Chapter-II

Experimental Details and Characterization Techniques

CHAPTER II

EXPERIMENTAL DETAILS AND CHARACTERISATION TECHNIQUES

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## Experimental Details and Characterisation Techniques

2.1   INTRODUCTION

Over the last two decades there has been progressive interest in fabrication of thin solid films of electrochromics materials. Now, it is well known that thin films of many transition metal oxides exhibit electrochromism. This kind of materials has significant place in production of "smart windows" designed for architectural purposes to control light transmittance. The application of these "smart windows" is quite wide and it is implemented into different kind of vehicles as aircrafts, spacecrafts etc. In addition different kind of devices, like smart window films were applied in fabrication of variable mirrors, photo-imaging systems, large area displays, solar energy collectors, in rear view mirrors for cars, to reduce excessive reflected light by dark shading induced by an electric signal, in cars to prevent the indoor heating by sun and more have been demonstrated.

Electrochromic windows are the most popular area of switching technology. Over the 10 years of the last century about 200 US and international patents have been granted on electrochromism. The smart windows are fabricated with five (or less) films- coatings to transparent conductors (TC) , electrolyte or ion conductor (IC) , counter electrode (CE) , and electrochromic film(EF): Glass/ TC / ion storage/ IC/ EF/TC/Glass

The device is designed in such a manner that provides intercalation and deintercalation with applied potential The chemical background of the process is usually described with following reaction for catholically coloring substances

MO_x (transparent) + yA^- + ye^- $\longrightarrow$ A_yMoO_x (Colored)

Intercalation

A_yMoO_x (colored) $\longrightarrow$ MO_x (transparent) + yA^- + ye^-
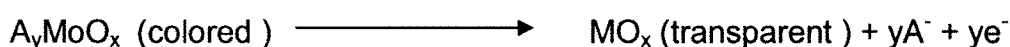
Deintercalation

Where,

A^+ is H^+, Li^+, Na^+, Ag^+.....

This is a simplified expression for possible reaction only for explaining the basic principles of electrochromism. In reality it is more complicated process and the electrochromism of different material is strongly related to the method of preparation, i.e. it is affected by structure, stoichiometry, binding condition and water content in the films. The no. of techniques has been developed for preparation of thin electrochromic films of molybdenum oxide such as thermal evaporation, sputtering and chemical vapor deposition. Electrochromic materials produced by this method show good characteristics. The molybdenum oxide thin solid films can be also fabricated by using some chemical methods like spray deposition, sol-gel deposition and electrodeposition.

The chemical bath method has the benefits of be easily realizable from the point of view of industrialization especially on large area devices, with the required electrochromic properties. The deposition process in the chemical bath goes through a colloidal state and it is well known that colloidal state of molybdenum oxide can be prepared from aqueous solution of maledict acid (H_2MoO_4) but this precursor does not give stable solutions upon hydrolysis and consequently rapid condensation and precipitation occurs if the solution is not stabilized. In the proposed method this problem is revealed over.

During last 10 years the global temperature risen by several degrees. The relatively inexpensive way of prevention of extra heat may become vital. The electro chromic material in future will take more significant place in these applications. In this work we presents a new chemical bath method for deposition of nanocrystalline thin solid films of molybdenum oxide on glass substrate coated with fluorine doped tin oxide. The method is simple and very fast. The easy preparation of these thin films encourage us to continue using this kind of system to produce vanadium doped molybdenum electro chromic oxide thin film

2.2   THIN FILM DEPOSITION TECHNIQUE

2. 2.1 Thin film deposition chamber

This section deals with fabrication of thin film deposition assembly and associated accessories. A thin film deposition chamber was designed and fabricated in our laboratory whose dimensions are 1.8X 0.8X 1.0 m. thin film deposition chamber maintains a clean, ambient atmosphere necessary for the deposition of thin films and protects the deposition system from the physical hazards. Cross-sectional view of deposition bath essentially consist of constant speed AC gear motor, oil bath and constant temperature system with magnetic stirrer, reaction container, substrate holder and temperature controller etc. shown bellow:
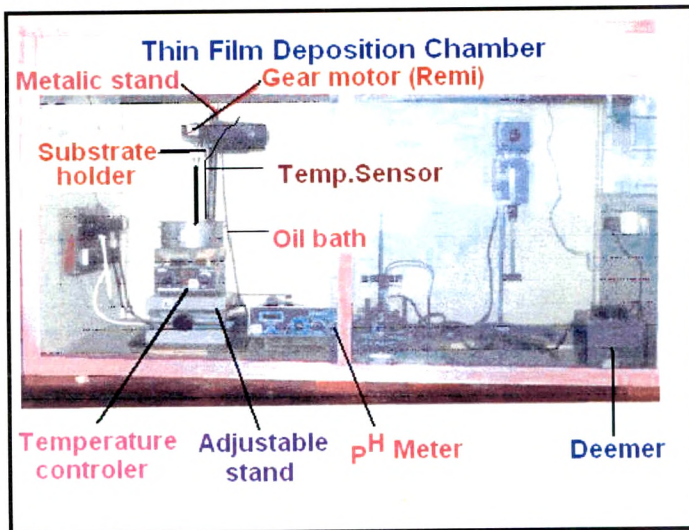

Fig.2.1 Thin film deposition chamber

2. 2.2. Constant temperature bath

The constant temperature bath of the dimension 3½ x 6' having temperature controller attachment was fabricated in our laboratory. In order to obtain uniform deposition temperature, 750 ml paraffin oil was kept in a bath. The constant temperature bath was then agitated using Remi-magnetic stirrer,

which was kept on movable stand for adjustment of the height to a required level.

2.2.3 Reaction container

The reaction container of the dimension 100 mm x 60 mm having 150 ml capacity was fabricated using borosil glass in University Scientific Instrumentation Centre (USIC), Shivaji University, Kolhapur. The reaction mixture was taken into this reaction container provided with magnetic needle at the bottom of the container. The container was kept in constant temperature bath. In order to avoid non-uniform heating of reaction container, glass ring was used to rest the reaction container. Glass ring was used to rest the reaction container in an oil bath.

2.2.4 Constant speed motor

A single phase A.C. gear motor type RU-56-36-HP, 1/8 Amps.1 was used for rotating the substrate at specified speed in a reaction container. A dimerstat-cum-regulator was provided to the motor for better speed control. The speed of the motor can be varied from 40 rpm to 100 rpm. The motor was fitted to a metallic stand having sufficient height to adjust the position of A.C. gear motor. A rotating shaft-cum-metallic rod of the dimension 20 x 0.5 mm was fitted to the motor and other end of the rod was attached to a substrate holder.

2.2.5 Substrate holder

Substrate holder is fabricated by using bakelite material of appropriate thickness in our laboratory and used for holding the substrate in horizontal position as shown in figure. The position of the motor was adjusted to a drilling machine stand in such a way that more than 2/3 portion of the substrates will dip into the solution container and substrates are exactly perpendicular to each other. The substrates were fitted to the bakelite disc of 5.3 cm in diameter and 1 cm thick with 4 slots cut into the disc in such a way that the rotating substrates did not touch the wall of the solution container, which may cause serious damage to the films. Thus continuous and proper bulk churning of the solution in the reaction container was made possible which helped in depositing uniform and better orientation of the crystallites.
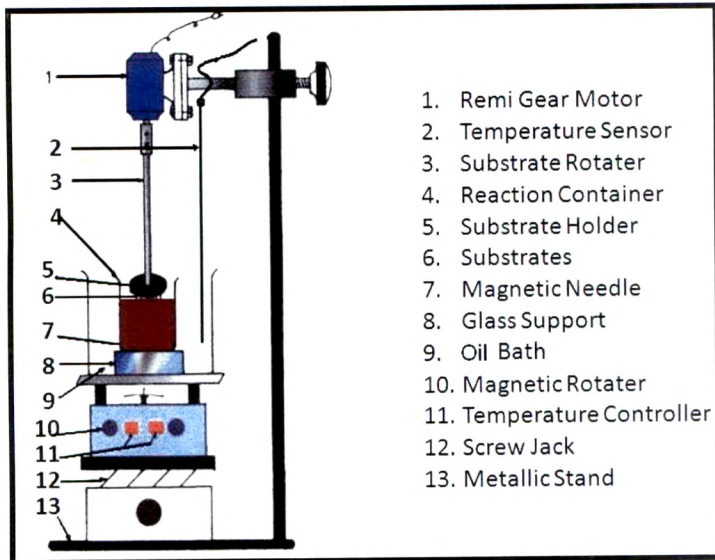
1. Remi Gear Motor
2. Temperature Sensor
3. Substrate Rotater
4. Reaction Container
5. Substrate Holder
6. Substrates
7. Magnetic Needle
8. Glass Support
9. Oil Bath
10. Magnetic Rotater
11. Temperature Controller
12. Screw Jack
13. Metallic Stand

Fig.2.2 Cross sectional view of thin film deposition assembly
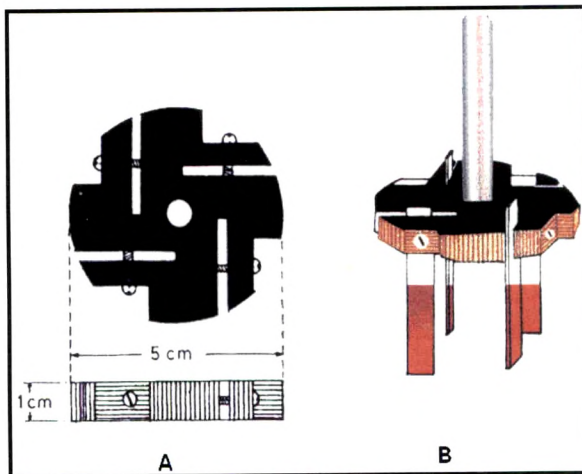

5 cm

1 cm

A

B

Fig. 2.3.a. Design of the substrate holder

Fig. 2.3.b. Cross sectional view of substrate holder

2. 2.6 Deposition of thin films

The glass substrate for the deposition of molybdenum oxide films were FTO coated substrates commercially available. Molybdenum oxide films were deposited from a chemical bath with optimized composition and process conditions.

2.3   Preparation of solution

2.3.1 Molybdenum oxide thin films

For the deposition of molybdenum oxide thin films 1.5 g of sodium molybdate were weighed and placed in a 100 mL beaker the salt was dissolved in 70 mL distilled water . For frequent performance of the deposition we encourage preparation of a stock solution. In the prepared solution 3 mL slightly acidic diethyl sulphate was added. After stirring the main volume of the sulphate remains insoluble as a second phase, in this order, the bath solution is prepared for film deposition.

2.3.2 Vanadium doped molybdenum oxide thin films

For the deposition of Vanadium doped molybdenum oxide thin films about 1.5 g of sodium molybdate were weighed and placed in a 100 mL beaker the salt was dissolved in 70 mL distilled water. For frequent performance of the deposition we encourage preparation of a stock solution. In the prepared solution 3 mL slightly acidic diethyl sulphate was added. After stirring the main volume of the sulphate remains insoluble as a second phase, then 1% of ammonium meta vanadate is added in this order to make the series of vanadium doped molybdenum oxide bath solution for film deposition.

2.3.3   Deposition of molybdenum oxide and Vanadium doped molybdenum oxide thin films

The glass substrates are immersed and the solution is heated on the plate of a magnetic stirrer. With the progressive increase in temperature, the $(C_2H_5)_2SO_4$ becomes more soluble. When the temperature reaches 75- 80 °C, all the $(C_2H_5)_2SO_4$ is dissolved. As a result of the hydrolysis of $(C_2H_5)_2SO_4$ the solution becomes acidic, and with the further increase in the temperature to a maximum of 95°C, the molybdenum oxide starts to deposit on the glass

substrates after a couple of minutes. The film thickness depends on the deposition time, which can vary from 2 to 15 min. The maximum thickness of the films from one bath was about 90 nm. The characterized thin films had thickness below 90 nm. It was found that the temperature needed for the beginning of the deposition is variable, depending on the concentration of the solute (at-starting time of deposition for solution with c = 0.1 mol/dm3, tb-starting time of deposition for solution with c = 0.2 mol/dm3.

2.4 Preparative parameters
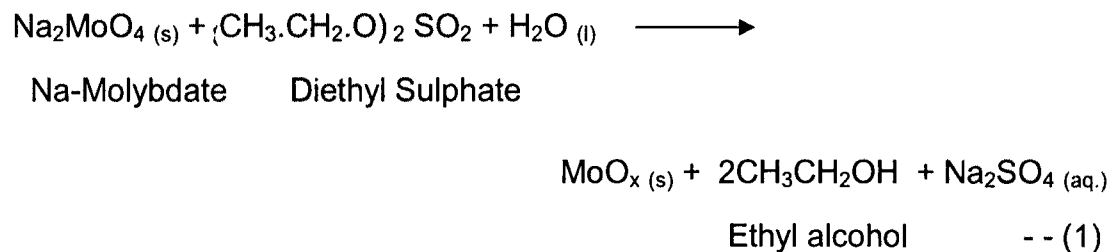
| Film Composition	MoO$_3$	Vanadium Doped MoO$_3$
Bath Composition	1.5 gm sodium molybdate + 3 ml diethyl sulphate + 70 ml distilled water	1.5 gm sodium molybdate + 3 ml diethyl sulphate + 70 ml distilled water + 1% ammonium meta vanadate
Deposition Temp.	90-95°C	90-95°C
P^H of the reaction mixture	7.4	6.5
Deposition Time	15 min.	15 min.
Substrate rotation	50 $\pm$ 2 rpm	50 $\pm$ 2 rpm

2.5 Reaction Mechanism and kinetics of thin film formation

The overall chemical reaction of the deposition process may be written as:

The reactions involved during the growth of Molybdenum oxide thin film are,

$$Na_2MoO_{4\ (s)} + (CH_3.CH_2.O)_2\ SO_2 + H_2O_{(l)} \longrightarrow$$

Na-Molybdate   Diethyl Sulphate

$$MoO_{x\ (s)} + 2CH_3CH_2OH + Na_2SO_{4\ (aq.)}$$

Ethyl alcohol   - - (1)

The reaction rate is controlled by the pH value. The H$_3$O$^+$ concentration depends on the reaction rate of the following reaction:

$$(CH_3.CH_2.O)_2\ SO_2 + 3\ H_2O \longrightarrow 2\ CH_3CH_2OH_{(aq.)} + H_3O^+ + SO_4^-\ (aq.) - -(2)$$
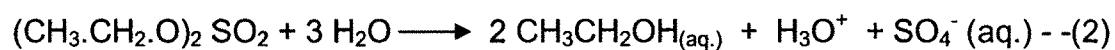
During this reaction diethyl sulphate undergoes hydrolysis by increase of H_3O^+(aq) concentration and pH decrease. The process is highly dependent on temperature and its increased value provides favorable increase of solubility of diethyl sulfate. Molybdic acid is slightly soluble in water and with increase of the concentration of H_3O^+ (aq) at elevated temperature precipitates as MoOx

$$MoO_4^{2-} {}_{(aq.)} + 2 H_3O^+ \longrightarrow MoO_3 {}_{(s)} + 3 H_2O \quad \text{------ (3)}$$
Thin film
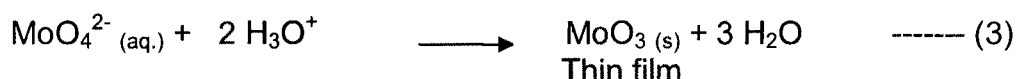
Most of the synthesized MoO_3(s) in the bath is precipitated and just a small part is a part of the thin solid film.

2.6 Characterisation of MoO₃ thin films

2. 6.1. Introduction

In the past years the advancement in science has taken place mainly with the discovery of new materials. Characterization is an important step in the development of exotic materials. The complete characterization of any material consists of phase analysis, compositional characterization, structural and surface characterization, which have strong bearing on the properties of materials. In this section different analytical technique used to characterize our thin films are described with relevant principles of their operation and working.

2.6.2. Optical absorption

The equilibrium situation in semiconductor can be disturbed by generation of carriers due to optical photon absorption. Optical photon incident on any material may be reflected, transmitted or absorbed. The phenomena of radiation absorption in a material is all together considered to be due to 1) inner shell electrons, 2) valence band electrons, 3) free carriers including electrons and 4) electrons bound to localized impurity centers or defects of some type. In the study of fundamental properties of the semiconductors, the absorption by the second type of electrons is of great importance. In an ideal semiconductor, at absolute zero temperature the valence band would be completely full of electrons, so that electron could not be excited to higher energy state from the valence band. Absorption of quanta

of sufficient energy tends to transfer of electrons from valence band to conduction band.The optical absorption spectra of semiconductors generally exhibits a sharp rise at a certain value of the incident photon energy which can be attributed to the excitation of electrons from the valence band to conduction band (may also involve acceptor or donor impurity levels, traps, excitons etc.) The conservation of energy and momentum must be satisfied in optical absorption process.

Basically there are two types of optical transitions that can occur at the fundamental edge of the crystalline semiconductor, direct and indirect. Both involve the interaction of an electromagnetic wave with an electron in the valence band, which is rose across the fundamental gap to the conduction band. However, indirect transition involves simultaneous interaction with lattice vibration. Thus the wave vector of the electron can change in the optical transition. The momentum change being taken or given up by phonon. Direct interband optical transition involves a vertical transition of electrons from the valence band to the conduction band such that there is no change in the momentum of the electrons and energy is conserved as shown in Fig. 2.4 (a). The optical transition is denoted by a vertical upward arrow. The forms of the absorption coefficient 'α' as a function of photon energy hν depend on energy of N (E) for the bands containing the initial and final states. For simple parabolic bands and for direct transitions [1-2].

$$\alpha = A (h\nu - E_g)^n / h\nu \qquad\qquad 2.1$$

Where A is a constant depending upon the transition probability for direct transition, n = 1/2 or 3/2 depending on whether the transition is allowed or forbidden in the quantum mechanical sense. E_g is the optical gap.

Let's visualize a situation given in Fig. 2.4 (b) where interband transition takes place between different k–states. Since these must satisfy the momentum conservation laws, the only way such transition can take place is through the emission or absorption of a phonon with wave vector q i.e.

$$k' \pm q = k + K \qquad\qquad 2.2$$

The transitions defined by equation (2.2) are termed as indirect transitions. For indirect transitions.

$$\alpha = A (h\nu - E_g)^n / h\nu \qquad\qquad 2.3$$

For allowed transition n = 2 and for forbidden transitions n = 3.

The band gap energy 'Eg' is determined by extrapolating the linear portion of the plot of $(\alpha h v)^n$ against hv to the energy axis at $\alpha = 0$.

While discussing the optical absorption edges observed in amorphous semiconductors the following assumptions are made: (a) the matrix elements for the electronic transitions are constant over the range of photon energies of interest and (b) K–conservation selection rule is relaxed. This assumption is made in amorphous semiconductors because near the band edges at least, $\Delta k \sim k$ and thus k is not a good quantum number. On E – k diagram such transitions would be non–vertical. However, no phonon absorption or emission processes are invoked to conserve momentum and all the energy required is provided by the incident photons. Such transitions are termed non–direct as opposed to indirect. Without knowledge of the form of N(E) at the band edges, and under the assumption of parabolic bands, the absorption in many amorphous material is observed to obey the relation (2.1) with n = 2. Thus absorption edge of many amorphous semiconductors can be described by a simple power law, at least over a limited range of the absorption coefficients, which enables an optical gap 'Eg' to be defined.
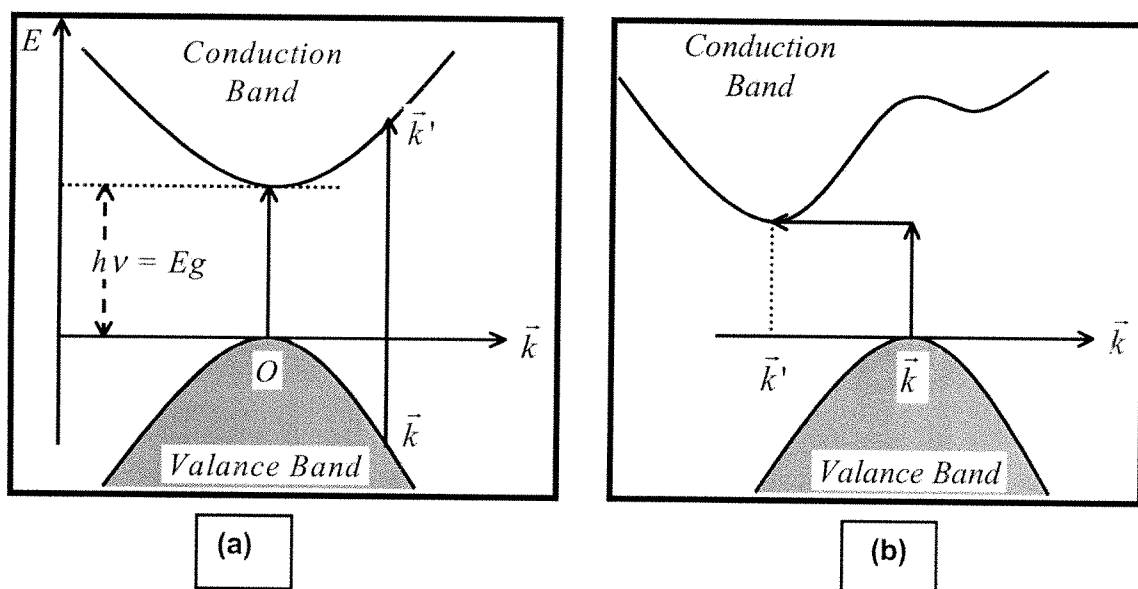

Fig. 2.4. "Direct interband optical transitions" for a) direct band and b) indirect band semiconductors. The transitions are represented by vertical arrow

2. 7.2. X- ray diffraction (XRD) technique

X-ray diffraction (XRD) is a powerful technique for determination of crystal structure and lattice parameters. The basic principles of X-ray diffraction are found in textbooks e.g. by Buerger [3], Klug and Alexander [4], Cullity [5], Tayler [6], Guinier [7], Barrett and Massalski [8].

Figure 2.5. Shows the schematics of X-ray diffractometer. Diffraction in general occurs only when the wavelength of the wave motion is of the same order of magnitude as the repeat distance between scattering centers. This condition of diffraction is nothing but Bragg's law and is given as,

$$2d \sin\theta = n\lambda \qquad\qquad 2.4$$

Where,

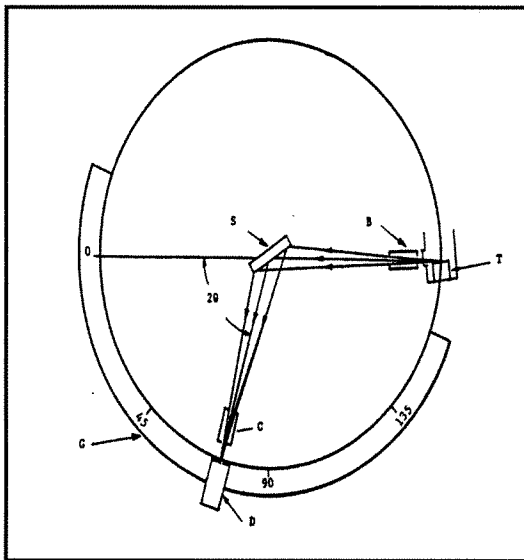|					
d	=	interplaner spacing	θ	=	diffraction angle
λ	=	wavelength of x-ray	n	=	order of diffraction

Figure 2.5. Schematic diagram of x-ray diffractometer. T, x-ray tube target; B & C, slit and collimator assemblies; S, sample holder; D, x-ray detector; G, goniometer scale graduated in degrees

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For thin films, the powder technique in conjunction with diffractometer is most commonly used. In this technique the diffracted radiation is detected by the counter tube, which moves along the angular range of reflections. The intensities are recorded on a computer system. The'd' values are calculated using relation (2.4) for known values of θ, λ and n. The X- ray diffraction data thus obtained is printed in tabular form on paper and is compared with Joint Committee Power Diffraction Standards (JCPDS) data to identify the unknown material. The sample used may be powder, single crystal or thin film. The crystallite size of the deposits is estimated from the full width at half maximum (FWHM) of the most intense diffraction line by Scherrer's formula as follows [7]

$$D = \frac{0.94\lambda}{\beta\cos\theta}$$

2.5

Where, D is crystallite size, λ is wavelength of X-ray used, β is full width at half maxima of the peak (FWHM) in radians, θ is Bragg's angle. The X- ray diffraction data can also be used to determine the dimension of the unit cell. This technique is not useful for identification of individuals of multilayers or percentage of doping material.

2.7.3 SEM- EDS profile

2. 7.3. Scanning electron microscopy

Scanning electron microscope (SEM) is an instrument that is used to observe the morphology of the solid sample at higher magnification, higher resolution and depth of focus as compared to an optical microscope [9]. When an electron strikes the atom, variety of interaction products are evolved. Figure 2.6. illustrates these various products and their use to obtain the various kinds of information about the sample. Scattering of electron from the electrons of the atom results into production of backscattered electrons and secondary electrons. Electron may get transmitted through the sample if it is thin. Primary electrons with sufficient energy may knock out the electron from the inner shells of atom and the excited atom may relax with the liberation of Auger electrons or X-ray photons. All these interactions carry information about the sample. Auger electron, ejected electrons and X-rays are energies specific to the element from which they are coming. These characteristic

signals give information about the chemical identification and composition of the sample.

Principle of scanning electron microscope

A well-focused mono-energetic (~25KeV) beam is incident on a solid surface giving various signals as mentioned above. Backscattered electrons and secondary electrons are particularly pertinent for SEM application, their intensity being dependent on the atomic number of the host atoms. Each may be collected, amplified and utilized to control the brightness of the spot on a cathode ray tube. To obtain signals from an area, the electron beam is scanned over the specimen surface by two pairs of electro-magnetic deflection coils and so is the C.R.T. beam in synchronization with this.
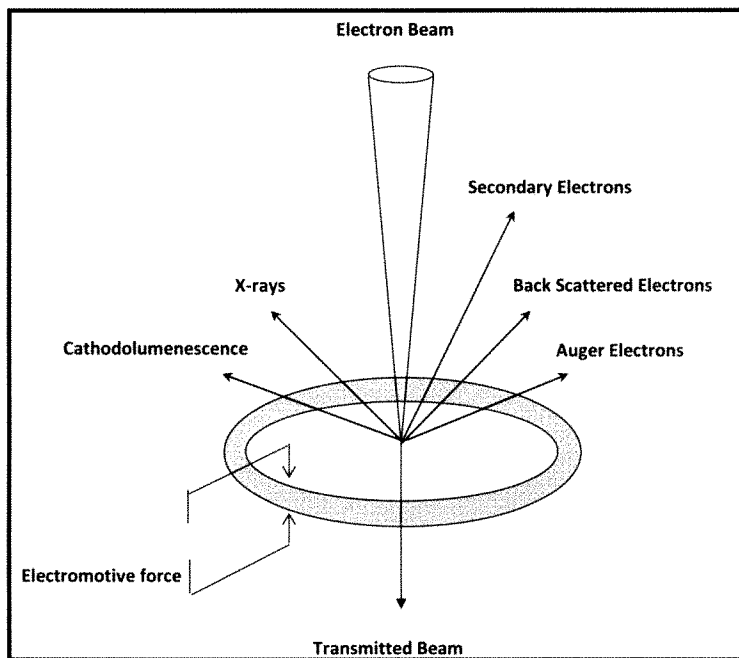

Figure 2.6. Variety of interaction products evolved due to interaction of electron beam and sample
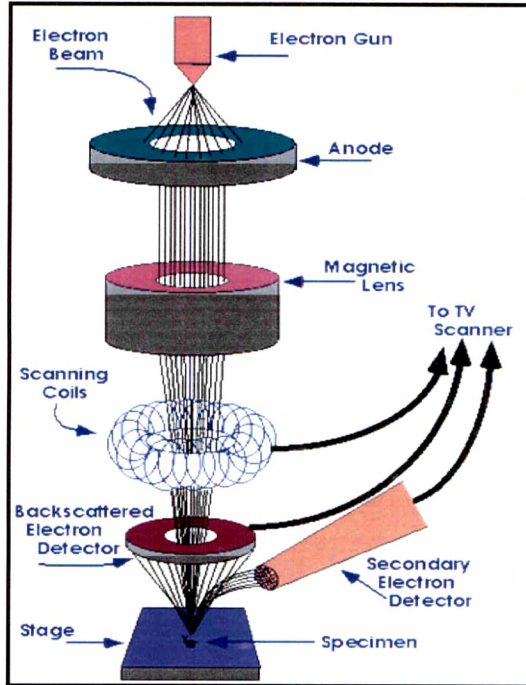
Figure 2.7 The ray diagram of scanning electron microscope

The signals are transferred from point to point and signal map of the scanned area is displayed on a long persistent phosphor C.R.T. screen. Change in brightness represents change of a particular property within the scanned area of the specimen [10].The ray diagram of scanning electron microscope is shown in Figure 2.7. The scattering cross section for back-scattered electrons is given as [11],

$$Q = 16.2 * 10^{-30} \left[\frac{Z}{E} \right]^2 \cot\left(\frac{\phi}{2} \right)$$ 2.6

Where, Z is atomic number and E is electric field.

Here the cross-section is proportional to Z^2. Hence, the back-scattered electrons are used for the Z contrast or for compositional mapping.

2. 7.4 Energy dispersive analysis by X-rays measurement (EDS)

In EDS technique a sample is made the target in an X- ray tube and is bombarded with electrons of suitable energy, it emits characteristics X-rays. This is the basis of a method of chemical analysis. The emitted X-rays are analyzed in an X-ray spectrometer and the elements present in the sample are qualitatively identified by their characteristics wavelengths. For compositions greater than or about 1% and elements separated by few atomic numbers, energy dispersion analysis is very useful because the intensities are increased about 100-Fold [12]. The resolution however, of an energy dispersion instruments is as much as 50 times less than the wavelength dispersion spectrometer using a crystal; thus overlapping of lines from nearby elements may occur. If a sample is irradiated with X-rays of sufficiently high energy, it will emit fluorescent radiation. This radiation may be analysized in an X-ray spectrometer and the elements present in the sample identified by their characteristics wavelengths. Study of thin films, ferrites, composites, biological samples and pharmaceutical samples are the common application areas.

2. 8.   Electrochromic characterization

Electro analytical techniques are concerned with the measurement of time related electrical quantities, such as charge or current and potential their relationship to the chemical reactions concerned.
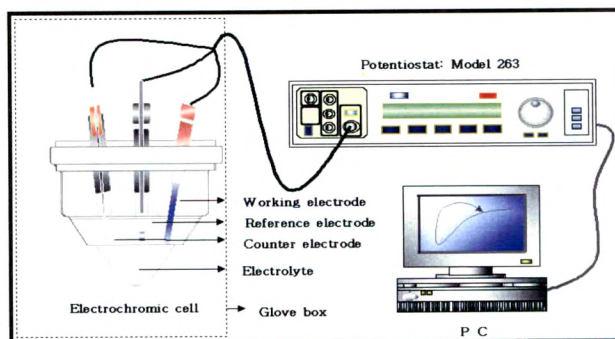

Fig. 2.8 Schematic diagram of the EC cell apparatus prepared for EC property measurements

Commercial Potentiostat CHI 400 electrochemical Analyser can be used for electrochromic characterizations of thin films.[13-14]The measurements requires an electrochemical cell with the three electrodes namely working, counter, and the reference, versus which the electrode potential are measured

◆ **Cyclic Voltammetery**

CV is the most widely used technique for acquiring qualitative information about electrochemical reactions taking place at the electrode – electrolyte interface. It offers a rapid location of redox potentials of the electroactive species in agitated or quiescent electrolyte and convenient evaluation of the effect of media upon the redox process[15-18].In CV the potential is continuously changed as a linear function of time in potential window + volts VS SCE and resulting current response is recorded. The resulting current versus potential plot is termed as a cyclic voltammogram. (Fig) .A smooth curve indicates that no well defined phase change occur during the reaction. Fig. illustrates a typical voltammogram for redox couple during a single potential cycle. It is assumed that only the oxidized ionic species are present initially, the mass transfer under concentration gradient is diffusion controlled and Fick's law of diffusion holds good for both oxidized and reduced ionic species. The redox potentials are predicted by Nernst equation given by,

$$E=E_o + (0.059/n) \log (C_o/C_r) \hspace{2cm} 2.7$$

Where, n= No. of electrons transferred

Co and Cr = concentration of oxidized and reduced ionic species

During a negative potential scan (coloration) in the first half cycle, as the applied potential approaches the characteristic reduction potential (Epc) predicted by Nernst equation, the cathodic current attains a peak value (Ipc). At least 90/n mV beyond the peak, the direction of applied potential is reversed. This helps in locating the presence of another reducible species in the bath.

During the reverse positive scan (bleaching) the reduced ionic species get oxidized and with similar trend the anodic current a peak value (Ipa) at an oxidation potential (Epa). If the redox reaction is reversible i.e.

maintain the surface concentrations of oxidized and reduced species as per the Nernst equation, the voltammogram is symmetrical otherwise it is asymmetrical.

- **Diffusion Coefficient**

It is the measure of ease with which an ionic speices can intercalate /deintercalate in the host. It is given by Randles and Sevick eqn

$$D^{1/2} = Ip/2.69 \times 10^5 . n^{2/3} . C.A.V^{1/2} \qquad 2.8$$

Ip=cathodic or anodic peak current

C=Concentration of ionic species

n=ionic charge

A=Area of film

V=Potential Scan Rate

- **Chronoamperometery (CA)**

CA involves stepping the potential of the working electrode from a value at which no Faradic reaction occurs to a potential at which the surface concentration of the electroactive species becomes effectively zero. The resultant current versus time is recorded. [19-22] the mass transport under the reversible condition is solely governed by Cottrell equation,

$$I_{(t)} = n.f.A.C.D^{1/2}/\pi^{1/2} t^{½} \qquad 2.9$$

Where, D= diffusion constant for the ionic species

Equation 2.9 indicates that, D is directly proportional to I^2.

- **Response Time**

The time required for the transition from colored to bleached state or vice-versa under the application of voltage pulse is termed as response or switching time. Though the magnitude of response time depends upon end use demand, a minimum switching time is necessary in advanced opto-Electronic EC devices.

- **Chronocoulometery (CC)**

The potential step experiment can also be used to record the charge versus time dependence [23-25]. Such a charge measurement is known as CC and is useful for measuring the quantity of intercalated/deintercalated charge.

● **Reversibility**

From the CC curves the amount of charges intercalated (Qi) and deintercalated (Qdi) during redox process are calculated. The electrochemical reversibility is calculated using the relation-[25-30].

Reversibility= Qdi / Qi   2.10

From the CV and CC analysis of electrochromic sample parameters like Reversibility, Response or switching time, Diffusion Coefficient and coloration efficiency can be determined.

2.9 Conclusion

The chemical bath deposition (CBD) is found to be most convenient method for deposition of MoO_3 and Vanadium doped MoO_3 thin films. CBD is simple, low cost and suitable method. In conclusion, this communication demonstrates that MoO_3 and Vanadium doped MoO_3 thin films have been successfully deposited using CBD.

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