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Thermodynamic Properties of MoO_3 Thin Films

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Abstract: 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. 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 gaso chromic 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. Many methods of preparation, physical and chemical methods, are used to prepare MoO_3thin films: chemical vapor deposition, magnetron sputtering, sol-gel technology, thermal evaporation technique and flash evaporation. Hence in the present study, thin films of MoO_3 were prepared by thermal evaporation and the structure, thermo emf of the prepared samples was studied. The diffraction pattern of MoO_3thin films deposited at room temperature indicating that the structure is amorphous in nature. The plot of thermo emf versus temperature difference between the two junctions is found to be linear indicating that the temperature dependence of thermo emf is the characteristic conduction of the films.

Keywords: MoO_3thin films, Thermal, Structure and Thermo emf.

INTRODUCTION

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 trioxide (MoO_3), one 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 micro batteries. 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[1].

WO_3, MoO_3 and Nb_2O_5 are well-known electrochromic materials that show cathodic coloration with H^+ or Li^+ ion insertion. As-deposited amorphous MoO_3 films are transparent, but when ions such as H^+ or Li^+ and electrons are electrochemically injected into these molybdenum oxide films, the color of the films changes to dark blue. However, despite three decades of intense studies, the physical mechanism of this color change is still not fully understood. The color change in the films is believed to be directly related to the double injection/ extraction of electrons and ions in the films, which can be written, in a simplified form, as

$$xM^+ + xe^- + a\text{-}MoO_3 \leftrightarrow a\text{-}M_xMoO_3$$

Where M = H, Li, etc. The current models suggest that the optical absorption of the ion-intercalated a-MoO_3 films is caused by electron exchange between adjacent Mo^{5+} and Mo^{6+} ions[2]. MoO_3 have a great technical interest, due to their optical and electronic properties. Indeed these transition metal oxides can be switched between two different optical states prompted by photo chromic, thermo chromic or electrochromic effect. These materials can be used in other applications such as solid state microbatteries. The sub-stochiometric films MoO_{3-x} with oxygen deficient contain excess metal atoms which act as doping centers; these centers control the electrical and optical film properties[3]. MoO_3 is a potential material because of its wide range of stoichiometry with interesting behaviour, which includes chromogenic and catalytic properties. This leads to the applications in electrochromic display devices, optical memories, gas sensors and lithium batteries. Different thin film deposition methods explored for the growth of molybdenum oxide films includes the thermal evaporation, electron beam evaporation, pulsed laser deposition, sputtering, electro-deposition, chemical vapour deposition and sol-gel process. Among these methods, thermal evaporation received considerable attention because it is industrially practiced method for generation of films at low temperatures with required chemical composition on large area substrates[4].

When MoO_3 intercalates Li^+, electrical energy stores in the electrode. Energy releases from the electrode when Li+ diffuses out. For electrochemical pseudo capacitor applications, the charge/discharge rate and the energy storage capacity are the most important parameters. Larger surface area and easy charge transport are required to achieve high charge/discharge rate[5, 6] MoO_3xerogel and aerogel, both offer large surface area, have been explored for such application and have demonstrated a current density of 6 C (C is about 150 mA h/g V_2O_5) without storage loss. However, MoO_3xerogel and aerogels are well-known to suffer from their structural stability; the porous structure readily collapses during Li^+ intercalation and extraction processes. Thermal evaporation is one of the most widely used, simplest and convenient techniques for the deposition of thin films. In this technique, the material can be evaporated by means of resistive heating or rf heating. This is done in a high vacuum, both to allow the vapour to reach the substrate without reacting with or scattering against other gas-phase atoms in the chamber and to reduce the incorporation of impurities from the residual gas in the vacuum chamber. Hence in the present study MoO_3 thin films were deposited by thermal evaporation method and the structure, thermo emf of the samples were studied.

EXPERIMENTAL

MoO_3 thin films were prepared on to Corning 7059 glass substrates by thermal evaporation of pure MoO_3 Powder (purity 99.99% obtained from MERCK) from an electrical heated molybdenum boat

kept at ~ 1823 K in a vacuum better than 8 x 10^{-6}Torr. A Hind High Vacuum 12A4 Coating unit was used for the deposition of the experimental films. A diffusion pump backed by a rotary pump was employed to produce the ultimate pressure of 3 x 10^{-6}Torr. Well cleaned Corning 7059 glass substrate along with suitable masks were mounted on a copper holder which was fixed on a tripod in the beljar. The source to substrate distance was fixed at 15 cm. After getting the ultimate vacuum of 5 x 10^{-6}Torr and the desired substrate temperature in the chamber, the glow discharge was initiated further ionically clean the substrates in the vacuum chamber. This was done for about two minutes. The system was allowed to reach the ultimate vacuum. When the power was fed to the boat, the material in the boat evaporated and the vapours reacted with the oxygen gas leading to film deposition on the substrate. The temperature of the boat during deposition was monitored by means of an optical pyrometer.

The substrates were maintained at the required deposition temperature and then, the molybdenum boat in which MoO_3 powder was kept. The shutter covering the substrates was opened when the temperature of the boat reached about 1823 K and it was maintained during the deposition of the films. The deposition rate observed by a quartz crystal thickness monitor was 10 A^0/sec. The structure of MoO_3 thin films was analyzed using a Philips X-ray diffractometer with CuKα (λ = 1.5418 A^0) target. The X-ray diffraction profiles were recorded in the scanning angle range 10-80^0 with a scanning speed of 1 deg./ min. The thermo emf of the prepared samples was studied between the temperature ranges from 275 to 325 K by using thermal probe method.

RESULTS AND DISCUSSION

The deposition parameters such as substrate temperature, deposition rate, film substrate combination, vacuum during the film deposition etc. greatly influence the physical and chemical properties of the oxide thin films. In the present investigation thin films of MoO_3 were prepared on Corning7059 glass substrates keeping all the deposition parameters fixed except the substrate temperature.

Structure: The X-ray diffraction profiles were recorded in the scanning angle range 10-80^0 with a scanning speed of 1 deg./ min. The X-ray diffraction pattern of room temperature deposited MoO_3 films assured their amorphous nature. **Fig. 1** shows a typical XRD pattern of one of the as deposited MoO_3 thin films.

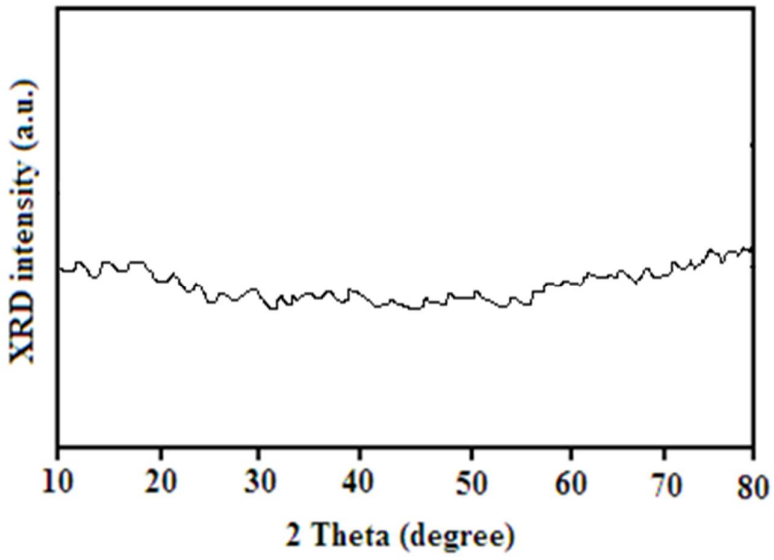

Fig. 1: XRD pattern of MoO_3 thin films deposited at room temperature

Thermo emf: The thermo power or Seebeck coefficient, of a material measures the magnitude of an induced thermoelectric voltage in response to a temperature difference across that material and the entropy per charge carrier in the material[7]. The temperature difference ΔT between the two ends of a material is small and then the thermo power of a material is defined approximately as:

$S = - \Delta V/\Delta T$

And a thermoelectric voltage of ΔV is seen at the terminals. The thermo emf of laser deposited MoO_3 thin film was studied in the temperature range from 275 K - 325 K by using thermal probe method is given in **Table-1**. The thermo emf was measured and the Seebeck coefficient of the material was also calculated. The plot of thermo emf versus temperature difference between the two junctions is found to be linear (**Fig. 2**) indicating that the temperature dependence of thermo emf is the characteristic conduction of MoO_3films. The thermo emf of MoO_3 films increased with the increasing of temperature. At low temperatures the Seebeck coefficient is observed to be high and the Seebeck coefficient decreases with increasing of temperature. The large values of thermoelectric power of MoO_3 thin films are typical of semiconductor behavior.

Table-1: Thermo emf versus temperature

Temperature (K)	Thermo emf (V)
275	0.482
280	0.518
285	0.812
290	1.028
295	1.314
300	1.691
305	1.988
310	2.218
315	2.698
320	3.192
325	3.694

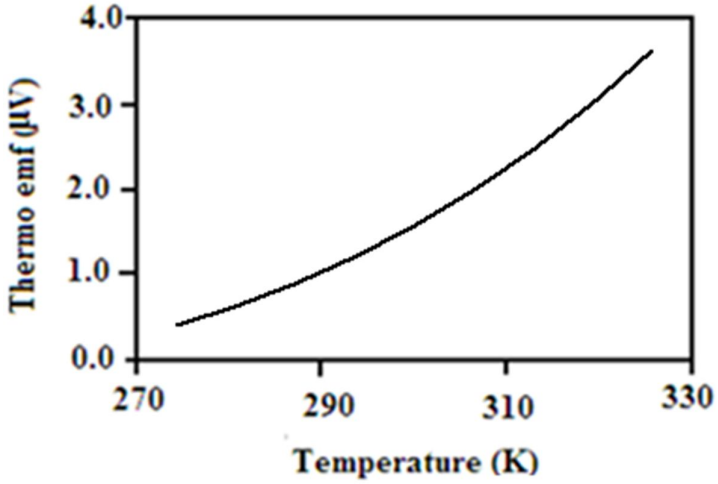

Fig. 2: Temperature dependence of the thermo emf of MoO_3 thin film

CONCLUSIONS

Thin films of MoO_3 were prepared by thermal evaporation method. The structure and thermo emf of the prepared samples were studied. The diffraction pattern of MoO_3 thin films deposited at room temperature indicating that the structure is amorphous in nature. The plot of thermo emf versus temperature difference between the two junctions is found to be linear indicating that the temperature dependence of thermo emf is the characteristic conduction of the films.

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