
CHAPTER - VI

SUMMARY AND CONCLUSION

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Molybdenum oxide, in the form of thin film is an interesting material to study. The reasons for this interest are numerous. It is a transparent, partially ionic 4d transition metal oxide, which exhibit interesting optical, and electrical properties. High optical efficiency and longer open circuit memory are the significant properties which attract researchers to study the electrochromic properties of these films. It is known that, the semiconducting and electrochromic properties of the films depend largely on their structure, which in turn depend on the method of preparation of the films. MoO₃ thin films have been prepared by various physical and chemical techniques. However, no reports can be found on the preparation of MoO₃ thin films by spray pyrolysis technique, which is simple and inexpensive one.

In this investigation, an attempt has been made to prepare MoO₃ thin films by spray pyrolysis technique (SPT). Ammonium molybdate solution was sprayed on to preheated amorphous and F.T.O. coated glass substrates. The pyrolytic decomposition of this solution results into the formation of thin solid MoO₃ films. The preparative parameters like substrate temperature, spray rate, solution concentration etc. have been optimized in order to obtain good quality

films. The structural optical and electrical properties of these films have studied. An attempt has been made to test the applicability of SPT to prepare electrochromic MoO_3 thin films, by forming a simple electrochemical cell with configuration, F.T.O./ MoO_3 /0.1N. H_2SO_4 /FTO Electrochromic properties of the cell have been studied by using electrochemical techniques.

The present work is divided into Five Chapters. Literature on characterization of MoO_3 is surveyed in Chapter-I and it is found that the physical properties of MoO_3 semiconductor are strongly dependent on the method of preparation. The variation in the optical, structural, electrical and electrochemical properties appeared in the literature, seem to depend sensitively on the sample, preparation conditions. A brief survey on other EC oxides is also included. Purpose of dissertation is stated in the same chapter.

Chapter-II introduces subject of electrochromism. It includes the basis of electrochromism definition of electrochromism, microstructural aspect, survey of different colouration methods, classes of electrochromic materials and configuration of electrochromic cell.

Chapter-III reports the preparation of F.T.O. coated glass substrates and deposition of MoO_3 thin films. Structural, optical and electrical properties of MoO_3 thin

films are studied with the help of various techniques and results are reported in Chapter-IV. Electrochromic properties using cyclic voltammetry, chronoamperometry, optical absorption, spectral transmittance and XRD are studied and discussed in Chapter-V.

Deposition of thin films by spraying solution onto the substrates is a simple and low cost technique, by which larger number of thin films on variety of substrates, (like glass, ceramic or metallic) can be prepared. In the present investigation MoO_3 powder dissolved in ammonia solution was sprayed onto the hot substrates. Amorphous and F.T.O coated glasses ($10-50 \text{ ohm}/\square$) were optimized in order to achieve uniform and adherent films. The substrate temperature was varied from 250° to 450°C in steps of 50°C . The spray rate, carrier air pressure, quantity of the solution to be sprayed and concentration of the spraying solution were $2.5 \text{ cc}/\text{min}$, $2.5 \text{ kg}/\text{cm}^2$, 50 cc and 0.05 M respectively. MoO_3 films prepared at different substrate temperatures were studied for their structural, optical and electrical properties.

The thickness of the films prepared at different substrate temperatures were measured. It is found that the film thickness decreases with increase in temperature. This is attributed to the increase in evaporation rate of the initial product with substrate temperature. Thickness varied from 1.56μ to 0.56μ .

The X-ray diffraction patterns of films were recorded in the range of angle 20° to 80° . The film crystallography was determined from XRD patterns. It is found that the films deposited at temperatures 250°C and 300°C were amorphous, while crystallization of the film was found to begin above 300°C . The films deposited at substrate temperature between 350 to 450°C were polycrystalline in nature with preferred orientation in (210) plane. Amorphous films were annealed for 6 hours at 500°C in air and analysed by XRD. It was observed that the amorphous films became polycrystalline, showing that the structure of film is substrate temperature dependent. The 'd' values of planes were calculated and compared with standard 'd' values taken from ASTM diffraction data files. For amorphous films the 'd' values were calculated for the peaks having more dominant counts than the background counts. The observed values are in good agreement with standard 'd' values and the composition of these films is found to be mainly of MoO_3 (Hexagonal phase).

The surface morphology of the films were studied by scanning electron microscopy. Scanning electron micrographs of the films prepared at 350°C and 400°C were taken with (X 5000) and (X 7000) magnifications. Inspection of these micrographs revealed that the films were continuous and grain size cannot be defined. The sample prepared at 400°C exhibit rough surface and full with flake like

structure.

Band gap energies of the films were estimated by analysing optical absorption spectrographs. The optical density (αt) of the films were recorded in the wavelength range of 350 to 850 nm at 300 K. In order to confirm the nature of the optical transition in MoO_3 film the plots of $(\alpha h\nu)^2$ versus $(h\nu)$ and $(\alpha h\nu)^{1/2}$ versus $(h\nu)$ were studied for a typical film. From this observation it is concluded that the optical absorption in MoO_3 film takes place through direct interband transitions with band gap energy 2.97 eV.

The absorption coefficient was of the order of 10^4 cm^{-1} and a steep absorption rise was observed on the shorter wavelength side for all the films. The recorded optical data were analysed for both possible direct allowed and direct forbidden optical transitions. From the plots of $(\alpha h\nu)^2$ versus $(h\nu)$ for all the films the bandgap energies were 2.6 eV, 2.97 eV, 2.97 eV, 2.97 eV and 2.82 eV for the samples prepared at substrate temperatures 250, 300, 350, 400 and 450°C respectively. From the plots of $(\alpha h\nu)^{2/3}$ versus $(h\nu)$ the values of band gap energies were 1.05 eV, 2.05 eV, 2.05 eV, 2.05 eV and 1.58 eV for the samples prepared at 250, 300, 350, 400 and 450°C respectively. These observations suggest that the optical transitions in MoO_3 takes place through both direct allowed and direct forbidden transitions.

The dark resistivity of the films were measured with two probe method in the temperature range 400 to 600 K. The room temperature (27°C) resistivity for amorphous films of the order of 10^6-10^7 ohm-cm, while for polycrystalline films it was of the order of 10^3 ohm-cm. This may be due to the improved crystallinity of the films at higher substrate temperatures.

The plot of $\log \rho$ versus $1/T$ consists of two regions, giving two activation energies corresponding to low and high temperature regions. For high temperature region the activation energy is varied from 0.05 to 0.25 eV and for low temperature region, is varied from 0.09 to 0.32 eV. It is seen that the value of activation energies in low and high temperature regions, increases with increase in the film thickness and hence with decrease in substrate temperature. This may be due to the combine effects of variation in crystallinity and dislocation density.

From the above discussion it is concluded that, structural, optical and electrical properties of spray pyrolyzed MoO_3 films depend strongly on substrate temperature.

In chapter V, the electrochromic properties of MoO_3 films are reported. It includes, cyclic voltammetry and chronoamperometry studies of an EC cell and structural and optical properties of the films after and before

In the study of chronoamperometry of polycrystalline MoO_3 film, it is found that initially there is a sharp decrease in colouration current and remains steady within about 10 seconds and the bleaching current decays more rapidly until all the colour leaves the film, then more slowly to an equilibrium value. The bleaching current was about 25 seconds. The colouration process was found to be rapid than bleaching.

The spectral transmittance of the cell was studied in terms of photocurrent during colouration. In the as deposited state, the film was transparent while on application of -0.4 V, the current was lowered by $6 \mu\text{A}$ at 650 nm, indicating that the film transmittance decreases after colouration.

As deposited and coloured films were subjected to XRD analysis and compared. It is found that the XRD peaks of coloured films are shifted from that of as deposited films. The shift may be due to the formation of molybdenum bronze.

The amorphous and polycrystalline films after and before colouration were subjected to optical absorption properties. Before colouration, polycrystalline films were almost transparent at wavelengths longer than 400 nm, while a marked increase in light absorption throughout the visible wavelength spectrum is observed for the coloured films. The

amorphous films before colouration were a transparent at wavelength longer than 550 nm, while after colouration absorption density increases beyond 550 nm. The absorbance change Δ ABS were about 0.9 (at 850 nm) and 0.24 cm^{-1} (at 770 nm) for polycrystalline and amorphous films respectively. This large increase in optical absorption is desirable for "Smart-window" applications.