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Characterization of molybdenum oxide films prepared by bias magnetron sputtering

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Thin films of molybdenum oxide were deposited on unheated glass substrates using dc magnetron sputtering method by sputtering of molybdenum target in the presence of oxygen and argon gas mixture under various substrate bias voltages in the range 0 to - 150 V. The effect of substrate bias voltage on the structure, electrical and optical properties was studied. From X – ray photoelectron spectroscopy studies revealed that the films formed on the unbiased substrates were substoichiometric with the presence of mixed oxidation states of Mo^{6+} and Mo^{5+}. As substrate bias voltage increased to – 120 V, the films were stoichiometric with oxidation state of Mo^{6+}. X-ray diffraction studies indicated that the films deposited on the unbiased substrates were amorphous in nature. The films formed at – 120 V were orthorhombic α – phase of MoO_3. The films deposited under unbiased condition showed high electrical conductivity of 3.6×10^{-4} Ω^{-1} cm^{-1} due to the amorphous nature, while those films deposited at the substrate bias voltage of -120 V showed the decrease in the electrical conductivity to 4.5×10^{-5} $\Omega^{-1} cm^{-1}$ due to the partial filling of oxygen vacancies. The unbiased films showed an optical band gap of 3.03 eV with the refractive index of 2.03. As the substrate bias voltage increased to -120 V the optical band gap of the films increased to 3.22 eV and refractive index increased to 2.13 due to the improvement in the crystallinity and packing density of the grown films.

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1. Introduction

Transition metal oxide films show wide variety of physical properties which make them as prime candidates for the exploration of structural properties in solids provides wide opportunities for technological applications. Among these transition metal oxides, molybdenum oxide (MoO_3) shows interesting structural, electrical and optical properties [1,2]. MoO_3 find applications as a cathode material in high density solid state microbatteries [2-4]. MoO_3 is considered as a chromogenic material since it shows electro-, photo- and gasochromic effects, and by virtue of these properties it is of scientific interest for the development of electrochromic display devices, optical switching and smart windows [5-8]. Nanocrystalline MoO_3 films find applications in gas sensors and lubricants [6,9]. In all these technological applications, the optimization of deposition conditions was very much essential to generate single phase MoO_3 films with required structural, electrical and optical properties. Different thin film physical deposition techniques such as thermal evaporation, electron beam evaporation, pulsed laser deposition and sputtering, and chemical deposition methods namely chemical vapour deposition, electrodeposition, spray pyrolysis and sol-gel process were used for preparation of MoO_3 films [3-18]. Among the physical deposition methods, dc magnetron sputtering received considerable attention because of the preparation of uniform films on large area substrates by sputtering of metallic molybdenum target in the presence of oxygen and argon gas mixtures. The physical properties of the dc magnetron sputtered films depend mainly on the deposition parameters such as the oxygen partial pressure, substrate temperature and substrate bias voltage. In order to achieve the crystalline films, the substrates are generally heated to high temperature during the deposition. This prevents the use of temperature sensitive substrates like plastics which are currently used for certain light weight devices. The effect of substrate heating can be achieved by ion bombardment during the growth of the films. The simple way of ion bombardment can be achieved by biasing the substrate during the deposition of the films in sputtering. In this investigation, an attempt is made in the preparation of MoO_3 films by dc magnetron sputtering under different substrate bias voltages and studied its influence on the growth and physical properties.

2. Experimental details

Molybdenum oxide films were deposited on glass substrates held at room temperature (303 K) by dc reactive magnetron sputtering method. Pure molybdenum of 50 mm diameter and 3 mm thick was used as sputter target. The vacuum system used for sputter deposition of the films was the combination of diffusion and rotary pumps which produce an ultimate pressure of 2×10^{-6} mbar. The required quantities of oxygen and argon gases were admitted in to the sputter chamber through fine controlled needle valves and their flow rates were monitored

individually employing Taylan mass flow controllers. The MoO_3 films were formed under different substrate bias voltages in the range 0 to - 150 V, and at an oxygen partial pressure (pO_2) of $2x10^{-4}$ mbar and sputtering pressure of $4x10^{-2}$ mbar. X - ray diffractometer (Seifert model 3003 TT) with Cu K_α radiation was used to determine the crystallographic structure of the films. Atomic force microscopy (AFM) was employed to characterize the surface morphology of the films using Digital Nanoscope. The core level binding energy and oxidation states of the films were analyzed by using X-ray photoelectron spectroscope (Model Kratos – Axis 165). The electrical resistivity of the films was measured using standard two probe technique. The optical transmittance and reflectance was recorded using double beam spectrophotometer (Hitachi model U-3400) in the wavelength range 300 - 1500 nm to determine the optical band gap and refractive index of the films.

3. Results and discussion

The physical properties of the MoO_3 films were highly influenced by the substrate bias voltage maintained during the deposition of the films. Fig. 1 shows the dependence of deposition rate of MoO_3 films on the substrate bias voltage. The deposition rate of the MoO_3 films formed on unbiased substrate was 21.3 nm/min. Deposition rate of the films increased to 23.4 nm/min with the increase of substrate bias voltage to - 120 V. The increase in the deposition rate with the increase of substrate bias voltage was attributed to the negative bias attract the positively charged molecules and clusters of the sputtered species in the plasma hence increased in the thickness of the deposited film. Further increase of substrate bias voltage to -150 V, the deposition rate start decrease and reached to a value of 22.8 nm/min. The decrease in the deposition rate at higher substrate bias voltages may be due to the bombardment of positively charged particles caused the number of molecules to resputter from the film surface. Such a dependence of deposition rate on the substrate bias voltage was also noticed by Yang et al. [19] in rf sputtered indium tin oxide films.

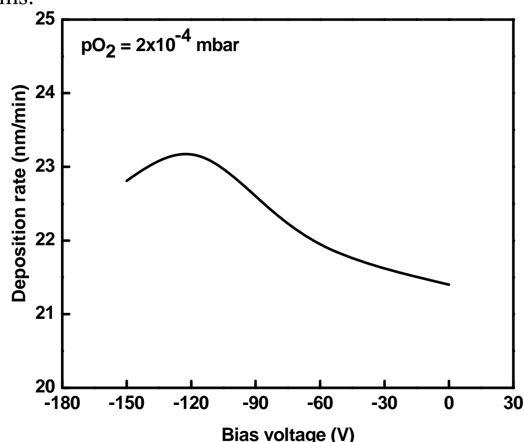

Fig. 1. Dependence of deposition rate of MoO_3 films on the substrate bias voltage.

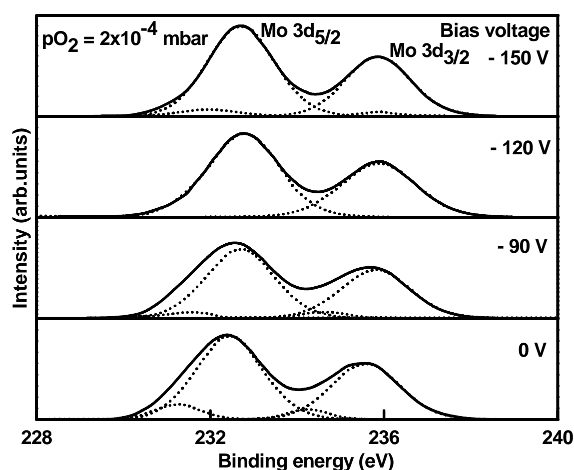

Fig. 2. XPS core level binding energy spectra of Mo 3d of MoO_3 films formed at different substrate bias voltages.

The core level binding energies and oxidation states in the deposited MoO_3 films was analyzed from the X – ray photoelectron spectroscopic studies. The survey scans for the films formed at different substrate bias voltages showed core level binding energy peaks characteristic of oxygen and molybdenum. The peak observed at about 531 eV was due to the core level of O 1s, the doublet located at 412 and 395 eV were the binding energies of Mo $3p_{1/2}$ and Mo $3p_{3/2}$respectively. The peaks situated at 232 and 235 eV correspond to the Mo 3d doublet. The peaks seen at about 65 and 35 eV were the core levels of Mo 4s and Mo 4p respectively. The peaks positioned at about 22, 7 and 5 eV were related to the binding energies of O 2s, O 2p and Mo 4p respectively [20]. The narrow scan spectra of Mo 3d doublet in the binding energy range 228 – 240 eV of the MoO_3 films formed at different substrate bias voltages are shown in Fig. 2. The films formed under unbiased substrate contained the core level binding energies of Mo $3d_{5/2}$ and Mo $3d_{3/2}$ at 232.44 and 235.58 eV respectively with spin orbit splitting of 3.14 eV as shown in the Fig. 2. This core level spectrum showed the asymmetric shoulders due the presence of mixed oxidation states of Mo^{5+} and Mo^{6+} of MoO_3. The deconvolution of the asymmetric peaks resulted the additional peaks at 231.23 and 234.38 eV respectively the Mo $3d_{5/2}$ and Mo $3d_{3/2}$ in the oxidation state of Mo^{5+} along with the Mo^{6+}. It indicated that the films formed under unbiased condition were substoichiometric [21] with the presence of mixed phase of MoO_3 and MoO_{3-x}. The films formed at substrate bias voltage of - 90 V, the spectrum also exhibited the asymmetric peaks of Mo $3d_{5/2}$ and Mo $3d_{3/2}$ at binding energy of 232.65 and 235.83 eV respectively. Further, increase of substrate bias voltage to - 120 V, the symmetric peaks of Mo $3d_{5/2}$ and Mo $3d_{3/2}$ were observed with the core level binding energies of 232.75 and 235.94 eV respectively, with the spin orbit spitting of 3.19 eV, which is the characteristic of Mo^{6+} oxidation state of MoO_3 as observed in electron beam evaporated films [22]. At

higher substrate bias voltage of – 150 V the core level binding energy peaks showed again the mixed phase of MoO_3 and MoO_{3-x}. The core level of O 1s also shifted towards lower core level binding energy side from 530.29 to 530.05 eV with the increase of substrate bias voltage from 0 to - 120 V respectively thereafter increased to 530.18 eV at higher substrate bias voltage of – 150 V. It revealed that the films formed at substrate bias voltage at - 120 V were single phase with the existence of Mo^{6+} oxidation state of MoO_3.

Fig. 3 shows the X-ray diffraction profiles of the films formed at different substrate bias voltages. The films formed under unbiased condition showed a broad band with out the presence of any diffraction reflections indicated the films were in amorphous nature. The films prepared at the substrate bias voltage of - 90 V showed the reduction in the intensity of the broad band with the presence of different peaks at 2θ = 12.62, 23.02, 25.5 and 38.9° related to the (020), (011), (040) and (060) reflections of MoO_3 indicated the films were in polycrystalline nature. The exhibited (020), (040) and (060) peaks correspond to α - phase MoO_3, while the (011) reflection with low intensity related to the β – phase of MoO_3. Hence the amorphous films could be crystallized into the mixed phase of α - and β - phase of MoO_3 when the bias voltage increased to - 90 V. At substrate bias voltage of - 120 V, the presence of (0k0) reflections clearly showed that the films formed were orthorhombic with layered structure of α - phase MoO_3. The substrate bias voltage further increased to – 150 V, the diffraction pattern exhibited the (110), (200) and (022) along with (0k0) reflections indicated the polycrystalline nature with the coexistence of α – and β - phase of MoO_3. The lattice parameter of the films formed at the substrate bias voltage of -120 V was a = 0.398, b = 13.860 and c = 0.369 nm which is in good agreement with the JCPDS data card No. 35-0609 [23]. In the present study polycrystalline films were obtained at substrate bias voltages ≥ - 90 V. The enhancement of crystallinity with the bias voltage may be attributed to the accelerated interaction of positive ions in the plasma with the growing surface. The substrate bias endues the positive ions with high energy, enhanced the diffusion of deposited particles and/or the relaxation of the growing surface was probably increased by the collision of the accelerated positive ions in the sheath of the plasma [24]. Therefore, application of negative bias voltage increases the energy of positively charged particles bombarding the substrate and initiates the process of sputtering from the surface of growing films. It can be understood that the ion bombardment on the substrates has a similar effect of substrate heating. To the best of our knowledge there were no reports on the substrate bias voltage influenced properties of MoO_3 films formed by magnetron sputtering. The amorphous to crystalline transformation with the substrate bias voltage was also observed in the indium tin oxide films formed at the bias voltage of - 50 V [25], cadmium oxide films formed at – 30 V [26] in dc reactive magnetron sputtering where as the tantalum oxide [26] films at –100 V by rf magnetron sputtered films.

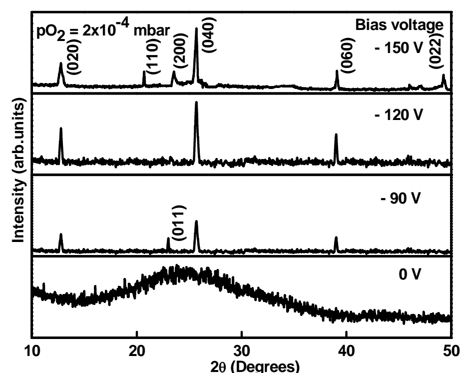

Fig. 3 X - ray diffraction profiles of MoO_3 films formed at different substrate bias voltages.

AFM images of MoO_3 films deposited at different substrates bias voltages are shown in figure 4. The surface morphology of the films significantly varied with the substrate bias voltage.

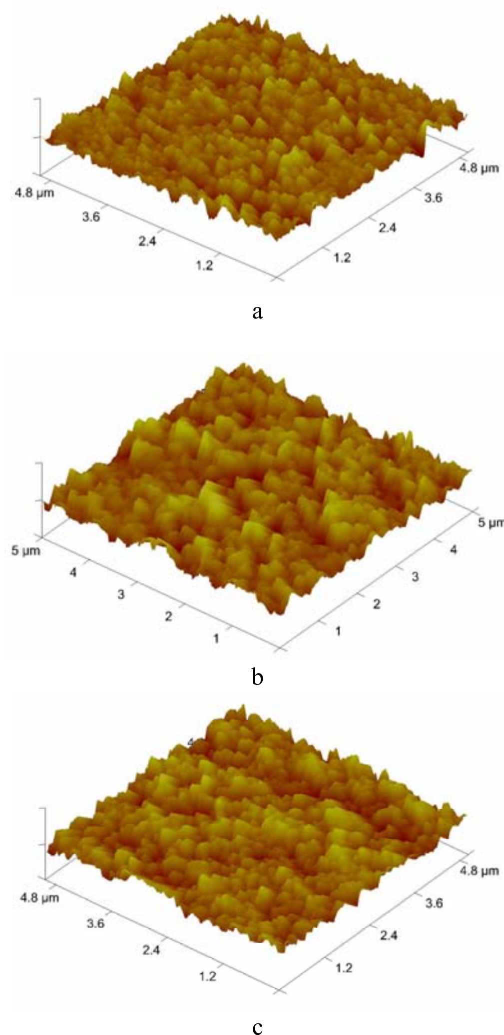

Fig. 4. AFM micrographs of MoO_3 films formed at different substrate bias voltages: a) 0 V, b) -120 V and c) -150 V.

The AFM micrograph of MoO_3 films formed under unbiased condition showed uniform grains and of spherical particles of small grains of various sizes because of the amorphous nature of the films. When the substrate bias voltage increased to – 120 V the size of the grain increased due to the polycrystalline nature and improved in the crystallinity of the films. These films showed pyramid like morphology which may exist by the accumulation of needle like crystallites [27] which enumerates the layered nature of MoO_3. At higher substrate bias voltage of – 150 V the grain size again decreased to a lower value. Many of the researchers reported the relation ship between the grain size and the energy of ions during sputtering. Yang et al. [19] reported that the grain size was larger in moderate range of negative bias voltage. At low bias voltages the adatoms mobility was low on the surface of the substrates. The low adatom mobility leads to smaller islands at the initial stage and therefore smaller size grains. At moderate substrate bias voltage (- 90 V to – 120 V) where adatom obtained more energy by ion bombardment, move more actively and form large sized grains [28]. At higher substrate bias voltages (≥ - 150 V) the ion bombardment on the film with high energy and consequently the high energy ions damage the films hence the decrease in the size of the grains [29].

The electrical conductivity of the films was influenced by the substrate bias voltage applied during the deposition. The dependence of electrical conductivity of the films on the substrate bias voltage is shown in figure 6. The film formed on unbiased substrates showed higher electrical conductivity of $3.6x10^{-4}$ $\Omega^{-1}cm^{-1}$ was due to the presence of oxygen ion vacancies. The electrical conductivity of the films decreased to $4.5x10^{-5}$ $\Omega^{-1}cm^{-1}$ with the increase of substrate bias voltage to - 120 V. The decrease of electrical conductivity with the increase of substrate bias voltage was due to the partial filling of oxygen ion vacancies. The films formed at higher substrate bias voltage of - 150 V showed a slight increase in the electrical conductivity to $6.5x10^{-5}$ $\Omega^{-1}cm^{-1}$ was due to the improvement in the crystallinity and oxygen ion vacancies generated by the partial dissociation of the constituent elements [30].

Fig. 6 shows the optical transmittance spectra of the films formed under various substrate bias voltages. It is seen from the figure that the optical transmittance of the films formed on unbiased substrate was low. The optical transmittance of the films increased with the increase of substrate bias voltage. The low optical transmittance at low substrate bias voltage was due to the oxygen ion vacancies. As the substrate bias voltage increased to - 120 V the density of scattering centers of molybdenum decreased there by increase in the optical transmittance. Further increase of substrate bias voltage to - 150 V a slight decrease in the transmittance was due to the oxygen ion vacancies.

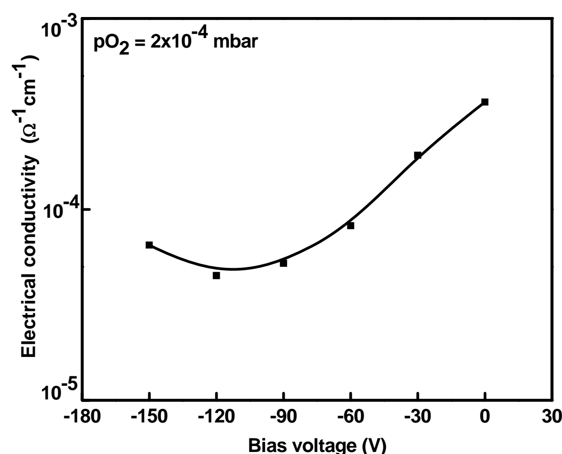

Fig. 5. Electrical conductivity of MoO_3 films formed at different substrate bias voltages.

A sharp absorption edge was observed around 400 nm in all the films. The increase of substrate bias voltage up to – 120 V leads to the shift in the optical absorption edge towards lower wavelength region thereafter it slightly shifted towards higher wavelength side. The optical absorption coefficient (α) of the films was evaluated from the optical transmittance data where the reflection losses were taken into consideration. The optical band gap of the films was evaluated from the plots of $(\alpha h\nu)^2$ versus photon energy (hν). The optical band gap of the films formed on unbiased substrates was 3.03 eV. The optical band gap of the films increased to 3.22 eV with the increase of substrate bias voltage to - 120 V. The increase of optical band gap with the increase of substrate bias voltage was due to the decrease of oxygen vacancies in the films. Further increase of substrate bias voltage to - 150 V the optical band gap decreased to 3.18 eV due to the creation of oxygen ion vacancies in the films. Julien et al. [31] reported the optical band gap of 3.37 eV in the films formed at room temperature by vacuum evaporation where those deposited at high substrate temperature of 573 K the band gap decreased to 2.80 eV due to the formation oxygen ion vacancies. Bouzidi et al. [18] were also observed the decrease in the optical band gap from 3.30 to 3.14 eV with the increase of substrate temperature from 523 to 573 K in the spray deposited films. However low value of 2.80 eV was obtained by Sivakumar et al. [14] in electron beam evaporation and Mohamed et al. [12] achieved a value of 2.60 eV in dc magnetron sputtered films.

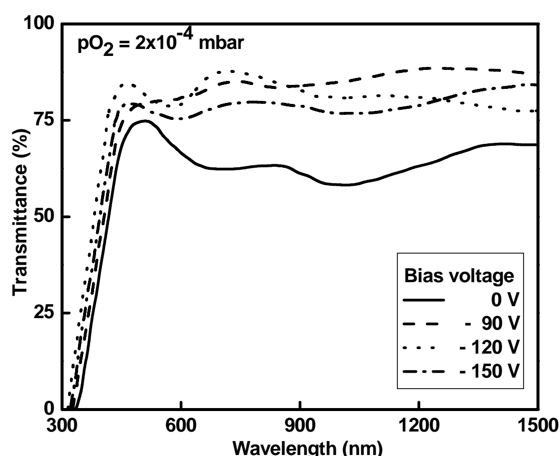

Fig. 6 Optical transmittance spectra of MoO_3 films formed at different substrate bias voltages.

The refractive index of the films was evaluated from the optical transmittance data using Swanepoel's envelope method. Figure 7 shows the wavelength dependence of refractive index of the films formed at different substrate bias voltages. The refractive index of the films was high at higher photon energies. It decreased with the increase of the photon energy in all the films. The refractive index of the films (at wavelength of 500 nm) increased from 2.03 to 2.13 with the increase of substrate bias voltage from 0 V to – 120 V due to improvement in the crystallinity and packing density of the films. Further increase of substrate bias voltage to – 150 V the refractive index decreased to 2.09 due to the formation of oxygen ion vacancies. In the literature it was reported that the refractive index of the films formed by thermal evaporation [32] was 1.8 while in the laser assisted deposition [33] showed the value of 1.9. In the present investigation the achieved refractive index of 2.13 at the substrate bias voltage of -120 V was in good agreement with the reports of Mohamed and Venkataraj [34] in dc magnetron sputtered films.

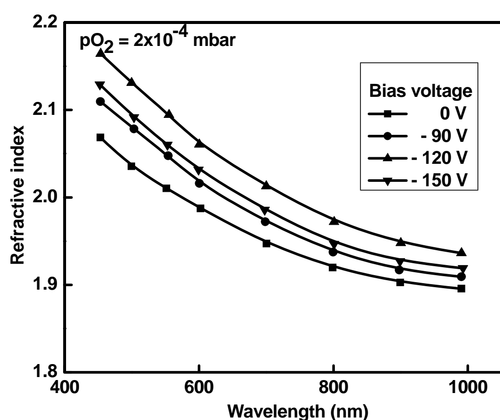

Fig. 7. Refractive index of MoO_3 films formed at different substrate bias voltages.

4. Conclusions

Molybdenum oxide films were formed on glass held at room temperature by sputtering of molybdenum target in an oxygen partial pressure of $2x10^{-4}$ mbar and sputtering pressure of $4x10^{-2}$ mbar under various substrate bias voltages in the range 0 to - 150 V using dc magnetron sputtering technique. The influence of substrate bias voltage on the structure, electrical and optical properties of the films was systematically investigated. From XPS studies it revealed that the films deposited on unbiased substrates were substoichiometric where as the films deposited at - 120 V were single phase orthorhombic α - phase MoO_3. It was also confirmed by the X- ray diffraction studies that the films formed at substrate bias voltages < -120 V were substoichiometric where as films deposited at - 120 V, the predominated (0k0) reflections indicated the preferential growth and suggest layered structure of α - phase MoO_3 films. The films formed on unbiased substrates showed high electrical conductivity of $3.6x10^{-4}$ $\Omega^{-1}cm^{-1}$, while those films deposited at the substrate bias voltage of - 120 V showed the decrease in the electrical conductivity to $4.5x10^{-5}$ $\Omega^{-1}cm^{-1}$ due to the partial filling of oxygen vacancies. The optical transmittance of the films increased with the increase of substrate bias voltage. The unbiased films showed an optical band gap of 3.03 eV with the refractive index of 2.03. As the substrate bias voltage increased to - 120 V the optical band gap of the films increased to 3.22 eV and refractive index increased to 2.13 due to the improvement in the crystallinity and packing density of the grown films. Further increase of substrate bias voltage to – 150 V the refractive index decreased to 2.09 due to the formation of oxygen ion vacancies.

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