Thickness dependent structural, morphological and optical properties of molybdenum oxide thin films

Sudesh Kumari^{1,2} · Kamaljit Singh^{1,2} · Palwinder Singh³ · Sanjay Kumar⁴ · Anup Thakur¹

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Abstract

Molybdenum oxide (MoO_3) is a chromogenic and a wide band gap *n*-type semiconductor. Thickness of thin films is usually observed to have significant influence on various properties of chromogenic materials. MoO_3 thin films of different thicknesses (100 nm, 200 nm and 400 nm) were deposited on glass substrates by thermal evaporation technique. The effect of thickness of deposited thin films on the structural, morphological and optical properties was investigated by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FE-SEM) and UV–visible spectroscopy. XRD analysis revealed the amorphous nature of deposited thin films of different thicknesses. FTIR spectrum showed the characteristic vibrations of intermolecular bonds in molybdenum oxide. The surface morphology of MoO_3 films showed nanoflakes like structures which became densely stacked with increase in film thickness and transformed to large grains with uniform coverage of the substrate surface with randomly oriented morphology. The transmission spectra revealed the slight increase in average transmittance in the visible-NIR region with increase in thickness of thin films. The optical band gap of the deposited thin films of different thicknesses was found to be increasing with increase in thickness of the films which may be attributed to decreased defect centres. The decrease in the values of Urbach energy with increase in thickness may be due to the increased homogeneity and decrease in scattering centres.

Keywords Molybdenum oxide · Optical properties · Thin films

1 Introduction

Transition metal oxides are known as chromogenic materials, owing to their ability to change their optical absorption properties on light irradiation (photo-chromic), heat absorption (thermo-chromic) and application of external electric field (electro-chromic) [1, 2]. These materials constitute an interesting group of semiconducting materials because of their technological applications in various fields such as smart windows and display devices [2], solid state micro-batteries [3, 4], electrochromic devices [1] and gas sensor [5]. Among the transition metal oxides,

molybdenum oxide (MoO_3) exhibits interesting structural, chemical, electrical and optical properties due to its high chemical and thermal stability, layered structure [6, 7] and chromogenic nature [8], its applicability in development of electrochromic display devices [9], smart windows, optical switching [2] and gasochromic switching [10]. It can be used as a cathode material in the development of solid state microbatteries [4] and as a catalyst in a variety of partial oxidation reactions [11]. MoO_3 can also be used as gas sensor [12, 13] and in organic light emitting diodes [14].

Molybdenum oxide is a wide band gap *n*-type semiconductor ($E_g \sim 3.20$ eV). It exhibits three different crystal

✉ Anup Thakur, dranupthakur@gmail.com | ¹Advanced Materials Research Lab, Department of Basic and Applied Sciences, Punjabi University, Patiala, Punjab 147 002, India. ²Department of Physics, Punjabi University, Patiala, Punjab 147 002, India. ³Institute of Nano Science and Technology, Mohali, Punjab 160 062, India. ⁴Department of Chemistry, Multani Mal Modi College, Patiala, Punjab 147 001, India.

structures, thermodynamically stable orthorhombic MoO_3 ($\alpha\text{-MoO}_3$), metastable monoclinic MoO_3 ($\beta\text{-MoO}_3$) and hexagonal MoO_3 (h-MoO_3). Many crystalline mixed-valence sub oxides with compositions between $\text{MoO}_{2.75}$ and MoO_3 are also known, that includes the γ and η phases of Mo_4O_{11} ($x \approx 2.75$), $\text{Mo}_{17}\text{O}_{47}$ ($x \approx 2.76$), Mo_5O_{14} ($x \approx 2.80$), Mo_8O_{23} ($x \approx 2.88$) and Mo_9O_{26} ($x \approx 2.89$) (in the monoclinic and triclinic ($\text{Mo}_{18}\text{O}_{52}$) phases) [15]. For the device applications, deposition of thin films of suitable thickness and optimization of their properties is required. Various deposition techniques have been employed to deposit molybdenum oxide thin films that include chemical vapor deposition [16], vacuum thermal evaporation [17], sol-gel coating [18], sputtering [19, 20], electro-deposition [21], flash evaporation [22] and spray pyrolysis technique [23]. Among these, vacuum evaporation is a widely used, reliable and highly efficient technique for depositing thin films of molybdenum oxide. This technique has very low chances of film contamination and does not damage the substrate. MoO_3 can be easily deposited as thin films with this technique since its melting and evaporation point [24] can be easily achieved by thermal evaporation. The films deposited by thermal evaporation are usually amorphous and sub-stoichiometric MoO_{3-x} [24, 25]. The oxygen vacancies present in the films can trap electrons and result in the formation of color centers [6]. These substoichiometric films find applications in photochromic, thermochromic and electrochromic devices [26, 27].

Limited literature has been reported on the effect of thickness on various properties of thermally evaporated molybdenum oxide thin films as compared to other deposition techniques for depositing molybdenum oxide thin films. The effect of thickness has been investigated and reported in this research work for the optimization of different properties of molybdenum oxide thin films.

2 Experimental details

Thin films of molybdenum oxide were deposited on glass substrates using thermal evaporation technique [28–30]. MoO_3 powder (99.99 % pure, Sigma Aldrich) as source material was used. High vacuum ($\sim 5 \times 10^{-6}$ mbar) inside the deposition chamber was maintained through out the deposition. The rate of deposition ($\sim 3\text{--}4$ Å/s) and thickness of films were measured *in-situ* by a digital thickness monitor (Hind High Vacuum DTM-101). By varying the amount of MoO_3 powder in evaporation boat, films of different thicknesses (100 nm, 200 nm and 400 nm) were deposited. Prior to the deposition of films, substrates were washed with water and cleaned ultrasonically at a temperature of 50°C for 45 min. Then the substrates were cleaned

with acetone and methanol and heated at 80°C for 1 h to remove any volatile impurities.

X-ray diffraction (XRD) patterns of the deposited films were recorded on a diffractometer with Cu-K_α radiation ($\lambda \sim 1.5406$ Å). Fourier transformed infrared (FTIR) spectra was recorded using FTIR spectrometer (Agilent Cary 630). The morphology of the deposited films was analyzed with Field emission scanning electron microscopy (FE-SEM) technique (HITACHI SU8010). The optical transmission of the films was recorded in the wavelength range 300–2400 nm using UV–visible–NIR spectrophotometer (Varian Cary-5000).

3 Results and discussion

3.1 Structural study

Figure 1 shows the XRD patterns of as-deposited molybdenum oxide thin films having thickness 100 nm, 200 nm and 400 nm. The presence of broad hump and absence of sharp peaks in the XRD patterns of as-deposited films confirms the amorphous nature. Touihri et al. [25] also obtained the similar results for 250 nm thick MoO_3 thin films.

The FTIR spectra of the MoO_3 thin films of different thicknesses are shown in Fig. 2. The FTIR spectra of thin film of thickness 100 nm showed the vibration bands at 446.7 cm^{-1} , 508.4 cm^{-1} which were assigned to the stretching vibration of O atoms in the O-Mo-O units. The bands at 573.2 cm^{-1} and 688 cm^{-1} were assigned to the bending vibration of O atoms in Mo-O-Mo units. Chibane et al. [31] have reported the similar

Fig. 1 X-ray diffraction patterns of molybdenum oxide thin films of different thicknesses

Fig. 2 Fourier transformed infrared spectra of molybdenum oxide thin films of different thicknesses

characteristic absorption bands of molybdenum oxide in the wave-number range 400–2000 cm^{-1} . For the thin film of thickness 200 nm, the FTIR spectrum showed the bands at 457.9 cm^{-1} , 580.2 cm^{-1} and 804.1 cm^{-1} . The band observed at 457.9 cm^{-1} was assigned to stretching vibration of O atoms in O-Mo-O units and the bands at 580.2 cm^{-1} , 804.1 cm^{-1} were assigned to bending vibration of O atoms in Mo-O-Mo units. FTIR spectrum of thin film of thickness 400 nm showed absorption bands at 421.4 cm^{-1} (assigned to stretching vibration of O atoms in O-Mo-O units), 758.9 cm^{-1} (associated with Mo-O stretching vibration) and 899.7 cm^{-1} (due to Mo=O stretching vibration).

3.2 Morphological study

The morphology of as-deposited MoO_3 thin films of different thicknesses have been characterized by FE-SEM, as shown in Fig. 3. It is clear from this figure that the morphology of film having thickness 100 nm was composed of irregular shaped nanoflakes like structures of different sizes that were randomly distributed. Film of thickness 200 nm was also composed of irregular nanoflakes that were more densely stacked. With further increase in thickness

of film (400 nm), the nanoflakes transformed to grains of irregular shapes. It is also confirmed from these images that the uniformity of films improves with increase in thickness. The change in morphology with thickness is also observed in $\text{Cu}_x\text{S}_y\text{O}_z$ thin film [32].

3.3 Optical study

The optical transmission spectra of as-deposited MoO_3 thin films of various thicknesses are shown in the Fig. 4. All the films exhibited high optical transparency better than 80 % from visible to NIR region. A slight increase in transmission with the increase in thickness of the films was observed which may be attributed to the increased homogeneity of thin films and decreased scattering centres. The appearance of fringes in transmission spectra is due to the optical interference effect and also confirm the uniformity of films [33, 34].

The optical band gap of molybdenum oxide thin films can be estimated from the optical transmission using Tauc's relation [35]:

$$\alpha h\nu = B(h\nu - E_g)^n \quad (1)$$

where α is the absorption coefficient, B is a constant, $h\nu$ is the photon energy, E_g represents the optical band gap and n is the exponent parameter related to the optical transition type. The value of n depends upon the optical transitions and it can take values $\frac{1}{2}$, 2, $\frac{3}{2}$ and 3 for direct allowed, indirect allowed, direct forbidden and indirect forbidden transition, respectively. For the molybdenum oxide thin films, the value of parameter n is $\frac{1}{2}$ indicating direct transition. The direct energy band gap values has been calculated from a plot of $h\nu$ versus $(\alpha h\nu)^2$ as shown in the Fig. 5. The value of band gap energy was obtained by extrapolating the linear portion of the curve to $h\nu$ axis at which the value of $(\alpha h\nu)^2$ becomes zero. Hence the optical band gap was 3.26 eV for film of thickness 100 nm, 3.32 eV for film of thickness 200 nm and 3.35 eV for film of 400 nm thickness. The increase in band gap with thickness may be attributed to the decrease in defect states. These results of optical band gap are in agreement with those reported in literature. Dhanasankar et al. [36] obtained band gap of multilayered molybdenum oxide films in the range 3.20 to 3.72 eV and reported the increase in band gap with thickness. Kumar et al. [37] obtained band gap of 3.56 eV for molybdenum oxide thin film deposited by spray pyrolysis technique.

The optical absorption spectrum of the semiconducting thin film consists of three regions: weak absorption region, absorption edge region and region of strong absorption [38]. Near the optical band edge, the exponential relation between absorption coefficient (α) and photon energy

Fig. 3 Field emission scanning electron microscopic images of the surface morphology of molybdenum oxide thin films of different thicknesses

Fig. 4 Optical transmission spectra of molybdenum oxide thin films of different thicknesses

($h\nu$) is known as Urbach empirical rule, which is given by the equation:

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_U}\right) \quad (2)$$

where α_0 is a constant, $h\nu$ is the incident photon energy and E_U is the band tail width (Urbach energy) of the localized states in the optical energy gap. This exponential part is called Urbach tail that appears in amorphous semi-conducting materials due to localized states which are extended in the band gap [39]. Taking the logarithm of both sides of above equation, one can obtain the equation of straight line given as:

$$\ln \alpha = \ln \alpha_0 + \left(\frac{h\nu}{E_U}\right) \quad (3)$$

Fig. 5 **a** Plot of $(\alpha h\nu)^2$ versus $h\nu$ and **b** Plot of $\ln(\alpha)$ versus $h\nu$ for molybdenum oxide thin films of different thicknesses

The reciprocal of slope of straight line of plot $\ln \alpha$ versus the incident photon energy ($h\nu$) gives the value of Urbach energy. Higher value of Urbach energy indicates the presence of more disorder and defects in the lattice that can introduce localized states at or near the conduction band level which then leads to increase in the band tail width E_U [38, 40]. Urbach energy for MoO_3 thin films was calculated from the reciprocal of slope of $\ln \alpha$ vs. $h\nu$ (Fig. 5b) and is 196.6, 188.6 and 175.1 meV for films of thickness 100 nm, 200 nm and 400 nm, respectively. The decrease in the values of Urbach energy with increase in thickness is due to the increased homogeneity and decrease in scattering centres.

4 Conclusions

Thin films of molybdenum oxide of different thicknesses were fabricated from molybdenum powder onto glass substrates using thermal evaporation method. XRD

analysis of as-deposited films revealed their amorphous nature. FTIR analysis revealed the characteristic absorption bands of molybdenum oxide. Surface morphological analyses revealed that the deposited films were composed of nanoflakes whose length and density varied with thickness. The optical transmittance of films indicated the good transparency of the deposited films. An increase in optical band gap and decrease in Urbach energy with the increase in thickness of the films was observed. This may be due to the increased homogeneity of thick films that led to decreased scattering centres.

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Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest.

Human and animals rights This article does not contain any studies with human participants or animals performed by the author.

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