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Chemosynthesis and characterization of electrochromic vanadium doped molybdenum oxide thin films

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ABSTRACT

A novel aqueous, relatively low temperature thin film growth technique has been developed to fabricate a new generation of smart and nanostructured metal oxide thin film material. Thin films of molybdenum oxide were produced by the chemical bath deposition method. Various levels of doping were achieved by adding small quantities of water soluble vanadium compound to the prepared solution of molybdenum oxide. The change in structural and optical properties in metallic phases were studied and compared to pure molybdenum oxide thin films. The thin films were characterized for their optostructural, morphological and compositional analysis using UV-Vis-NIR spectroscopy, XRD, SEM and EDS techniques. The electrochemical performance of pure and doped thin films was studied in $0.5M H_2SO_4$ as an electrolyte.

Keywords: Thin films; Chemical synthesis; Optical properties; Electrochromism; Scanning electron microscopy (SEM); X-ray diffraction.

INTRODUCTION

Electrochromism describes a phenomenon of color change in a persistent but reversible manner produced by electrochemically induced oxidation reduction reactions [1]. Electrochromism is the phenomenon of coloration or bleaching (optical modulation) of certain transition metal oxide thin films by the application of dc voltage. Electrochromism is an emerging area having applications in smart windows, information displays, automobile windshields and medical electronics [2].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. One of the widely studied, yet not understood in detail ,the thin films of molybdenum oxide (MoO₃), among the other transition metal oxides, MoO₃ exhibits interesting structural, chemical, electrical and optical properties. MoO₃ finds application as a cathode material in the development of high-energy density solid-state micro batteries. Molybdenum

oxide films and nanocrystals also find application in sensors and lubricants [3–16]. The coloration and bleaching in these electrochromic films is due to the intercalation of charge in the molybdenum oxide lattice.

$$MoO_3 + xM^+ + xe^- \rightarrow Mx MoO_3^{-x}$$

Where e^{-i} is the electronic charge, M is the charge balancing ion like H⁺, Li⁺, Na⁺ and K⁺.

The electrochromic properties depend upon the growth technique [2].Presently, considerable efforts are going on to improve the switching speed, coloration efficiency and color neutral property of the molybdenum oxide thin films. The color neutral property is desired in the architectural application hence vanadium doping is expected to enhance the color neutral property in molybdenum oxide thin films. Since the electrochromic effect in molybdenum oxide based thin film is controlled through electrochemical reduction and oxidation by ion intercalation and deintercalation, the electrochemical properties are of interest. Thin films of molybdenum oxide have been deposited by various physical and chemical methods. In present work we have prepared MoO_3 thin films by using simple chemical bath deposition (CBD) technique. This method is inexpensive and does not require sophisticated vacuum equipment. The chemical bath methods have the benefit of being easily realizable from the point of view of industrialization, especially on large area devices, with the required electrochromic properties. [17, 18].

MATERIALS AND METHODS

A simple chemical bath deposition (CBD) technique was employed to deposit pure MoO_3 and vanadium doped MoO_3 thin films onto glass substrates and FTO coated quartz using sodium molybdate as a precursor and diethyl sulphate. Before the substrates were introduced into the reaction bath, they were boiled in chromic acid for 2 hr and kept in it for 12 hr then washed with detergent and finally rinse in acetone before use. This is to ensure presensitised substrate surface and nucleation site for thin film formation.For the preparation of MoO_3 thin films following experimental procedure was used, 1.5 gm of sodium molybdate was dissolved in 70 ml distilled water taken in 100ml beaker(0.1 M). To this solution, 3 ml slightly acidic diethyl sulphate was added. The clean and dry glass substrate were fitted to bakelite substrate holder and dipped in the above solution. The speed of substrate rotation was kept 40–50 rpm. The solution bath was kept at 90 -95 °C for 15 min. After 15 minutes there was white colored and uniform deposition of molybdenum oxide on glass substrates. As deposited thin films were dried in constant temperature oven at 110 °C.

For the preparation of vanadium doped MoO_3 thin films, 1.5 gm of sodium molybdate was dissolved in 70 ml distilled water(0.1 M). To this solution, 3 ml slightly acidic diethyl sulphate and 1 % of ammonium metavanadate was added as a dopant. Rest of the procedure is same as described above. After 15 minutes there was faint yellow colored and uniform deposition of vanadium doped molybdenum oxide on glass substrates. As deposited thin films were dried in constant temperature oven at 110 °C.

The structural phase of thin films was determined by X-ray diffraction analysis [PW-1710 diffractometer] with Cu K α target having wavelength 1.542 A⁰. The surface morphology was

studied using scanning electron microscopy. [SEM: JEOL JSM – 6360A Analytical scanning electron microscope]. The compositional analysis was carried out using energy dispersive X-Ray spectrometery. [EDS: JEOL JSM – 6360A Analytical scanning Electron microscope]. The optical transmittance was measured using UV-Vis-NIR spctrophotometer.[Hitachi Model 330-Japan] in the wavelength range of 300-850 nm.The thickness of films was determined by surface profiler [AMBiOS XP-1]. The electrochemical intercalation and deintercalation of electrons and H⁺ ions was carried out in a potentiostat [EG & G model verstat – II PAR 362] controlled by a personal computer [Electrochemistry software M 270] in three electrode cell configuration with 0.5M H₂SO₄ as the working electrode and the saturated calomel electrode (SCE) as the reference electrode.

RESULTS AND DISCUSSIONS

3.1 Growth Mechanism of pure and vanadium doped MoO_3 thin films

Pure MoO_3 and vanadium doped MoO_3 thin films are prapared by simple chemical bath deposition using sodium molybdate and diehyl sulphate as a precursor. The reactions involved during the growth of molybdenum oxide thin films are as follows-

 $Na_2MoO_{4(s)} + H_2O \rightarrow MoO_4^{2^-}_{(aq)} + 2Na^+ \quad \dots \qquad (1)$

The reaction rate is controlled by pH value. For the increased precipitation Of MoO_3 , the protonium ion formation was done by hydrolysis of diehyl sulphate in the temperature range of 90^0 C.

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

This process is highly dependent on temperature and its increased value provides favorable increase of solubility of diethyl sulphate. Finally formation of MoO_3 thin film was done by reaction between molybdic acid and protonium ion as follows-

$$MoO_4^{2-}{}_{(aq.)} + 2 H_3O^+ \longrightarrow MoO_3{}_{(s)} + 3 H_2O \qquad (3)$$

Thin film

The overall reaction for formation of MoO₃ thin film is given by equation 4

 $\begin{array}{rl} Na_2MoO_{4\ (s)} +\ (CH_3.CH_2.O)_2\ SO_{2(l)} + H_2O_{(l)}\\ Na-Molybdate & Diethyl\ Sulphate \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ &$

3.2 XRD Studies

Structural identification of MoO_3 and vanadium doped MoO_3 films were carried in the range of angle 2 θ between 10° to 100°. Fig.1a and 1b shows the XRD patterns for as deposited MoO_3 and vanadium doped MoO_3 thin films respectively. Fig.2a and 2b shows the XRD patterns for MoO_3

and vanadium doped MoO₃ thin films annealed at 500°C respectively. Improvement in crystallinity was observed upon annealing the films for 3 hr at 500 °C. The observed XRD patterns were compared with JCPDS card (71-0566, 72-0448 and 74-0050) for MoO₃ and vanadium doped MoO₃ which confirms α - orthorhombic phase of MoO₃ and vanadium doped MoO₃. The well defined peak is (310) in the XRD patterns.



Fig.1b. XRD pattern of as deposited vanadium doped MoO₃ thin film



Fig.2b. XRD pattern of vanadium doped MoO_3 thin film annealed at $500^\circ C$

The average crystallite size of MoO_3 and vanadium doped MoO_3 in the film was determined from the prominent peak (310) by using Scherer formula

Where,

- λ is the wavelength
- B is the angular line width at half maximum intensity, and
- θ is the Bragg's angle

The average crystallite size of MoO₃ is 47.0 nm and vanadium doped MoO₃ is 47.08 nm.

3.3 Optical Studies

The optical absoption spectra of MoO_3 and vanadium doped MoO_3 films were recorded in the wavelength range of 350 to 650 nm. The variation of absorption coefficient (α) with photon energy (hv) is given as

$\alpha = A (hv-Eg)^n / hv$ ----- (6)

A is constant, hv is photon energy (eV), Eg is band gap energy of semiconconductor (eV) and n is index number depending on mode of transition). Where, α is absorption coefficient (cm⁻¹) which can be calculated by using the absorbance value measured for a particular wavelength (λ) and film thickness (t) using equation

$$\alpha = 1/t \log (Io/It) \qquad (7)$$

The plot of $(\alpha.h\nu)^2$ versus h ν for pure MoO₃ and vanadium doped MoO₃ is shown in Fig.3a and 3b respectively. The band gap determined near the absorption edge by extracting the absorption edge by the straight-line portion of the plot to the energy axis and direct band gap energy. For pure MoO₃ band gap is 3.1 eV and for vanadium doped MoO₃ it is 2.8eV. The band gap value was found to decrease after vanadium doping.







Fig 3b. The plot of $(\alpha h v)^2$ vs hv of vanadium doped MoO₃ thin film

3.4 SEM/EDS studies

Fig.4a and 4b shows SEM micrographs of pure MoO_3 and vanadium doped MoO_3 thin films. It was observed that the surface smooth and dense morphologies without any cracks. Fig.5a and 5b shows EDS patterns for pure MoO_3 and vanadium doped MoO_3 thin films.



Fig. 4a SEM of MoO₃ thin film



Fig. 4b SEM of vanadium doped MoO₃ thin film

The EDS patterns clearly reveal the presence of Mo, V and oxygen in films without any impurity.



3.5 Electrochemical Studies

For electrochemical studies 0.5 M H_2SO_4 electrolyte solution was used with graphite as counter electrode and saturated calomel as reference electrode. The simultaneous electrochemical intercalation and deintercalation of electrons and H^+ ions was carried out.

3.5.1 Cyclic Voltammograms (CV)

Cyclic voltammograms (CV) were recorded for MoO_3 as well as vanadium doped MoO_3 films with the linear potential sweep between ± 0.5 mV at a scan rate of 10mVs^{-1} and are shown in Fig.6.

When a negative potential was applied blue color was observed, indicating oxide reduction followed by H^+ ions intercalation. After the reversal of potential the anodic current started to flow corresponding to the deintercalation process. There is a well-defined anodic peak for the film, indicating H^+ insertion– removal process is highly reversible process with little hystersis.



Fig. 6. Overlay of CV for MoO3 and vanadium doped MoO3 thin films

The area of the hysteresis curves height and position of anodic and cathodic peaks are closely related to the electrochemical processes occurring in MoO_3 as well as vanadium doped MoO_3 thin films. The cathodic and anodic peak current density increases with doping, indicating that the H⁺ ions easily diffuse in the vanadium doped MoO_3 . The diffusion coefficient of H⁺ ions is calculated by using the Randles-Servcik equation

$$D^{1/2} = Ip/2.69 \times 10^5 .n^{2/3} .C.A.V^{1/2}$$
 ------(8)

Where,

Ip - Cathodic or anodic peak current, C - Concentration of ionic species,

N - Ionic charge, A - Area of film, V - Potential Scan Rate.

By substituting all the values, the diffusion coefficient at the 10 mVs⁻¹ scan rate is $1.21 \times 10-10$ cm²/s and $2.64 \times 10-10$ cm²/s for intercalation and deintercalation processes for the MoO₃ and vanadium doped MoO₃ films. It clearly shows that diffusion coefficient increases with Vanadium doping.

3.5.2 Chronoamperometry (CA)

Chronoamperometry (CA) data were recorded for the MoO_3 and vanadium doped MoO_3 films with the potential being stepped from $\pm 0.5V$ for 10 s and shown in Fig. 7.



Fig.7.Overlay of CA for MoO3 and vanadium doped MoO3 thin films

The higher bleaching current arises from the good conductivity of molybdenum bronze $(HxMoO_3)$ and rapid decays in current are due to conductor-to-insulator transition. On the other hand, insulator to- conductor transition during coloration is slow. The response time for coloration (tc) and bleaching (tb) were calculated from the CA data and are listed in Table 1. All the films show fast colour-bleach kinetics. The bleaching kinetics is always faster than the coloring rate owing to the well-defined different mechanisms. The bleaching speed is governed by the space charge limited current flow of cations through the bulk of the film whereas in the coloring mode the potential barrier at the MoO_3 - electrolyte interface and the number of H⁺ insertion play a critical role.

3.5.3 Chronocoulomatery (CC)

The number of H+ ions intercalated and deintercalated with respect to time was measured using chronocoulometry (CC) studies. Fig.8 shows charges intercalated/ deintercalated versus time transients at $\pm 0.5V$ for the step of 10 s for the MoO₃ and vanadium doped MoO₃ films.



Fig.8.Overlay of CA undoped and vanadium doped MoO3 thin films

In the forward scan the charges are intercalated into the film by diffusion process. CC of MoO_3 and vanadium doped MoO_3 films, recorded at a potential step of $\pm 0.5V$ for 10 s. resulting in coloration due to reduction of Mo^{+6} to Mo^{+5} states. In the reverse scan the intercalated charge is removed from the film, resulting in bleaching due to oxidation of Mo^{+5} to Mo^{+6} states. The reversibility of the films was calculated as a ratio of charge de-intercalated (*Q*di) to charge intercalated (*Q*i) in the film. Interestingly, it was observed that the reversibility increases as the vanadium doping. The electrochromical properties calculated form CV, CC and CA are listed in Table 1.

Samples	Response Time		Dovorsibility
	tc sec	tb sec	Reversionity
MoO ₃	7	4	55 %
Vanadium doped MoO ₃	5	1	73 %

Table No.1 CC and CA data of MoO₃ and vanadium doped MoO₃ thin films.

The doping of vanadium creates structural disorder in the MoO₃. Due to doping α -orthorhombic phase nature with the porous structure opens up more channels for the charge insertion/deinsertion during the intercalation/deintercalation process, which may leads to increase in the reversibility of the films as compared with the MoO₃ films.

CONCLUSION

The doping effect of vanadium on the structural, optical and electrochromic properties of MoO_3 thin films have been studied systematically. X-ray analysis show that films are α - orthorhombic. It is seen that, vanadium doping can lead to significant surface morphology changes in MoO_3 . It was observed that band gap decreases with vanadium doping.

It has been observed that crystallographically oriented MoO_3 films show poor electrochromic performance. An interesting way to overcome this deficiency is to dope vanadium at the MoO_3

host matrix, which modifies its physicochemical properties and improve the existing electrochromic characteristics. The possible beneficial effects of doping on the electrochromic host material are improved durability, color neutrality, a larger switching potential range or faster reaction kinetics.

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