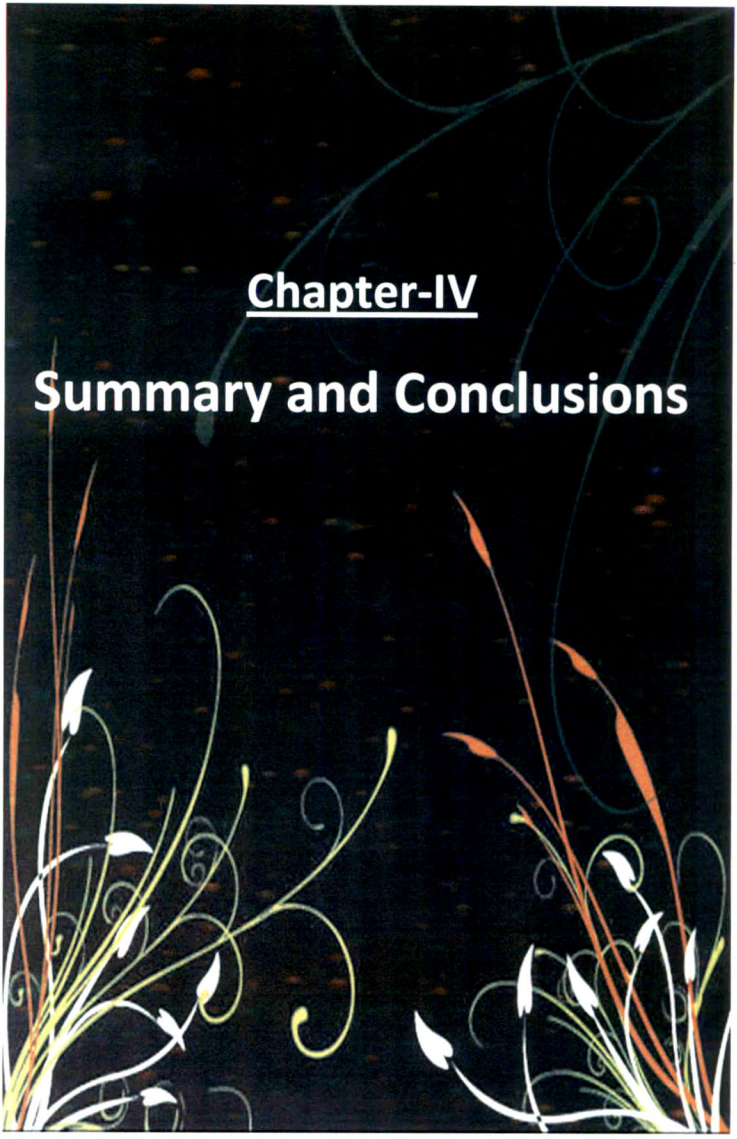

CHAPTER IV

SUMMARY AND CONCLUSION

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Introduction

Electrochromics is a healthy blend of basic Chemistry and Physics thin film science, device technology and market opportunities. Use of electrochromic transition metal oxides as smart windows in an interactive architecture of buildings provide better option for energy saving. A quantative analysis reveals that a smart window can save an energy equivalent to that generated by a solar cell at it's highest efficiency of 17%.Hence developments in electrochromics will remain a vital field for endeavors of various kinds in coming years. An electrochromic transition metal oxides are characterized by it's ability to sustain reversible and persistent change in optical properties under the application of proper voltage. An electrochromic device is essentially a rechargeable battery in which the electrochromic electrode is separated by a suitable solid or liquid electrolyte from a charge balancing counter electrode. The colour changes balancing are achieved by charging and discharging of this electrochemical cell with applied voltage of few volts.

Electrochromic optical switching devices known as chromogenic devices or smart windows can be used for variety of application one of the most promising applications is for the regulation of incident solar energy and glare in buildings, vehicles, ships, aircrafts and spacecrafts. Utilisation of electrochromic materials shows about 25% for buildgings and 11% for automobiles the potential for glass based glazing technology is very large.

Electrochromic products already in the market place are automobile mirrors and eyeglasses. Prototypes are being tested for sunroofs and visors. These devices can also be used for large area information displays where high switching speed is not required. However the market penetration of electrochromic devices in India is marginal owing to their high cost. Thus cost effective electrochromic devices are a need of time.

The transitions from a highly transmitting bleached state to a partly reflecting or absorbing colored state over the visible solar spectrum make these materials most useful. The well known materials to exhibit

electrochromism are transition metal oxides, which are ion insertion materials are of two types

1) Cathodically coloring – those which reduced in colored state
2) Anodically coloring- those which an oxidized in colored state

In 1970, electrochromism was first time demonstrated by S.K.Deb in thin films of tungsten oxide. Renewed interest in this area started in mid 1980 for large area applications and the developments has been growing ever since. The electrochromism is reported in many inorganic transition metals oxides like WO_3, MoO_3, Nb_2O_5, NiO, V_2O_5 etc of these extensively investigated electrochromic materials. MoO_3 and vanadium doped MoO_3 thin film show pronounced electrochromism due to it's interesting structural, optical 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.

It is known that electrochromic properties strongly depend on the synthesis techniques at suitable preparative parameters.In this respect we have chemically synthesized transition metal oxide namely MoO_3 and Vanadium doped MoO_3 thin films. Mo –oxide thin films can be prepared by variety of physical, chemical and electrochemical methods like sputtering, chemical vapour deposition, thermal oxidation, sol-gel, electrodeposition, anodization etc.

In the present investigation, Vanadium doped and undoped molybdenum trioxide thin films have been prepared from aqueous bath onto a conducting and non conducting substrates using simple chemical bath deposition method. The preparative parameters such as concentration of the precursor solution, pH of the bath solution, bath temperature, deposition time and agitation of substrate etc. of the films have been optimized. It is seen that preparative parameters strongly influence on growth of MoO_3 thin film as well as Vanadium doped MoO_3 thin film. The characterization of these films are carried out using, UV-visible absorption spectrophotometry, X-ray diffraction (XRD), Scanning electron microscopy (SEM), Energy Dispersive X-ray

Analysis(EDS) and Cyclic Voltammetey, Chronoamperometery and Chronocolometery.

The quantum of the research work that was carried out is presented four chapters.

Chapter I divided into two parts, part A deals with the theoretical background of transition metal oxides, Chromism in transition metal oxides including thermochromic, photochromic, piezochromic materials and also electrochromic materials. It also deals with basis of electrochromism.

Part B deals with introduction to thin films are summarized followed by thin film deposition techniques, it includes physical as well as chemical methods of thin film deposition. In electrochemical methods basic chemical bath deposition is described. Then modified chemical bath deposition, which is known as arested precipitation technique is described in detail.

Chapter II describes experimental details for the deposition of thin films of MoO_3 and Vanadium doped MoO_3 by the chemical bath deposition technique.This chapter also gives theoretical information of characterization techniques used for the characterisation of MoO_3 and Vanadium doped MoO_3 thin films.It deals with systhsis of thin films by chemical bath deposition technique. The substrate cleaning, preparation of the precursor solutions and experimental setup for chemical bath depositon technique. The various preparative parameters such as solution concentration, bath temperature, pH of the bath, and deposition time, of the films were optimized. It also includes growth mechanism and kinetics of film formation.

The various preparative parameters and deposition condition are as follows-

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 ± 2 rpm	50 ± 2 rpm

The probable chemical reaction involved in formation of MoO_3 thin films-

$Na_2MoO_{4\,(s)} + (CH_3.CH_2.O)_2\,SO_2 + H_2O$

Na-Molybdate Diethyl Sulphate

$$\longrightarrow MoOx_{(S)} + 2CH_3CH_2OH + Na_2SO_{4\,(aq)} \text{---(1)}$$

Thin Film Ethyl Alcohol

$$(CH_3.CH_2.O)_2\,SO_2 + 3\,H_2O \longrightarrow 2\,CH_3CH_2OH_{(aq.)} + H_3O^+ + SO_4^-{}_{(aq.)} \text{------(2)}$$

$$MoO_4^{2-}{}_{(aq.)} + 2H_3O^+ \longrightarrow MoO_{3\,(s)} + 3\,H_2O \text{ ------- ----------(3)}$$

Thin film

As grown samples are thin relatively thin uniform, smooth and tightly adherent to the substrate support. The color of the deposit for MoO_3 is white and that of Vanadium doped MoO_3 is slightly yellowish.

This chapter also describes various characterization techniques for thin film. It includes optical absorption spectroscopy , X-ray diffraction and scanning electron microscopy used for determination of optical band gap, structure determination and surface morphology of the films respectively. The EDS technique is discussed further, which is used for compositional study of

the film. Electrochrimic properties are discussed on the basis of cyclic voltametery, chronoamperometery and chronocolometery.

Chapter III, It is fully devoted to optostructural, morphological, compositional and electrochromic investigation of MoO_3 and Vanadium doped MoO_3 thin films.

The optical studies were performed in the wavelength range 250-650 nm and the absorption spectra were evaluated to determine the absorption coefficient (α), optical energy gap (Eg). The optical band gap for MoO_3 thin film is 3.1 eV and Vanadium doped MoO_3 thin film is 2.8 eV respectively. It was observed that band gap decreases with doping

MoO_3 and Vanadium doped MoO_3 thin films were characterized by X – ray diffraction technique using Cu- Kα radiation (λ=1054056 A°) from the diffractograms, it was found that the as grown thin films shows nanocrystalline in nature The observed d- values were compared with standard d- values JCPDS data, and found to be good agreement with d- values. The X-ray analysis showed that MoO_3 and Vanadium doped MoO_3 thin films are α-orthorhombic in nature with grain size 47 and 47 nm.

The morphological and compositional studied of the films were carried out using SEM-EDS technique. The results obtained reveals the surface morphology of the films. From SEM study it is observed that, less uniformly distribution of particles with large intergrannular spacing in them.

Chapter III also described electrochromic characterization and electrochromic application of MoO_3 and Vanadium doped MoO_3 thin films. From CV, CA and CC analysis of electrochromic sample parameters like reversibility, response or switching time and diffusion coefficient was determined. CV for MoO_3 and Vanadium doped MoO_3 in the potential range ± 0.5V vs SCE at different scan rate was recorded. The films turns blue at - 0.5V vs SCE and it retrieves to it's transparent state at + 0.5V vs SCE.The process intercalation and deintercalation process takes place according equation 1.1 &1.2. It was also seen that cathodic peak current (Ipc) and anodic peak current (Ipa) increases with increase in scan rate. A linear relationship implies that the reaction is diffusion controlled. Diffusion

Coefficient found to be 1.21 X 10^{-10} cm^2/s & 2.64 X 10^{-10} cm^2/s for undoped and doped thin film respectively. From CA and CC response time and reversibility calculated.

Samples	Response Time		Reversibility
	tc sec	tb sec	
MoO_3	7	4	55 %
Vanadium doped MoO_3	5	1	73 %

Chapter IV, This chapter is pertaining the summary and conclusions drawn on the present investigation.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.

Chemical bath deposition is applied successfully to deposit stichiometric, adherent and uniform deposition of thin film form.Optical absorption shows that band gap decreases with Vanadium doping.X-ray diffraction confirmed the phase formation in MoO_3 and Vanadium doped MoO_3 thin films. The films are mechanically stable no cracks are observed in the low magnification SEM image. The electrochromic studies show that Vanadium doping enhances electrochromism.