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Coloration of molybdenum oxide thin films synthesized by spray pyrolysis technique

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A B S T R A C T

Photochromiccoatings of molybdenum oxide films were deposited on glass substrates by spray pyrolysis technique. The samples were prepared at two substrate temperatures of 250 °C and 400 °C using spray time varying between 1 and 5 min while the other spray operating parameters are fixed at their optimum values. The crystalline nature and crystallite size of the films were investigated by grazing angle X-ray diffraction. The surface topography was characterized by atomic force microscopy roughness data and particle size histograms. The X-ray diffraction patterns prove that the films deposited at substrate temperature of 250 °C and different spray time are amorphous while the films deposited at 400 °C and different spray time are crystalline with only α-phase. The particle size distribution for the prepared samples are found to be in the range from 70 to 100 nm. The particle size distribution tends to be narrow as the spray time increases which indicates the improvement in homogeneity of the samples. The optical absorption spectra of selected colorless samples before and after UV light irradiation was recorded. Two distinct absorption bands were observed: a sharp one related to the energy gap and a broader one at lower energy of 1.03 eV to which the blue color of the sample after UV irradiation is related. This latter band is fitted with three sub-bands E$_1$, E$_2$ and E$_4$ using a Lorentzian model. The intensity and position of these sub-bands depended on UV light exposure time. The sub-bands E$_1$ and E$_4$ are related to the bulk and surface paramagnetic color centers while the E$_2$ band is related to pairing diamagnetic color centers.

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1. Introduction

Non-stoichiometric MoO$_3$ thin films may be prepared by different techniques. The oxygen deficiency in these materials MoO$_{3-x}$ gives rise to surplus of metal atoms that work as doping centers. The optical properties of the Molybdenum trioxide have been dominated by these doping centers [1–3]. The non-stoichiometric MoO$_3$ can be predominantly linked with color centers that are formed, particularly by oxygen vacancies that trap electrons. Such non-stoichiometric Molybdenum trioxide thin films manifest very important thermochromic and photochromic properties that may be used for smart windows [4,5]. However, there is as yet somewhat debate regarding the formation of different color centers in amorphous MoO$_3$. Schirmer et al. [6] proposed that coloration is similar to that

produced by amorphous WO$_3$ films. Such cases, the electronic transitions among the different oxidation states of molybdenum (Mo^{5+}, Mo^{6+}) cause the optical absorption bands of the films [6]:

$$h\nu + Mo^{5+}(A) + Mo^{6+}(B) \rightarrow Mo^{5+}(B) + Mo^{6+}(A) \qquad (1)$$
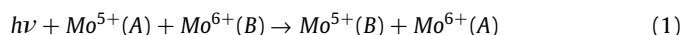
Based on this assumption, small polarons are formed as a result of electron trapping in the Mo^{5+} sites, such electrons polarize their surrounding lattice. These small polarons absorb the incident radiation and jump between A and B sites. This model is analogous to that presented by Deb [7], who observed that the properties of color centers in WO$_3$ are very similar whether generated by photochromism, or electrochromism.

Molybdenum oxide has different crystalline polymorphous stable orthorhombic α-MoO$_3$, metastable β-MoO$_3$ and the metastable phase MoO$_3$. It is known that MoO$_3$ exists in different oxide states, sub-oxides, hydro-oxides and crystalline hydrates [3]. The MoO$_3$ hydrates comprise monoclinic dihydrate (MoO$_3$ 2H$_2$O), (MoO$_3$ H$_2$O), (MoO$_3$ 1/2H$_2$O), and (MoO$_3$ 1/3H$_2$O) [4]. The hydrated MoO$_3$ is pre-

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pared by acidification of sodium molybdate (Na_2MoO_4) solution. The phase transition have been observed in hydrated MoO_3 from thermogravimetric (TG) and X-ray diffraction (XRD) results [8].

In this study, spray pyrolysis is used to prepare non-stoichiometric thin films of MoO_3 on glass substrates, as a simple, low cost and mass production technique. Optimum preparation conditions are determined to allow the formation of MoO_3 with high photo chromic performance. The effect of the UV illumination time on the absorption spectra of the samples is studied to pursue the coloration process.

2. Experimental

The spray pyrolysis set-up to prepare MoO_3 is described elsewhere [8]. Several parameters are relevant to the spray pyrolysis system such as, distance between nozzle orifice and substrate surface, nozzle shape and dimensions, precursor material and concentration, 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 as follows: (i) solution flow rate 0.3 ml/s; (ii) filtered and dried compressed air 6 N cm^{-2}; (iii) distance between nozzle orifice and substrate surface 30 cm; (iv) precursor $MoCl_5$ (the used $MoCl_5$ is chemically pure 99.95%); and (v) solution molarity 0.2 M. Two groups of samples are prepared at fixed substrate temperatures one at 250 °C while the other at 400 °C. The spray time is varied from 1 to 5 min. Table 1 shows the different states for the prepared MoO_3 thin films. The used substrates are transparent glass slices for microscope (Menzel - Gläser, Germany $2.5 \times 1.5 \times 0.1$ cm^3).

2.1. Sample characterization

The structure information for the prepared MoO_3 thin films such as crystallite size, crystallinity and amorphisity, and phases have been explored by grazing angle X-ray powder diffractometer (GAXRD). The data were recorded at ambient condition in step scanning mode, using a computer controlled X-ray diffractometer (PANalytical Empyrean) with Cu kα 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 2θ range of $10°-70°$, 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 [9]. The surface topography of the prepared films is studied by examination of roughness obtained from 2D atomic force microscope AFM images. The AFM model (WET-SPM, Scanning Probe Microscope, Shimadzu, Japan) was used to record the AFM images. Specific samples are selected to study the coloration processes when exposed to UV lamp ($\lambda = 254$ nm) (Spectronics corporation USA). Double beam spectrophotometer (Jasco V-530 model) is used to record the absorption

spectra in the wavelength range of 190–2500 nm. The absorption bands are deconvoluted and fitted by Lorentzian model.

3. Results and discussion

3.1. Sample structure

The GAXRD patterns for MoO_3 films are given in Fig. 1. All samples depict their crystallinity, since their GAXRD patterns show clear and defined peaks. As the spray time increases, the (0k0) intensity show reasonable increase, the (020) plane has the most significant increase. This indicates that the (020) is the main growth plane.

The planes corresponding to each 2θ are assigned according to JCPD files card number 05-0508 which declare that the prepared samples are pure orthorhombic α-MoO_3 without any other phases such as β-MoO_3.

There is a weak intensity peak which appeared at $2\theta = 11.528°$ for all samples with negligible change in intensity. This peak is not accounted in literature. The peak is an indication of the monoclinic hydrated MoO_3 (JCDD No.: 72-1051) formation with small quantity. Such a peak is expected since the synthesis is conducted in an aqueous medium. This suggestion is supported by previously reported data [10]. The obtained results are consistent to a great extent with that reported in literature [11].

3.2. Sample morphology

The 2D AFM images of particle size distribution recoded for the MoO_3 films deposited at constant deposition temperature of 400 °C and different spray time ranging from 1 to 5 min are shown in Fig. 2 (a)–(e). The AFM images show uniform spherical and belt like particles of various sizes. The size of these particles increased with increasing spray time up to 3 min due to the polycrystalline nature and improved crystallinity. The samples deposited at spray time greater than 3 min showed pyramid like morphology that may have occurred due to the aggregation of belt like crystallite [12], which depicts the layered nature of MoO_3. The average particle size were estimated statistically by taking the summation of all particle size and divided by it is number (see Fig. 3 (a)–(e)). The slight increase in particle size with increasing spray time may be due to the low mobility of ad atoms on the film surface. This observation is consistent with the reported results for MoO_3 deposited by sputtering [13].

The obtained results are also compatible with those obtained from SEM images and XRD patterns [14]. A typical AFM images show that the size of the particles are found to be in the range from 70 to 100 nm. The particle size distribution for samples deposited at substrate temperature 400 °C and varied spray time (1–5 min) is elucidated by AFM histogram given in Fig. 4 (a)–(e). It is obvious that the particle size distribution tends to be narrow as the spray time increase which indicates the improvement in homogeneity of the samples.

The combined results depict that the MoO_3 films deposited at 400 °C and different spray time are crystalline with only α-phase with (0k0) plane giving the layer structure. Table 2 illustrates the average roughness and mean radius of particles for MoO_3 samples prepared at 400 °C and different spray time. Table 2 shows clearly the increase trend of particle size except only at the values at 4 and 5 min. Also, the film presents a large belt structure at short spray time due to the onset of spread nuclei formation followed by their growth at the beginning of spray deposition. After the formation of the first and second layers the upward growth accompanied with surface tension phenomenon is enhanced and allowing the formation of spherical structures. These results are consistent with those reported in literature [9,15-18].

Table 1
The crystalline nature of the samples at different preparation conditions of MoO_3 thin films.

Time	Temperature	
	250 °C	400 °C
1 min	Amorphous irradiated by UV light	Polycrystalline
2 min	Amorphous	Polycrystalline
3 min	Amorphous	Polycrystalline
4 min	Amorphous	Polycrystalline
5 min	Amorphous	Polycrystalline