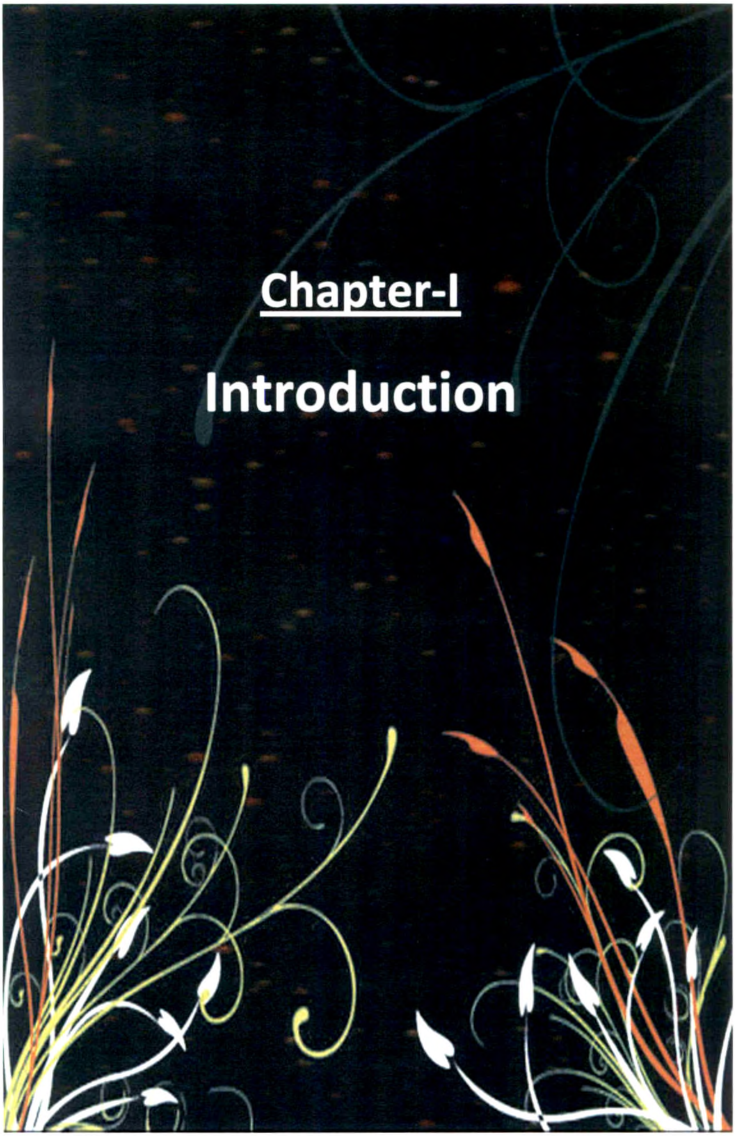

Chapter-I

Introduction

CHAPTER I

INTRODUCTION

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Chapter I

INTRODUCTION

Section – A

LITERATURE SURVEY OF TRANSITION METAL OXIDES

1.A.1 Introduction to Transition Metal Oxides

Transition metal oxide are the promising materials for various scientific technologies. They have attracted a great deal of interest and have been most extensively investigated. Pure stiochiomeric form of the transition metal oxides are good insulators at room temperature. Transition metal oxides, containing atoms with unfilled d-shells, possess multiple oxidation states and exhibit the phenomenon of mixed valence. Because of this property they are generally subject to various chemical and structural transformations under the action of different external perturbations, such as heat treatment, photon irradiation, electron and ion bombardment or electrochemical treatment. These transformations, in turn, are accompanied by significant modifications of the optical, electrical and other properties As an example, one can mention the effect of laser modification of TiO_2, V_2O_5, Nb_2O_5 and Ta_2O_5[1] thin films. Of all the transition metal compounds, the vanadium–oxygen system is truly remarkable and even, in a certain sense, unique.

In early years transition metal oxides have been prepared by thermal decomposition of metal compounds. These oxides have not been prepared as pure stiochiomeric form, extrinsic conduction always dominates at ordinary temperature. Although these oxides are custmarily identified with their chemical formula. The reasons for the increasing number new applications of these oxides are good mechanical, chemical and electrochemical stability, high electrocatalytic activity, good solar absorption coefficient, high surface area and good electrochromic properties. Due to the diverse structural, magnetic, electrical and optical properties of transition metal oxides, they found widespread applications in different fields like, optoelectronics, microelectronics, solid state ionics [2-4] microbatteries and electrochromic display devices [4-5]. Transition metal oxides have been studied intensively by theoretical and experimental techniques [4-6]. They show metal-semiconductor transition,which implies an abrupt change in optical and electrical properties [7]. That is why this oxide is used in thermal sensing and switching. Transition metal oxides based materials are known to display several types of chromogenic effects [8], as a window for solar cells [9] and for transmittance modulation in smart windows with potential applications in architecture and automotives [10]. It shows an atypical behaviour because it can not be defined exactly either as a cathodically or as anodically coloring material. Transition metal oxide exhibit multi-colored electrochromism allowing the use in electrochromic (EC) displays color filters and other optical devices [11].

Electrochromism is well known in numerous inorganic and organic substances.Among the inorganic class, almost all the intresting materials are transition metal oxides that are employed in the form of thin films.Most of the research work to develope highly transperant and conductive film has been consisting transition metal oxide's

Transition metal oxides of W,Ti,V,Nb,Ta and Mo exihibit cathodic electrochromisms and oxides of V, Cr, Mn,Fe,Co, Ni, Rh and Ir anodic electrochromisms. Vanadium shows both anodic and cathodic electrochromism. In 1969 Deb published results showing that color centres could be formed in thin films of tungsten oxides by the application of an electric field. Deb firstly used the term "electrochromism" for tungsten oxide film, which was previously only associated with some organic compounds Inorganic electrochromic materials such as Molybdenum Oxide change their transmittance when ions and electrons are injected into the material by an application of an electric field.

Transition metal oxides with diverse structures, properties, and phenomena have been the focus of much attention in recent years in view of their scientific and technological applications. Molybdenum oxide (MoO_3), among the other transition metal oxides, exhibits interesting structural,chemical, electrical, and optical properties. MoO_3 finds application as a cathode material in the development of high-energy density solid-state microbatteries. It is considered as a promising chromogenic/electrochromic material, as it exhibits electro and photochromic effects by virtue of which the material is of much interesting for the development of electrochromic display devices, optical switching devices, display devices, and smart window technology. Molybdenum oxide films and nano-crystals also find application in sensors and lubricants . In all these technological applications, optimization of the growth conditions to produce pure phase of MoO_3 thin films with controlled structure, morphology, optical and electronic properties is important. Therefore, an understanding of the growth mechanism, microstructure formation and surface modification as a function of growth conditions is prime requisite. Understanding of the composition, structure, and phase of the grown MoO_3 films since the properties and performance of the resulting films are mainly governed by their microstructure. MoO_3 exists in polycrystalline, the thermo-dynamically stable orthorhombic α MoO_3 phase. Synthesis of crystalline MoO_3 films requires higher temperatures, where the compositional deviation is very common resulting in the formation of layers with Mo in the reduced state.

Transition metal oxides are largely studied with respect to their electrochromic properties, for applications as smart windows and display devices. Molybdenum trioxide, compared to tungsten trioxide, has a comparatively lower coloration efficiency. However, the closer position of its optical absorption peak to the human eye sensitivity peak makes this material a very attractive electrochromic material . Mixed films based on W/Mo oxides are expected to exhibit an enlarged optical absorption band. This could originate from increased electron transitions between the two types of metallic site in the two-component material.

Investigations of transition metal oxide films are connected with their application as the active layers in electrochromic devices, mainly smart windows. A very important feature of the films is their optimal structure (crystalline orthorhombic with a unique layered structure of the MoO_3 film and an amorphous, porous structure in the cases of WO_3 and mixed MoO_3-WO_3 films), all permitting easily intercalation of ions. For an electrochromic device, a high optical transmittance of the active metal oxide layer is very important. To improve the initial transmittance, structural changes of the films are necessary.

1.A.2 Transition metal Oxides Of VIB group Elements

Essentially all of the oxides are constructed from one type of building blocks MoO_6 octahedra with a central transition metal atom.(Mo) surrounded by blocks are connected either by corner sharing or by a combination of corner- sharing and edge sharing and many different crystal structures are known.

The transition metal oxides offer a wealth of unique physical, chemical, electronic, optical, magnetic, and thermal properties which have occupied scientists and engineers for decades. The Transition metal oxides of VIB offer many convenient physical effects which can be harnessed for different microelectronic device applications.

Chromium, with its $[Ar]3d^5$,$4s^1$electronic configuration,provides unique 3*d*-orbital mixing in the chemical bonds that it makes, and this leads directly to its multivalent character *(+2,+3,+4,+5)* which can be affected by crystal structure, habit, defects, and external redox electron transfer. Chromium forms a very large number of oxides, although only a select few provide the stability needed for microelectronic devices, and these include CrO_3,CrO_2 and CrO_5 has been intensively studied for its metal-insulator phase transition (MIT) that occurs at a very technologically useful temperature of 67^0C. A similar MIT has been observed in CrO_3, CrO_5 has also been intensely studied for its electrochromic and thermochromic effects which can be harnessed for electro-optical device applications. The unique structure and properties of both of these oxides will be briefly reviewed, along with their more promising device applications. New materials are also being developed in the Chromium oxide family. Several of these will also be discussed in terms of their future promise for applications to microelectronic devices, sensors and systems.

Transition metal oxides of VIB are well known for their wide variety of physical and chemical properties. Many of these materials undergo phase transitions with interesting structural, electronic and magnetic behavior Some exhibit high temperature superconductivity and exciting optical properties or high catalytic activity. Among these molybdenum oxides represent an important class of materials due to their large variety in crystal structures and physical/chemical properties. They cover a wide range of electronic properties from metals to semiconductors and insulators and are, therefore, used in many technological applications. Examples are Molybdenum oxide based electrical and optical switching devices, write-erase media, light detectors, critical temperature sensors, infrared spatial light modulators. Further, molybdenum trioxide forms n- and p-type semiconductor phases, which are of technological interest. The rich and diverse chemistry of these oxides results mainly from two interrelated factors. First, the metal ions can adopt different formal oxidation states in the oxides, ranging from +2 to +5 in the case of vanadium and from +4 to +6 in the case of molybdenum. Second, the ions can exhibit quite different 137 coordination geometries described by octahedra, pentagonal bipyramids, square pyramids, or tetrahedra, where the different local units share comers and/or edges and/or faces. Many of these oxides are described by a defined composition (single or mixed valency oxides) while others exhibit a wide range of compositions. Molybdenum oxides form a large group of materials resulting from the ability of molybdenum to possess different formal oxidation states as well as different local coordination .

Tungsten trioxide (WO_3) is a prototype d^0 oxide based on a framework of comer sharing $W0_6$ octahedra. The formal oxidation state of tungsten is 6+, although due to strong covalency, the W ions do not carry the full 6+ charge. The neighbouring oxide ReO_3 has a simple cubic structure with an Re-O-Re angle of 180°, but in WO_3 rotation and distortion of the WO_6 octahedra gives rise to a series of lower symmetry phases: there are at least five bulk phase transitions between 100 K and 1000 K. A monoclinic phase γ-WO_3 is stable between 290K and 603K. It has cell parameters a = 7.297A, b = 7.539A, c = 7.688A and P = 90.91° and belongs to the space group $P2_1/n$. The y-WOs structure represents a (2x2x2) superstructure based on an idealised cubic unit cell of dimension about 3.7A (256). Crystals of WO_3 cleave most easily to expose (001) surfaces, which because of the monoclinic symmetry are distinct from (100) and (010) surfaces.

Stoichiometric monoclinic tungsten trioxide is an insulator at 300K with a band gap of about 2.6eV. However, WO_3 readily becomes oxygen deficient to form WO_3-X with variable oxygen composition parameter X. This oxygen deficiency greatly influences the bulk electronic transport properties by introducing donor electronic states into the upper half of the bulk bandgap: charge book keeping requires that each oxygen vacancy converts two W(VI) ions to W(V).

1.A.3 Molybdenum Oxide Thin Films

A report on preparation and properties of sodium and potassium molybdenum bronze. Crystals was made by A. Wold et al. [12] They studied pure molybdenum oxide crystals grown in electrolytic reduction of MoO_3 – Na_2MoO_4 mixture at 675^0C

In systematic study on optical and photoelectric properties of single crystal prepared by sublimation method and thin films of molybdenum trioxide (MoO_3) was reported by S.K.Deb [13] for the first time. A broad colour band was observed after UV irradiation.

Measurement of ESR and Optical spectra of the potassium and sodium molybdenum bronzes was reported by P.G. Dickens [14] An electron transfer proposed as follows :-

$$M + Mo^{6+} \longrightarrow M^{+} + Mo^{5+}$$

R.B. Dzhanelidze [15] studied optical and photoelectric properties of MoO_3 single crystal and thin films. While electron microcroscope observations of thin platelets of MoO_3 were reported by L.A Bursi [16]

Electrochromic was given wide spread attention through work of S. K. Deb [17] on WO_3 thin films.

M R. Tubbs [18] studied optical properties, color centres and holographic recording of MoO_3 layers and reported some possible applications of MoO_3 layers in image recording and holography. Thin layers of MoO_3 on to glass and silica substrate were obtained by evaporating material from electrically heated tantalum boats at a vacuum of 10^{-5} torr.

Thomas Arnoldussen [19] reported electrical properties, electrochromism and photochromism in amorphous MoO_3 films in various ambients.

Krishnakumar [20] have prepared MoO_3 films by physical vapour deposition and have reported their optical and electrical properties. They found that films exhibit photochromism upon UV radiation.

The electrochemical insertion of Lithium, Sodium and Magnesium in Orthorhombic MoO_3 thin films was studied by M. E. Spahr [21]

The electrochromic properties of crystalline molybdenum oxide thin films are described by S. Tarsame [22]

The present status and future of electrochromic material has been adequately reviewed by Somani [23]

R. S. Patil [24] have prepared MoO_3 films by electrodeposition and have reported their structural and optical properties.

1.A.4 Applications Of VIB Group Transition Metal Oxides

The VIB transition metal oxides of offer a wealth of unique physical, chemical, electronic, optical, magnetic, and thermal properties which have occupied scientists and engineers for decades. Metallic oxides are important materials from the standpoint of both fundamental and applied science. Particularly, tungsten and molybdenum oxide films have been the focus of extensive scientific investigations due to their prospective technological applications in electrochromic devices, gasochromic sensors, and electrocatalysis. However, their most intensively investigated property so far is the electrochromism. WO_3 films are considered one of the most viable options in emerging electrochromic technology, being applicable for regulating the throughput of radiant energy in smart windows and antidazzling mirrors. These oxides have also been used as "templates" in the synthesis of composites of the type transition metal oxide/conducting polymer, generating promising results in the area of cathodic materials in secondary lithium batteries. The transition metal oxides with electrochromic properties have attracted much interests in recent years, since their potential applications in many important technological areas, such as in smart windows , self-dimming rear mirrors, electrochromic displays and sensors etc. Due to the diverse structural, magnetic, electrical and optical properties of transition metal oxides, they found widespread applications in different fields like, optoelectronics, microelectronics, solid state ionics, microbatteries and electrochromic display devices. That is why this oxide is used in thermal sensing and switching.

The unique structure and properties of both of these VIB oxides will be briefly reviewed, along with their more promising device applications. New materials are also being developed in the vanadium oxide family. Several of these will also be discussed in terms of their future promise for applications to microelectronic devices, sensors, and systems. As a catalyst in refractories, as a ceramics colorant, in the manufacture of vanadium salts, as a flux, and as a dye. Two grades are offered. They are used in a variety of applications, including chemical and environmental catalysts, Behnfield and Stretford gas processing, coloring compounds, batteries, dye fixants, and vitamins Due to its high thermal coefficient of resistance, Mo and W oxide finds use as a detector material in bolometers and microbolometer arrays for thermal imaging. It also find an application as ethanol sensor in ppm levels (up to 0.1 ppm). Possible new uses include the preparation of bismuth vanadate ceramics for use in solid oxide fuel cells. Another new application is in redox batteries, a type of flow battery used for energy storage, including large power facilities such as wind farms.

Chromium oxide thin films are of great interest due to the wide variety of their technological applications. The most stable phase is the corundum structured Cr_2O_3. This form of oxide has important industrial applications, for instance in catalysis and solar thermal energy collectors. Currently, low-reflective Cr_2O_3/Cr films are widely used as black matrix films in liquid crystal displays. As this chromium oxide is an insulating antiferromagnetic material it is also suitable as a tunnel junction barrier.

VIB transition metal oxides with diverse structures, properties, and phenomena have been the focus of much attention in recent years in view of their scientific and technological applications.

Molybdenum oxide (MoO_3), among the other transition metal oxides, exhibits interesting structural, chemical, electrical, and optical properties MoO_3 finds application as a cathode material in the development of high-energy density solid-state microbatteries. It is considered as a promising chromogenic/electrochromic material, as it exhibits electro-, photo-, and gasochromic effects by virtue of which the material is of much interest for the development of electrochromic display devices, optical switching coatings, display devices, and smart window technology .Molybdenum oxide films and nano-crystals also find application in sensors and lubricants.

Due to the diverse structural, magnetic, electrical and optical properties of VIB transition metal oxides, they found widespread applications in different fields like, optoelectronics, microelectronics, solid state ionics, microbatteries and electrochromic display devices. Mo- oxygen systems have been studied intensively by theoretical and experimental techniques. They show metal-semiconductor transition, which implies an abrupt change in optical and electrical properties. That is why this oxide is used in thermal sensing and switching.VIB oxide based materials are known to display several types of chromogenic effects, as a window for solar cells and for transmittance modulation in smart windows with potential applications in architecture and automotives .

The Mo oxides offer many convenient physical effects which can be harnessed for different microelectronic device applications molybdenum oxides have for many decades attracted much attention for their rich and unique physical properties which pose intriguing questions as to their fundamental origins as well as offering numerous potential applications for microelectronics, sensors, and microelectromechanical.

Trasition metal oxides of VIB has been recognized as one of the better photocatalysts in heterogeneous photocatalytic applications as it combines two important complementary features for a photocatalyst good UV absorption efficiency for the light harvesting process and good adsorption capacities, due particularly to the density of OH− groups of amphoteric character. However, the band gap energy requires that near-UV light be used to photoactivate this very attractive photocatalyst .Unfortunately, in solar energy applications only ~3% of the solar light is absorbed. It would be advantageous, therefore, if this metal oxide semiconductor (SC) could be photosensitized by visible light.

Trasition metal oxides of VIB have been widely used as an essential part of many photoelectronic devices, such as flat panel displays, electroluminescent devices, thin film transistor, and solar cells, because of their unique properties of high electrical conductivity and high optical transmittance.

1.A.5 Chromism In Transition Metal Oxides

Compounds that change color visibly and reversibly when subjected to a change intheir environment (heat, light, pressure, electrons, etc.), are known as chromogenic materials. Transition metal oxides exihibit different types of chromism. There are four major categories–electrochromic (EC), thermochromic (TC), photochromic (PC) and piezochromic (PEC). The change in optical properties can be in the form of absorption, reflectance, or scattering. The change can be either within the visible, or beyond visible spectrum. Chromogenesis is one of the most exciting, but also complex research topics. The two major types are the nonelectrically activated and electrically activated types. The non-electrically activated type includes photochromics, and thermochromics .

1.A.5.1 Thermochromic (TC) Materials.

They change reversibly color with changes in temperature Fig. 1.1. They can be semi-conductor compounds, liquid crystals or metal compounds. Thermochromic materials change color by a process which involved athermally induced chemical reaction or a phase transformation. The change in color happens at a determined temperature, which can be varied by doping the material.Thermochromism is seen in a large number of organic and certain transition metal oxides.The phase change in a transition metal oxides can cause a significant change in its electronic properties from an insulator to semiconductor transition or from a semiconductor to metallic state when a "critical" temperature is exceeded. Some of these compounds are Fe_3O_4, NbO_2, NiS, Ti_2O_3 and VO_2[4].Vanadium dioxide, VO_2 has also been considered for window applications. By substitutional doping of vanadium in VO_2, an improvement on the transformation temperature can be achieved. They return to their original condition when they go back to the starting temperature. Some materials exhibit hysteresis during their heating and cooling cycle

Fig. 1-1. Thermochromic materials change reversibly color when they are heated or cooled.

1.A.5.2 Photochromic (PC) Materials.

They change material state from transparence to color when they are exposed to light, and revert to transparency when the light is dimmed or blocked. The change of PC material is one of the oldest phenomena in switching and dates back to the 1880s. Generally PC materials are energy absorptive.Basically the physical phenomenon involved is the reversible change of a single chemical species between two energy states that have different absorption spectra. The changes in states can be induced by electromagnetic radiation, usually UV light. PC materials have potential in advanced glazing. The main application is in the field of sunglasses. To become photochromic a special glass containing metal halides such as AgCl or AgBr is made. A special heat treatment of this composition causes the formation of photosensitive silver halide crystals with 15 nm in size. When UV light of the wavelength between 300-400 nm illuminates the glass, the metal halide crystals disassociate into metallic silver and the halide. The effect causes visible absorption 3 takes place. When the UV light is removed, the metal-halide molecule recombines thermally to its original form and as a result the glass becomes more transparent. Photochromic lenses automatically lighten and darken depending on changing daylight conditions, even behind a windshield.

1.A.5.3 Piezochromism

Piezochromism is the reversible colour changed caused by mechanical grinding. This induced colour change reverts back to its original colour if the material is left in the dark over time or dissolved in an organic solvent. A chemical that displays this phenomenon is diphenylflavelene.

1.A.5.4. Electrochromic (EC) Materials

Until now EC materials have been finding several applications like in smart windows anti-dazzling rear view mirrors, switchable motorcycle helmet Fig. 1.3, for contrast-enhancement in some emissive display devices and in non-emissive large-area color display for information advertisement. The smart windows are of great interest for special fields in architectural glazing of building and sunroof of automotive. Furthermore, they have no moving parts and the maintenance costs are minimal. The absorption or reflection of light in the visible and near infrared region can be adjusted according to the environment with an applied electric field or voltage (~5 V). In other words they are able to turn a transparent glazing into a color tinted glazing and then turn it back again. Thus a dynamic control of solar energy radiation and infrared radiation can significantly lower the air conditioned energy consumption in hot summer and cold winter.

Fig. 1-2. South facing view of a portion of the 8 x 17 m Electrochromic E-Control™ glass made by Flabeg and installed in the Stadtsparkasse Dresden am Altmarkt. The left portion of the window is colored. (Source: H. Wittkopf, Flabeg.) [25].

The study of electrochromic materials is an interdisciplinary field. In an electrochemical cell of EC devices the discharged positive ions (guest atoms) are free to diffuse in a thin solid film (electrode) of host material, modifying its electronic structure to create a colored material. The change is also thought as an oxidation-reduction reaction in chemistry, using either inorganic or organic compounds,and the color change can occur at either the anode or the cathode thin film. There are two major class materials, the ion-insertion/extraction type such as tungsten trioxide, Tungsten trioxide (WO_3). The WO_3 is ubiquitous and one of the best choices for the primary working electrode material in EC devices. It is common one as an active EC layer for potential application in advanced glazing and large area displays. The WO_3 is one of the best EC performances due to its high charge capacity and long-term cyclability. It goes blue on insertion of Li or other metal, hydrogen and guest atoms.

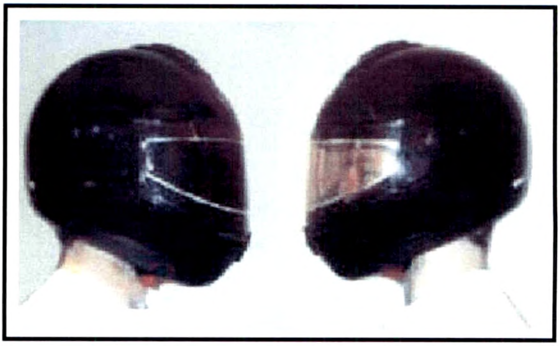

Fig. 1-3. Switchable motorcycle helmet visor made by ChromoGenics. Shown are two colorations of the visor (Credit: C. Granqvist, ChromoGenics.)

The well-known to exhibit the electrochromics are transition metal oxides, which are ion insertion materials and are of two types

- Cathodically colouring: Those with reduced colored state.
- Anodically colouring: Those with oxidised colored state.

Oxides of W, Mo, Ti, and Nb color under charge insertion and are referred to as cathodic EC materials, whereas oxides of Ir and Ni color under charge extraction and are called anodic EC materials, Vanadium oxide is of an intermediate nature and displays features of weak cathodic and anodic coloration in different wavelength regions. MoO_3 thin film show pronounced electrochromism due to its interesting structural and electronic properties. It is a 4d transition metal Oxide which can be switched between two different optical states [transparent and absorbing] by photochromic, thermochromic or electrochromic effect

◆

Electrochromism

An electroactive species often exhibits new optical absorption band or a new color whenever there occur a charge transfer or redox reaction (Reduction or Oxidation). If the change is reversible (Coloration and bleaching) then it termed as electrochromism. Many organic and inorganic materials exhibit electrochromism. For example: - The ferrocyanide ions in aqueous solution are pale yellow but on electrochemical oxidation exhibit brilliant yellow color. The original pale yellow state is restored on electrochemical reduction. As the colour state is observed upon oxidation, the material is called anodically colouring.

Tungsten oxide is another classical example which shows a transition from pale yellow to deep blue on electrochemical reduction. Upon electrochemical oxidation, it regains it's original colour. As the colored state is observed upon reduction the material is called cathodically colouring.

The most extensively studied inorganic system in tungsten oxide (WO_3) also called tungsten oxide, compromising of W^{6+}. When small amount of W^{5+} is introduced during growth, intense optical changes can be seen upon electrochemical reduction or oxidation.

An electrochromic species can be a conducting liquid, solid or thin film. For anodically colouring thin film diped in an electrolyte anion incorporation and cation expulsion occur,while for cathodically colouring thin film,cation incorporation and anion expulsion occur during optical changes.The transferring ion is called the counter ion.The ionic diffusion rate will determine the rate of electrochromic operation.

Electrochromic(EC) materials are able to change their optical properties in a reversible and persistent way under the action of a voltage pulse. This change may be due to the formation of colour centres or defect complexes or an electro-chemical reaction that produces a colored compound. An electrochromic material must posses both ionic and electronic conduction. Electrochromic is a reversible and persistent change in the optical properties of the material caused by an applied electric field or current.

Transition metal oxides are large band gap semiconductors which are completely transparent in visible region of electromagnetic spectrum.

The ionic insertion in the lattice by electrochemical oxidation reduction renders them coloration and their conductivity increases by orders making them metallic. A wide scope persists systematic study of electrochromism in thin films of transition metal oxides.

◆ Basis of electrochromism

EC materials are characterized by their ability to sustain reversible and persistent optical changes under the action of an applied electric field, as a result of which intercalation/deintercalation of small ions and charged compensating electrons takes place .

Electrochromism is based on the formation of colored compound from oxides of polyvalent metal upon insertion or extraction of small ions like H^+or OH^-, K^+, Li^+, F^- etc. according to following reactions :-

For cathodically colouring material-

$MO_n + xA^- + xe^- \longleftrightarrow A_xMO_n$ 1.1

For anodically colouring material-

$MO_n + xA^- + xH^+ \longleftrightarrow A_xMO_n$ 1.2

Where,

M is metal atom

e^- Is an electron

H^+ is proton

A^+ is an intercalated ion like H^+ or Li^+

$A^-$is an intercalated ion like OH^- or F^-

n depends on the particular type of oxide and

X may have in value between 0 to 1

In cathodically colouring EC material the coloration takes place upon intercalation (insertion) of H^+ or Li^+ ion and bleaching takes place upon deintercalation (extraction) of H^+ or Li^+ ions. Colored compounds (bronzes) are partially reduced oxides of polyvalent metal which contain the cation of reducing element (H^+ or Li^+).

In anodically colouring EC material the coloration takes place upon intercalation of OH^- ions and bleaching takes place upon deintercalation of OH^- ions. For anodic colouring EC materials reaction can be written in terms of both $OH^-$and H^+ ions, which usually required hydrated forms of oxides. The position of equilibrium depends on the Gibb's free energy of formation and on the ionic activities of the ingredients.

◆ EC devices

An EC device may have variety of configurations depending on the end application. The basic elements of an EC device are

- Two transparent conducting layers

- An active electrochromic layer
- An electrolyte in liquid or solid state and
- An ion storage media which may be another electrochromic layer or may be an integral part of the conducting layers.

This sandwitch configuration allows a reversible reaction to cycle between the EC material and ion storage media, with simultaneous injection of electrons or holes and protons or ions depending on the material. Under the action of electric field, movement of ions from electrolyte and electrons through the electrode take place. The variation of the electron density in the electrochromic material leads the modulation of optical properties. This mechanism is possible due to appropriate electronic and the ionic conductivities of electrode and electrolyte respectively.

◆ **Appearance of an EC devices**

The appearance of the electrochromic device is of paramount importance. The electrochemically acquired colour should be uniform and even, rather than patchy or streaked. A common cause of patchiness is inhomogeniety of electrochromic material, which can sometimes be avoided by improved deposition method. More difficult to control but commonly observed, is intensity gradient caused by an unevenness of the applied electric field across the electrochromic surface resulting in more intense coloration at the edges. A highly uniform conductive supporting electrode will ensure a more even appearance.

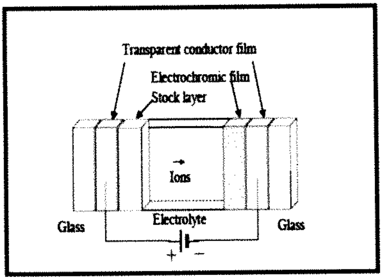

Fig. 1-4. A Basic Electrochromic film device structure

Section – B

THEORETICAL BACKGROUND OF THIN FILM TECHNOLOGY

1.B.1 Basics of thin film technology

Thin films are thin material layers ranging from fractions of a nanometer to several micrometers in thickness. Electronic semiconductor devices and optical coatings are the main applications benefiting from thin film construction. Some work is being done with ferromagnetic thin films as well for use as computer memory. Ceramic thin films are also in wide use. The relatively high hardness and inertness of ceramic materials make this type of thin coating of interest for protection of substrate materials against corrosion, oxidation and wear. In particular, the use of such coatings on cutting tools may extend the life of these items by several orders of magnitude. The engineering of thin films is complicated by the fact that their physics is in some cases not well understood. In particular, the problem of rewetting may be hard to solve, as there is ongoing debate and research into some processes by which this may occur.So a thin film is defined as a low dimensional material created by condensing, one by one, atomic/ molecular/ ionic species of matter. The thickness is typically less than several microns. Whatever be the film thickness limit, an ideal film can mathematically be defined as a homogeneous solid material contained between two parallel planes and extended infinitely in two directions (say x, y) but restricted along the third direction (z), which is perpendicular to the (x, y) plane. The dimension along the z-direction is known as film thickness (t). Its magnitude may vary from a limit $t \rightarrow o$ to any arbitrary value say to 10 µm or more but always remaining much less than those along the other two directions i.e. x and y. Thin films differ from the thick films. Thick film is defined as low dimensional material created by thinning a three dimensional material or assembling large clusters/ aggregates/grains of atomic/molecular/ionic species.

Thin film technology is a relatively young and ever growing field in the physical &chemical sciences which is confluence of materials science, surface science, applied physics, applied chemistry. Thin film technology has its objectives in the provision for scientific bases for the methods & materials used in thin film electronics. Additionally; it provides a sufficient data in the area of applications to permit for understanding of those aspects of the subject that might still be termed an 'art'. Thin film of metals were probably first prepared in a systematic manner by Michael Faraday, using electrochemical methods. Thin films have a no. of applications in various fields.Few of them are A.R.coatings, solar energy converters, transistors, coating, technology,, interference filters, polarisers, narrow band filters, solar cells, photoconductors, IR detectors, waveguide coatings, temp. Controlled aerospace devices, photothermal solar coatings (such as black chrome, Nickel, cobalt etc.) Magnetic films in recording device, superconducting films, microelectronic devices, diamond films, and high coatings are used for engineering applications, corrosion resistive thin film coatings and decorative thin film coatings etc.The enormous flexibility provided by the thin film growth processes allows the fabrication of desired geometrical, topographical, physically crystallographic & metallurgical microstructures into two or less dimensions and to study the structure sensitive properties.

Thin-film technologies are also being developed as a means of substantially reducing the cost of photovoltaic (PV) systems. The rationale for this is that thin-film modules are expected to be cheaper to manufacture owing to their reduced material costs, energy costs, handling costs and capital costs. However, thin films have had to be developed using new semiconductor materials, including amorphous silicon, copper indium diselenide, cadmium telluride and film crystalline silicon. In all cases, these technologies face major technical and financial hurdles. Thin film properties are strongly dependent on the method of deposition, the substrate materials, temperature, rate of deposition and composition. Ultra thin films are two dimensional micro materials which are obtained by one of the established techniques falling under the headings such as physical vapour deposition(PVD), chemical vapour deposition (CVD), electrochemical deposition(ECD), arrested precipitation technique (APT).The films can be further cut into a desired dimensions and geometry by one or more micro lithographic techniques. By using any one of these techniques falling & or therof,thin films of the order of 0.1 to o.4 um or even less can be obtained on a variety of surfaces like metals, ceramics, insulators, plastic etc. The tailoring of the materials properties basically involves numerous inherent characteristics of nucleation & growth kinetics of thin film formation . The creation of matter in a deposition process involves adsorption, desorption, condensation and migration of an atoms to reach critical nucleation stage. These processes take place under supersaturation, rapid thermalisation and non equilibrium thermodynamics conditions.

1.B.2 Growth of the thin film

Thin films are deposited on a substrate by thermal evaporation, chemical decomposition and the evaporation of source materials by the irradiation of energetic species or photons for a variety of applications. Thin films growth exhibits the following features:

- The birth of thin films of all materials created by any deposition technique starts with a random nucleation process followed by Nucleation and growth stages.
- Nucleation and growth stages are dependent upon various deposition Conditions, such as growth temperature, growth rate, and substrate chemistry.
- The nucleation stage can be modified significantly by external agencies, such as electron or ion bombardment.
- Film microstructure, associated defects structure, and thin film stress depend on the deposition conditions at the nucleation stage.
- The crystal phase and orientation of the films are governed by the deposition conditions.

The basic properties of film, such as film composition, crystal phase and orientation, film thickness, and microstructure, are controlled by the deposition conditions. Thin films exhibits unique properties that can not be observed in bulk materials.

1.B.3 Thin film deposition techniques

The properties of thin films are extremely sensitive to the method of preparation, several techniques have been developed (Depending on the desired film properties) For the deposition of the thin films of the metals,alloys,ceramic,polymer and superconductors on a variety of the substrate materials.Each methods has it's own merits & demerits and of course no one technique can deposit the thin films covering all the desired aspects such as cost of equipments, deposition conditions & nature of the substrate material etc.Thin film deposition techniques are broadly classified under two heading as listed in table 1.1.

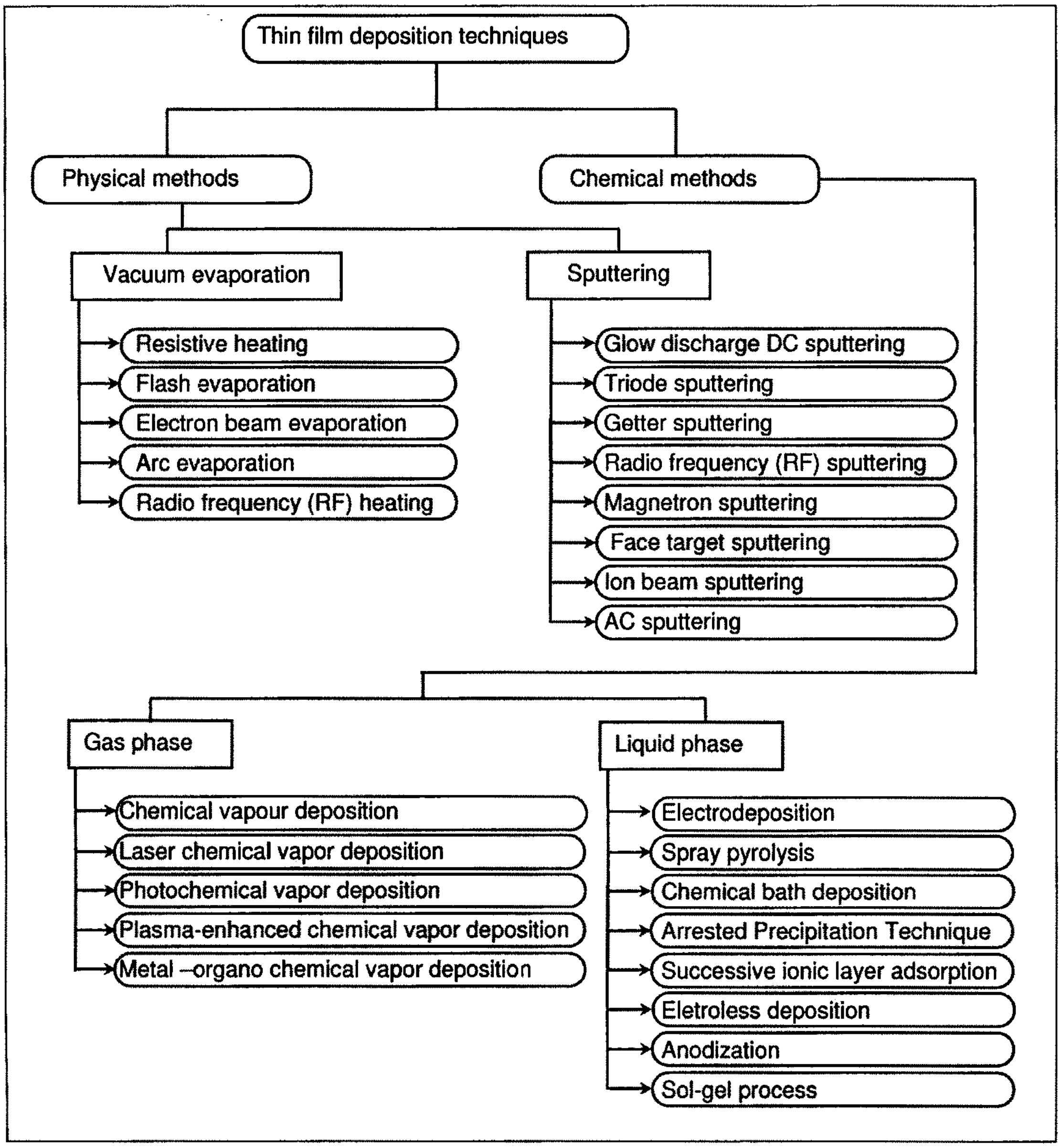

Table 1-1. Classification of thin film deposition techniques

1.B.3.1 Physical techniques,

- **Physical vapour deposition technique (PVD)**

Thin films play an important role in present day for the technological development & techniques of the film deposition offer a major key to the fabrication of solid state microelectronic devices. Physical vapour deposition is also known as thermal evaporation. It is one of the oldest techniques, is still widely used both in laboratory & industry. It is very simple & convenient technique. The three basic steps involved in the deposition are as follows.

- Generation of vapour from the condensed phase, solid or liquid.
- Transfer of vapour from source to the substrate.
- Condensation of vapour on substrate surface to form the solid film.[26-27]

- **Sputtering deposition**

Bombardment of a surface with high velocity positive ions causes the surface atoms to be ejected. This ejection of atoms from the surface due to bombardment by positive ions, usually inert is commonly known as sputtering. When the ejected atoms are made to condense on a substrate, thin film deposition takes place. Various theories have been put forward to account for the mechanism of cathode sputtering. Several works on the subject of sputtering technique on thin film deposition are available.

1.B.3.2 Chemical techniques

Another major technology for depositing thin films and coatings consists of the chemical methods including thin film formation by chemical processes in the gas or vapour phase as well as from liquid phases. Chemical deposition techniques are the most important tools for deposition of the thin films owing to their versatility in depositing a large no. of metals & compounds at a relatively low temperature. The various chemical deposition processes are as follows.

- Electro deposition
- Spray pyrolysis
- Chemical vapour deposition
- Anodisation

- Screen printing
- Chemical bath deposition
- Arrested precipitation technique.

◆ Electro deposition

It is a process of depositing a substance on the electrode by electrolysis, the chemical changes being brought about the passage of a current through an electrolyte. The phenomenon of electrolysis is governed by the Faraday's laws, when a metal electrode is immersed in a solution containing ions of that metal, a dynamic equilibrium M. M_n + x (M- Metal atom & X =S, Se, Te) is set up.

The electrode gains a certain charge on itself which attracts oppositely charged ions & molecules holding them at electrode / electrolyte interface. A double layer consisting of an inner layer of water molecules interposed by preferentially adsorbed ions & outer layer of the charge opposite to that of the electrode is formed. During deposition ions reach the electrode is formed. During deposition ions reach the electrode surface, stabilizes on it, release their ligands, release their charges and undergo electrochemical reaction. The rapid layer depletion of the depositing ions from the double layer is compensated by a continuous supply of fresh ions from the bulk of the electrolyte. The factors influencing the electro deposition process are, I] current density I] bath composition iii] pH of the electrolyte IV] temperature of the bath v] agitation VI] electrode shape.

◆ Spray pyrolysis

This is a thermally stimulated reaction between the clusters of liquid vapour atoms of different spraying solutions of the desired compound onto a substrate maintained at elevated temperature. The sprayed droplets on reaching the hot substrate undergo pyrolytic decomposition and form a single crystal or cluster of crystallites of the product. The other volatile byproducts and excess solvents escape in the vapour phase.

The thermal energy for decomposition, subsequent recombination of the species, sintering & recrystallisation of the crystallites is proved by hot substrate. The nature of the fine spray droplets, with the help of a carrier gas depends upon spray nozzle. The growth of a film by a spray pyrolysis is determined by nature of the substrate, solution as well as spray parameters. The films are general strong and adherent, mechanically hard, pinhole free & stable with temperature and time. The morphology of the films is general rough and that will depend upon the spray conditions. The surface of the substrate gets affected in the spray process and the choice is limited to glass, quartz, ceramics or oxides, nitride or carbide coated substrates.

◆ Chemical vapour deposition (CVD)

This method consists of the condensation of compound from the gas phase onto a substrate where reaction occurs to produce a solid deposit. A liquid or solid compound is made gaseous by volatilization and is caused to flow either by a pressure difference or by carrier gas to the substrate. The chemical reaction is initiated at or near the substrate surface to produce the required samples on the substrate. The possible reactions which are involved in CVD are thermal decomposition, hydrogen reduction, nitridation, oxidation, chemical transport reaction and combined reactions. In most of the reactions, the deposition is heterogeneous in nature. Certain important features common to all these methods are,

- CVD set-ups are simple & have fast recycle time,
- Deposition of the compounds, multi components and control of their stoichiometry is possible.
- High deposition rates are achieved,
- Objects of complex shapes and geometries can be coated
- Epitaxial layer of high perfection & low impurity content can be grown.
- In situ. Chemical vapour etching of the substrates prior to the deposition is possible.

The factors affecting the deposition, uniformly, composition and properties of the films are,

- Thermodynamics & reaction kinetics involved in the deposition process are very complex & difficult to understand.

- High temperature in the process lead to the diffusion, alloying or to a limited choice of the substrate materials.
- Uniformity of the deposit & making of the substrates is usually difficult.
- Higher substrate temperature is required as compared to PVD process.

◆ Anodisation

This is an electrolytic process where the metal is made the anode in suitable electrolyte. The surface of the metal is converted into its oxide having decorative, protective & other properties by passing an electric current. The required oxygen originates from the electrolyte used. The pH of the electrolyte plays an important role in obtaining the coherent films. The thickness of the oxide layer depends on the type of metal, applied voltage, time and temperature of the bath.

◆ Screen printing

It is a essentially a thick film process in which paste containing the desired material is screen printed by a conventional method onto a suitable substrate to define conductor, resistor or a device pattern. Subsequently the substrate is fixed under appropriate conditions of the time & temperature to yield rugged components bonded to the substrate. The substrates which have smooth surface, capability of withstanding at higher temperature, mechanical strength, high thermal conductivity & good electric properties & are compatible with film material pastes are used.

◆ Arrested precipitation technique

It is also called solution growth or controlled precipitations or arrested precipitation which has attracted a great deal of attention because of its overriding advantages over the other conventional methods. A significant quanta of work is available in the literature.

The film properties required for a particular application can bring about by using various deposition techniques. The chemical methods are economical and easier than that of the physical methods. But there is no ideal method to prepare thin films, which will satisfy all possible requirements. Among the chemical methods, the Chemical bath deposition is the most popular today because large number of conducting and semiconducting thin films can be prepared by this technique[28-30]

- It is simple, inexpensive and does not require sophisticated instrumentation.
- It is ideally suited for large area thin film depositions; substrate surfaces of both accessible and non-accessible nature could easily be deposited.
- The deposition is usually at low temperature and avoids oxidation or corrosion of the metallic substrates.
- Slow film formation process facilitates better orientation of the crystallites with improved grain structures over the substrate surface.
- Stoichiometry of the deposits can be maintained since the basic building blocks are ions instead of atoms.
- An intimate contact between reacting species and the substrate material permits pinhole free and uniform deposits on the substrates of complex shapes and sizes.
- Dissociation rate of organometallic complex to release free metal ions for reaction is well control by maintaining the pH of reacting solution.
- Wide varieties of conducting / nonconducting substrate materials can be used.
- Doped and mixed films could be obtained by merely adding the mixant / dopant solution directly into the reaction bath.
- Electrical conductivity of the substrate material is not an important criterion.

1.B.4 Chemical bath deposition (CBD)

Films can be grown on either metallic or nonmetallic substrates by dipping them in appropriate solutions of metal salts without the application of any electric field. Deposition may occur by homogeneous chemical reactions usually reduction of metal ions in solution by a reducing agent. If this occurs on a catalytic surface, it is called an electro less deposition (autocatalytic).

Silvering is the most widely used for this technique, metallic as well as mixed film sulphides, and selenides) and other alloys can be deposited. For nonmetallic surfaces a sensitizer has to be used. The growth rate & degree of crystallinity depends upon the temperature of the solution. The main advantage of this method is to deposit the films on non-accessible surfaces such as rounded glass tubes.

The chemical bath deposition is the simplest of the chemical methods, and it has many advantages as;

- It is simple & does not require any sophisticated instrumentation.
- It is ideally suited for large area depositions & substrate surfaces of both accessible & non accessible nature could easily be deposited.
- The deposition is usually at low temperature and avoids the oxidation or corrosion of the metallic substrates.
- It is possible to obtain uniform & large area semiconductor deposits on a variety of substrate materials.
- Thickness of the deposits can be controlled from few nanometers to micrometer by variation in the preparative parameters.
- As compared to the other thin film deposition techniques, chemical bath deposition process can be used conveniently for deposition of a variety of materials.

1.B.4.1 Factors governing the chemical bath deposition

It is the most suited method for deposition thin films. However, the growth of film is found to be governed by the various factors such as bath composition, the pH, and deposition time & deposition temperature.

◆ **Bath composition**

The growth rate and quality of the deposited films was greatly influences by the concentration of the reacting species. The films deposited by using low concentration are thin and nonuniform. This observation can be relates to the insufficient supply of ionic species at such concentration levels. On the other hand when concentration of the species was increased, the quality and uniformity of the films goes on increasing and the films were thick.

This is true up to a certain level of concentration and then saturation in the growth process was observed.

◆ **The pH**

It is the most important factor in the Chemical bath deposition. Thus the desired films were obtained on the substrate surface by optimizing the P^H value of its bath solution which avoids the deleterious effects.

◆ **Deposition time**

Growth of the thin film by chemical bath deposition is time dependent. The deposition time of the film affects film thickness.

◆ **Deposition temperature**

The temperature dependence of growth rate shown by literature survey that the rate of deposition increases with bath temperature resulting into formation of fine grained structure.

1.B.5 Aim and objective of present research work

There has been an increase in the interest in metal oxide thin films during past few decades because of their promising use in various fields of science and technology. Tungsten and molybdenum oxide thin films are being extensively studied for their use as gas sensors, as electrodes in microbatteries and electrochromic application. Various deposition techniques such as Electrodeposition, Chemical vapour deposition, Chemical deposition, Thermal deposition and Sputtering are being used to deposite MoO_3 thin films. It is observed that physical properties like morphology, porosity, water content and crystallinity as well as the optical and electrical properties of these thin films are critically sensitive to the preparation method and conditions. It is possible to tailor the properties of the thin film material by controlling the preparation conditions which in tern make the film suitable for a particular application. Therefore selection of an appropriate preparation technique and optimization of preparatory conditions play vital role.

Depending on the type of device, its geometry and expected performance, one can employ an appropriate deposition technique and control the preparatory conditions.

Chemical bath deposition has many attractive features and have the benefit of being easily realizable from the point of view of industrialization, especially on large area devices, with the required electrochromic properties. Because of its simplicity, low cost and feasibility. In recent years chemical bath deposition thin films are playing important role in energy conversions, solar selective coatings, Optoelectronic devices, gas and humidity sensors etc.

With this view, it was decided to deposit thin films of molybdenum oxide and vanadium doped molybdenum oxide by chemical bath deposition and to study their electrochromic properties. In the present research work a novel route is exploited for the first time.

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