Preparation and Characterization of Molybdenum Trioxide Thin Films Grown by Two-Step Method: DC Sputtering and Plasma Oxidation

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Abstract

Nanostructured molybdenum trioxide (MoO_3) films as environmental friendly materials can be used in various filed such as electrochemical energy storage devices, rechargeable batteries and gas sensors. In this work, nanostructured MoO_3 thin films were successfully grown on quartz substrates by two-step method. In the first step, molybdenum films were deposited on quartz substrates by DC magnetron sputtering technique. Then the plasma oxidation of molybdenum films was used to prepare molybdenum oxide. The effect of plasma oxidation power and thermal annealing on the structural, morphological and optical properties of the MoO_3 films were investigated by different analysis including XRD, AFM, RBS and spectrophotometry. XRD results indicated that the plasma powers effectively influenced the structure of films. The RBS analysis confirmed the presence of Mo and O elements. The AFM images showed that an increment of plasma power leads to decrease the roughness of films and annealing effectively changed the morphology of films. Furthermore, the optical transmittance decreases by increment of the plasma oxidation powers.

Keywords: MoO_3, Plasma Oxidation, Thin Film, Sputtering, Nanostructure.

1. Introduction

Nowadays transparent metal oxides with wide range of applications owing to their attractive physical, electrical and optical properties have been the matter of many researches. In the meantime considerable attention has been paid to transition metal oxides such as molybdenum trioxide (MoO_3). Commonly molybdenum trioxide presents three phases: orthorhombic α-MoO_3, monoclinic β-MoO_3 and hexagonal h-MoO_3 [1]. The α-MoO_3 is thermodynamically stable in nature and has a layered structure. MoO_3 has an intrinsic anisotropy and can form different morphologies such as: nano rods, nanowires, nanobelts, nano sheets, nano tubes and nano spheres [2]. Moreover, the superiorities of low cost, nontoxic nature, chemical stability, high theoretical specific capacity and the environmentally friendly nature make nanostructured MoO_3 exceptional electrode material for rechargeable batteries capacitors [3]. Also, MoO_3 is a promising material for a lot of applied fields such as: gas sensors, catalysts, electrochemical energy storage devices, display devices, smart windows and battery electrodes [2-4]. Various techniques have employed to produce MoO_3 thin films e.g. sol gel-spin coating [5], thermal evaporation [6], magnetron sputtering [7], laser ablation [8] and thermal oxidation [9]. An alternative method for preparation of metal oxide is plasma oxidation that has several advantages over other oxidation techniques such as fast oxidation rate and ease of forming uniform and dense layer [10]. Therefore in this investigation, oxygen plasma treatment of molybdenum films was employed to prepare molybdenum oxide.

The focus of this research is to investigate the effect of plasma treatment power and thermal annealing on structural, morphological and optical properties of molybdenum oxide films.

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2. Materials and Methods

2.1 Thin Film Deposition

The molybdenum oxide (MoO_3) thin films were grown on quartz substrates using two-step method. In the first step molybdenum films were deposited on quartz (1cm×1cm) substrates by employing DC magnetron sputtering. A pure metal Mo (99.999%) target was used for deposition of films in a DC magnetron system (EDS -160).

In order to remove any surface contamination, all of the substrates were washed with ethanol and acetone for 10 min ultrasonically and were dried in N_2 gas then were transferred to sputtering chamber and were placed 6 cm away from target after that the chamber was evacuated with rotary and diffusion pumps until 6×10^{-5} mbar.

Pure argon was used as sputtering gas. Prior to deposition, the target was pre-sputtered for 10 min. Next, the shutter was swept and deposition was carried out for 10 min in constant working pressure of 3.9×10^{-2} mbar. In second step, the prepared Mo thin films were exposed to the oxygen plasma in a cylindrical plasma system [10] at different plasma powers of 5, 10 and 15 W for 30 min.

The plasma chamber pressure was 2.5×10^{-1} mbar during the plasma treatment.
The thin films which exposed to the oxygen plasma in different plasma treatment powers named, Q_1, Q_2, Q_3. In the last step the samples, which prepared in the prior stage, were annealed in an electrical furnace at 600 °C for 30 min under a constant oxygen (99.999%) flow.

2.2 Characterization

The structural properties of films were identified by X-ray diffraction (XRD, Philips, PW 3710) using Cokα radiation (λ=1.7890 A°). The morphology of thin films was studied by atomic force microscope (AFM, Park Scientific Instrument, Auto probe CP USA) in contact mode. The optical transmittance spectra of prepared films were measured using a UV-Vis spectrophotometer (Perkin Elmer's LAMBDA 2) in the wavelength range from 200 to 1100 nm. The composition of films was determined via Rutherford back scattering spectroscopy (RBS).

3. Results and Discussions

3.1 Structural Characterization

Fig. 1.a and Fig. 1.b show the X-ray diffraction patterns of MoO_3 thin films provided at different plasma treatment powers and those which subsequently annealed.
By exposing the Mo thin films to the oxygen plasma at different powers, the XRD patterns showed a polycrystalline structure of MoO_3 films. According to Fig. 1.a the peaks located at 2θ about 49.76° and 78.16° correspond to (141) and (152) reflections of orthorhombic phase of α-MoO_3 (JCPDS Data file: 00-035-0609) and (141) planes grow preferentially.
Repetition of crystallography directions in the samples prepared at different plasma treatment powers indicates that the films orientation was not affected by plasma treatment power but intensity changing of the peaks reveals that crystal quality was absolutely touched by plasma treatment powers.
The XRD patterns of annealed samples (Fig. 1.b) show a polycrystalline nature of the films too.
After thermal annealing, the intensity of peaks increased for samples prepared at plasma power of 10 and 15 w.
Most of the time when the films exposed to heat treatment, the atoms adopt a more regular settlement which lead to a polycrystalline nature of the films and better crystallinity [1,11].
The best crystallinity created at the power of 5w before annealing (Sample Q1) and at the power of 10W after annealing (sample Q2A). Comparison between XRD patterns of samples Q1 and Q1A shows in plasma power of 5 w preferred crystal orientation was not affected by thermal annealing and it is the same in both samples. Whereas in other samples, annealing lead to a change in crystal orientation. The opposition of surface energy and strain energy can lead to some changes in preferred orientation [11].
The XRD patterns of annealed samples reveals by increasing the plasma power, the intensity of the peaks increased with the exception of sample Q3A that was prepared at high plasma power of 15W. Also the number of the peaks in sample Q3A beside Q3, increased that can be due to the high energy of the atoms which caused repeated nucleation during heat treatment that is responsible for the formation of nano-grains [1,11,12].
The absence of dross peaks, offers the accumulation of high pure molybdenum trioxide in all samples.

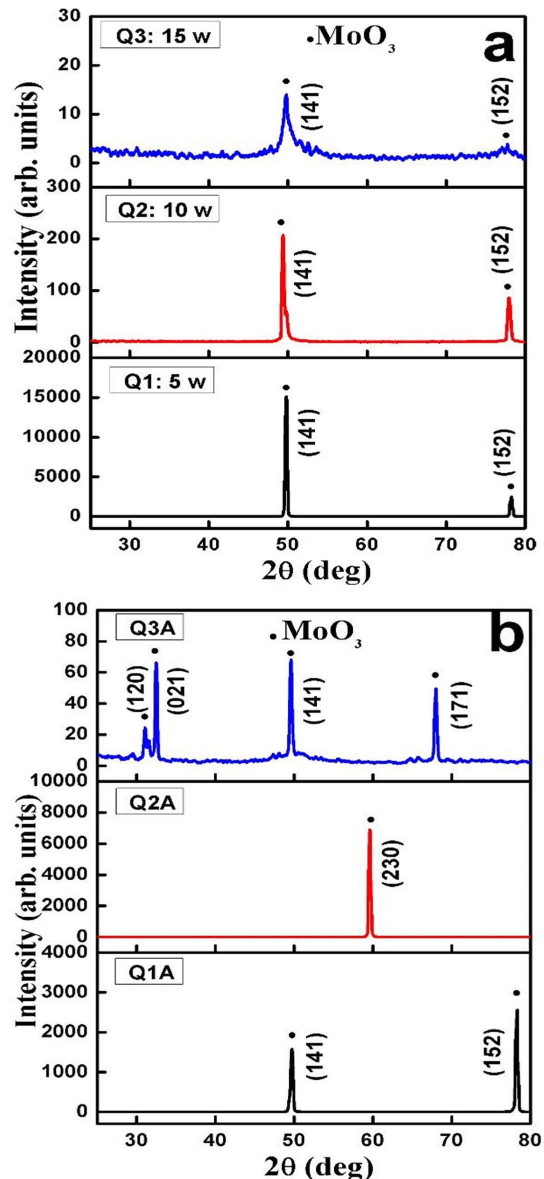

Fig. 1. XRD patterns of MoO_3 films prepared at different plasma oxidation powers: (a) before annealing and (b) after annealing.

3.2. Morphological Characterization

The two and three dimensional AFM images of prepared films are shown in Figs 2 and 3. The scanning area was 2×2µm^2. The AFM images show that the surface morphology of the films grown at different plasma treatment powers was changed. Before annealing the grain size of prepared films decreased with plasma power and at same time, the film roughness decreased and the films became uniform. After annealing, the surface morphology was changed. The grain size and the films roughness were increased. This increment is attributed to the combining of tiny grains and formation of larger grains.

The morphology of films before annealing exhibits more uniform of the nanograins and smooth surface. Also, the histogram of the surface height distribution profiles shows a shape of Gaussian distribution that confirmed the homogeneity of the films. Figs 3a and 3b illustrates the variation of the root mean square (RMS) roughness and average roughness of films with plasma treatment power before and after annealing respectively(Fig. 4.).

3.3. RBS Analysis

The constituent elements of the films were obtained using RBS analysis. Typical RBS spectrum of selected samples Q1A and Q2A is shown in Fig. 5.a and Fig. 5.b. It can be seen in Fig. 5.a and Fig. 5.b that in addition to the silicon, which is related to the substrate, molybdenum and oxygen, are existence elements in the films, and there is no trace of impurity in the films. On the other hand, the ion scattering from Mo atoms occurs at higher backscattering energy. This is because the backscattered energy of the incident ions is depending on the atomic mass of the elements from which the ions backscatters. The atomic masses of the elements are 15.99, 28.09 and 95.94 for O, Si and Mo respectively and the Mo is the heaviest among the elements either in the film or in the substrate [1].

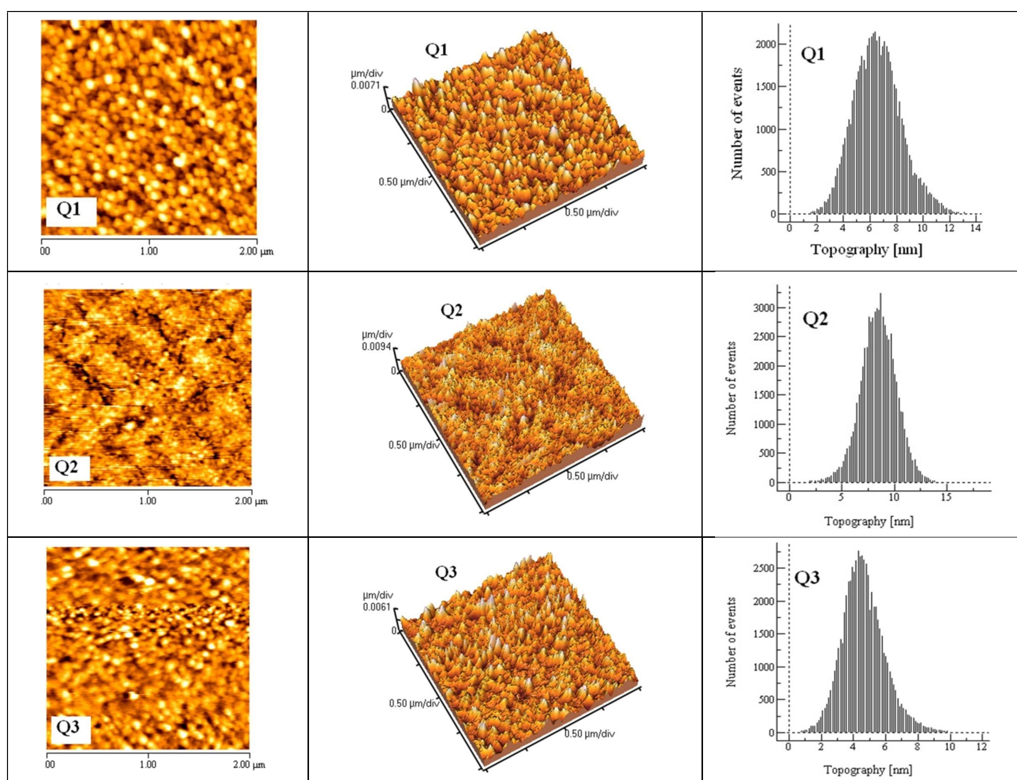

Fig. 2. 2D and 3D AFM micrographs along with corresponding topographic histogram images of MoO_3 films prepared at different plasma oxidation powers.

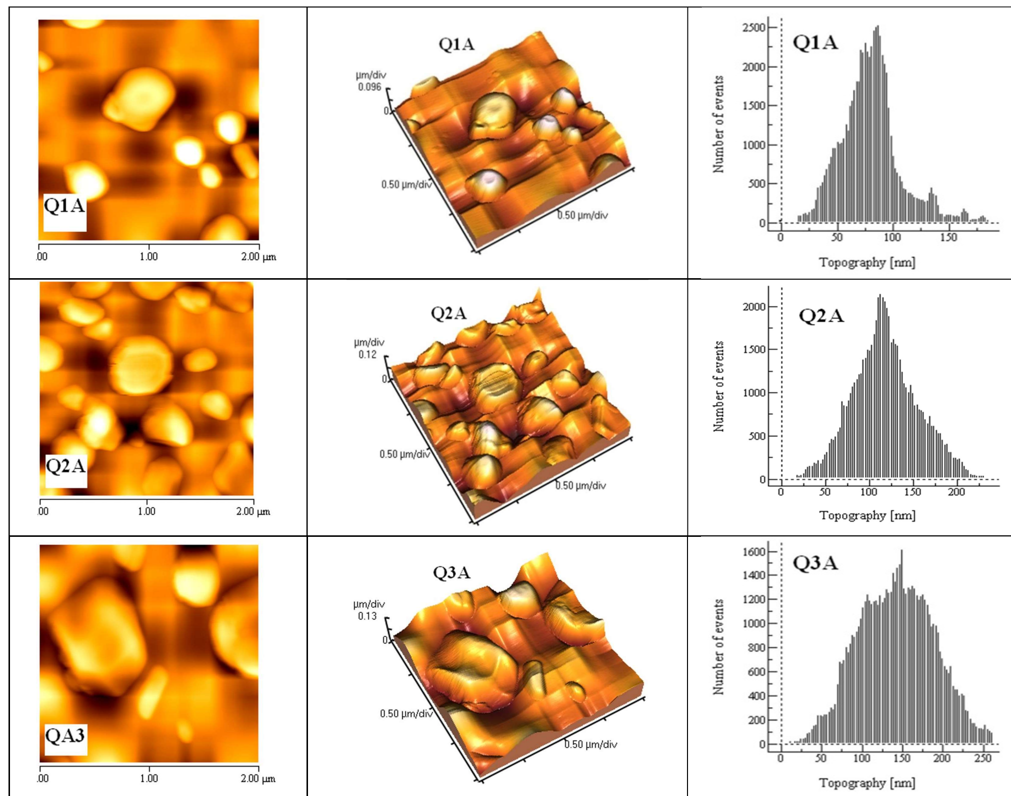

Fig. 3.2D and 3D AFM micrographs along with corresponding topographic histogram images of the MoO_3 films prepared at different plasma oxidation powers after annealing.

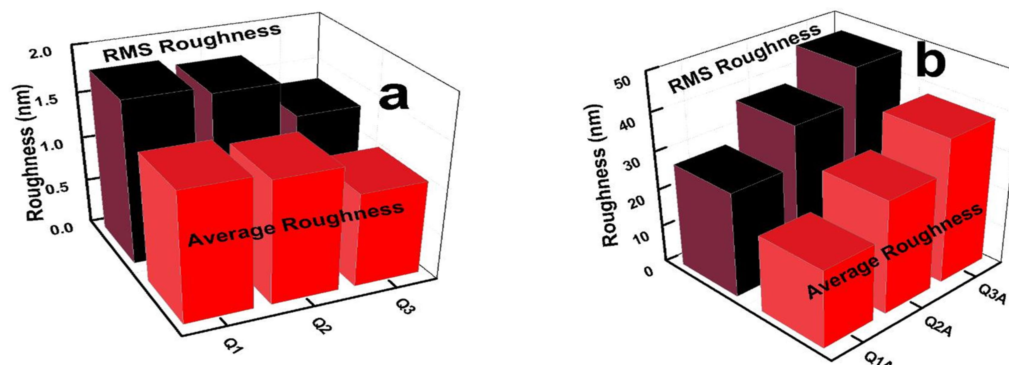

Fig. 4. Variation of roughness versus plasma oxidation powers (a) before annealing and (b) after annealing.

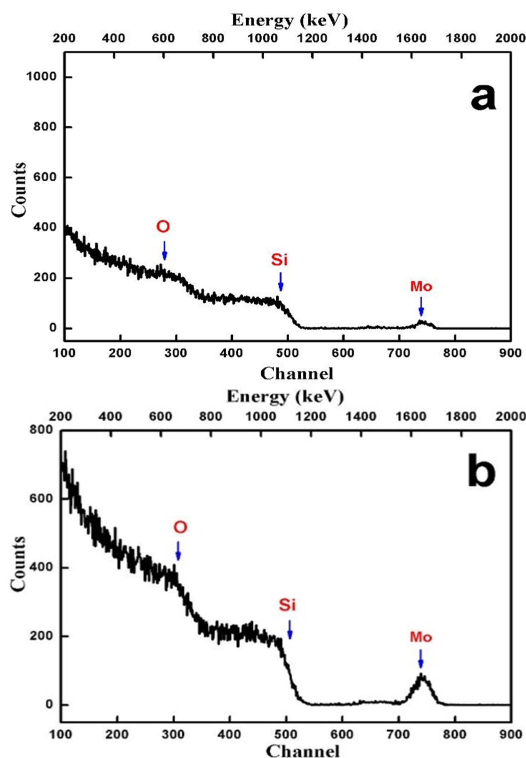

Fig. 5. RBS spectrum of the MoO_3 films grown on quartz substrates at different plasma oxidation powers (a: 5w) and (b: 10w) after annealing.

3.4. Transmittance Spectra

The optical transmittance spectra recorded in the wavelength ranging 200-1100nm are shown in Fig 6 as a function of plasma power. We can observe that, the optical transmission decreases as the plasma oxidation powers increases and the optical absorption edge shifted towards larger wavelength. The maximum transparency was obtained for the sample prepared at plasma power of 5w. According to XRD results the best crystallinity was obtained for this sample.

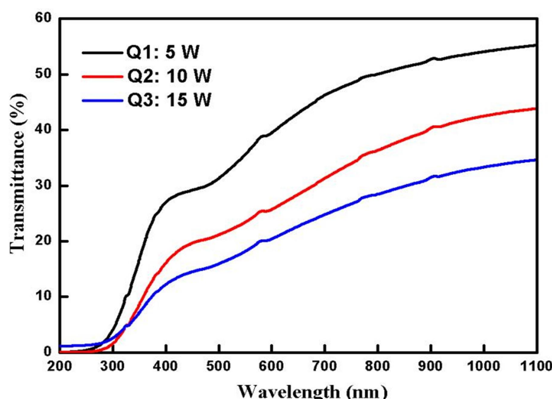

Fig. 6. Optical transmittance spectra of MoO_3 films prepared at different plasma oxidation powers.

4. Conclusions

From the present investigation, it can be concluded that:

1. The structural studies by XRD analysis showed the polycrystalline nature of MoO_3 with orthorhombic structure.
2. By increasing the plasma power the crystallinity of films decreased.
3. The AFM results exhibited that after annealing, the grain size and the films roughness was increased due to the combining of tiny grains and formation of larger grains.
4. The best crystallinity and homogeneity of films was observed before annealing in samples prepared at low plasma oxidation power of 5w.

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