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# Synthesis, characterization and structural control of nano crystalline molybdenum oxide $MoO_3$ single phase by low cost technique

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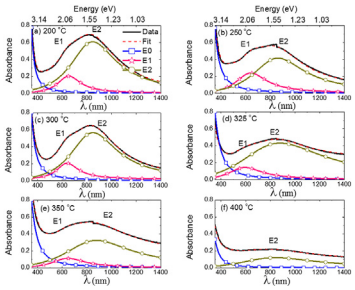
## HIGHLIGHTS

- Single phase α-$MoO_3$ nano crystalline $MoO_3$ thin films have been synthesized.
- Amorphous-to-crystalline phase transition occurs at 325 °C for $MoO_3$ thin films.
- A clear change in the Uv–Vis absorption spectrum for the $MoO_3$ thin films.
- The colors of films are changed from sky blue to deep blue.
- The plasmonics peak positions are depending on the substoichiometry of the $MoO_3$.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Thermodynamically stable α- $MoO_3$ thin film is prepared without any other phases of the molybdenum oxides. Simple and low coast spray pyrolysis technique is used. Growth conditions are optimized to produce pure α- $MoO_3$ with controlled crystallite size and surface morphology. Small angle (GAXRD) diffractometer is used to elucidate the structure. Profile shape function (PSF) model is made for the experimental data. WinFit software is going first to fit (PSF) to use the refined profile parameters for determination of crystallite size and internal residual strain. The (GAXRD) patterns prove the existence of α- $MoO_3$ only with layered structure, indicated by the appearance of only (0k0). The calculated crystallite sizes and the strain are found to range from 10 to 28 nm and 0.28%–0.05% respectively. Ultraviolet and Visible transmission measurements were performed over a wavelength range 190–2500 nm on the $MoO_3$ thin films synthesized by spray pyrolysis technique at different substrate temperature. The two sub-bands corresponds to the electronic transition between the molybdenum oxidation states $Mo^{4+}$, $Mo^{5+}$ and $Mo^{6+}$ are observed. Quantitative information on the temperature-induced blue shift of the sub-bands was obtained by fitting the spectra with Lorentz functions. The transition from $Mo^{5+}$ to $Mo^{6+}$ oxidation states show a blue shift up to Tc = 325 °C. Above Tc, the transition $Mo^{5+}$ to $Mo^{6+}$ increases more drastically, resulting in an anomaly in the temperature-induced shift at Tc. The anomaly can be attributed to the amorphous-to-crystalline phase transition at 325 °C. In addition, both refractive index and extinction coefficient are calculated as a function of substrate temperature.



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## 1. Introduction

Molybdenum oxide ($MoO_3$) is a material which has potential for application as photochromicand electrochromic smart windows for light modulation [1–4]. ($MoO_3$) can exist in three crystalline phases ($\alpha$, $\beta$ and hexagonal) depending on the preparation technique and its relevant parameters. The thermodynamically stable $\alpha$-phase $MoO_3$ has a layered structure consisting of double layers of $MoO_6$ octahedral held together by covalent force [5]. The optimization of growth conditions to produce pure phase with controlled structure and morphology for certain application is important.

Several experimental studies have been made on the structural and optical properties of the molybdenum oxide. These studies have been motivated by scientific and technological interest [6,7]. They are a model system relatively easy in preparation by using many deposition techniques [8,9]. It has a great potential for applications including solar cell, flat panel displays, batteries, photodetector, optical devices, sensors and electronics [10,11]. For this reason, large efforts have been undertaken for reliable understanding of the basic properties of the molybdenum oxide nanostructure. The electronic and optical properties of molybdenum oxide are closely correlated with their geometrical structure, namely their amorphous and crystalline structure, which results from using different substrate temperatures during the deposition process. Experimentally, Tarsame et al. [12] have investigated structural and optical properties of amorphous and crystalline molybdenum oxide thin films. The author concluded that the as-deposited $MoO_3$ films by thermal evaporation under high vacuum are amorphous films got crystallized by increasing the annealing temperature up to 350 °C [12]. He found that the XPS core level analysis shows the presence of three-oxidation state in as-deposited films while there is only one oxidation state in the crystalline films. However, one can observe in his optical measurements two sub-band transitions in the crystalline films.

In the present work, an attempt is made to deposit nanostructure Molybdenum oxide films on glass substrates using spray pyrolysis, as a simple and cost effective technique. The objective of this work is to define and optimize the preparation conditions allowing deposition of pure $\alpha$-phase $MoO_3$ films for chromogenic smart windows. In the present work, we investigate the effect of substrate temperature on the appeared absorption bands. These bands have been fitted and deconvoluted using Lorentz model. We studied the effect of sub-stoichiometry on the tuning of plasmonics feature in the molybdenum oxide films. The spectral weight and energy of the arising sub-bands are correlated with the change in substrate temperature. In addition, refractive index and extinction coefficient were calculated.

## 2. Experiment

The spray pyrolysis set-up to prepare $MoO_3$ is described elsewhere [13]. It consists of a locally made glass nozzle, peristaltic pump, air compressor, air flow meter, and hot plate, provided with control circuit to adjust its temperature via Cu/Cu constantan thermocouple. The substrate on the heater surface and the spraying nozzle are settled in a glass enclosure to maintain temperature stability. The spray system is enclosed in a fumed cupboard provided with a fan to remove the byproduct gases. The glass substrate ($1.5 \times 2.0 \times 0.1$ cm) is cleansed chemically and ultrasonically. There are several parameters relevant to the spray system such as, nozzle shape and dimensions, precursor material and concentration, distance between nozzle orifice and substrate surface, flow rates of gas and solution, spray time and substrate temperature. Each of the above parameters is manipulated one at a time to produce films with reasonable adherence and homogeneity. It is found that the optimum parameters for the prime deposited films are:

- Precursor, $MoCl_5$.
- Solution molarity, 0.2 M.
- Solution flow rate, 0.3 ml/s.
- Distance between nozzle orifice and substrate surface, 30 cm.
- Filtered and dried compressed air, 6 N $cm^{-2}$.

The 0.2 M spray solution is formed by dissolving Molybdenum penta-chloride (Merck 99.6% purity) in bidistilled water. Filtered and dried compressed air is used as carrier gas. The above mentioned conditions are fixed at their optimum values. The prepared films are classified to two groups. The first one is that prepared at fixed spray time (5 min) and varying the substrate temperature from 200 °C to 400 °C. The second group is that deposited at fixed substrate temperature 400 °C and different spray time, ranging from 1 to 5 min.

The structure information for the deposited samples such as, amorphisity and crystallinity, phases, crystallite size and strain are explored by grazing angle X-ray powder diffractometer (GAXRD). The data are collected at ambient temperature in step scanning mode, using a computer controlled X-ray diffractometer (PAN analytical Empyrean) with Cu k$\alpha$ radiation ($\lambda$ k$\alpha$ = 1.5406 Å) operated at 30 mA and 45 KV provided with (GAXRD) attachment. The film diffraction patterns are scanned in the $2\theta$ range of $10^\circ - 70^\circ$. With scan step 0.02°, counting time 20 s/step and grazing angle 2.5° of incident X-rays. A Quartz standard sample was used for determining the zero shifts and the instrumental profile under the same data collection conditions of the investigated samples. Crystallite size and strain analysis were determined by using WinFit program [14]. The surface morphology is examined by SEM. The obtained data are correlated with the prepared parameters. The Uv–Vis transmittance has been measured at room temperature in the energy range 190–2500 nm using a double beam spectrophotometer. The glass substrates were used as a reference through the measurements of T -$\lambda$ for the samples.

## 3. Results and discussion

### 3.1. XRD measurements

The films deposited at 325 °C are sky blue while those deposited at 350 °C and 400 °C are deep blue and light blue respectively. All samples are examined by GAXRD to elucidate their structure. It is found that films deposited at substrate temperature lower than 325 °C and spray time less than 5 min are amorphous as shown in Fig. 1.

The onset of crystallization is seen at 325 °C since two clear week peaks appeared at $2\theta = 23.32^\circ$ and 25.63°. The samples prepared at 350 °C show a new peak at $2\theta = 27.29^\circ$ besides the preceding ones at 23.32° and 25.63°. The samples deposited at 400 °C show six clear peaks. Three of which have high relative intensity at $2\theta = 12.72^\circ$, 25.63° and 38.86° while the other three have weaker intensity at $2\theta = 23.32^\circ$, 27.29° and 67.45°. The interplaner space d corresponding to each $2\theta$ is calculated using Bragg's formula $n\lambda = 2\,d\sin\theta$. The obtained d values for the investigated films deposited at substrate temperature ranging from 325 °C to 400 °C at fixed spray time 5 min are indexed with JCPDS files (05-0508) which depict the consistency between the data, are given in Table 1.

The planes corresponding to each $2\theta$ and d values are assigned according to JCPDS files (05-0508). The comparison between these data, declare that the prepared samples are orthorhombic $\alpha$- MoO3 without any other phase such as $\beta$- MoO3 or hexagonal MoO3. Lattice parameters for the investigated samples are calculated using