lambda_2} \left( \frac{\lambda_3 \lambda_4}{\lambda_3 - \lambda_4} \right) \quad \ldots(2.4)
\]

Having determined the refractive index, \( n \) from equation (2.4), the thickness, \( d \) of thin film sample was calculated by using equations (2.2) or (2.3).

Finally, the variation of refractive index, \( n \) with photon wavelength, \( \lambda \) was determined from the positions of two successive fringes in the reflectance spectra equation (2.4). The refractive index was fitted with Cauchy’s dispersion formula [Heavens (1965)]:

\[
n(\lambda) = A + \frac{B}{\lambda^2} \quad \ldots(2.5)
\]

The absorption coefficient, \( \alpha \) was calculated from the transmittance and reflectance values by the relationship:

\[
\alpha = \frac{1}{d} \ln \frac{(100-R)}{T} \quad \ldots(2.6)
\]
where $d$ is the film thickness and $R$ and $T$ are % reflectance and transmittance values. WO$_3$ and MoO$_3$ are indirect band gap semiconductors and the band gap was calculated from the Tauc’s relationship [Tauc (1968)]:

$$(\alpha h\nu)^n = A(h\nu-E_g)^\frac{1}{2} \quad \text{....(2.7)}$$

where $A$ is a constant, $h\nu$ is the incident photon energy, $E_g$ is the optical bandgap. For indirect transitions the exponent takes the value $n=1/2$. The optical bandgap of WO$_3$ and MoO$_3$ thin films was determined by plotting graphs between $(\alpha h\nu)^{1/2}$ and photon energy $(h\nu)$, and by extrapolating the straight line section of the plot to the energy axis.

2.6. **Electrical Properties**

The electrical conductivity of thin film samples was measured by two-probe set up by making two Al contacts on the top surface of thin films with a gap of about 1 cm between them. The variation of current with voltage was recorded at a regular interval of 2 V. The conductivity of films was calculated using the formula:

$$\sigma = \frac{l}{Rwd} \quad \text{....(2.8)}$$

where $R$ is the resistance of the film, $w$ is width of the contacts, $l$ is the length of gap between the contact and $d$ is the thickness of the film. The conductivity increases exponentially with temperature and the relation between the conductivity and the temperature is given by:

$$\sigma = \sigma_o \exp \left( -\frac{\Delta E_a}{kT} \right) \quad \text{....(2.9)}$$

where $\sigma$ is the conductivity at a temperature $(T)$, $\sigma_o$ is a constant. From the Arrhenius plots the activation energy, $\Delta E_a$ of film is determined by:

$$\Delta E_a = 1000\text{mk} \quad \text{....(2.10)}$$

where $k$ is the Boltzmann constant and $m$ is the slope of the linear fit curve.

2.7 **Field Emission Scanning Electron Microscopy (FESEM)**

The scanning electron microscope (SEM) utilizes a focused beam of high-energy electrons to generate a variety of signals at the surface of sample as shown in
Fig. 2.7. These accelerated electrons carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions. These signals reveal information about the sample including external morphology (texture), chemical composition, crystalline structure and orientation of the sample [Zaefferer (2011)]. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD) that are used to determine crystal structures and orientations. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. The SEM is also capable of performing analyses of selected point locations on the sample.

Field Emission Scanning Electron Microscope (FESEM) has certain advantages over SEM because of its better resolution than SEM. The source of electrons in SEM is tungsten hairpin or LaB₆ while for FESEM the source is cold, thermal, or Schottky element. SEM does imaging up to micrometer resolution while FESEM can go up to few nanometer range. FESEM has more brightness and its filament has more lifetime in comparison to SEM. Therefore FESEM is better than SEM.

![Systematic diagram of FESEM](image)

**Fig. 2.7:** Systematic diagram of FESEM [Kumar (2011)].
Fig. 2.8 below is the photograph of Zeiss Supra 55 Field Emission Scanning Electron Microscope (FESEM) that was used to analyze the surface morphology of the samples. The samples were coated with a thin gold layer prior to FESEM studies in order to reduce the surface charging effects.

The elemental compositions of samples were measured by Energy Dispersive Spectroscopy (EDS) performed on X-Max 50 mm² detector (Oxford Instruments, UK).

Fig. 2.8: Photograph of Zeiss Supra 55 FESEM.

2.8 Atomic Force Microscopy (AFM)

Atomic force microscope (AFM) is a very high-resolution type of scanning probe microscopy (SPM), with resolution of the order of fraction of a nanometer. Fig. 2.9 illustrates the basic design and working principle of an AFM. It is used to measure the roughness of a surface at high resolution. AFM uses a cantilever with a very sharp tip to scan over a sample surface. As the tip approaches the surface, attractive force between the surface and the tip cause the cantilever to deflect towards the surface. However, as the cantilever is brought even closer to the surface, such that the tip makes contact with it, increasingly repulsive force takes over and causes the cantilever to deflect away from the surface [Binnig et al. (1986)].

AFM operation is usually described as one of three modes, according to the nature of the tip motion:

- contact mode, also called static mode
- tapping mode, also called intermittent contact
• non-contact mode

**Fig. 2.9:** Systematic diagram illustrating the working principle of an AFM.

AFM measurements on thin films were carried out on Parks Instrument XE-70 microscope in contact mode using a scan rate of 1 Hz (**Fig. 2.10**). The cantilever provided with XE-70 was a silicon rectangular shaped cantilever for use in contact mode which had a small spring constant in the range: 0.01 to 3 N m$^{-1}$ to respond with sensitivity to the tiny force between the atoms. The probe tip used in the contact mode had a thickness of about 1 μm to achieve a small spring constant.

**Fig. 2.10:** Photograph of Parks Instrument XE-70 atomic force microscope.
2.9 **Transmission Electron Microscopy (TEM)**

Transmission electron microscopy (TEM) is a technique in which a beam of high energy electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through. The basic schematic diagram of a TEM is given below (Fig. 2.11). An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, photographic film, or a CCD camera. TEM is capable of imaging at a significantly higher resolution than light microscopes, owing to the small de Broglie wavelength of electrons. This enables the instrument's user to examine the fine detail even as small as a single column of atoms, which is thousands of times smaller than the smallest resolvable object in a light microscope. At smaller magnifications TEM image contrast is due to absorption of electrons in the material, thickness and composition of the material. At higher magnifications complex electron-wave interactions modulate the intensity of the image.

![Systematic diagram of TEM](image)

**Fig. 2.11:** Systematic diagram of TEM [Yaacob (2012)].

The size and shape of WO$_3$ and MoO$_3$ nanoparticles were studied on Jeol 200 kV Transmission Electron Microscope (Fig. 2.12). For this, the powdered sample was sprinkled on carbon coated copper grids and the d-spacing of interference fringes was determined. From d-spacing the crystal plane was identified.
2.10 Raman Spectroscopy

Raman spectroscopy is a technique which provides information about the vibrational, rotational and other low frequency transitions in molecules. It is based on inelastic scattering of monochromatic light, usually from a laser source in the visible, near infrared, or near ultraviolet range. Inelastic scattering means that the frequency of photons in monochromatic light changes upon interaction with a sample. Photons of the laser light are absorbed by the sample and then re-emitted. The laser light interacts with phonons or other excitations in the system, resulting in the up or down shift of the energy of the laser photons. The shift in energy gives information about the vibration modes in the system whose schematic is shown in Fig. 2.13. The shifting of the frequency (or wavenumber) of the scattered photons in comparison with original monochromatic frequency is called the Raman effect. The measurement of this shift by Raman spectroscopy can be used to study vibrational properties of solid and liquid samples.
1. A molecule with no Raman-active modes absorbs a photon with the frequency $v_0$. The excited molecule returns back to the same basic vibrational state and emits light with the same frequency $v_0$ as an excitation source. This type of interaction is called an elastic Rayleigh scattering.

2. A photon with frequency $v_0$ is absorbed by Raman-active molecule which at the time of interaction is in the ground vibrational state. The photon’s energy is transferred to the Raman-active mode with frequency $v_m$ and the resulting frequency of scattered light is reduced to: $v_0 - v_m$. This Raman frequency is called Stokes frequency.

3. A photon with frequency $v_0$ is absorbed by a Raman-active molecule, which at the time of interaction, is already in the excited vibrational state. Excessive energy of excited Raman active mode is released, the molecule returns to the basic vibrational state and the resulting frequency of scattered light goes up to $v_0 + v_m$. This Raman frequency is called Anti-Stokes frequency.

Fig. 2.13: The systematic diagram of a Raman spectrometer [Ricbard Brundle et al. (1992)].
When a molecule is in an electric field $E$, the electron cloud and nuclei become polarized resulting in an induced dipole moment $P$. The size of the dipole moment induced by a field of magnitude $E$, classically is given by the polarizability, $\alpha$ of the molecule:

$$P = \alpha E \quad ...(2.11)$$

The intensity of the Raman scattering is seen to be proportional to the derivative of the polarizability(squared): thus, the polarizability must change linearly with vibrational motion for Raman scattering to occur. The greater the change, the more intense is the Raman scattering. If $\alpha$ is unchanged or at a minimum/maximum, there is no Raman scattering. Since $P$ and $E$ are vector quantities, the polarizability tensor, $\alpha$, is defined by nine coefficients (second rank tensor). However, because $\alpha_{xy} = \alpha_{yx}$, $\alpha_{xz} = \alpha_{zx}$, $\alpha_{yz} = \alpha_{zy}$ there are only six independent coefficients.

![Fig. 2.14: Photograph of Renishaw inVia Reflex micro Raman spectrometer.](image)

Raman studies were performed on thin film and powdered samples of WO$_3$ and MoO$_3$ on Renishaw inVia Reflex micro Raman spectrometer equipped with a 514.5 nm and 488 nm Ar ion laser (50 mW), 2400 lines/mm diffraction grating, a suitable edge filter for recording the Stokes spectra and a CCD detector (Fig. 2.14). Measurements were done at room temperature in the backscattering geometry, in the wave number range of 30 to 2000 cm$^{-1}$ and at a spectral resolution of 1 cm$^{-1}$. 

68
2.11 Magnetic Properties

The dc magnetization (M) measurements were carried out on WO$_3$ nanoparticles as a function of temperature (T) and magnetic field (H) on a Vibrating Sample Magnetometer (VSM) (Cryogenic Ltd., UK). Magnetization as a function of magnetic field was recorded over +50 to −50 kOe applied magnetic field at various temperatures.

For zero-field-cooled (ZFC) magnetization measurements, the sample was first cooled from room temperature down to 5 K in zero magnetic field. After applying the magnetic field at 5 K, the magnetization was measured in the warming cycle with field on. Whereas, for field-cooled (FC) magnetization measurements, the sample was cooled in the same field (measuring field in the ZFC case) down to 5 K and the FC magnetization was measured in the warming cycle under the same field.

2.12 Gas Sensing Properties

To study the gas sensing properties, films were prepared on an alumina tube and two Al contact were made on the top surface of the film and nichrome coil was inserted inside the tube, the former acted as a heating element. The gas sensor was put in a dessicator of volume 10 liters (Fig. 2.15). The upper half of the desiccator had a provision for introducing known volumes of H$_2$S and other gases with gas tight microliter syringes.

![Fig. 2.15: Schematic of the gas sensor apparatus.](image)

Electrical resistance of films was measured by applying 10 V DC across the Al electrodes and current was measured with an auto-ranging digital picoammeter (Keithley Model 485) connected in series with the sensor element. The sensor signal (response), S, is defined as:
Where $R_a$ and $R_g$ are sensor resistances in air and gas-air mixtures respectively. Since Al electrodes were on top, our measurements represented changes in the surface properties. The sensor characteristics were measured at six operating temperatures of 433 K, 453 K, 473 K, 493 K, 523 K and 550 K. To study gas response of the sensor elements, known volumes of $\text{H}_2\text{S}$ and $\text{C}_2\text{H}_5\text{OH}$ vapours were introduced into the test chamber and changes in current flowing through the sensing element were continuously monitored with an auto-ranging digital picoammeter. The time taken for the current to rise to its maximum value after the introduction of gas was taken as the 100% response time. To measure the recovery time of the sensor, we opened the top half of the test chamber, allowing the surrounding air to flow into the lower half containing the sensor, the time taken for the current to decrease to its initial value was taken as the 100% recovery time.

The following parameters are important for gas sensing:

**Sensor Signal:** It defined as the ratio of resistance of the sensing element in the presence of test gas to the value of its resistance in air.

**Sensitivity:** It is defined as the ratio between a small change in sensor signal to a small change in the input signal (gas concentration).

**Selectivity:** It is the ability of a sensor to detect a target gas without being affected by the presence of other interfering gases.

**Response time:** It is typically defined as the time taken by the sensor to attain the 90% of maximum value of the output signal after being exposed to a target gas.

**Recovery time:** It is typically defined as the time taken by a sensor to come back to 90% of its original state when the target gas is removed.
Bibliography


