



## Development of Molybdenum trioxide ( $\text{MoO}_3$ ) by spin coating method for photovoltaic application

L.Chibane<sup>1</sup>, MS.Belkaid<sup>1</sup>, M. Pasquinelli<sup>2</sup>, H.Derbal-Habak<sup>2</sup>, J-J. Simon<sup>2</sup>, D.Hocine<sup>2</sup>, O.Boudia<sup>3</sup>

<sup>1</sup>Laboratory of Advanced Technologies of Genie Electrics (LATAGE)  
Faculty of Electrical and Computer Engineering  
Mouloud Mammeri University (UMMTO), BP 17 RP 15000, Tizi-Ouzou, Algeria  
E-mail: [chibane83@yahoo.fr](mailto:chibane83@yahoo.fr), [belkaid\\_ms@yahoo.fr](mailto:belkaid_ms@yahoo.fr)

<sup>2</sup>Aix-Marseille University, Institut Matériaux Microélectronique Nanosciences de Provence  
IM2NP CNRS UMR 6242  
Campus de Saint-Jérôme, Avenue Escadrille Normandie Niemen – Service 231, F-13397 Marseille Cedex 20, France  
E-mail : [marcel.pasquinelli@univ-cezanne.fr](mailto:marcel.pasquinelli@univ-cezanne.fr)

**Abstract.** Molybdenum trioxide,  $\text{MoO}_3$ , thin films have been deposited on glass substrates by Spin-coating method using ammonium heptamolybdate tetrahydrate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ ) as a single source precursor of Mo and O and. They were subjected to atmospheric heat treatment at different temperatures (200°C, 400°C and 500°C).  $\text{MoO}_3$  thin films obtained, were characterized using X-ray diffraction techniques (XRD), Scanning Electron Microscopy (SEM), Energy Dispersed Spectroscopy (EDS) and integrating sphere. The XRD patterns of annealed films show the formation of  $\text{MoO}_3$  in a polycrystalline phase, formation of  $\text{MoO}_3$  was also confirmed by EDS. The SEM photographs show that the thin films obtained are in layer-type structure and their grains size increases with increasing of annealing temperatures. The measurement results of integrating sphere show that the  $\text{MoO}_3$  thin film prepared at 500°C transmit about 72% and reflect about 12% of the visible spectrum.

### Key words

Material,  $\text{MoO}_3$ , oxide, lamellar, photovoltaic

## 1. Introduction

Molybdenum trioxide,  $\text{MoO}_3$ , is a transition metal oxide with a layer-type structure, composed of layers of distorted  $\text{MoO}_6$  octahedra in an orthorhombic crystal [1, 2]. Because of its layered structure,  $\text{MoO}_3$  is primarily studied in relation to its electrochromic and photochromic properties, for application as smart windows and display devices [3, 4]. It also used in gas sensing and catalytic research fields[5]. However this material has band gap value (1,7eV) well-matched to the solar spectrum [6], which makes it interesting to be an active element in a solar cell (absorber layer). In order to elaborate  $\text{MoO}_3$  in thin films shape, a number of methods have been used, including Atmospheric Pressure Chemical Vapor Deposition (APCVD) method[6], Thermal Spray method [7], Electrosynthesis method [2], chemical vapor transport method (CVT) [8,9], magnetron sputtering method [5] and

several others. Each method provides various advantages and disadvantages. In this work, thin films of  $\text{MoO}_3$  were deposited at atmospheric pressure on glass substrates, by Sol-Gel method using a Spin Coating process, which is a low cost technique and it could produce large area thin films as well.

## 2. Experimental procedure

### 2.1. Materials used

$\text{MoO}_3$  thin films were prepared on glass substrates, using ammonium molybdate tetrahydrate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ ) precursor as a single source of Mo and O, dissolving into de-ionized water at 0.15g/ml mass concentration. To obtain homogeneous solution we used a magnetic stirrer and add some catalysts.

### 2.2. Deposition of $\text{MoO}_3$ thin films

By using a nozzle an excess amount of the prepared solution is placed on the glass substrate (Fig.1), which is then rotated at a controlled rotational speed of about 1000 rpm for a period of 5min in order to spread the fluid by centrifugal force and evaporate the solvent. Before removing the coated substrate, the rotational speed had been increased to 3000 rpm to eliminate any grain of undissolved precursor. After that, it was transferred to a high temperature furnace under atmospheric conditions for heat treatments. The chemicals reacted on the substrate and form the desired solid thin film. The deposition was performed on several substrates at different heat treatment temperatures (200°C, 400°C and (500°C) for 30 min heat treatment time.

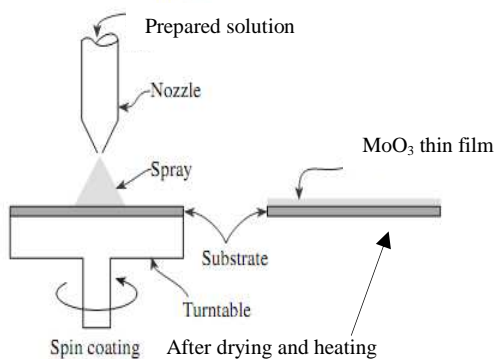


Fig.1.Stapes of dip- coating method

In order to study the properties of the thin films obtained, They were characterized using X-ray diffraction techniques (XRD), Scanning Electron Microscopy (SEM), Energy Dispersed Spectroscopy (EDS) and integrating sphere.

### 3. Results

#### 3.1. Crystallographic Structure

##### A. X-ray powder diffraction results

The X-ray diffraction spectra of the thin films prepared at different baking temperatures (200°C,400°C and 500°C) are shown in Fig.2 (a, b, c). From the XRD spectra we observed that the film prepared at 200°C (a) is completely amorphous in nature but films prepared at 400°C (b) and 500°C (c) are crystalline. It was also observed from the XRD spectra that the film prepared at 500°C is more crystalline than that at 400°C. Comparison of the prominent peak positions (2 $\theta$ -values) of the XRD spectra with the ASTM data file for MoO<sub>3</sub> (file n°00-035-0609 from published crystal structure data of Kihiborg (1963)) revealed that the product is phase MoO<sub>3</sub>, which crystallizes in the orthorhombic system with space group Pbnm (62), lattice parameters  $a = 3,96300$ ,  $b = 13,8600$ ,  $c = 3,660$ . Seen from Fig.2.c. The planes of the thin film prepared at 500°C heat treatment are indicated in the XRD spectra. The Peak positions (2  $\theta$ ), their Intensity (I) and  $hkl$  index of MoO<sub>3</sub> are listed in table 1.

#### 3.2. Morphological and chemical characterization

##### A. SEM results

The obtained thin films were gray in color and their thickness was estimated from 0.2 to 0.4 micrometer. Fig.3 display the SEM pictures with two different magnifications for each pattern, prepared by sol-gel method and air-annealed in a muffle furnace at different heat treatment temperatures ( 200°C,400°C and 500°C) for 30 min. In Fig.3a it shows that the surface morphology of MoO<sub>3</sub> thin film prepared at 200°C , exhibits a relatively smooth and completely covered surface , characteristic feature of an amorphous film. In this pattern the lamellar aspect of MoO<sub>3</sub> is not observed which is certainly due to the low annealing temperature. The powder XRD pattern verifies that this product is amorphous in nature (Fig.2a).It

shows in Fig.3b and Fig.3c that MoO<sub>3</sub> films obtained at 400°C and 500°C are crystalline and consist of rectangular crystallites having a lamellar structure, characteristic feature of the Molybdenum trioxide thin films. The crystallites are randomly oriented.

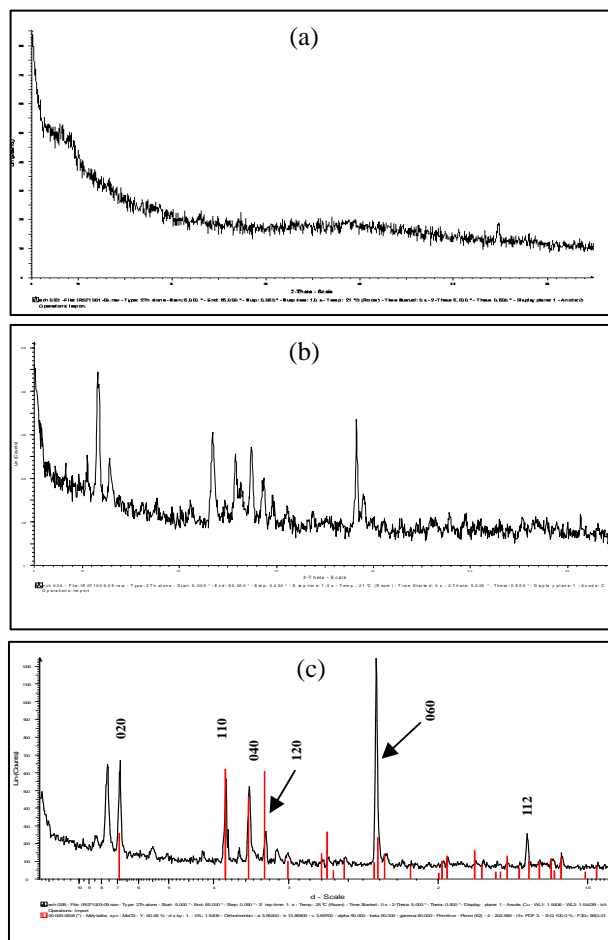


Fig.2. X-ray diffraction spectra of MoO<sub>3</sub> thin films prepared at different baking temperatures (200°C,400°C et 500°C°)

Tab.1. Peak positions (2  $\theta$ ), Intensity (I) and  $hkl$  index of MoO<sub>3</sub>

Peak position (2 $\theta$ )	Intensity (I)	$hkl$
12.780	36	020
23.340	77	110
25.700	38	040
25.880	31	120
38.980	21	060
55.200	10	112
58.840	11	081

Comparing Fig.3b and Fig.3c we deduce that the obtained films for the same annealing time (30min) at higher temperature have a larger size and more symmetrical morphology than those at lower temperature. The crystallites average size of film annealed at 400°C is estimated at 0.6 $\mu$  micrometer and for the film annealed at 500°C it is of about 2  $\mu$ .

## B. EDS results

Fig.4 shows EDS spectrum of film prepared at 500°C. The peaks present in this figure are those characteristics of oxygen (O K), molybdenum (Mo L) and sodium (Na K) which correspond to the constituents of the thin film deposited.

Tab.2 display mass concentration (Wt %) and atomic concentration (At %) of constituents of the film prepared at 500°C. It observed that the atomic concentration ratio Mo / O is of about 1 / 3, confirming the formation of thin film of MoO<sub>3</sub>. The presence of Na peak is certainly due to the presence of impurities in the annealing furnace during heat treatments.

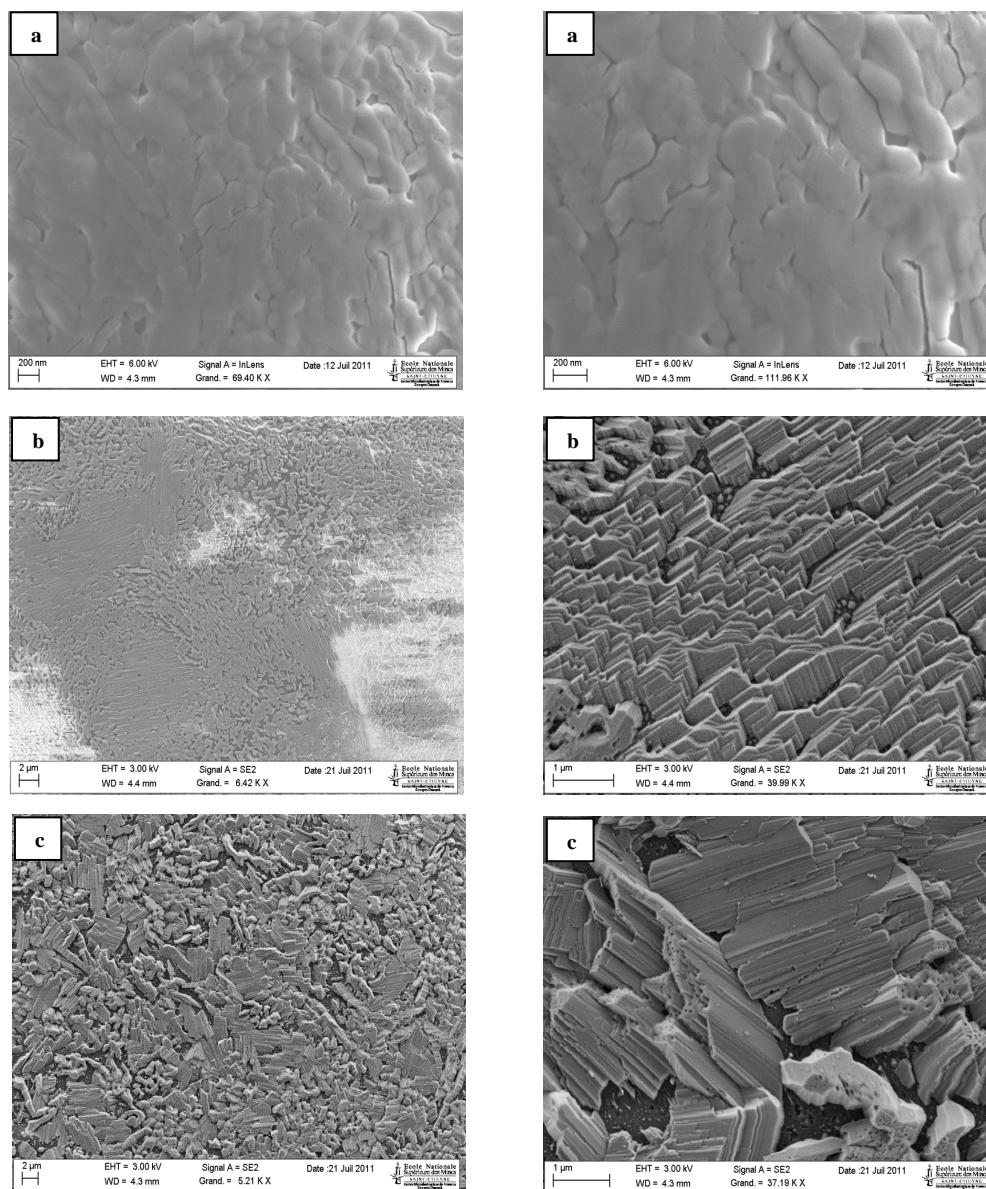


Fig.3.SEM pictures with two different magnifications for each pattern, prepared by sol-gel method and air-annealed at different heat treatment temperatures (200°C, 400°C and 500°C) for 30 min

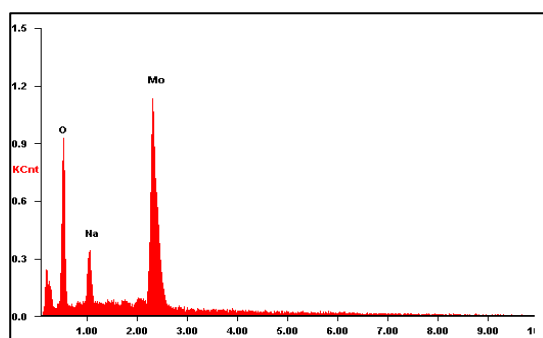


Fig.4. EDS spectrum of film prepared at 500°C

Tab.2. Mass concentration (Wt %) and atomic concentration (At %) of constituents of the film prepared at 500°C.

Element	Wt %	At %
O K	35.89	70.72
NaK	05.29	07.26
MoL	54.69	17.97

### 3.3. Optical characterization

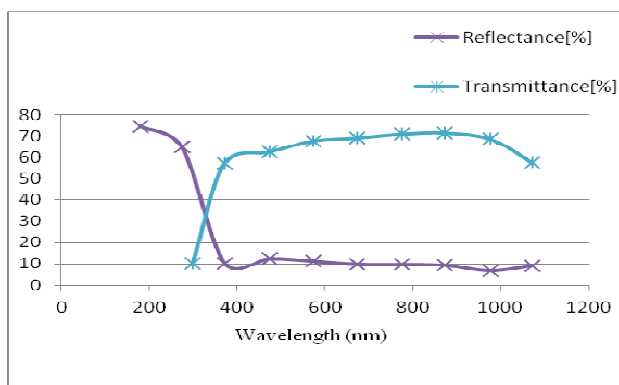


Fig.5. Transmittance and reflectance spectra of film prepared at 500°C

Fig.5 shows the transmission and reflection spectra of the  $\text{MoO}_3$  film prepared at 500°C heat treatment temperature. It observes that the transmittance of this film in the visible range spectrum is within the range 60-72 %, while the reflectance is around 12%. This result is consistent with works of K.A.Gesheva et al. [6] and K. A. Gesheva et al.[10].

## 4. Conclusion

$\text{MoO}_3$  thin films have been successfully deposited by Spin-coating method which is a low cost technique, using  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  as a single source precursor of Mo and O. The deposited films showed good adherence towards the substrates. The XRD patterns of film prepared at 500°C show the formation of  $\text{MoO}_3$  which crystallizes in the orthorhombic system. Using EDS technique, it observed that the atomic concentration ratio Mo / O of film prepared at 500°C is of about 1 / 3, confirming the formation of the  $\text{MoO}_3$  thin film. It is also found that the reaction temperature is very important for the formation and morphology of the prepared  $\text{MoO}_3$  thin films. The transmittance of  $\text{MoO}_3$  thin film annealed at 500°C is within the range 60-72 % in the visible range spectrum; while the reflectance is around 12%. The results obtained in this work demonstrate the potential of the sol-gel method for preparation of  $\text{MoO}_3$  thin films that may be useful for photovoltaic applications.

## Acknowledgement

Author "L. Chibane" is grateful to MS. Belkaid Professor and Researcher at LATAGE laboratory (Tizi-Ouzou, Algeria), IM2NP Laboratory (Marseille, France), all those who contributed to the achievement of this work.

## References

- [1] Wells, A.F. , Structural Inorganic Chemistry, 1984, Oxford: Clarendon Press. ISBN 0-19-855370-6.
- [2] Features, R. S. Patil, M.D. Uplane, P. S. Patil ,Electrosynthesis of Electrochromic Molybdenum Oxide Thin Films with Rod-Like, 2008, Int. J. Electrochem. Sci., 3 259 – 265.
- [3] Ferreira, F. F.; Souza Cruz, T. G.; Fantini, M. C. A.; Tabacniks, M. H.; de Castro, S. C.; Morais, J.; de Siervo, A.; Landers, R.; Gorenstein, A. Solid State Ionics. 2000, 136-137, 357.
- [4] Lin Shih-Yuan , Wang Chih-Ming , Kao Kuo-Sheng , Chen Ying-Chung , Liu Chan-Chih, Electrochromic properties of  $\text{MoO}_3$  thin films derived by a sol-gel process, 2010, Journal of sol-gel science and technology , vol. 53, n°1, pp. 51-58.
- [5] C. Imawan , H. Steffes, F. Solzbacher, E. Obermeier, A new preparation method for sputtered  $\text{MoO}_3$  multilayers for the application in gas sensors, 2001, Sensors and Actuators B: Chemical Volume 78, Issues 1-3, 30 August, Pages 119-125.
- [6] K.A.GESHEVA,T.IVANOVA and A.SZEKERES, Photovoltaic and photoactive materials Properties, 2002, Technology and applications,313-316.
- [7] J. Torres, L. D López-Carreño, L. C. Moreno, H. M. Martinez, A. P. Pardo, and J.E,  $\text{MoO}_3$  Thin Films Prepared by Thermal Spray Using Ammonium Molybdate,2009,Advanced Materials VIII Encontro da SBPMat , Rio de Janeiro .
- [8] M Ferroni, V Guidi, G Martinelli, M Sacerdoti, P Nelli, G Sberveglieri,  $\text{MoO}_3$ -based sputtered thin films for fast  $\text{NO}_2$  detection, 1998, Sensors and Actuators B: Chemical Volume 48, Issues 1-3, 285-288.
- [9] Young Jung Lee et al, Chemical vapour transport synthesis and optical characterization of  $\text{MoO}_3$  thin films , 2009, J. Phys. D: Appl. Phys. 42 115419.