Structural, Morphological and Optical Properties of Bias Sputtered MoO_3 Films

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Abstract: Molybdenum oxide (MoO_3) films were deposited by RF magnetron sputtering of molybdenum target on unheated glass and silicon substrates in an oxygen partial pressure of $4x10^{-2}$ Pa and at different substrate bias voltages in the range from 0 V to -150 V. Effect of substrate bias voltage on the structural, morphological and optical properties of the MoO_3 films was investigated. XRD studies indicated that the films formed on unbiased substrates were amorphous. Polycrystalline with α- phase MoO_3 were achieved at substrate bias voltage of -150 V were of mixed phase of α- and β- phase MoO_3. The microstructure of the films transforms into needle like structure when deposited at higher substrate bias voltages. The optical band gap of the films increased from 3.03 eV to 3.12 eV and refractive index increased from 2.02 to 2.12 with increase of bias voltage from 0 V to -100 V.

Keywords: Molybdenum oxide thin films, RF magnetron sputtering, Bias voltage, Structural, Morphological, Optical properties.

I. INTRODUCTION

Among these transition metal oxides, molybdenum oxide (MoO_3) have much importance in sensing of ethanol [1], nitrogen oxide [2] and carbon monoxide gases [3], solid state microbatteries [4], catalyst [5], electro-chromic devices [6], and solar cells [7] and light emitting diodes [18-20]. Different thin film physical deposition techniques such as thermal evaporation [8], pulsed laser deposition [9], electrodeposition [10], DC magnetron sputtering [11] and RF magnetron sputtering [12] for the preparation of MoO_3 thin films. The influence of sputter power on the structural and optical properties of molybdenum oxide films were earlier reported [13]. In the present investigation, MoO_3 films were deposited by RF sputtering at various substrate bias voltages in the range from 0 V to -150 V. The influence of substrate bias voltage on the structural, morphological and optical properties of the MoO_3 film were studies systematically and presented the results.

II. EXPERIMENTAL

MoO_3 films were deposited on glass and silicon substrates by RF magnetron sputtering method. The sputter system pumped by diffusion and rotary pump combination to produce ultimate pressure of $2x10^{-6}$ mbar. Pure molybdenum of 50 mm diameter and 3 mm thickness was used as sputtering target. The required quantities of oxygen and argon gases were admitted into the sputter chamber through fine controlled needle values. MoO_3 films were formed at different substrate bias voltages in the range from 0 to -150 V, at fixed oxygen partial pressure of $4x10^{-4}$ mbar and sputter pressure of $4x10^{-2}$ mbar. Thickness of the films was measured using Vecco Dektak depth profilometer. X-ray diffraction was used to determine the crystallographic structure of the films. Scanning electron microscope was employed to analysed the surface morphology of the films. Chemical binding configuration of the films was studied with Fourier transform infrared spectrophotometer in the wavenumber range 400 – 1500 cm^{-1}. Optical transmittance of the films was recorded using Perkin-Elmer double beam spectrometer in the wavelength range 300 – 1500 nm in order to determine the optical band gap and refractive index.

III. RESULTS AND DISCUSSION

A. Deposition rate:

The deposition rate of the films was determined from the thickness and duration of the deposition. Deposition rate of the films formed under unbiased condition was 8.2 nm/min. It increased to 9.7 nm/min with increase of substrate bias voltage from 0 to -150 V as shown in the figure 1. The thickness of the films investigated was in the range 0.98 - 1.16 μm. The increase of thickness increase in the substrate bias was due to the negative bias attracts the positively charged sputtered species and clusters in the plasma.

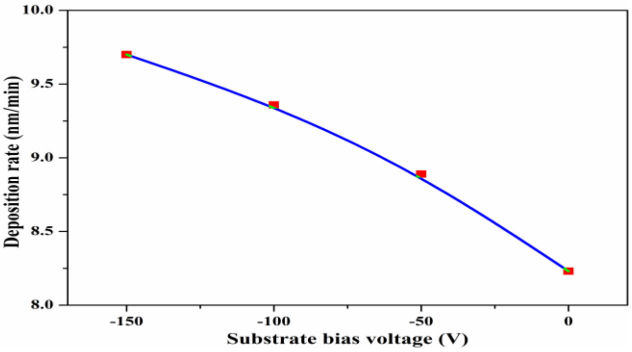

Fig. 1. Variation of deposition rate with substrate bias voltage of MoO_3 films

B.Structural properties:

Figure 2 shows the X-ray diffraction profiles of the films formed at different substrate bias voltages. The films formed under unbiased substrates showed a broad absorption band without presence of absorption bands revealed the amorphous nature. The films prepared at bias voltage of -50 V showed different peaks at 2θ = 12.64 and 25.5° related to the (020) and (040) reflections indicated the growth of orthorhombic α-MoO_3 phase. The lattice parameters achieved were (a = 3.962°A, b = 13.858°A and c = 3.697°A). The achieved lattice parameters were in good agreement with JCPDS data [card no 35-0609]. As the substrate bias voltage increased to -100 V the intensity of (020) peak enhanced sur to improved crystallinity. Further increase of bias voltage to -150 V the films showed the (020), (011), (110) and (040) peaks. The peaks located at (011) and (110) correspond to theβ-MoO_3 along with α-phase which indicated that the grown films were of mixed phase. It revealed that the single phase of α- MoO_3 were obtained at -100V. The increase of crystallinity with the bias voltages is due to accelerated interaction of positive ions in the plasma with growing surface with increased energy [14]. Amorphous to crystalline transformation takes place with the bias voltage was noticed in sputter deposited tin oxide films formed at substrate bias voltage of -50 V [15] and in RF magnetron sputtered tantalum oxide films at bias voltage of -100 V [16]. The crystallite size of the MoO_3 films calculated by using Debye-Scherrer's relation [17]

$$D = k\lambda / \beta\cos\theta \qquad (1)$$

where k is a constant which is a value of 0.89 for copper kα radiation, β the full width at half maximum intensity of the X-ray diffraction peak measured in radians and θ the diffraction angle. The crystallite size of the films increased from 6 to 11 nm with increase of substrate bias voltage from -50 V to -100 V later decreased to 3 nm at higher substrate bias voltage of -150 V. The decrease in the crystallite size at higher bias voltage of -150 was due to decrement in the crystallinity of the films.

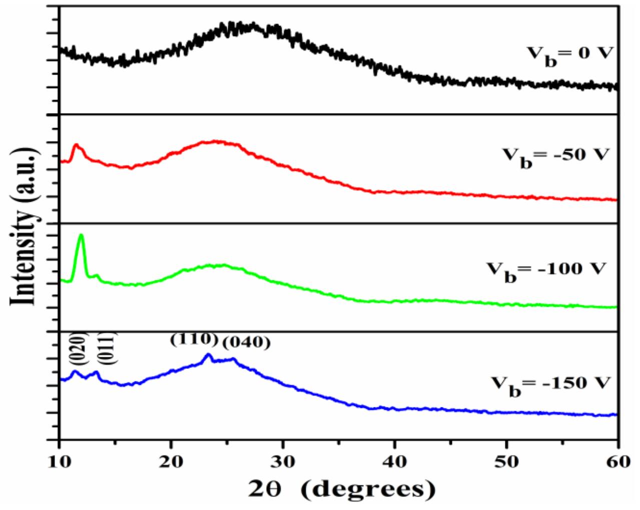

Fig. 2. XRD profiles of MoO_3 films

C.Fourier transforms infrared studies:

The Fourier transform infrared spectra of MoO_3 films formed on silicon substrates at different substrate bias voltages are shown in figure 3. The FTIR spectra of unbiased films have broad band in between wavenumbers 600 and 1000 cm^{-1}. The FTIR spectra of the films formed at -50 V showed a band at 811 cm^{-1} related to the stretching vibrational mode of Mo = 0. A weak band located at 569 cm^{-1} was related to the presence of transverse optical vibrations of Mo-O-Mo, which attributed to the wide range of bond angles and bond lengths [18]. When substrate bias voltage increased to -100 V the broad band was observed at 818 cm^{-1} with weak band at 568 cm^{-1}. The broad band shifted towards higher wavenumber side and weak bond shifted towards lower wavenumber side. Further increase of substrate bias voltage to -150 V the broad band observed at 819 cm^{-1} and weak bond at 568 cm^{-1}. The intensity of IR absorption band was increased with increase of substrate bias voltage. This may be due to the ad-atom high bias mobility at voltages which improves the crystallinity of the films.

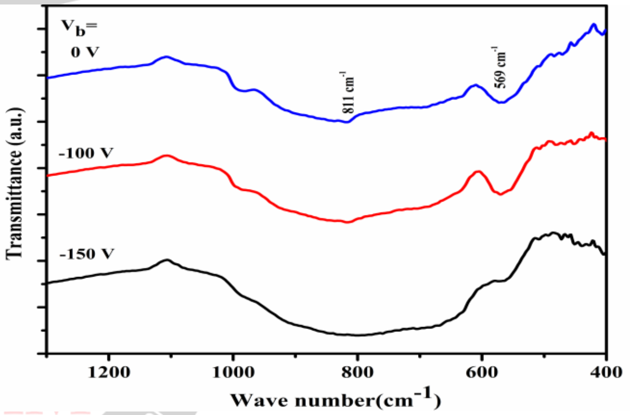

Fig. 3. FTIR spectra of MoO_3 films at different bias voltages (a) 0 V, (b) -100 V and (c) -150 V

D. Surface morphology:

Scanning electron microscopic images of MoO_3 films deposited at different substrate bias voltages are shown in figure 4. Microstructure analysis of the films reveals that the dense grains were observed at low substrate bias voltages. Microstructure of the films transform into needle like structure when deposited at higher substrate bias voltage (-100 and -150 V). Formation of such needle like morphology was also observed by Ramana et al. [19] in DC magnetron sputtered films. Nivas et al. [20] also obtained MoO_3 nano rods of 1.2 μm length and 200 nm diameters in RF magnetron sputtering followed by annealing at temperature of 673 K. This needle shaped grains were grown due to enhanced ad-atom mobility at high bias voltages to promote the growth of larger size grains in the films.

DOI : 10.35291/2454-9150.2021.0020

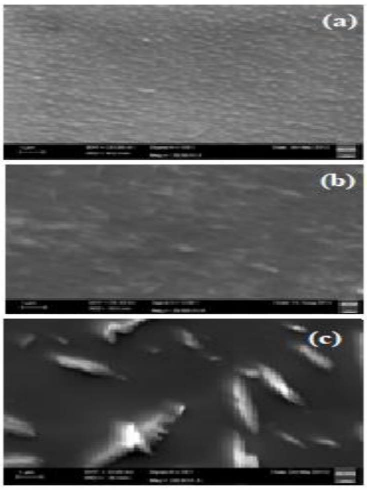

Fig. 4. SEM Images of MoO_3 films formed at bias voltages (a) 0V, (b) -100 V and (c) -150 V

E. Optical properties:

The optical transmittance spectra of the MoO_3 films formed at different substrate bias voltages are shown in figure 5.

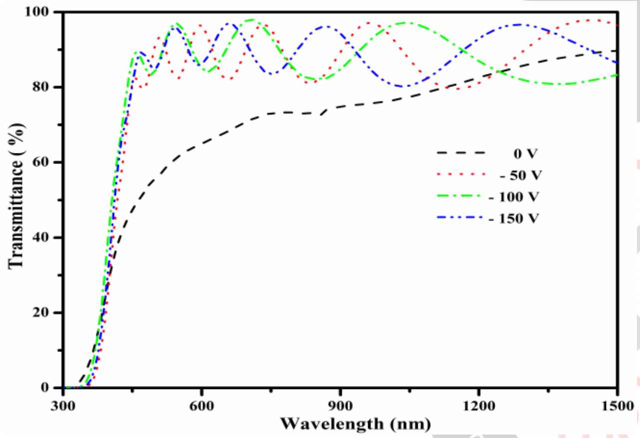

Fig.5. Optical transmission spectra of MoO_3 films formed with different substrate bias voltages

The optical transmittance was low in the case of the films formed on unbiased substrate due to the oxygen ion vacancies. As the bias voltage increased to -50 V and -100 V, the transmittance of the films increased due to decrease in the density of scattering centers of molybdenum. Further increase of the bias voltage to -150 V a slight decrease in the transmittance was due to the oxygen ion vacancies. A sharp absorption edge was observed at around 400 nm in all the films.

The optical absorption coefficient (α) of the films was evaluated from the optical transmittance (T) and thickness (t) if the deposited film using the relation

$$\alpha = -(1/t)\ \ln T\ \ (cm^{-1}) \qquad (2)$$

The optical transitions between the valance and conduction bands can be understood by recording wavelength dependence of optical transmittance. Optical absorption in the films followed Tauc's relation [21],

$$\alpha h\nu = A(h\nu - Eg)^x \qquad (3)$$

where A is a constant, Eg the energy band gap, hν the energy of the incident photon and x a constant. Optical band gap was determined from the plot of $(\alpha h\upsilon)^2$ versus photon energy of the films formed with different substrate bias voltages is shown in figure 6. The optical band gap of films deposited at unbiased condition was 3.03 eV. The optical band gap of the films increased to 3.12 eV with increase of substrate bias voltage to -100 V. The increase of optical band gap with increase of bias voltage was due to decrease of oxygen ion vacancies in the films. Further increase of the bias voltage to -150 V, the bandgap decreased to 3.08 eV due to creation of oxygen ion vacancies. Bouzidi et al. [22] observed the decrease in the optical band gap from 3.30 to 3.14 eV in spray deposited films.

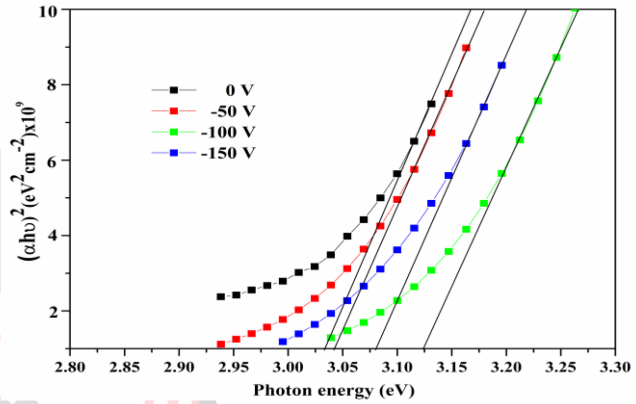

Fig. 6. Plots of $(\alpha h\upsilon)^2$ versus photon energy of MoO_3 films

The refractive index (n) of the films was calculated from the interference fringes of the optical transmittance using Swanepoel envelope method [23] by relation

$$n(\lambda) = [N+(N^2 - no^2n_1^2)\ ½]^{1/2} \qquad (4)$$

where

$$N(\lambda) = (n_on_1)(T_M-T_m)/T_MT_m)]+(n_o^2-n_1^2)^{1/2} \qquad (5)$$

where TM is the transmittance maxima, Tm the transmittance minima in the interference spectrum, no the refractive index of the medium air and n1 the refractive index of the substrate of glass.The refractive index of the films at 600 nm wavelength increased from 2.02 to 2.12 with the increase of bias voltage from -50 V to -100 V due to improvement of crystallinity and packing density. Further increasing to -150 V, the refractive index decreased to 2.09 due to formation of oxygen ion vacancies. This is in coincides with the results of Mohamed et al. *[18]* in DC magnetron sputtered films.

IV. CONCLUSION

MoO_3 films were deposited on glass plates and silicon substrate held at room temperature by RF magnetron sputtering at a fixed oxygen partial pressure of $4x10^{-4}$ mbar and at different substrate bias voltages in the range from 0 V to -150 V. X-ray diffraction studies suggest that the

DOI : 10.35291/2454-9150.2021.0020

MoO_3 was orthorhombic at low substrate bias voltages, and polycrystalline at bias voltages > -100 V. SEM images at higher bias voltages consists needle like morphology due to better ad-atom mobility. FTIR studies indicated the shifting of Mo = O and Mo - O - Mo bonds with increase of substrate bias voltages explain the improvement of crystallinity of the films. The optical transmittance of the films increased with increase of substrate bias voltage. Optical band gap of unbiased films was 3.03 eV with refractive index of 2.02. The optical band gap and refractive index increased to 3.12 eV and 2.12 respectively with bias increased to -100 V, due to improvement in the crystallinity. For a higher bias voltage of -150 V, the band gap is 3.08 eV and refractive index was 2.09 due to formation of oxygen ion vacancies.

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DOI : 10.35291/2454-9150.2021.0020