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Structural and electrical characterization of magnetron sputtered MoO$_3$ thin films

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Abstract: Thin films of molybdenum oxide were deposited on glass and crystalline silicon substrates using dc magnetron sputtering method by sputtering of molybdenum target in the presence of oxygen and argon gas mixture under various oxygen partial pressures in the range 8x10$^{-5}$ - 8x10$^{-4}$ mbar. The glow discharge characteristics of the molybdenum cathode under various oxygen partial pressures were studied. The effect of oxygen partial pressure on the core level binding energy, structure, mechanical and electrical properties of the films was systematically studied. The films formed at oxygen partial pressures < 2x10$^{-4}$ mbar contained the MoO$_3$ and MoO$_{3-x}$ phases. The films deposited at oxygen partial pressures of 2x10$^{-4}$ mbar were stoichiometric with single phase orthorhombic α-MoO$_3$. The electrical conductivity of films decreased from 4x10$^{-5}$ to 1.6x10$^{-6}$ Ω$^{-1}$ cm$^{-1}$ with increase of oxygen partial pressure from 8x10$^{-5}$ to 8x10$^{-4}$ mbar.

1. Introduction
Molybdenum oxide (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 [1-3]. Different thin film deposition methods explored for the growth of molybdenum oxide films includes the thermal evaporation, electron beam evaporation, pulsed laser deposition, sputtering, electrodeposition, chemical vapour deposition and sol-gel process [4-8]. Among these methods, dc magnetron sputtering received considerable attention because it is industrially practiced method for generation of films at low temperatures with required chemical composition on large area substrates. In this investigation an attempt is made in the preparation of MoO$_3$ films by dc reactive magnetron sputtering under various oxygen partial pressures and studied its influence on the structural and electrical properties of the deposited films.

2. Experimental details
Molybdenum oxide films were deposited on glass and silicon (111) substrates held at temperature of 473 K by sputtering of molybdenum target of 50 mm diameter under various oxygen partial pressures (pO$_2$) in the range 8x10$^{-5}$ - 8x10$^{-4}$ mbar. The detail of the deposition system was given elsewhere [9].The sputter chamber was evacuated to an ultimate pressure of 5x10$^{-6}$ mbar by using diffusion pump backed by rotary pump. The required quantity of oxygen and argon gases were admitted into the sputter chamber through fine controlled needle valves and followed by mass flow controllers. The glow discharge characteristics of the molybdenum cathode under various oxygen partial pressures were studied. The core level binding energies and oxidation states of the films were analyzed by using
X-ray photoelectron spectroscopy. The crystallographic structure of the films was determined by X-ray diffraction. The surface morphology of the films was analyzed with atomic force microscope. The microhardness of the films was measured using nano indenter. The electrical properties of the films were measured using standard four probe technique.

3. Results and discussion
3.1 Glow discharge characteristics
Glow discharge characteristics of the molybdenum target in the magnetron assembly under different oxygen partial pressures were carried out at different cathode currents. The dependence of molybdenum cathode potential on the oxygen partial pressure is shown in figure 1. At a constant cathode current of 250 mA the cathode potential initially increased from 490 to 567 V with the increase of oxygen partial pressure from $7 \times 10^{-5}$ to $1 \times 10^{-4}$ mbar. Further increase of oxygen partial pressure to $4 \times 10^{-3}$ mbar, the cathode potential decreased to 486 V. At low oxygen partial pressures the reduction in the ionization collision caused an increase in the cathode potential. The decrease of cathode potential at higher oxygen partial pressures was due to the oxidation of molybdenum target.

Figure 1 Variation of molybdenum cathode potential with oxygen partial pressure

The oxide has higher secondary electron emission coefficient than the elemental molybdenum target, hence low cathode potential required at higher oxygen pressures to achieve the same cathode current [10]. Such a dual nature of variation in the cathode potential with the oxygen partial pressure was also observed in magnetron sputtering of metallic target of tantalum in the presence of reactive gas of oxygen during the deposition of tantalum oxide films [11]. In order to study the effect of oxygen partial pressure on the structural and electrical properties, the MoO$_3$ films were formed by sputtering of molybdenum target under various oxygen partial pressures in the range $8 \times 10^{-5}$ - $8 \times 10^{-4}$ mbar and at a constant substrate temperature of 473 K. The deposition rate of the MoO$_3$ films was highly influenced by the oxygen partial pressure maintained during the preparation of the films. The deposition rate of the films formed at low oxygen partial pressure of $8 \times 10^{-2}$ mbar was 19.2 nm/min. It gradually increased to 23.5 nm/min with the increase of oxygen partial pressure to $2 \times 10^{-4}$ mbar while at high oxygen partial pressure of $8 \times 10^{-4}$ mbar the deposition rate of the films decreased to 14.2 nm/min. The initial increase in the deposition rate with the increase of oxygen partial pressure was due to the increase of the sputtering power since the cathode potential increased with the increase of oxygen partial pressure at a fixed cathode current. The decrease of deposition rate at higher oxygen partial pressures was related to the chemical reaction between the target surface of molybdenum and the reactive gas of oxygen and forms the oxide layer on the target [12]. Scarminio et al. [13] were also observed the similar behaviour of higher deposition rate at lower oxygen partial pressures in rf sputtered molybdenum oxide films.
3.2 X-ray photoelectron spectroscopy

The survey scan of X-ray photoelectron spectra of the MoO$_3$ films contained the characteristic peaks of molybdenum and oxygen. The narrow scan spectra of the Mo 3d doublet core levels of the films formed at different oxygen partial pressures are shown in figure 2. The core level binding energy of Mo 3d$_{5/2}$ decreased from 232.69 to 231.87 eV with the increase of oxygen partial pressure from 8x10$^{-5}$ to 8x10$^{-4}$ mbar. The shape of the core level spectrum of the films formed at oxygen partial pressure of 8x10$^{-5}$ mbar was asymmetric indicated the presence of mixed oxidation states of molybdenum in MoO$_3$ films. The films deposited at oxygen partial pressure of 2x10$^{-4}$ mbar showed the symmetric peaks of Mo 3d$_{5/2}$ with the core level binding energy of 232.49 eV and Mo 3d$_{3/2}$ of 235.64 eV and with the spin orbit splitting of 3.15 eV indicated the characteristic of Mo$^{6+}$ oxidation of MoO$_3$ [8]. The films formed at higher oxygen partial pressure of 8x10$^{-4}$ mbar showed the mixed oxidation states of Mo$^{4+}$, Mo$^{5+}$ and Mo$^{6+}$. Such a mixed phase of molybdenum oxide films were also achieved in rf reactive sputtered films formed at different oxygen partial pressures [14]. The core level binding energy of pure oxygen (O 1s) peak is 531.0 eV. The core level binding energy value of the films decreased from 530.44 to 529.77 eV with the increase of oxygen partial pressure from 8x10$^{-5}$ to 8x10$^{-4}$ mbar respectively. The decrease in the binding energy of O 1s with the increase of oxygen partial pressure was attributed to the bonding of oxygen with molybdenum to form molybdenum oxide [15].

3.3 Structure and surface morphology

Crystallographic structure of the films was analyzed by the X-ray diffraction. X-ray diffraction profiles of the MoO$_3$ films deposited at different oxygen partial pressures are shown in figure 3. The presence of diffraction peaks revealed that the films were polycrystalline in nature. The films formed at low oxygen partial pressure of 8x10$^{-5}$ mbar showed the (020), (011), (040) and (060) reflections of MoO$_3$. Another reflection of (111) corresponds to the unoxidized molybdenum. Scarminio et al. [13] also reported that the films deposited by rf sputtering at low oxygen partial pressures exhibited the metallic behaviour and with the increase of oxygen partial pressure, the films were transformed into stoichiometric MoO$_3$. The presence of (020), (040) and (060) reflections related to α - phase of MoO$_3$ while the (011) reflection connected to the β- phase of MoO$_3$ [16]. Hence the coexistence of mixed phases of α- and β- MoO$_3$ films along with elemental molybdenum was achieved at lower oxygen partial pressure of 8x10$^{-5}$ mbar. When oxygen partial pressure increased to 2x10$^{-4}$ mbar, the films showed only the (0k0) reflections indicated the orthorhombic α - phase of molybdenum oxide. Further increase of oxygen partial pressure to 8x10$^{-4}$ mbar the presence of (002) along with (0k0) reflections indicated the presence of α - and β- phase of MoO$_3$. Such a change of phase in MoO$_3$ was
also noticed with the oxygen partial pressure in pulsed laser deposited films [17]. From the XRD studies it revealed that the oxygen partial pressure of $2 \times 10^{-4}$ mbar is an optimum to produce single phase orthorhombic $\alpha$-phase MoO$_3$ films. The surface morphological studies of the sputtered MoO$_3$ thin films were carried out by using atomic force microscopy. AFM images of the MoO$_3$ films deposited at different oxygen partial pressures are shown in figure 4. The AFM images demonstrated that the sputtered MoO$_3$ films were homogenous and uniform. MoO$_3$ film deposited at low oxygen partial pressure of $8 \times 10^{-5}$ mbar shows the uniform and needle like structure of various sizes. The size of initially formed nuclei would be small when films deposited at low oxygen partial pressure of $8 \times 10^{-5}$ mbar. When the oxygen partial pressure increased to $2 \times 10^{-4}$ mbar, the films showed columnar growth combined with the large needle like grains. At this oxygen partial pressure large size grains were observed. Further increase of oxygen partial pressure to $8 \times 10^{-4}$ mbar, the films exhibited rare small grains were observed.

The stress developed in the films was determined from the XRD data. The variation of stress developed in the MoO$_3$ films with the oxygen partial pressure is shown in figure 5. It seen that the deposition stress is compressive at lower oxygen partial pressures i.e. from $8 \times 10^{-5}$ mbar to $1 \times 10^{-4}$ mbar which attributed to the lattice distortions produced by energetic particles (reflected Ar neutrals/sputtered Mo atoms) striking of the film [18,19]. The stress observed at an oxygen partial pressure of $8 \times 10^{-5}$ mbar was -583 MPa. When oxygen partial increased to $2 \times 10^{-4}$ mbar, the tensile stress starts to build up due to the densification of the films. This densification clearly indicated that the transformation of mixed phase of MoO$_3$ thin films to stoichiometric MoO$_3$ as confirmed from XPS and XRD. Further increase of oxygen partial pressure above $2 \times 10^{-4}$ mbar, there is a small increase in tensile stress. Therefore the intrinsic stress in the sputtered MoO$_3$ thin films can be compressive or tensile stress, depending on the mass, flux and energy of the particles striking the film. Mohamed et al. [20] found that the stress of -824 MPa at oxygen partial pressure of $3.9 \times 10^{-4}$ Pa and it decreased sharply with increase oxygen partial pressure.
3.4 Mechanical properties
The microhardness of sputtered MoO$_3$ films formed at different oxygen partial pressures is shown in figure 6. The microhardness of the MoO$_3$ films at low oxygen partial pressure of 8x10$^{-5}$ mbar was 0.6 GPa. The low microhardness in the films formed at low oxygen partial pressure was due to the presence of mixed phase of molybdenum oxide along molybdenum. The higher hardness of the MoO$_3$ films deposited at higher oxygen partial pressures can be attributed to the composite structure.

3.5 Electrical properties
Figure 7 shows the variation of electrical conductivity of MoO$_3$ films with the oxygen partial pressures. It was observed that the electrical conductivity decreased with the increase of oxygen partial pressure. The electrical conductivity of films formed at low oxygen partial pressure of 8x10$^{-5}$ mbar showed high value of 4x10$^{-5}$ Ω cm$^{-1}$ due to the presence of metallic molybdenum along with MoO$_3$. The films formed at oxygen partial pressure of 2x10$^{-4}$ mbar showed the electrical conductivity of 1.2x10$^{-5}$ Ω cm$^{-1}$. The low electrical conductivity of 1.6x10$^{-6}$ Ω cm$^{-1}$ was achieved at higher oxygen partial pressure of 8x10$^{-4}$ mbar. Low value of electrical conductivity at higher oxygen partial pressure of 8x10$^{-4}$ mbar might be due to the slight excess of oxygen in the films. Decrease in the electrical conductivity with the increase of oxygen partial pressure was attributed to the partial filling of oxygen vacancies in the films.

4. Conclusions
Molybdenum oxide films were formed on glass and silicon substrates held at substrate temperature of 473 K by sputtering of molybdenum target under various oxygen partial pressures in the range 8x10$^{-5}$ -
8x10^{-4} mbar using dc magnetron sputtering technique. From XPS studies it revealed that the films deposited at 2x10^{-4} mbar were stoichiometric with Mo^{6+} state. It was also confirmed by the X-ray diffraction studies that the films deposited at oxygen partial pressure of 2x10^{-4} mbar, contained the (0k0) reflections indicated the layered structure of α- phase MoO_3 films. Films deposited at the oxygen partial pressure of 2x10^{-4} mbar showed columnar growth combined with the large needle like grains. The microhardness of the films increased from 0.6 to 1.5 GPa and the electrical conductivity of films decreased from 4x10^{-5} to 1.6x10^{-6} Ω·cm^{-1} with increase of oxygen partial pressure from 8x10^{-5} to 8x10^{-4} mbar.

References