Chapter III

Experimental

3.1 Characterization of the samples by X-ray diffraction

Identification of phases in samples was carried out by X-ray diffraction. The instrument used was D 500 model of M/s Siemens Germany, Cu K$_{\alpha1}$ ($\lambda = 1.5406$ A$^\circ$) radiation with nickel as the filter was used. Bulk samples were finely ground using a mortar and pestle, mounted on a sample holder (which does not show any X-ray diffraction peaks in the region of studies) and used for the diffraction studies. Samples in the form of thin films over substrates were also kept on the sample holder and studied. Normal scan rate employed was 0.05$^\circ$/sec while in the case of slow scan experiments the scan rate employed was 0.5$^\circ$/min.

3.2 Electrical characterization of materials

Electrical conductivities of MoO$_3$ and WO$_3$ and oxide systems based on these binary oxides were measured in this work. A frequency response analyser (Model SI 1255 of Solartron, M/s Schlumberger, UK) coupled with an electrochemical interface (Model 1286 of Solartron, M/s Schlumberger, UK) in the frequency range of 1 Hz - 1MHz was used for this purpose. Normally an applied voltage of 250 mV is used in all the measurements. Samples in the form of powder were compacted into pellets by compressing them using die and plungers made of WC and a pellet press. The compaction was generally carried of at a pressure of $\sim$ 4 tons. The pellets were generally 10mm in diameter and 2 to 2.5 mm in thickness. The pellets were then sintered at an appropriate temperature and these sintered pellets were used for electrical conductivity measurements. The set up used for mounting a pellet and measuring its conductivity is shown in Fig.3.1. This consists of a one end closed ($\sim$ 12.5 mm OD and 11mm ID) quartz tube having a cut-out at the closed end. The sample pellet sandwiched between two platinum electrodes was placed at the bottom of this quartz tube through the cut-out. Alumina discs were placed below the bottom electrode and on top of the upper electrode. The open end of the quartz tube was secured to a stainless steel (SS) coupling through a Veeco-type fitting. Two springs, which hang from the (SS) coupling, were connected to this quartz tube using two hooks provided in the tube. Another quartz tube ($\sim$ 10 mm dia) closed flat at both ends was placed over the stack of sample pellet and alumina discs. An additional spring was kept between the SS coupling and the top of the closed inner quartz
Fig. 3.1: Schematic representation of the set up employed for electrical conductivity measurements
tube. This arrangement of springs kept the platinum electrodes well pressed on the sample pellet. Platinum wires of 1 mm thickness that were attached to the platinum electrodes served as electrical leads. These leads were insulated using alumina beads and tubes, and were taken through O-ring sealed fittings provided at the top of the SS coupling. A stainless steel sheathed type K thermocouple was positioned close to the sample pellet by using another O-ring sealed fitting present in the SS coupling. This sample holder assembly was placed inside a bigger quartz tube (~ 45 mm diameter), which was also connected to the SS coupling through an O-ring Seal. The SS coupling had tubes for gas inlet and outlets provided with needle valves. When Au, Ag and graphite electrodes were to be used, discs made of the desired material were placed between the sample pellet and platinum electrodes and measurements were made. The whole set up was kept inside the isothermal zone of a vertical resistance furnace. The temperature of the sample was controlled to ± 1 K at a chosen temperature using a PID controller.

3.3 Characterization of thermal behavior of samples

In the present work thermal analysis studies were carried out using a simultaneous thermogravimetry/differential thermal analysis (TG/DTA) instrument of M/s Rheometric Scientific, UK (Model STA 1500). Mass of the sample taken and the heating rate employed varied from experiment to experiment and they are described in the respective chapters. Experiments were carried out in different gaseous atmospheres either in static or dynamic conditions. The flow rate of the gas under dynamic conditions was generally 30 ml/min. When the experiments were carried out in the presence of large fraction of NH₃, air was suitably purged through the instrument so that the corrosive attack of the instrument by NH₃ can be avoided. The reference material used was α-Al₂O₃.

Differential scanning calorimetric experiments were carried out using a Model calorimeter supplied by M/s Mettler Toledo, USA. A known quantity of the sample (~50 mg) which was sealed inside a thin aluminium crucible was used as sample. An empty aluminum crucible was employed as reference.

3.4 Fabrication of sensors

3.4.1 Porous pellet sensors

For making porous pellets to be tested as sensors, the sample powder was first mixed with polyvinyl alcohol binder. The powder was then made into pellets of 10
mm diameter and 2 to 3 mm thickness, using the pellet press. The pellets were then slowly heated to 573 K to remove the binder followed by sintering at an appropriate temperature to yield rigid porous pellets. The porosity of the pellets was measured using pycnometry.

3.4.2 Thin film sensors

In the present work thin films of MoO₃ and WO₃ were made using Pulsed Laser Deposition (PLD) technique and tested for their gas sensing properties.

Pulsed Laser Deposition is a thin film growth technique in which photonic energy is coupled to a target of bulk starting material via electronic process [67]. In this technique, high intensity laser pulses of short wavelength are focused using focusing lenses on the surface of the target. On the surface, they are partially absorbed and the absorbed radiation is immediately converted into electronic excitations. The excited electrons transfer their energy to the lattice within a few pico seconds resulting in heating of the surface to a depth of 1/α, where α is the characteristic optical absorption coefficient of the material. The thermal diffusion length for a material, \( l_{\text{ther}} \) is given by

\[
    l_{\text{ther}} = 2\sqrt{Dt}
\]

where D is the thermal diffusivity and t is the pulse duration. If thermal diffusivity 'D' is smaller than 1/α, then the sample will be heated down to a depth of 1/α independent of the pulse duration. Because of the high energy deposited, the volume of the material that gets heated up is converted into vapour and a plume is generated. By positioning a substrate at a suitable location, films of the target material can be obtained. Substrate can be maintained at elevated temperatures so as to enhance film growth process. Pulsed laser deposition can be employed for deposition of films of metal and ceramic materials. Most of the materials show strong absorption in the wavelength range of 200 nm to 400 nm. Hence, if a laser light of wavelength in this region is used, the penetration depth into the target material will be short and removal of thin layers would be possible. In the present work, thin films of sensor materials were made using a pulsed excimer Laser, (KrF; \( \lambda = 248 \text{ nm} \)) Lumonics, Canada) operating at 20 Hz.

The layout of the PLD assembly used in this work for making thin films is shown in Fig.3.2. The laser from the source is passed through an optical window of a SS vacuum chamber and is focused on the surface of the target. The chamber is pumped down by a Turbo Molecular Pump (TMP) and has provisions to let in gases with precisely known flow of gases. Using a butterfly valve mounted between the vacuum chamber and the TMP, and by maintaining a constant flow of oxygen gas into the

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Fig. 3.2: Lay out of PLD assembly
chamber, the chamber could be maintained at different pressures of oxygen. Through the ports provided in the chamber, target and substrate holders are mounted. The target holder is rotatable using a DC motor so that ablation is not confined to one spot on the target but uniformly spread out on its surface. Interaction of laser beam with the target material causes the ejection of luminous plume as shown in the Fig.3.3. Material from the laser plume is then allowed to re-condense on a substrate attached to a substrate holder. The substrate can be heated to a desired temperature by means of a heating facility provided in the substrate holder and this enhances the film growth process on the substrate. Conditions such as substrate temperature, oxygen partial pressure, energy density at the laser spot etc., need to be optimized for growth of films and they varied for MoO₃ and WO₃. The conditions employed in each case are presented in the respective chapters. Thickness of the films deposited was measured by means of a surface profiler (model Dektak-3 of M/s Veeco/Sloan Technology, USA). Substrates used for deposition of thin films were polycrystalline alumina and quartz.

3.5 Testing of Sensors

The schematic of the glass chamber used for sensor studies is shown in Fig.3.4. Total volume of the glass chamber is 700 ml and is provided with a port for injecting the gas inside the chamber through a chromatographic septum. It has inlet and outlet provisions to enable purging out the gas ambient from the chamber after completion of a test with air flow. Sensors either in the porous pellet or thin film forms were mounted on a special holder which was placed inside the chamber through a port as shown in the Fig.3.4. The sensor holder has provision to make electrical contacts (Pt) to the electrodes of the sensor. Silver wires attached to these Pt electrical contacts are brought out of test chamber through the sensor holder. The sensor holder also houses a thermocouple for accurate measurement of the temperature of the sensor. The chamber was kept inside a horizontal resistance furnace and was heated to a desired temperature for carrying out the gas sensing studies. The temperature of the sensor was controlled at the desired temperature within ±1K using a PID controller.

Semiconducting oxide sensors require non-interacting metallic electrodes to monitor the change in conductivity during its sensor action. In the case of porous pellet sensors, these electrodes can be made by sandwiching the pellet in between metal plates/foils of similar dimensions. In this work platinum foils were used as electrodes for
Fig. 3.3: Interaction of laser plume with the target material and ejection of luminous plume from the material.
Fig. 3.4 : Schematic representation of sensor set up used for studying the sensing characteristics of the samples
porous pellets sensors. While studying gas sensing characteristics of pure MoO₃, electrodes made of Au and graphite were also used.

Metal oxides such as MoO₃ are characterized by their high resistivity. When they are made into thin films, the film exhibits very high resistance which poses measurement problems. To overcome this, special type of electrode system called interdigitated electrode (IDE) was used. Sensor film was deposited over these IDEs. These electrodes were also made by pulsed laser deposition. For depositing IDEs the substrate was masked with a stainless steel mask of interdigitated pattern and platinum metal was deposited by ablating a high-density platinum target. The photograph of both the mask and the pattern after deposition of platinum on the surface of the substrate is shown in Fig.3.5.a and 3.5.b respectively. Using this deposition technique, interdigitated electrodes with a gap of 400μm between two adjacent electrodes could be made.

The sensing action of a semiconducting oxide sensor material towards an analyte gas is measured in terms of the variation in the conductance of the material and the parameter measured is the resistance of the material present either as thin films or as porous pellet. A typical experiment to measure the sensing characteristic of the sensor towards an analyte gas is as follows. At a chosen temperature, the sensor is equilibrated till a steady base line resistance in air is observed and the resistance of the sensor was measured using an electrometer (Model No. 7150 of M/s Solartron, UK). Adequate quantity of the analyte gas is then injected into the test chamber so that resulting concentration is in the desired concentration level in air (ppm). Change in resistance of the pellet is measured as a function of time till a steady value is reached. The chamber is then purged with air and the sensor is allowed to reach the initial value of the resistance before the next experiment is carried out. This experiment is repeated for other analyte gases of interest. Sensitivity is defined in different ways in literature and this aspect was already discussed in Chapter-I. In the present work, percentage sensitivity is used and is calculated using the formula

\[
\% \text{Sensitivity} = \left( \frac{R_a - R_d}{R_a} \right)
\]

where \(R_a\) = resistance of sensor in clean air and \(R_d\) = resistance of the sensor in air containing the analyte gas.

As discussed in Chapter-I, characteristics of a sensor towards a particular analyte gas vary with temperature. By measuring the sensitivities as a function of
Fig. 3.5: (a) Mask used for making Interdigitated electrodes (b) Electrode pattern deposited over the substrate
temperature for a fixed concentration of different gases of relevance including the target analyte gas, optimum temperature for operation of the sensor for sensing the analyte gas can be derived. For a sensor material the temperature at which sensitivity is maximum is generally different for different analyte gases. In our studies, sensing characteristics of a sensor for different analyte gases viz. NH₃, H₂ and LPG were first studied in the temperature range of 500K to 673K. Sensitivity of the sensor as function of analyte gas concentration was then studied at the temperature where the sensor showed maximum sensitivity towards a particular analyte gas compared to other analyte gases.

The response and recovery times of a sensor towards an analyte gas are very important parameters that decide the utility of the sensor. In this work responsivity time is taken as the time taken by the sensor for attaining the steady state resistance from its initial resistance in clean air after exposure to air that contains the analyte gas. Recovery time is defined as the time taken for the complete recovery of resistance of the sensor to its initial value in air when it is exposed to clean air after its exposure to the air containing the analyte gas. As in the case of response time, recovery time of a sensor towards an analyte gas differs depending upon the sensor material and the operating temperature.

3.6 Characterization of samples by spectroscopic methods

X–Ray photoelectron spectroscopy

Valence state of elements in the sensor material before and after its exposure to the analyte gases were investigated using X–ray Photoelectron Spectroscopy. The instrument used was VGESCA LAB MK II apparatus with 150 mm hemispherical analyzer at a band pass energy of 20 eV. X–ray used was Al Kα (1486.6 eV). Samples were used as fine powders supported on Indium foil. The measurements were carried out at room temperature and at a pressure of 2.3×10⁻⁸ mbar. The binding energies of electrons were calibrated against the C1s line assumed to correspond to 284.6 eV.

Electron Paramagnetic Resonance

In the present investigation EPR spectrum of MoO₃ samples were recorded using Bruker ESP – 300 spectrometer operated at X–Band frequency (9.5 GHz using 100 KHz field modulation). Diphenyl picryl hydrazyl radical (DPPH) was used as a field marker. Measurements were carried out at room temperature.
**Infrared Spectroscopy**

Infrared spectra were recorded for the samples prepared from ammonium heptamolybdate tetrahydrate and subsequently stored under ambient conditions using FTIR MB-100 spectrometer of M/s Bomem, Canada. IR spectra were also recorded for a) the MoO$_3$ samples heated at different temperatures viz. 373, 473, and 573 K in flowing argon atmosphere for 5 h and b) the samples which were first heated at 573 K under flowing argon and then stored in ambient air for a few days. Samples for IR spectra were prepared in argon atmosphere glove box by dispersing about 1 - 2 mg of MoO$_3$ in ~ 100 mg moisture free KBr (spectroscopy grade of M/s E-Merck, Germany) and compacting as thin discs.

**3.7 Morphological Characterization of samples**

**Scanning Electron Microscopy**

Morphology of the MoO$_3$ and Ag$_6$Mo$_{10}$O$_{33}$ specimens before and after exposure to NH$_3$ containing air were investigated by scanning electron microscopy using a Philips Scanning Electron Microscope, model No. XL 30. Grains which exhibited morphological changes were subsequently investigated by Energy Dispersive X-ray Analysis (EDAX) for evaluating possible composition variations as result of the chemical interaction. A Philips Energy Dispersive X-ray Analyzer, Model, NEWXL 30 was used for this purpose.

**Transmission Electron Microscopy**

The morphology and particle size of mixed systems of MoO$_3$ – TiO$_2$ were determined from the micrographs obtained from a JEOL 200 CX, 200 kV transmission electron microscope (TEM) having 2 Å$^6$ resolution. The crystallites were dispersed in butanol by sonication and deposited on a carbon grid. Those crystallites projecting out through the holes in the carbon grid were selected and oriented with respect to the electron beam using the goniometer.

**Atomic Force Microscopy**

Morphology of the laser ablated thin films of MoO$_3$ before and after annealing in air was studied using atomic force microscopy. Model NSE of M/s Digital Instruments USA was used for this purpose.