

STRUCTURAL AND VIBRATIONAL PROPERTIES OF SPRAY PYROLYSED MOLYBDENUM OXIDE THIN FILMS

A. Bouzidi^{}, N. Benramdane^{*}, M. Medles^{*},
S. Bresson^{**}, C. Mathieu^{**},
B. Khelifa^{**}, R. Desfeux^{**}, M. El Marssi^{***}*

^{*} Laboratoire d'Elaboration et de Caractérisations des Matériaux, département d'électronique, Faculté des Sciences de l'Ingénieur, Université Djillali Liabes, BP89, Sidi Bel Abbès, 22000, Algérie

^{**} Université d'Artois, Faculté Jean Perrin, Rue Jean Souvraz, Lens, SP18, 62307, France

^{***} Laboratoire de Physique de la Matière Condensée, Université de Picardie Jules Verne, 33 rue St. Leu, Amiens, 80039, France

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MoO₃ thin films were prepared by spray pyrolysis technique by using 0.1 M of molybdenum chloride (MoCl₅) dissolved in deionized water on glass substrates heated at different temperatures. Influence of substrate temperature T_s on structural and vibrational properties is discussed; X-ray diffraction characterization revealed that the films are monoclinic for 200 °C and become orthorhombic above 225 °C. Raman spectra of the films were reported and explained the transformation phase.

Keys words: structural properties, vibrational properties, molybdenum trioxide.



Attouya Bouzidi

Organisation: Djillali LIABES University.

Education: Djillali LIABES University (1989-1994), Magister (1997), Doctorat d'état (2004).

Experience: Teaching (maître de conférence) at Djillali LIABES University (1997 – today), member in Scientific research projects (1998 – today)

Main range of scientific interests: thin films, optical properties of semiconductors.

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- 2 publications in Solar Energy Materials and Solar Cell.
- 1 publication in Microelectronic Engineering.
- 1 publication in Molecular Physics Reports.

Introduction

Transition metal oxide films have a great technical interest for their optical and electronic properties. Indeed, these materials can be switched between two different optical states prompted by photochromic, thermochromic or electrochromic effect [1]. Moreover, a number of these oxides such as MoO₃, V₂O₅, and V₆O₁₃ are promising cathode materials for rechargeable lithium batteries [2-4].

MoO₃ thin films were prepared by various techniques, such as reactive sputtering [5], chemical vapor deposition [6], pulsed laser deposition [7], oxygen plasma assisted molecular beam epitaxy [8] and flash evaporation [9]. We have used spray pyrolysis technique to fabricate molybdenum oxide thin films. The detailed study of structural and optical properties of MoO₃ thin films prepared by spray pyrolysis technique has been reported in a previous work [10] and shows that structural and optical properties of these films depend on substrate temperature.

The temperature dependence of the phonon spectrum has been investigated previously by Julien et al [11], the same authors have studied the substrate temperature dependence of flash evaporated MoO₃ thin films properties [9], but as far we know the effect of substrate temperature on vibrational properties of MoO₃ thin films prepared with spray pyrolysis technique has not been studied. So, in this paper, our objective is a comparative study of the spray pyrolysed MoO₃ vibrational and structural properties according to the substrate temperature.

Experimental details

Thin films were deposited by spray pyrolysis technique on glass substrates at different temperatures varying from 200 °C to 300 °C. Spraying solution of Molybdenum chloride (MoCl₅) dissolved in deionized water, with 0.1 M concentration is used. The description of spray pyrolysis technique has been reported previously [12].

Structural characterization was carried out at room temperature in the $\theta-2\theta$ scan mode using a Rigaku Miniflex diffractometer ($\text{CuK}_{\alpha 1}$ radiation, $\lambda = 1.5406 \text{ \AA}$). Raman spectroscopy measurements were performed at room temperature in a backscattering microconfiguration using the 514.5 nm line from an Ar-ion laser focused on the surface as a spot of $1 \mu\text{m}$ in diameter and with a power density of $\sim 3 \text{ MW/cm}^2$. The scattered light was analysed with a Jobin Yvon T64000 spectrometer, equipped with a liquid nitrogen cooled CCD detector. The spectrometer provided a wave number resolution better than 3 cm^{-1} .

Results and discussion

Structural properties

X-ray diffraction patterns of molybdenum films prepared at different substrate temperatures are given in Fig. 1.

At 200°C , the pattern exhibits (011) and (200) peaks with low intensity. These peaks are indexed by comparing the experimental data (measured inter-reticular distances d_m) with the JCPDS card No. 47-1081, corresponding to the $\beta\text{-MoO}_3$ (monoclinic phase, $P2_1/c$ space group (No. 13)). This phase has been obtained by thermal treatment of spray dried powders of aqueous molybdic acid solutions [13] and by pulsed laser deposition [7].

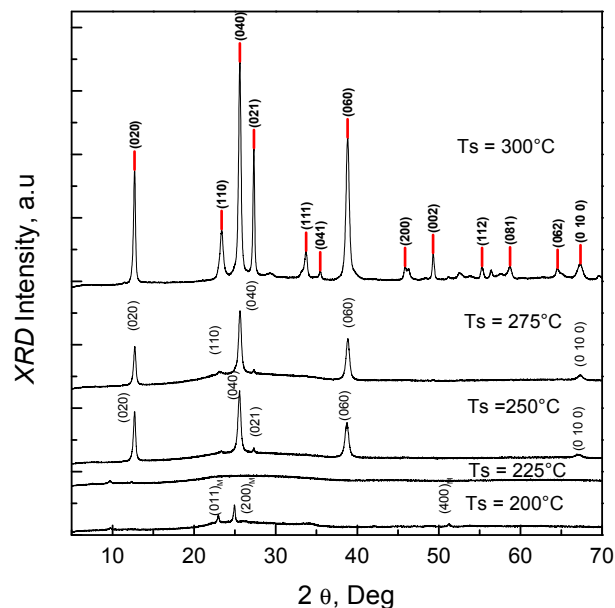


Fig. 1. X-ray Diffraction spectra of spray pyrolysed samples prepared for different substrate temperatures with 0.1 M of spray solution MoCl_5

At 225°C , the diffraction spectrum shows a large band suggesting a disorder in the structure due probably to the $\beta\text{-MoO}_3$ and $\alpha\text{-MoO}_3$ mixture.

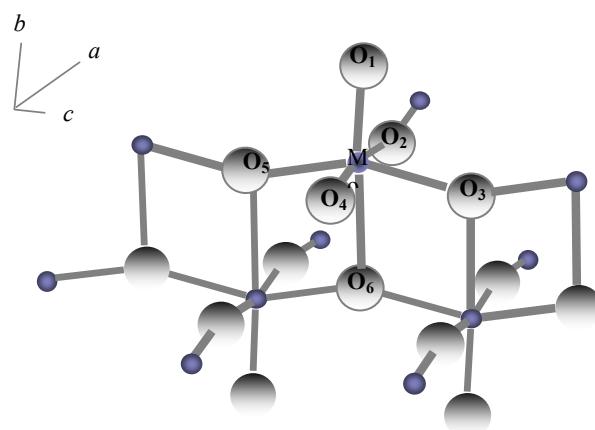
At 250°C and 275°C , the (0k0) peaks predominate indicating a preferential growth and suggesting layered

structure of the films. The grains have the b -axis perpendicular to the substrate surface. Indeed, the $\alpha\text{-MoO}_3$ can be described as a layered structure in which each layer is built up of MoO_6 octahedra at two levels connected in the direction to c axis by edge and corner sharing so as to form zig-zag rows, in the direction to the a axis the octahedra are connected by corners sharing [14] (see Fig. 2). Our result is similar to that obtained in literature for flash evaporated MoO_3 thin films [9].

At the higher temperature 300°C , the pattern exhibits several peaks in different directions indicating the thin films polycrystalline nature. A good agreement is observed between the inter-reticular distances of thin films deposited in the range from 250 to 300°C and those of JCPDS file (card N° 05-0508) corresponding to the orthorhombic phase ($\alpha\text{-MoO}_3$).

The experimental lattice parameters are $a = 3.973 \text{ \AA}$, $b = 13.902 \text{ \AA}$ and $c = 3.692 \text{ \AA}$ [10], which are in good agreement with the literature data ($a = 3.962 \text{ \AA}$, $b = 13.858 \text{ \AA}$ and $c = 3.697 \text{ \AA}$) [15]. Moreover, the grain size increases with increasing substrate temperature, its values are about 21 nm for the range ($250\text{--}275^\circ\text{C}$) and 26 nm for 300°C [10]. The $\alpha\text{-MoO}_3$ spray pyrolysed films are light colored at low temperature and become deeply greyish when the substrate temperature increases. This fact suggests that the number of defects increases due to oxygen vacancies formation in the films and induces a decrease of the optical gap of MoO_3 [9, 16].

In order to confirm our hypothesis that the large band observed on the diffraction spectrum at 225°C is attributed to the mixed phase during the transformation from $\beta\text{-MoO}_3$ to $\alpha\text{-MoO}_3$ and to affine our obtained results, we present the study of spray pyrolysed MoO_3 vibrational properties according to the substrate temperature.



Mo-O₁: 1,67 Å; Mo-O₂: 2,25 Å; Mo-O₃: 1,95 Å;
Mo-O₄: 1,73 Å; Mo-O₅: 1,95 Å; Mo-O₆: 2,33 Å

Fig. 2. Structure of $\alpha\text{-MoO}_3$ (zig-zag chains of octahedra [14])

Raman micro-spectroscopy

The obtained Raman spectra in the range 80-1100 cm^{-1} for samples prepared by spray pyrolysis at substrate temperatures varying from 200 $^{\circ}\text{C}$ to 300 $^{\circ}\text{C}$, are shown in Fig. 3 and 4.

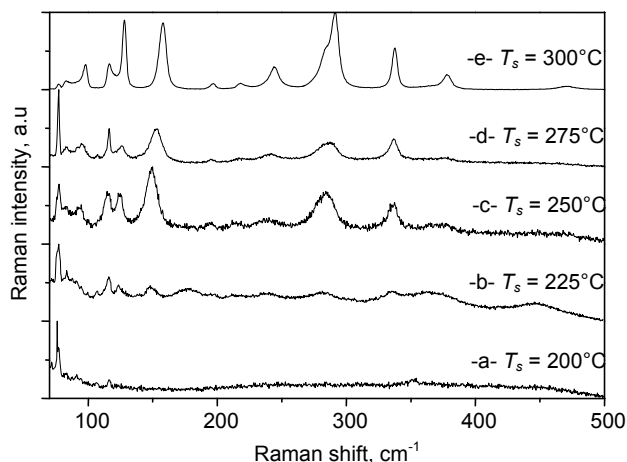


Fig. 3. Raman spectra in the frequency range 80 to 550 cm^{-1} of MoO_3 films prepared at different substrate temperature

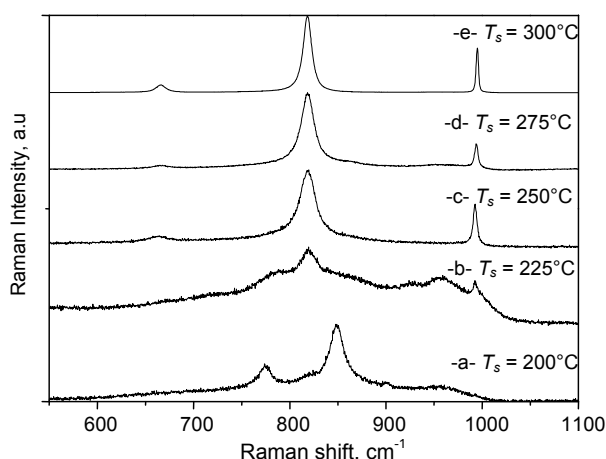


Fig. 4. Raman spectra in the frequency range 550 to 1100 cm^{-1} of MoO_3 films prepared at different substrate temperature

Vibrational study in 80-550 cm^{-1} spectral region

In the range 80-550 cm^{-1} , we can observe that the vibrational behaviors of the different samples are not the same. Thus, the spectra can be separated on three parts: the first concerns the vibrational behavior of the sample prepared at 200 $^{\circ}\text{C}$, the second part amounts to $T_s = 225$ $^{\circ}\text{C}$ and the thin films prepared at $T_s = 250$ to 300 $^{\circ}\text{C}$ correspond to the last part. All the observed bands in Fig. 3 and 4, are summarized and compared with previous literature data in Table 1.

For the sample prepared at $T_s = 200$ $^{\circ}\text{C}$, in the spectral range 80-550 cm^{-1} , we can only observe some very weak peaks below 200 cm^{-1} , above this frequency value we notice weak peak at 355 cm^{-1} . This band has been observed for $\beta\text{-MoO}_3$ phase [7, 17] and can be assigned by deformation bending mode δOMO_3 . Moreover, in Fig. 5, we present the Raman spectrum of this sample in the range 72 to 80 cm^{-1} . A resolved doublet at the bands 76 and 77 cm^{-1} , is observed. The peak at 76 cm^{-1} has a width at half maximum smaller than the second peak. However, we know the existence of a plasma ray in this spectral range. So, it is reasonable to assign the band at 76 cm^{-1} to this ray plasma and the band at 77 cm^{-1} to our material. In the literature [7], the band at 77 cm^{-1} corresponds to a vibrational mode of $\beta\text{-MoO}_3$. This result must be confirmed by the spectral study on the range 550-1100 cm^{-1} .

Table 1

Experimental frequencies (cm^{-1}) and assignment of the Raman active modes of orthorhombic MoO_3

This work (cm^{-1})	E. Haro-Poniatowski et al [7]	Eda [18]	Assignment [19]
995, s	995, s	995	$A_g, B_{1g} \nu \text{O}=\text{Mo}$
818, vs	819, vs	819	$A_g, B_{1g} \nu \text{OMO}_2$
666, w	667, w	666	$B_{2g}, B_{3g} \nu \text{OMO}_3$
471, w	471, w	471	$A_g, B_{1g} \nu \text{OMO}_3$
378, m	379, m	378	$B_{1g} \delta \text{O}=\text{Mo}$
364*, vw	365, w	366	$A_g \delta \text{O}=\text{Mo}$
337, m	337, m	338	$A_g, B_{1g} \delta \text{OMO}_3$
291, s	291, s	291	$B_{3g} \delta \text{O}=\text{Mo}$
284*, m	283, m	283	$B_{2g} \delta \text{O}=\text{Mo}$
244, m	245, m	246	$B_{3g} \delta \text{OMO}_2$
218, w	217, w	217	$A_g \delta \text{OMO}_2$
197, w	198, w	197	} Other deformation modes
158, s	158, m	159	
128, s	129, w	129	
116, m	115, m	117	
98, m	98, m	100	
83, w	82, s	84	

w = weak, m = medium, s = strong, vs = very strong, * fitted frequency value

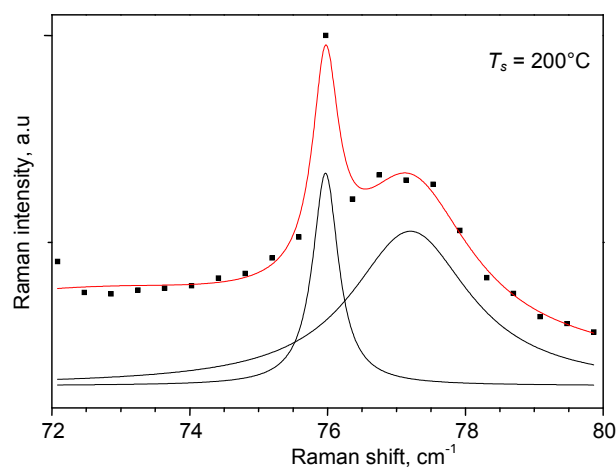


Fig. 5. Raman spectra in the frequency range 72 to 80 cm^{-1} of $\beta\text{-MoO}_3$ films prepared at 200 $^{\circ}\text{C}$

When the substrate temperature reaches 225 °C, some weak broad peaks are observed at 158, 238, 281, 336, 372 and 447 cm^{-1} , a well resolved doublet appears at 116 and 124 cm^{-1} and medium peak is observed at 148 cm^{-1} . The bands at 238, 281, 336, 372 cm^{-1} are near to the ones observed in literature for α -MoO₃ [17, 18, 19] (Table 1). In comparison with the previously Raman studies on β -MoO₃ or α -MoO₃, it seems that the weak broad peak at 447 cm^{-1} has not indexed. However, it can explain the disorder in the structure.

For the third part ($T_s = 250$ to 300 °C), we always observe in the Fig. 3 a medium peak, nearby to 337 cm^{-1} . A strong peak with shoulder appear near 290 cm^{-1} in the case of the sample prepared at 300 °C, whereas we notice a broad peaks at same frequency value for 250 and 275 °C, all these bands are due to the Raman-active bending modes [19]. In order to analyse the peak shape, lorentzian fitting is used in 270 to 300 cm^{-1} spectral region (Fig. 6), the curve fittings confirm the existence of shoulder bands (fitted frequencies values labeled * in Table 1), it is clearly that the $\delta\text{Mo}=\text{O}$ vibrations corresponding to frequencies of 284 and 291 cm^{-1} are closely dependant to substrate temperature and the intensity ratio (I_{291}/I_{284}) increases as function of T_s .

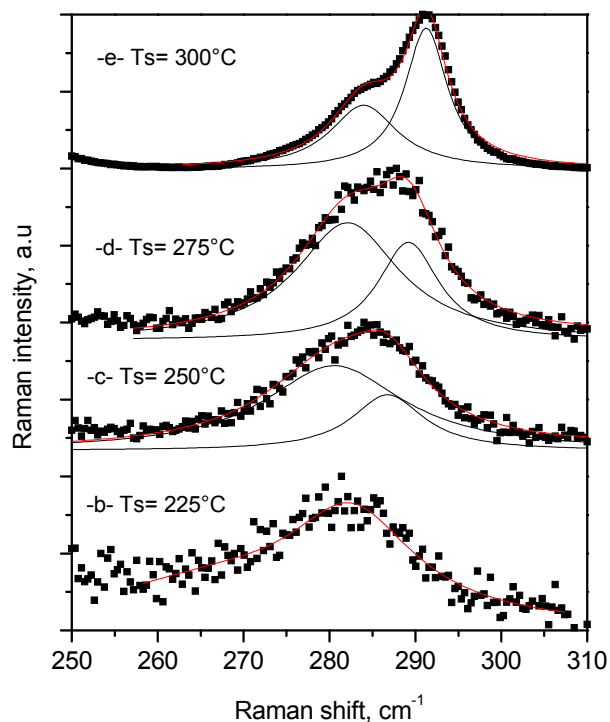


Fig. 6. Analysis of the peaks 284 and 291 cm^{-1} as a function of substrate temperature

The line shifted from 149 cm^{-1} to 153 cm^{-1} (Fig. 3, c, d) is assigned to B_{1g} mode (translational rigid MoO₄ chain mode, T_b), when substrate temperature reaches 300 °C, a strong band at 158 cm^{-1} is observed and assigned to A_g mode (translational rigid MoO₄ chain mode, T_b).

The resolved doublet at 116 and 124 cm^{-1} is always observed with a shift of 5 cm^{-1} for 124 cm^{-1} band at 300 °C, these bands are assigned respectively to B_{2g} , B_{3g} modes (translational rigid MoO₄ chain mode, T_c).

We can notice that the different modes for MoO₃ thin film prepared at 300 °C are more resolved than films prepared at 250 or 275 °C.

Vibrational study in 550-1100 cm^{-1} spectral region

In Fig. 4, a, the more intense peaks at 849 cm^{-1} and 774 cm^{-1} can be assigned to the stretching vibrations of Mo–O bonds in the expected corner-sharing octahedral Mo–O–Mo and the weak peak observed at 901 cm^{-1} indicates a stronger distortion of the MoO₆ octahedra. The monoclinic MoO₃ contains two crystallographically independent octahedra, shown the disorder at the Mo and O sites; its ReO₃ structure is analogous to WO₃. Indeed the Raman spectrum of MoO₃ thin film prepared at 200 °C (Fig. 3, a and Fig. 4, a) is similar to WO₃ as described in the literature [7, 13]. This spectrum exhibits other very weak bands at 818 and 957 cm^{-1} that are determined by lorentzian fit of the experimental spectrum. The very weak band at 818 cm^{-1} corresponds to stretching vibration of Mo–O–Mo suggesting the slight presence of α -MoO₃ in thin film deposited at 200 °C.

For $T_s = 200$ °C, the band at 957 cm^{-1} was observed at 951 cm^{-1} by S.H. Lee et al [5] for sputtered amorphous MoO₃. The authors assigned to Mo=O stretching mode of terminal oxygen atoms possibly on the surfaces of the cluster, these terminal oxygen bonds are created by breaking of Mo–O–Mo bonds at the corner-shared oxygen, which are common to two octahedron [13], T.Ono et al [20] have observed this band at 955 cm^{-1} for MoO₃ catalyst exchanged with O¹⁸ that assigned to vibration of Mo–O¹⁸ bond.

When the substrate temperature reaches 225 °C, the peaks being particularly broad, indicate the poor crystallization of film, confirming the X-ray diffraction measurements. The 848 cm^{-1} and 774 cm^{-1} characteristic peaks of β -MoO₃ becomes very weak and the band at 957 cm^{-1} becomes more intense due to disorder increase in film. According to $T_s = 200$ °C, additional peaks at 819 cm^{-1} and 992 cm^{-1} appear, these modes characterizing the α -MoO₃ are assigned respectively to Mo–O₍₂₎–Mo and Mo=O₍₁₎ stretching vibrations. That's why it is reasonable to think that at $T_s = 225$ °C, we have a mixture of α -MoO₃ and β -MoO₃. The weak band observed at 924 cm^{-1} is not mentioned by other experimental works and it can be explained by film disorder. Above 225 °C, further the stretching vibrations modes at 819 and 994 cm^{-1} , a weak band is observed at 666 cm^{-1} , that assigned to OMo₃ bridging stretching vibrations. With the increasing substrate temperature, a shift toward the mode frequencies characteristic of orthorhombic phase (α -MoO₃) is observed and the bands become well resolved. The band at 994 cm^{-1} is more intense which confirm the layered structure of the film. The bands corresponding to orthorhombic phase are assigned according to α -MoO₃ single crystal studied by

Py and Maschke [19] and summarized in Table 2, our results are in good agreement with those reported in literature [7, 9, 17-19].

Table 2
Experimental frequencies of Raman active modes of MoO₃ spray pyrolysed thin films deposited at different substrate temperatures

β -MoO ₃ [7]	This work, °C					α -MoO ₃ [19]
	200	225	250	275	300	
76 (s)	76					
91	91	83	83	83	85	83
		90*	93	94	98	99
130 (w)	116	116	115	116	116	116
		124	124	126	128	129
		148	149	153		154
		158			158	158
176						
194						
237 (w)		195*	195	195	197	198
		214*	214	217	218	217
283 (w)		238	239	241	244	246
		281	279*	280*	284*	283
310 (w)			287*	288*	291	291
349 (m)	355	336	337	336	337	338
391 (w)		372	373	374	378	365
						379
414 (w)						
		447				
774 (s)	774		662	666	666	473
		819*				666
849 (vs)	849	784*	818	818	818	819
		855*				
904 (m)	901					
		924				
		957				
		960				
		992	992	994	995	995

w = weak, m = medium, s = strong, vs = very strong, * fitted frequency value

Conclusion

MoO₃ thin films were prepared by spray pyrolysis technique on glass substrate with a temperature variation from 200 to 300 °C. The films exhibit respectively a monoclinic structure at low temperature and an orthorhombic structure at high temperature. The structural results reveal that the films structure changes with substrate temperature.

The samples were characterized also by Raman spectroscopy; the results confirm the temperature dependence of the nature of the film. At 200 °C the Raman frequencies correspond to β -MoO₃. A mixture of monoclinic and orthorhombic structure is observed at

225 °C, the spectrum is particularly broad for this temperature, which explains the poor film crystallization and the absence of peaks in XRD diagram. Above 250 °C, all frequencies Raman corresponding to α -MoO₃ are observed and confirm the XRD results.

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