Chapter-7

Structural and Morphological Control of Magnetron Sputtered Molybdenum Oxide thin Films

Chapter 7

7.1 Introduction

The density of state of material is proportional to its size. Transition metal oxides have a wide range of structural, physical, and chemical properties. They have a wide range of industrial applications as a result of this. The uppermost shell d-electrons, oxygen vacancies, crystal imperfections, stacking defects, and grain boundaries all affect their characteristics. [380] Because of its wide range of stoichiometry and fascinating behavior, such as chromogenic and catalytic characteristics, molybdenum oxide (MoO_3) is a promising material for a many electronic applications among these transition metal oxides. Controlled structural morphology, microstructure, specific optical and electrical properties of MoO_3 films are significant in a variety of applications. [381] Electro chromic display devices, optical memory, gas sensors, and lithium ion batteries are one of its applications. [382-384] Electron beam evaporation, pulsed laser deposition, electro-deposition, Thermal evaporation, sputtering, chemical vapor deposition, and the sol-gel technique are some of the thin film deposition methods investigated for the fabrication of molybdenum oxide films. [385-389] The electrical, structural properties of the material can be tuned by proper selection of synthesis technique. Among these approaches, RF magnetron sputtering has gained a lot of interest since it is a widely used method for depositing thin films with the desired chemical composition on large areas of substrates at low temperatures. This approach produces microstructure and nanostructure films that are homogeneous, pristine, better crystalline properties, sticky, and have a consistent chemical composition. This approach allows for large-scale fabrication of these films. An attempt is made to deposit Molybdenum oxide thin films using RF reactive magnetron sputtering at various oxygen partial pressures, and different temperatures. In this chapter, RF reactive

magnetron sputtering was used to fabricate thin films of molybdenum oxide (MoO_x) with varied oxygen flow rates and a deposition pressure of $2x10^{-2}$ Torr. RF Sputtered MoO_x films were investigated for their stoichiometry, composition, chemical binding energy, and electrical properties. Thermodynamically stable orthorhombic -phase, monoclinic -phase, high-temperature monoclinic modification MoO_3-II -phase [390], and hexagonal h-phase occur in MoO_3. -MoO_3 has a layered structure. Several technological uses of MoO_3 films have been documented in the literature, including catalyst [391], electro chromic devices [381, 392], lithium-ion batteries [393], super-capacitor [394] , gas sensor and lubricants [395, 396].

The as deposited films were annealed in O_2 ambient at different temperatures in the range 300 - 500°C. X-ray diffraction (XRD) studies suggest that the as-deposited film has a cubic Mo structure and the films annealed at 500 °C for 1 hour in O_2 ambient were polycrystalline and all of the peaks that identified, are corresponding to orthorhombic α-MoO_3. Raman spectroscopy of thin film also reveals the orthorhombic crystal structure and is in good agreement with previous reports. Moreover, Field emission scanning electron microscope (FESEM) images of the films annealed at 500°C exhibited flake like structures due to improvement in the crystallinity. The kinetic energy of the sputtered Mo particles appears to be important in influencing the ultimate film quality, according to these findings. This flake like sheets indicates the layered structure of MoO_3 crystals. The resistivity of the film annealed at 500°C is increases, which is maybe due to granular surface morphology with high roughness. The findings suggest that these structures could be used as thin film solar cell and other electronic devices in oxide micro- and Nano electronics.

7.2 Methods and characterization

7.2.1 Fabrication of film

Mo thin films were prepared by RF (radio frequency) magnetron sputtering system on a soda lime glass substrate with a Mo target (diameter, 63.5 mm; purity, 98% Mo). Before deposition, surface contaminations of the substrate were ultrasonically cleaned with acetone and methanol for 15 min, respectively and then dried by nitrogen gas. Schematic of a RF magnetron sputtering set up is given in Figure 7.1 (a). Firstly chamber was pumped to base pressure of $8x10^{-6}$ Torr by rotary and turbo pump and then Ar flow was introduced and working pressure was set at $2x10^{-2}$ Torr. The distance between the target and substrate was kept at 5 cm. Prior to the Mo depositions; the target was pre-sputtered for 15 min to remove impurities and possible oxidation from the target surface.

7.2.2. Characterization

The 100 W RF power was supplied to the sputter target using RF power generator. After the deposition, the Mo thin film was placed in a high-temperature furnace under atmospheric conditions. O_2 gas was used and furnace temperature was raised to 300°C, 400°C and 500°C for thermal annealing for 1 hour. Schematic of the furnace which was used to anneal the Mo thin film samples is shown in Figure 7.1 (b). The experimental parameters that are used in magnetron sputtering and furnace are given below the figures 7.1(a) and 7.1(b). The as-deposited films and the annealed films at different temperatures were characterized by studying their crystallographic structure, surface morphology, and electrical properties. The structural properties of the films were determined by X-ray diffractometer (XRD) (Stoe, X'pert PRO) using Cu $k_\alpha$irradiation. Raman spectroscopy of molybdenum compounds is well established for the characterization of molybdenum oxide based catalysts and materials. Raman spectroscopy provides useful information about the

degree of crystallization or about structural defects. Hence, Raman spectroscopy is suited for the characterization of MoO_x based materials. [397, 398] The morphological properties were investigated by atomic force microscopy (AFM) (Park scientific instruments atou probe cp) and field emission scanning electron microscopy (FESEM) (Hitachi S4160) and the sheet resistivities of the samples were collected by Four Point Probe (MELLER) at room temperature. These analyses were employed to explore of how thermal annealing affected the MoO_x thin films structure, morphology and electrical properties.

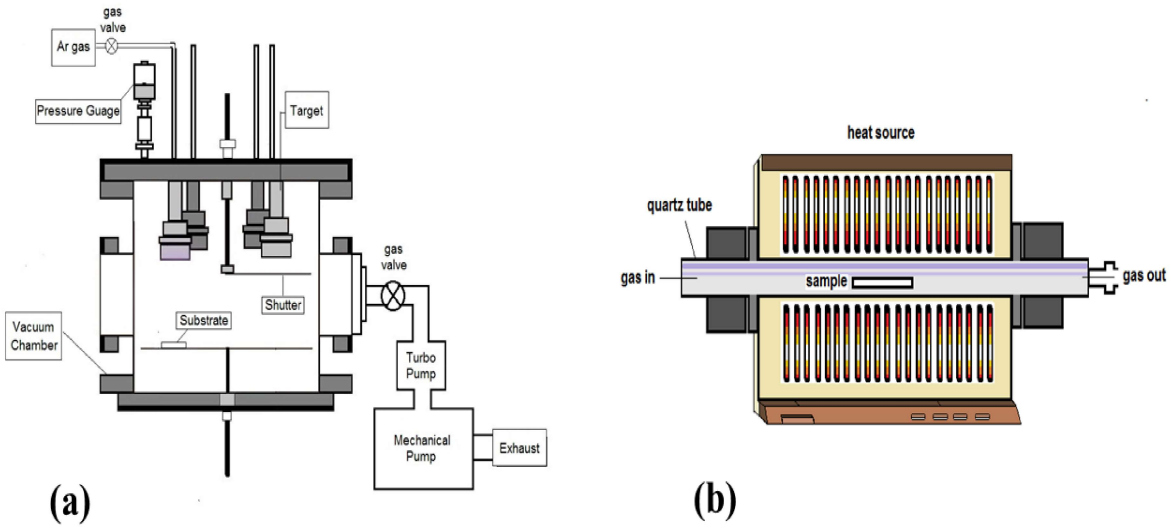

Figure 7.1: Schematics of (a) RF magnetron sputtering, (b) furnace and experimental conditions.

7.3 Results and discussion

7.3.1 Structural studies

Figure 7.2 shows the XRD profiles of as-deposited and the MoO_x films annealed at different temperatures. The as-deposited film shows a diffraction peak at 39.75° corresponds to the Mo cubic structure. While after exposure to O_2 atmosphere for 1hr at 300°C, formation of oxide layer occurred as the metallic peak of Mo is progressively replaced by weak peaks at

36.8 and 42° related to monoclinic MoO_2. In this temperature, the weak oxidation of the Mo film started and the annealing temperature was not enough to achieve stoichiometric structure of the molybdenum oxide. When the Mo film annealed at 400°C for 1hr, the spectrum was mainly composed of the monoclinic MoO_2. The intense peak at ~26° and two weak peaks at ~23° and 28° correspond to α-MoO_3 phase. In this temperature, the film has the mix phase structure and formation of stoichiometric α-MoO_3 phase started. The phase of the as-deposited film completely changed to α-MoO_3 phase after annealing at 500°C for 1hr. All of the peaks, that are identified, are corresponding to orthorhombic α-MoO_3. Furthermore, three reflections (020), (040) and (060) were observed in the XRD profile, relating to the formation of a layered structure of MoO_3. From XRD studies, it is clear that the annealing temperature of 500°C is an optimum to produce orthorhombic α-phase MoO_3 film. The results achieved are in accordance with the reports of where α- and β- phase films were achieved by annealing of RF magnetron sputtered MoO_3 films in the temperatures in the range 623 - 673 K, and single phase α- MoO_3 films at 723 K.

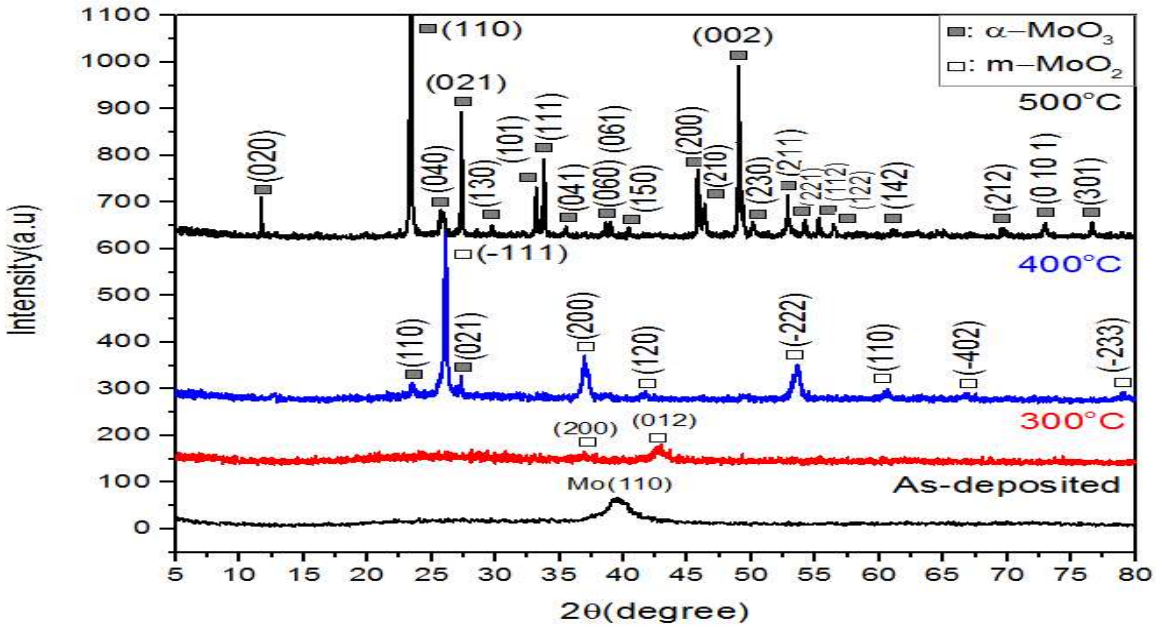

Figure 7.2: XRD spectra of as-deposited Mo and Annealed MoO_x Films at 300, 400 and 500 °C

7.3.2 Surface morphology

Figure 7.3 shows the FESEM images of the as-deposited and annealed films. Image of as-deposited film shows cauliflower like structures of various sizes, which can clearly be observed. The film annealed at 300°C for 1hr represents smooth and non-structured surface morphology due to the formation of a thin oxidized layer on its surface. After annealing Mo film at 400°C for 1hr, the new grains formed on the film, which is attributed to a reaction between a surface and oxygen. The surface morphology of the film annealed at 500°C entirely changed as shown in the image. The particle shape converted to flake like grains with length of ~1µm and the width of 500nm. Moreover, it is easy to observe the crystals are composed of a series of flake like sheets that indicated the layered structure of MoO_3

crystals. This can correspond to the presence of the (0k0) peaks observed in the XRD pattern by R. Naouel et al.[399] have synthesized a similar layered structure of α−MoO_3 under hydrothermal conditions. The morphological studies revealed that, the annealing temperature strongly influenced on the surface morphology of the films. At a higher annealing temperature of 500°C the particles achieved required thermal energy to promote the formation of the films with larger grain sizes, due to the coalescence of neighboring crystallites driven by thermal energy. Inset in figure 7.3 shows another FESEM image of 500°C annealed film with resolution of 3µm. The surface consists of elongated crystallites that randomly oriented.

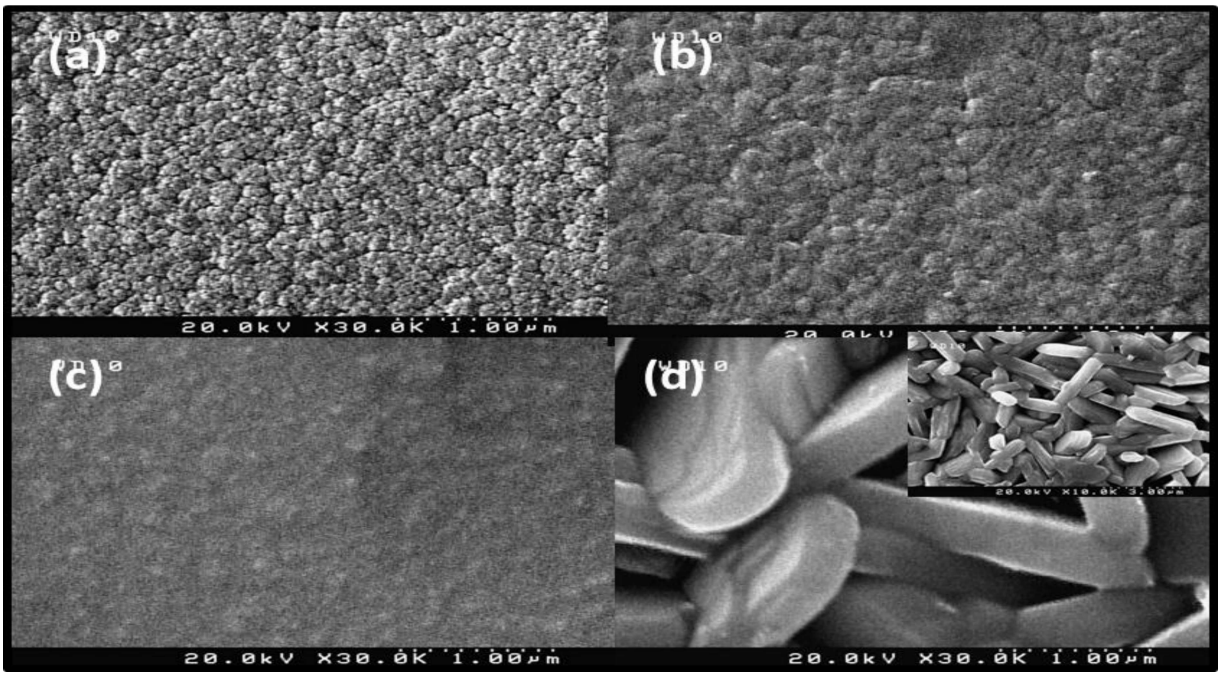

Figure 7.3: FESEM images of (a) as-deposited Mo, (b) annealed at 300°C, (c) annealed at 400°C and (d) annealed at 500 °C MoO_x films (inset 3µm scale)

Figure 7.4 shows the 2D and 3D AFM images of the samples before and after annealing. The as-deposited film shows the uniform and needle like structure that composed of small grains. After annealing at 300°C, the film again showed needle like structure with decreasing in height of grains. When the annealing temperature increased to 400°C, the film showed the large conical structure of various sizes. With further increase of temperature to 500°C, the surface morphology drastically changed and the large pyramid like grains of the order of several microns leading to a non-uniform film surface. AFM parameters are summarized in table 7.1. It is observable that the root mean square surface roughness (RMS) first decrease from 13.21 to 10.24 nm at 300°C then increase to 15.17 nm at 400°C. The Decreasing of the RMS at 300°C can attributed to the formation of oxidized smooth layer on the surface. In 400°C thermal energy helps particles to move on the surface and the neighboring grains can combine with each other to form large scale grains and increase surface roughness. After annealing at 500°C the RMS of the film gradually increase to 96.25 nm. In this temperature, thermal energy also increases the grains scale and the surface roughness much more than the annealing at 400°C. This large increase of roughness together with the XRD data confirms the formation of polycrystalline α-MoO_3 phase. Other AFM parameters decrease and increase in the same manner. It is notable that the morphology of the films significantly varied at different annealing temperatures.

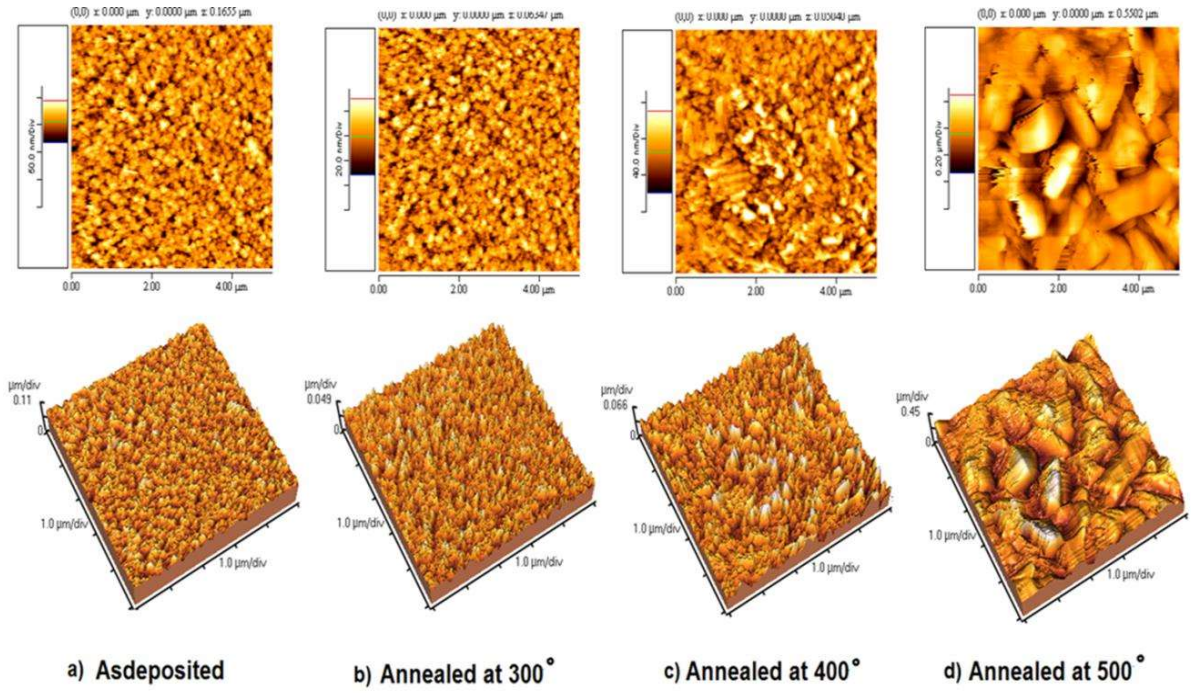

Figure 7.4: 2D and 3D AFM images of (a) as-deposited Mo, (b) annealed at 300ºC, (c) annealed at 400ºC and (d) annealed at 500 ºC MoO_x films

7.3.3 Electrical properties

The electrical resistivity of the as-deposited film and the films annealed at 300°C, 400°C and 500°C is shown in table 7.1. It is obvious that the film exhibited low resistivity at 300°C, indicating the metallic nature which is due to the low oxidation. The films annealed at 300°C and 400°C showed the resistivity of 45.6 Ω/cm and 480 Ω/cm. More oxidation of film cause large increase in the resistivity of film annealed at 400°C. The resistivity of the film annealed at 500°C is very high that was out of range. This high resistivity maybe due to granular surface morphology with high roughness that electron traps in large vacancies between grains in agreement with AFM and SEM images. As a result of this study the electrical resistivity of the films was efficiently influenced by the annealing temperature.

Table 7.1: Roughness and electrical resistivity measurement for as-deposited, annealed at 300, 400 and 500°C samples.

sample	Mean Ht (nm)	R_{pv} (nm)	R_{RMS}(nm)	R_a(nm)	ρ(Ω/cm)
As-deposited	158.7	221.2	13.21	10.30	4.6
Annealing at 300°C	59.97	98.12	10.24	8.26	45.6
Annealing at 400°C	67.71	132.7	15.17	11.76	480
Annealing at 500°C	565.7	899.3	96.25	74.81	Out of range

The crystal structures of the films annealed at 400°C and 500°C were characterized by Raman spectroscopy. From figure 7.5 (a), the Raman spectrum shows peaks at 491.67, 565.76, 578.19 and 729.79 cm^{-1}. The position of peaks is in good agreement with that reported values for monoclinic MoO_2. In figure 7.5 (b) peaks at 368.66, 381.99 and 473.75 cm^{-1} corresponds to deformation modes and peaks at 669.52, 822.71, and 998.47 cm^{-1} refer to stretching modes. [400] All the peaks confirm the orthorhombic crystal structure and are in good agreement with previous reports. [401, 402] In the literature, Raman peaks are assigned to the terminal oxygen (Mo = O) stretching mode at 995 cm^{-1}, the triply connected bridge-oxygen (Mo_3-O) stretching mode at 665 cm^{-1}, and the doubly connected bridge-oxygen (Mo_2 –O) stretching mode at 818 cm^{-1}. It is clear that peaks shift forward from

MoO_3 Raman peaks during the annealing process. The intensity of the peaks indicates a highly ordered structure.

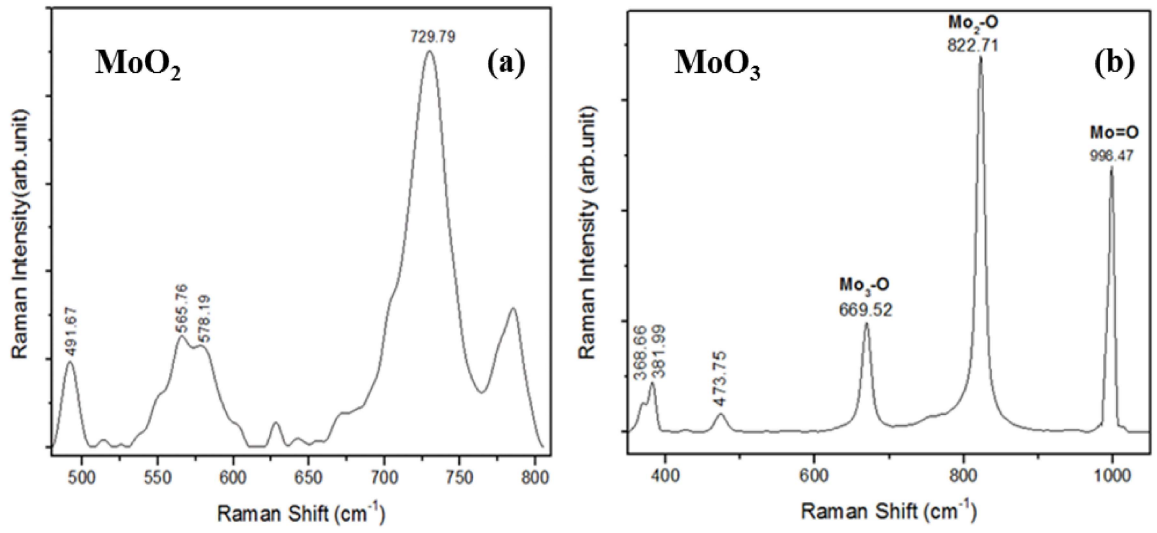

Figure 7.5: Raman spectra of (a) MoO_2 and (b) MoO_3 films

7.4. Conclusion

In the present work, effect of annealing in O_2 ambient was investigated on the physical properties of the Molybdenum thin films. The morphological and structural studies revealed that, the annealed films exhibited the layered structure at high annealing temperatures with enhancement in the crystallinity. The film annealed at 500 ^oC was of flake like structure, due to the coalescence of neighbouring crystallites driven by thermal energy by annealing. The change in surface morphology with different annealing temperatures was due to the modification of grain growth into nanocrystalline with uniform size of crystallites. The high resistivity obtained in the case of the sample annealed at 500^oC, which can be explained by the granular surface morphology with high roughness that electron traps in large vacancies

between grains. In conclusion from this chapter, we found that the structural, morphological, and electrical properties of the films were efficiently influenced by the annealing temperature.