

## Effect of thermal treatment on the CO and H<sub>2</sub>O sensing properties of MoO<sub>3</sub> thin films

**M Torres-Luengo, H M Martínez, J Torres and L D López-Carreño**

Grupo de Materiales con Aplicaciones Tecnológicas, GMAT. Departamento de Física, Universidad Nacional de Colombia, Bogotá, Colombia

E-mail: mtorresl@unal.edu.co

**Abstract.** MoO<sub>3</sub> thin films were prepared on Corning glass substrates using the chemical spray pyrolysis technique. A 0.1 M solution of ammonium molybdate tetrahydrate was used as precursor one. 5ml and 20 ml of the precursor solution was sprayed with the substrate temperature maintained at 623 K. Thermal treatment involved drying at 393 K for 8 h with continuous N<sub>2</sub> flow, followed by a vacuum annealing at 473 K for 2 h in a residual inert atmosphere. XRD indicates that the crystallographic structure corresponded to the orthorhombic  $\alpha$ -MoO<sub>3</sub> phase. Electrical characterization was carried out in a system operating under high vacuum conditions. The samples could be cooled down to LN<sub>2</sub> temperature and heated in a controlled way up to 473 K. To elucidate the electrical response of the films to CO and H<sub>2</sub>O exposure, the I-V characteristic curve was measured over the whole temperature range. The electrical resistance of the films decreased with increasing temperature. In 5 ml films, the sensitivity to both gases increased which thermal treatment, reaching values between 40% and 60% at room temperature. On the contrary, the 20 ml films' sensitivity decreased almost half of their original values after thermal treatment.

### 1. Introduction

Because of its technological importance, scientific research in the thin films-based gas sensor field has shown a significant increase over the last years. From a technological point of view, efficiency and low cost of production are some of the most important features in the development of these devices [1–4]. The operating principle of these devices is based on the changes in the sensor's electrical resistance induced by gas-surface electrostatic interactions. Semiconductor transition metal oxides have been widely used as a detection material. Among these, molybdenum trioxide has received special attention. Thin films have been prepared using different techniques, and their properties depend on the method as well as the parameters used during the preparation process. The physical-chemical properties of MoO<sub>3</sub> thin films prepared through spray pyrolysis and their potential application as a gas sensor have been studied, and the effect of the deposition parameters on the crystallographic structure, morphology, and opto-electronic properties have also been widely reported [5–10].

### 2. Experimental procedure

MoO<sub>3</sub> thin films were deposited on Corning glass substrates using the spray pyrolysis technique. A 0.1 M solution of ammonium heptamolybdate tetrahydrate ((NH<sub>3</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O) was used as a precursor. Specific details of the spray pyrolysis equipment and the substrate's cleaning procedure have already



been described [11]. Regarding the present article, two types of samples were prepared: 5 and 20 ml of the precursor solution was sprayed onto substrates maintained at 623 K, respectively. The thermal treatment involves two steps: a drying process at 393 K in atmospheric pressure under continuous N<sub>2</sub> flow for 8 hours and an annealing at 473 K in a vacuum with a residual gas mixture of N<sub>2</sub>, Ar and H<sub>2</sub> for 2 hours.

The films' crystallographic structure was studied using an XPert PRO PANAnalytical X-ray diffractometer. X-ray diffractograms were taken in a 2 $\theta$  range 10° - 70°, with a step of  $\Delta 2\theta = 0.02^\circ$  and an exposure time of 2s per step using Cu-K $\alpha$  radiation ( $\lambda=1.5406\text{\AA}$ ) and Bragg -Brentano geometry.

The films' I-V characteristic curves were measured via the two-point technique on a separate high-vacuum system that operates at a base pressure of about 10<sup>-5</sup> mbar. In this system, the samples' temperature can be varied in a controlled way in the range 133-473 K. The samples' temperature was measured with a K-type thermocouple attached to the sample.

In order to measure the I-V curves, two comb-shaped aluminum electrodes were deposited through thermal evaporation in a high vacuum (10<sup>-5</sup> mbar base pressure). Cu wires were attached to the aluminum electrodes using silver staining (GA18573 Leitsilver BioChemika) [12]. An AC-voltage 20 V peak-to-peak and 0.05 Hz signal provided by a digital PeakTech 4070 signal generator was used as excitation source.

The current through the sample was measured using a Keithley 617 digital high-impedance electrometer. I-V curves were recorded using an automatic data acquisition system.

The interaction of CO and H<sub>2</sub>O molecules with the MoO<sub>3</sub> thin films' surface was studied by measuring the relative change of the films' electrical resistance, which is obtained from the measured I-V curves. Before exposing the sample to a CO or H<sub>2</sub>O atmosphere, the film was heated to 473 K at a 10<sup>-5</sup> mbar residual gas pressure in order to clean it through desorption the sample's surface. After that, CO or H<sub>2</sub>O was injected into the HV-chamber until a 10<sup>-2</sup> mbar pressure was reached. Then, the film was cooled down to 133 K using LN<sub>2</sub>.

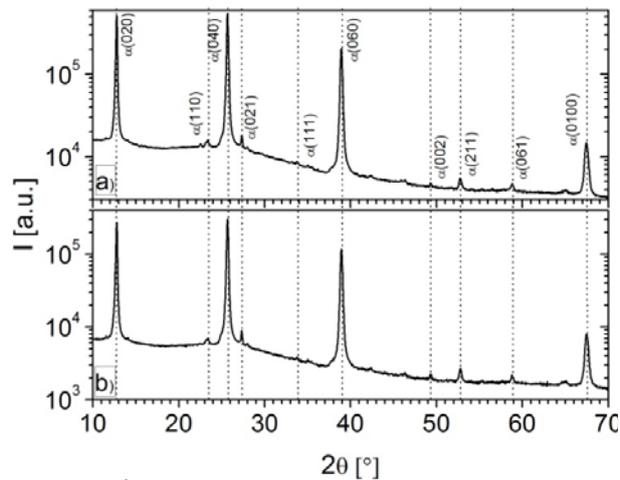
### 3. Results and discussion

#### 3.1. X-ray diffraction (XRD)

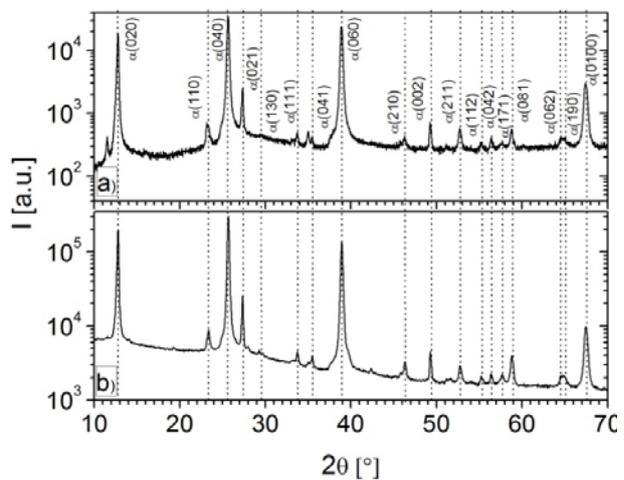
It is well known that MoO<sub>3</sub> can exist in two crystallographic forms: the  $\alpha$ -phase, which presents an orthorhombic structure, and the  $\beta$ -phase, with a monoclinic structure. Figure 1 shows the XRD spectra of the samples deposited with a 5 ml solution. According to crystallographic card JCPDS-ICDD 00-005-0508, the prepared samples' structure corresponds to the orthorhombic  $\alpha$ -MoO<sub>3</sub> phase. Analysis of the diffraction peak's integrated intensity suggests that MoO<sub>3</sub> films grow with a preferred orientation along the [0k0] direction. This characteristic behavior has already been reported [11].

From the X-ray spectra, the lattice constants were also calculated. For thermally untreated films, values of  $a=3.96\text{\AA}$ ,  $b=13.86\text{\AA}$  and  $c=3.69\text{\AA}$  were determined. These values are consistent with those reported in the crystallographic card for MoO<sub>3</sub>-powder samples. In all cases, the maximum discrepancy does not exceed 0.2%. As can be seen in Figure 1 (lower spectrum), thermal treatment has no significant effect on the MoO<sub>3</sub> films' crystallographic structure.

For the films deposited with 20 ml of solution, the X-ray spectra analysis (figure 2) shows that the MoO<sub>3</sub> films also have an orthorhombic-type crystalline structure. Diffraction patterns were also indexed by comparing them with JCPDS-ICDD card 00-005-0508, and the presence of a single  $\alpha$ -MoO<sub>3</sub> phase was confirmed. Lattice parameters obtained from the diffraction peaks' positions are also in agreement with those obtained for the MoO<sub>3</sub> films deposited with 5 ml of solution. A preferred growth along the [0k0] direction was also observed. As in the previous case, no effect on the crystallographic structure can be observed as a result of thermal treatment.



**Figure 1.** 5 ml  $\alpha$ -MoO<sub>3</sub> XRD patterns of a) non-thermally treated films and b) thermally treated films.



**Figure 2.** 20 ml  $\alpha$ -MoO<sub>3</sub> XRD patterns of a) non-thermally treated films and b) thermally treated films.

Although the MoO<sub>3</sub> films' crystallographic structure analysis does not suggest significant effects resulting from the thermal treatment, effects are more evident for the MoO<sub>3</sub> films' electrical properties, as is discussed in the next section.

### 3.2. Electrical Properties

Sensitivity was used as a figure of merit in order to quantify the effect of CO or H<sub>2</sub>O adsorption on the MoO<sub>3</sub> films' electrical properties. In this case, the sensitivity  $S$  is defined as:

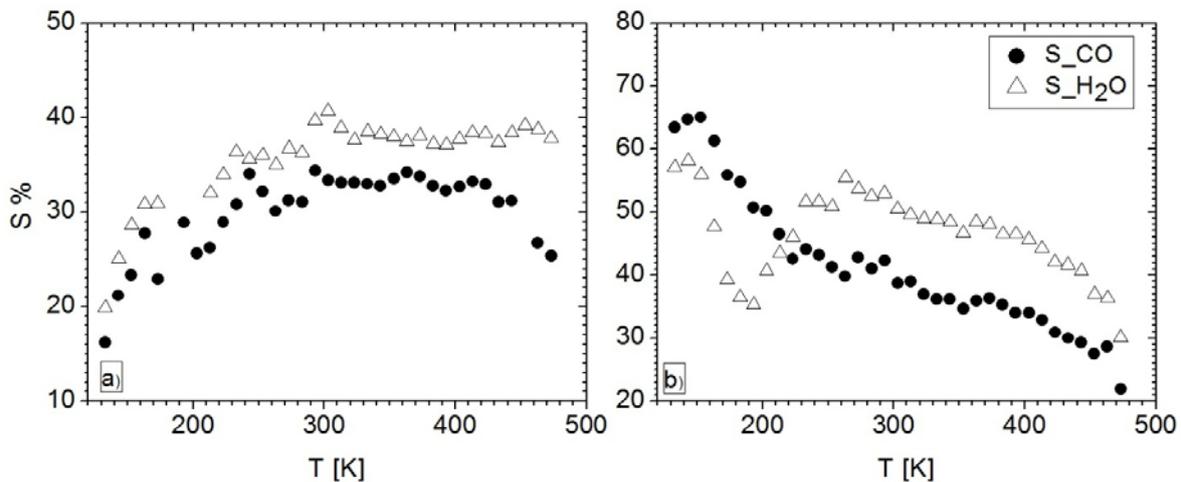
$$S=100 \cdot (R_a - R_g) / R_a \quad (1)$$

where  $R_a$  and  $R_g$  are the film's electrical resistance measured in a vacuum and in the corresponding gas atmosphere, respectively.

In all cases, the I-V characteristic curve of the  $\alpha$ -MoO<sub>3</sub> thin films deposited with 5ml of volume exhibits a linear behavior over the whole temperature range studied. A similar behavior was found after CO and H<sub>2</sub>O adsorption. Regardless of thermal treatment, the MoO<sub>3</sub> films' electrical resistance decreases with increasing temperature of the films. On the contrary, prior to thermal treatment, the I-V characteristic curve of films deposited with 20 ml of volume exhibits a non-linear behavior, which is more evident for temperatures lower than 253 K. Ohmic behavior is restored throughout the whole operating temperature range after thermal treatment.

In high vacuum conditions, the 5 ml MoO<sub>3</sub> films' electrical resistance varies from 100 k $\Omega$  to 500 M $\Omega$ , depending on the film's temperature. After thermal treatment, the variation range of the electrical resistance increases by at least an order of magnitude. In the case of the MoO<sub>3</sub> films deposited with 20 ml of volume, in vacuum conditions the electrical resistance varies between 5 M $\Omega$  and 2000 G $\Omega$ . However, after thermal treatment, values of the MoO<sub>3</sub> films' electrical resistance in the range 70 k $\Omega$  to 10  $\Omega$  were found. In this case, the films' electrical resistance decreases by two orders of magnitude after thermal treatment.

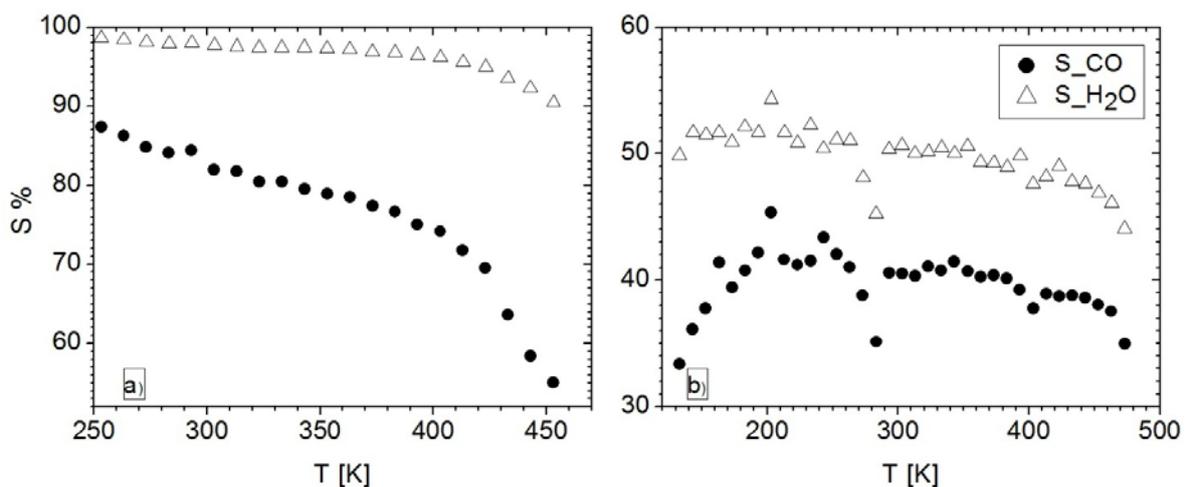
The effect of thermal treatment on the CO and H<sub>2</sub>O sensitivity for MoO<sub>3</sub> films deposited with 5ml of volume is shown in Figure 3. For both gases, and prior to thermal treatment (left graph), the percentage relative change at the lowest temperature of the electrical resistance is close to 20%. For these films, the CO and H<sub>2</sub>O sensitivity gradually increases as the operating temperature is raised. For a film's temperature close to room temperature, the sensitivity tends to stabilize, reaching values of around 33% and 38% for CO and H<sub>2</sub>O, respectively.



**Figure 3.** 5ml  $\alpha$ -MoO<sub>3</sub> sensitivity as a function of temperature for a) non thermally treated films and b) thermally treated films.

Conversely, after thermal treatment, the CO and H<sub>2</sub>O sensitivity reaches values close to 60% at the films' lowest measured temperature. When the operating temperature increases, the sensitivity for CO and H<sub>2</sub>O gradually decreases to 20% and 30%, respectively. The H<sub>2</sub>O sensitivity curve shows an untypical behavior characterized by the presence of a local minimum located near 190 K. At this temperature, a significant increase in the total pressure of the system there was also observed. These correlated events could be attributed to H<sub>2</sub>O desorption from the MoO<sub>3</sub> film's surface.

The CO and H<sub>2</sub>O sensitivity curves for the films deposited with 20 ml of volume are shown in Figure 4. In this case, regardless of the thermal treatment, the percentage relative change of the electrical resistance due to gas adsorption diminishes with increasing temperature of the films. For thermally untreated films, it was not possible to obtain a reference curve in the lower temperature range measured because of the nonlinear I-V characteristic curve measured in this region. Despite that, for temperatures above 253 K, the H<sub>2</sub>O sensitivity remains practically constant, with values close to 100%, showing a slight decrease around 390 K, where it reaches a value of 90%. The CO sensitivity varies from 88% at the lowest measured temperature up to about 75% around 400K. After thermal treatment, the sensitivity for both gases remains constant along the whole measured temperature range, with values near to 50% and 40% for H<sub>2</sub>O and CO, respectively.



**Figure 4.** 20ml  $\alpha$ -MoO<sub>3</sub> sensitivity as a function of temperature for a) non thermally treated films and b) thermally treated films.

#### 4. Conclusions

In this paper, we compared the structural, electrical, and sensing properties of MoO<sub>3</sub> thin films. The effects of thermal treatment on these properties were also studied.

Results obtained from XRD revealed a single orthorhombic phase of  $\alpha$ -MoO<sub>3</sub> and showed that an increase of the deposited volume of the solution also increases the number of diffraction peaks observed, but they do not vary significantly with thermal treatment.

However, thermal treatment increases the percentage relative change of the electrical resistance, due to the interaction of CO and H<sub>2</sub>O molecules with the MoO<sub>3</sub> films deposited with 5 ml of volume. When the volume of the deposited precursor solution is increased, thermal treatment has an opposite effect, and it also eliminates the nonlinear behavior in the I-V characteristic at low operating temperatures. Despite this, both gases have reducing effects on MoO<sub>3</sub> thin film's sensitivity properties.

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