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# Study of structure of the $TiO_2$–$MoO_3$ bilayer films by Raman spectroscopy

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ABSTRACT

In this work, $TiO_2$–$MoO_3$ films were easily prepared by dip-coating technique and metallo-organic decomposition process (MOD). Raman analyses indicate the formation of $TiO_2$ in anatase phase and orthorhombic phase of $\alpha$-$MoO_3$. It was observed that the Raman bands intensities attributed to $TiO_2$ and $MoO_3$ oxides were dependent on the number of decomposition–deposition cycles (DDC). The different number of DDC generates films with different thicknesses and the Raman signal was sensitive to this variation. Raman analyses provided qualitative information about the bilayer structure of the bi-component $TiO_2$–$MoO_3$ films, which was confirmed by scanning electron microscopy. In this direction, the dip-coating technique and MOD process can be an efficient strategy to facile preparation of many samples to be used in applications.

## 1. Introduction

Transition metal oxides are indicated as an interesting class of materials because of their potential applications as catalysts, sensors, and photochromic devices [1–4]. Bi-component metal-oxide films are interesting materials because they can provide a better performance in some applications that is related with the cooperative effect of the components in the same structure [5]. Sputtering and vacuum evaporation are the most common techniques used to prepare metal-oxide thin films [5–7]. These techniques allow good thickness control. However, they are very expensive and require extensive time to prepare few samples. Ronconi et al. [8] showed the possibility of preparing thin films with controlled thickness combining the dip-coating technique and the metallo-organic decomposition process (MOD). This method consists in the thermal decomposition of a metallo-organic compound, leading to the solid of interest formation on the substrate. The deposition step is performed using dip-coating technique [8]. The MOD methodology has also been used to prepare size-controlled nanoparticles with great success [9,10]. The ability to deposit films over large-area substrates and the low-cost production facilities are some of the advantages of the dip-coating technique and MOD process [8].

Other aspect which is related to metal-oxide thin films studies is the number of techniques used to characterize these materials such as X-ray diffraction, X-ray photoelectron spectroscopy, atomic force microscopy and scanning and transmission electron microscopy [11–13]. Those techniques are very important to study the samples, but in some cases the number of techniques can be reduced to few techniques such as Raman spectroscopy, which can be complemented with electron microscopy. This combination can provide enough information to study and describe metal-oxide thin films features such as composition [14], phase identification [15], hetero-structure [16], morphology [17], nanoparticles and grain size [18]. Also, Raman spectroscopy is a fast and nondestructive technique, which may be advantageous when compared with others characterization techniques.

In this work, single $TiO_2$ and $MoO_3$ thin films were prepared as well as bi-component $TiO_2$–$MoO_3$ thin films. The intention was that each layer in the thin film should be made of only one oxide. The films were prepared by dip-coating technique using titanium and molybdenum metallo-organics compounds as source of the respective oxides. The $TiO_2$–$MoO_3$ structure has been investigated mainly by Raman spectroscopy.

## 2. Experimental

### 2.1. Chemicals and substrate preparation

The metallo-organic compound titanium(IV) di-(*n*-propoxy)-di-(2-ethylhexanoate), hereafter named $Ti(Prop)_2(Hex)_2$, was synthesized as described elsewhere [19]. Molybdenum(VI) 2-ethylhexanoate, $Mo[OOCCH(C_2H_5)C_4H_9]_6$, denominated Mo$(Hex)_6$, was purchased from Strem Chemicals and used as received.

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They were separately dissolved in hexane, forming the solutions with the concentrations 0.51 mol $dm^{-3}$ to $Ti(Prop)_2(Hex)_2$, 0.28 and 0.44 mol $dm^{-3}$ to $Mo(Hex)_6$. The concentrations of Ti and Mo precursors solutions were determined from the thermogravimetric analysis experiments. Quartz slides (1.0 cm wide × 2.0 cm long × 0.1 cm thick) were cleaned in a boiling 10% neutral detergent solution (Extran) for 2 h and rinsed with distilled water. Subsequently, the slides were soaked into $HNO_3$ solution (0.2 mol $dm^{-3}$) for 3 h, under heating, rinsed with distilled water and dried in hot air flow.

### *2.2. Films deposition*

Single $TiO_2$ and $MoO_3$ films were prepared by dip-coating technique, using the quartz slides as substrates. The substrates were dip-coated in the respective precursor solution. After each coating, the samples were placed in a furnace and heated in the same heating ramp (10 °C $min^{-1}$), but in different temperatures (600 °C for Ti precursor and 500 °C for Mo precursor) for 30 min. After reaching room temperature, other coatings were applied until the required number was completed (3 or 6 depositions). This procedure was named decomposition–deposition cycles (DDC). Finally, the single $TiO_2$ and $MoO_3$ films samples were placed in a furnace for 5 h, for thermal treatment, at 600 °C and 500 °C, respectively. The same methodology was employed in the bi-component $TiO_2$–$MoO_3$ films preparation. The samples were named $TiO_2(x)$–$MoO_3(y;z)$, where 'x' and 'y' refer to the number of DDC, and 'z' refer to the concentration of the $Mo(Hex)_6$ solution. It was defined 100 mm $min^{-1}$ as withdrawal speed and 60 S as immersion time to all depositions in the dip-coating procedure.

### *2.3. Characterization techniques*

Thermogravimetric analyses were carried out at a ramp rate of 10 °C $min^{-1}$, in air flow rate of 50 $cm^3$ $min^{-1}$ (using TGA/DTA–TA Instruments SDT Q600). Raman measurements were obtained using a Renishaw Raman Microprobe Imaging System 3000 coupled to an optical microscope with spatial resolution of 1.5 μm and spectral resolution of 2 $cm^{-1}$. The He–Ne laser ($\lambda$ = 632.8 nm) power was estimated to be 8 mW. The laser light was focused onto the sample using a 50× objective lens (Olympus). The sample $TiO_2(4)$–$MoO_3(4;0.44)$ was also analyzed by Confocal Raman Microscopy (CRM) using a NTEGRA spectra – AFM/Confocal Raman in the same condition. This measurement was made at different positions in the film surface by moving the laser in the *Z* axis. Also, the surface morphology/topography was analyzing using the same AFM microscope in tapping mode. Samples were fixed over metallic sample holders, coated with gold and analyzed by scanning electron microscopy (SEM) in a JEOL JSM 6360 with 20 kV voltage. Ti and Mo qualitative elemental analyses were obtained by energy dispersive X-ray spectroscopy (EDS) using the same SEM.

## 3. Results and discussion

The metallo-organic precursors $Ti(Prop)_2(Hex)_2$ and $Mo(Hex)_6$ thermogravimetric analyses are shown in Fig. 1. Four weight loss events are observed in the $Ti(Prop)_2(Hex)_2$ thermogravimetric curve. The first one is related to the propoxide groups decomposition, which is completed at about 28% in weight loss, and can be comparable to the calculated value of 26%. The second and third events caused an approximate 53% weight loss and are associated with the 2-ethylhexanoate group decomposition (Fig. 1). The Ti precursor thermal decomposition is completed below 500 °C, with a total weight loss at about 81%. The last event happened at 483 °C and it is associated with the elimination of residual carbon. In order to prepare $TiO_2$ thin films without residual carbon the temperature of 600 °C was chosen, based on the thermogravimetric data, for the thermal decomposition of $Ti(Prop)_2(Hex)_2$.

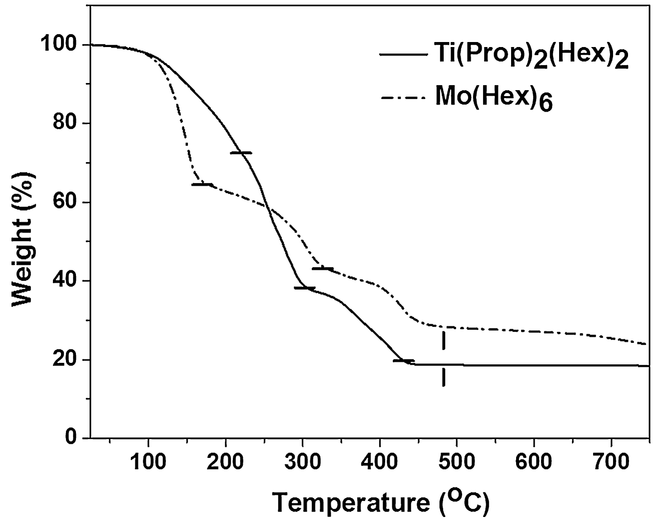

**Fig. 1.** TG curves of the $Ti(Prop)_2(Hex)_2$ and $Mo(Hex)_6$ metallo-organic precursors.

Three events can be observed in the $Mo(Hex)_6$ thermogravimetric curve (Fig. 1). The first one is completed at 175 °C, with weight loss at about 35%, and it is related to an excess of 2-ethylhexanoic acid present in molybdenum(VI) 2-ethylhexanoate. The other two events are associated with the 2-ethylhexanoate groups weight loss, at about 37%. They were completed below 500 °C (Fig. 1). Mo precursor thermogravimetric curve does not show a stable profile after compound thermal decomposition. This happens because $MoO_3$ is volatile after 550 °C [20]. Consequently, weight loss is increased when the temperature is higher than 550 °C. According to these observations, 500 °C was chosen as the thermal decomposition temperature to $Mo(Hex)_6$, thereby avoiding the presence of residual carbon and a high weight loss due to $MoO_3$ volatility.

The bands at 143 and 635 $cm^{-1}$, assigned to $TiO_2(6)$ in anatase phase [21], are observed in the Raman spectrum for $TiO_2$ film (Fig. 2). These bands are attributed to $E_g$ modes characteristic of the $TiO_2$ anatase [21]. Also, bands correspond to quartz, which was

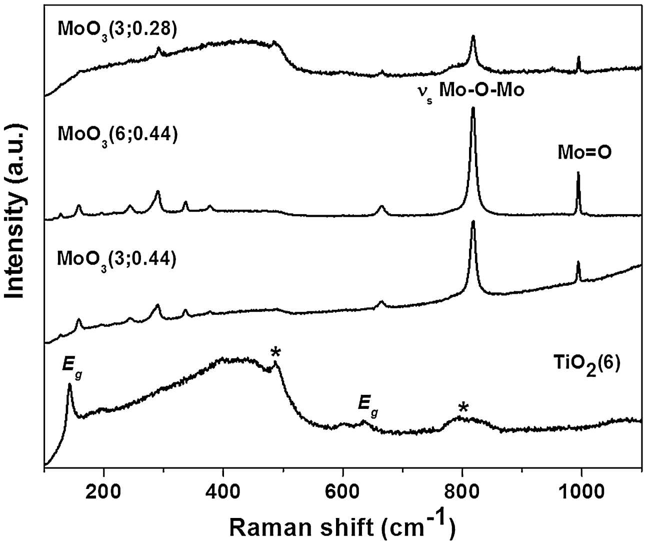

**Fig. 2.** Raman spectra of the $TiO_2$ and $MoO_3$ thin films samples.