Structural Characterization of Tin and Molybdenum Oxides Thin Films Deposited by RGTO

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In this paper the oxidation process of Sn/Mo mixed oxides for sensing applications was explored with the aim of investigating the structural properties of these materials and eventually understanding possible relations with functional behaviors. The films were deposited by sputtering following the rules of RGTO (rheothaxial growth and thermal oxidation) and annealed in humid synthetic air at 500, 600, and 700 °C. This is the first time that those materials are deposited by the RGTO technique. The characterization was performed by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDXS), glancing incidence X-ray diffraction (GIXRD), and micro-Raman mapping. It is shown that because of the fabrication process, as a function of the annealing temperature, an addition of a molybdenum layer on tin films determined the formation of oxides species different from that occurring on pure tin films. The Mo content in films treated at 600 and 700 °C decreased, probably because of the molybdenum oxides evaporation.

Introduction

The increased demand of monitoring the pollution of urban environments has determined the need for developing small, cheap, and low power consuming devices to replace the current analytical instrumentation. In particular, thin film sensors have been widely studied because of their small size, high sensitivity, and very low power consumption.[1]

The majority of chemical sensors used for monitoring toxic and inflammable gases are based on semiconducting metal oxides, as for example SnO_2 and MoO_3,[2] since they are stable in air at relatively high temperatures. In particular, tin dioxide has received a great deal of attention as a functional material. The main interests in tin dioxide are nowadays linked to its use as a selective oxidation catalyst of hydrocarbons and in solid-state sensors for reducing gases to be used in the fuel industry, environmental protection, and biotechnology. Moreover, the sensitivity to a specific gas of SnO_2-based sensors can be tuned by doping with different cations (see for example refs 3−5). It was shown that SnO_2 doped by Mo is sensitive to alcohol detection;[5] it leaves almost unchanged the response to NO_2,[6] and it has a low response to CO.[7] However, it is also reported that when mixed Mo−Sn oxides are formed, the response to CO increases.[8] A. Chiorino et al.[9] reported the characterization of pure and Mo-doped SnO_2 nanosized powders prepared by sol−gel and used in thick films gas sensors. The achieved goal was to obtain powders and films of nanosized particles with a sharp size distribution, stable of thermal treatments up to 850 °C. In the XRD patterns of these films only the cassiterite phase can be detected. On the other hand, Ivanovskaya et al.[7] examined the effect of the Sn-to-Mo ratio in the formation of the oxides in sensors prepared by sol−gel. Finally, in the literature different deposition techniques have been considered, showing that physical and structural properties are strongly dependent upon the method of preparation of the films.[10,11]

In this paper we have analyzed $SnO_2−MoO_x$ thin films deposited by the rheotaxial growth and thermal oxidation (RGTO) technique and annealed at different temperatures. The aim is to investigate the structural properties of these materials and the oxides formation processes. Since the conduction properties strongly

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depend on defects of nature and on crystallite size, chemical composition, and morphology of the film, this study is mandatory to understand, to develop, and to improve materials with tailored performances for gas sensors applications.

To our knowledge, this is the first time that those materials are deposited by the RGTO technique.

Experimental Section

Deposition. Thin film deposition was performed by dc sputtering for Sn and RF sputtering for Mo in an argon atmosphere with a pressure respectively of 2×10^{-3} and 7×10^{-3} mbar. The sputtering plant (Alcatel 450 SCM) operated at 50 W (dc power) for Sn deposition and 150 W (RF power) for molybdenum. All the targets are certified by Target Materials Inc. at 99.9% purity. Sn (about 3000 Å) was deposited at 400 °C (temperature higher than that of the melting point), followed by the deposition of Mo (about 150 Å) at 300 °C. The calculated deposition rates were 2.7 and 0.28 nm/s for Sn and Mo, respectively. The final thickness was checked by a profilometer. At 100 °C, the samples were cooled at room temperature for 1 h. Three samples were annealed at 500, 600, and 700 °C, respectively, in an oven under a controlled flux of humid synthetic air (70 RH) and the oxidation process was achieved as follows: (a) heating from room temperature up to 250 °C at 2 °C/min; (b) annealing for 4 h at 250 °C; (c) increasing the temperature to the chosen values (500, 600, and 700 °C) at the rate of 1.3 °C/min; (d) annealing at this temperature for 30 h; (e) cooling to the room temperature (−2 °C/min).

This procedure was adopted to avoid stresses or cracks in the layers and to obtain homogeneous oxidation processes.

Scanning electron microscopy (SEM) analyses were performed by a Cambridge Stereoscan 260 microscope equipped with a Link Analytical probe for energy-dispersive X-ray spectroscopy (EDXS).

Wide-angle X-ray diffraction (WAXRD) and glancing incidence X-ray diffraction (GIXRD) spectra were collected by a Bruker "D8 Advance" diffractometer equipped with a Göbel mirror. The angular accuracy was 0.001° and the angular resolution was better than 0.01°. The Cu Kα line of a conventional X-ray source powered at 40 kV and 40 mA was used and the average crystallite sizes were calculated by means of the Topas P program.[12]

Micro-Raman spectra were collected by a Dilor Labram spectrograph. The exciting source was a HeNe laser (632.8 nm) with a power of less than 10 mW at the sample. The microscope was coupled confocally to the spectrograph. A 100× objective with a numerical aperture NA = 0.9 and a confocal hole opened at 200 μm were used. Suppression of the exciting line was obtained with a holographic notch filter. The spectra were measured at room temperature.

Discussion

Far from being thoroughly clarified, the oxidation of tin has still several issues to be addressed. It is recognized that oxidation kinetics depends on thin film deposition and doping.[13]

In the present work, the addition of a molybdenum overlayer produced some interesting morphological and structural features of the films. We have considered four samples: one just cooled at room temperature after the deposition and three annealed at 500, 600, and 700 °C, respectively, as described in the Experimental Section.

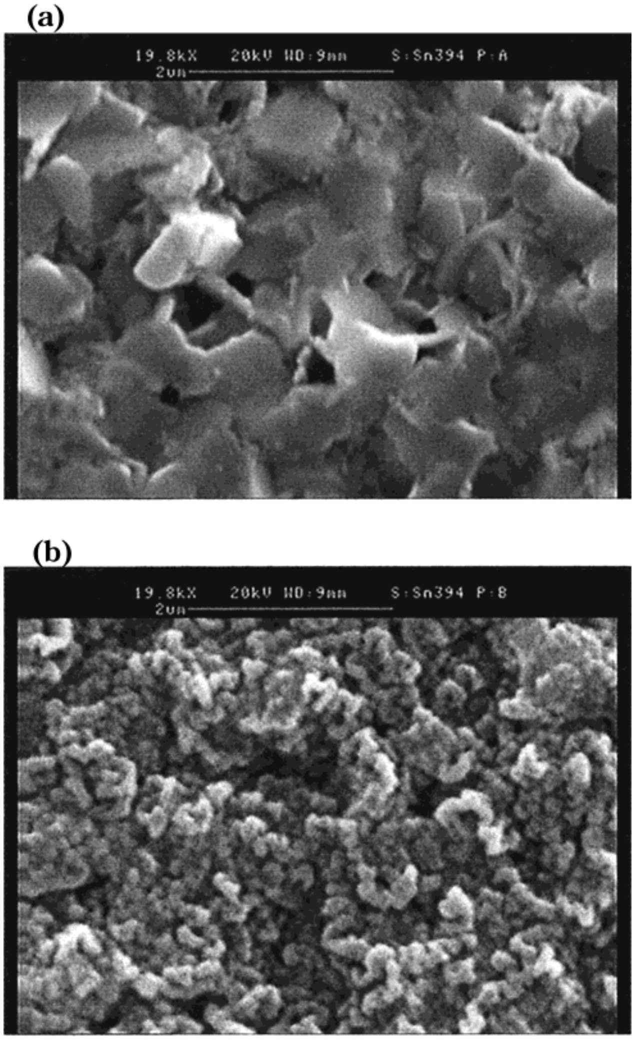

Figure 1. SEM micrographs of the (a) not annealed sample and (b) sample annealed at 600 °C.

Table 1. Mo Content as a Function of the Temperature Annealing, Obtained by the EDXS Analysis

element	sample annealing	wt %	wt % σ
Mo L	100 °C	7.66	0.50
Mo L	500 °C	4.14	0.29
Mo L	600 °C	2.17	0.27
Mo L	700 °C	2.04	0.26

Figure 1a shows an SEM micrograph of the sample cooled at room temperature and not annealed. In this figure a platelike crystallite shape is evident, different from the typical spheres obtained for pure Sn films.[14] Figure 1b shows an SEM micrograph of the sample annealed at 600 °C, where the shape of the crystallites is cylindrical and still different from that obtained for the same treatment of pure Sn films.[15]

From EDXS analysis a qualitative reduction of the Mo content with the increasing of the annealing temperature increases was observed (see Table 1).

For all the annealed samples the WAXRD patterns (not reported here) showed the presence of only the cassiterite phase, despite the alumina substrate contribution. Moreover, peaks analysis showed that all the films had a similar nanocrystalline microstructure with

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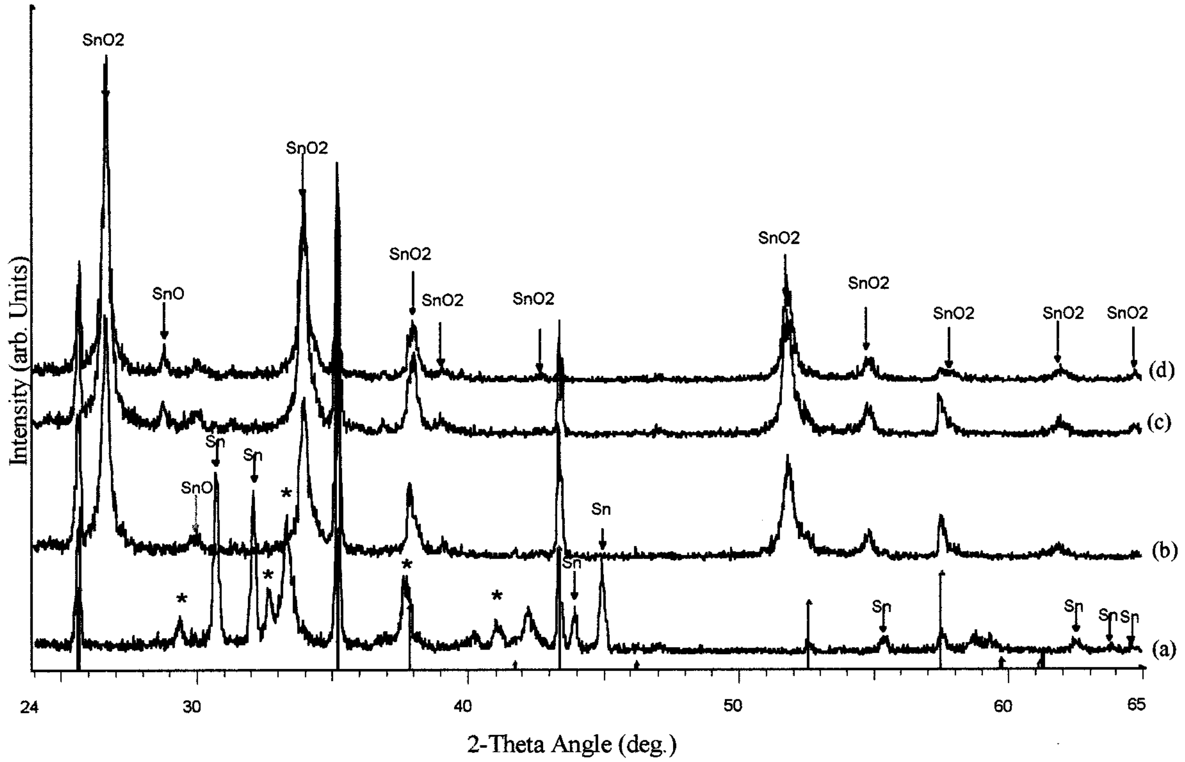

Figure 2. GIXRD spectra of a Sn−Mo film as deposited (a), after the annealing at 500 °C (b), after the annealing at 600 °C (c), and after the annealing at 700 °C (d). The glancing incident angle was fixed at 0.2°. All the samples were deposited on Al_2O_3 substrates and the Al_2O_3 reflections (JSPDS, card no. 741081) are reported (vertical bars). The stars indicate reflections tentatively attributed to an Sn and Mo mixed oxide.

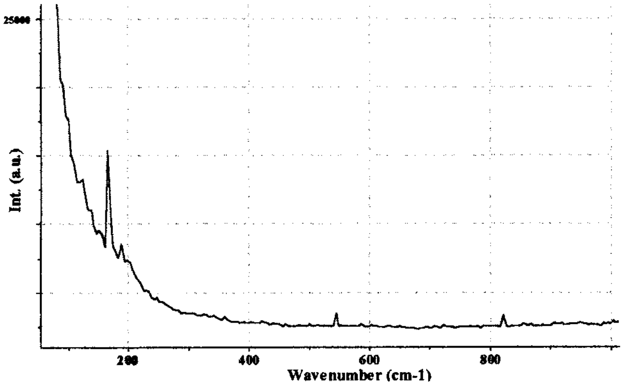

Figure 3. Raman spectra of the not annealed sample.

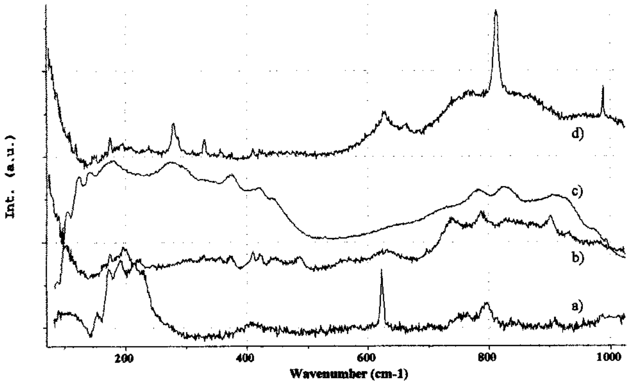

Figure 4. Raman spectra of the sample annealed at 500 °C. The (a) and (b) and (d) spectra are collected at three different points. The band at about 630 cm^{-1} is characteristic of the A_{1g} mode of SnO_2 cassiterite. As a reference, the Raman spectra of Mo(110) oxidized single crystal has been reported (Figure 4c). Pure MoO_3 exhibits a spectrum with intense bands at 157, 284, 666, 818, and 995 cm^{-1}. These bands have been detected in the spectrum collected in the third point (4d).

an average crystallite size of 30−35 nm, suitable for gas-sensing applications.

Among the available techniques for structural characterization, GIXRD is a basic technique for the analysis of thin layers. In fact, for small incidence angles the GIXRD becomes more surface sensitive and the contribution from the substrate can be suppressed.

The GIXRD spectra collected for all the samples are shown in Figure 2. The incidence angle was fixed at 0.2°. For the not annealed sample, the tin metallic phase is detected (JSPDS, card no. 040673) whereas in all the annealed samples the SnO_2 cassiterite phase appeared. (JSPDS, card no. 710652). In this figure, the patterns of the two SnO phases reported in the JSPDS (card no. 060395 and 040673) are also shown as a reference. No reflections from pure metallic molybdenum or molybdenum oxide phases were detected.

In a previous paper[16] the oxidation of pure tin layers deposited by RGTO onto alumina substrates have been investigated with the aim of identifying the different steps of this process. It has been shown that at least three phases coexisted at 450 °C (Sn, SnO, and SnO_2), whereas the film appeared homogeneous after annealing treatments above 550 °C, when only the cassiterite phase was detected.

Differently, after the annealing at 500 °C in the Mo−Sn−O films considered in this work, the cassiterite coexisted with the SnO phase characterized by the reflection at 29.9° (2θ) (JSPDS, card no. 060395). In the

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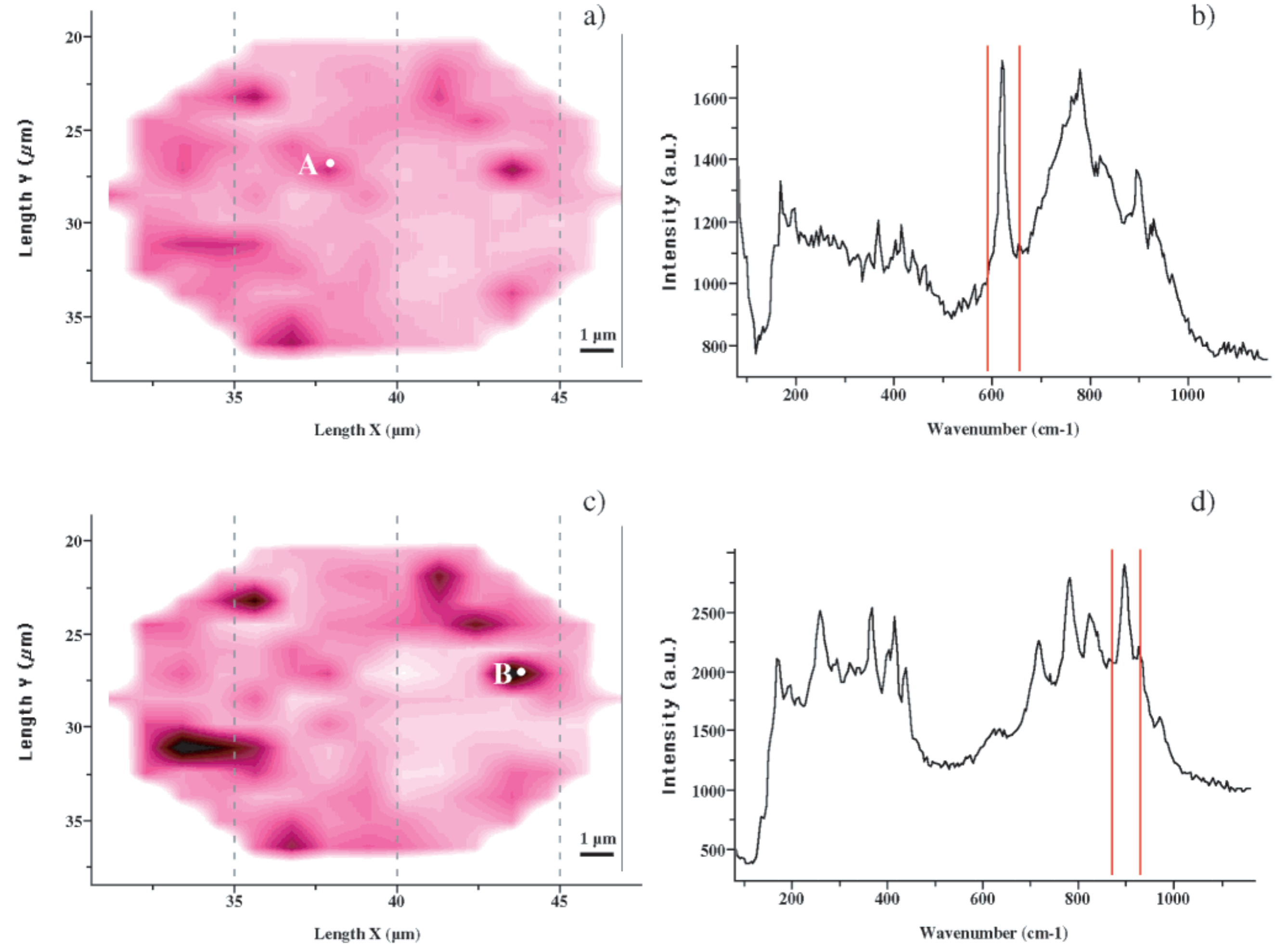

Figure 5. The micro-Raman map of the sample annealed at 500 °C. In Figure 5a the A_{1g} mode of SnO_2 cassiterite is mapped and in Figure 5c a molybdenum oxide band (see Figure 5d) is mapped. The spectra collected in the points A and B of the map are reported in Figure 5b and 5d.

sample treated at 600 °C another SnO phase appears (JSPDS, card no. 040673) identified by the reflection at 28.7° (2*θ*). These three phases were still detected in the sample annealed at 700 °C**.**

Figure 2a shows the GIXRD pattern for the not annealed sample. The stars indicate the reflections due to the film. Their positions are close to that of the SnO_2 phase, card no. 781063 of JSPDS. The differences in peaks positions and intensities may be attributed to a substoichiometry of the film and/or to the presence of the molybdenum in this phase. The high intensity of the reflection at 33.5° (2*θ*) may be due to the presence of molybdenum or tin molybdenum mixed oxides. Indeed, a few molybdenum oxides have a strong reflection at about 33.5° (2*θ*) (JSPDS, card no. 800347, 731538, 720448, etc.), as some tin and molybdenum mixed oxide (JSPDS, card no. 470464 etc.).

The GIXRD results are confirmed by Raman experiments. Indeed, in the not annealed sample a band at 170 cm^{-1} is present (see Figure 3) and it can be attributed to a substoichiometric phase of tin dioxide.[16,17] Consistently, Geurts et al.[17] found an XRD pattern for this substoichiometric phase similar to that found in this work. However, in our samples the temperature of formation of this phase is lower than that found by Geurts, probably because of the presence of molybdenum.

Figure 4 shows the Raman spectra of the sample annealed at 500 °C, collected in three points of the surface. In Figure 4a the A_{1g} mode of SnO_2 cassiterite[18] at about 630 cm^{-1} is present, while in Figure 4b intense bands peaked at 737, 787, 830, and 900 cm^{-1} are evident. As a reference, the Raman spectra of the oxidized surface of a Mo (110) single crystal is reported (Figure 4c). This pattern does not correspond to that of MoO_3 (see below) and the corresponding phase has not yet been identified. The bands obtained in the Raman spectrum of oxidized Mo (110) are similar to those in Figure 4b. Thus, in this sample segregations of molybdenum oxides have been demonstrated. Figure 4d shows Raman spectra collected in a third point for the sample annealed at 500 °C. Here, Raman bands appear at 150, 170, 282, 630, 665, 813, and 990 cm^{-1}. Pure MoO_3 exhibits Raman bands at 157, 284, 666, 818, and 995 cm^{-1}. The ratio of bands intensities for the MoO_3 is reported in Figure 4d. The band at 170 cm^{-1} may be attributed to a substoichiometric phase of tin dioxide (see Figure 3) and the band at 630 cm^{-1} corresponds to the A_{1g} mode of SnO_2 (see Figure 4a). This spectrum

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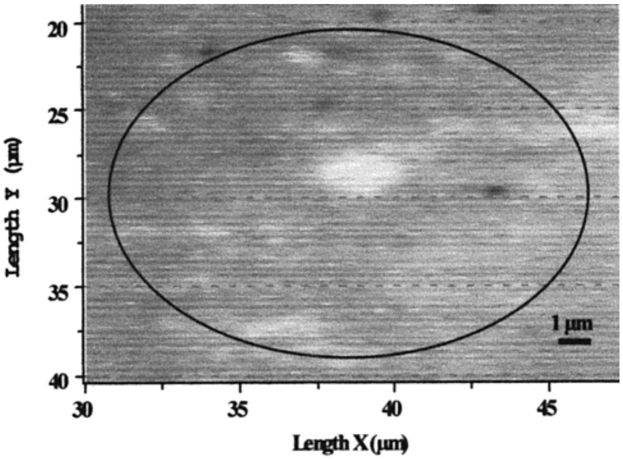

Figure 6. Video image collected from a region of the layer after annealing at 500 °C. The circle indicates the area mapped in Figure 5.

allows the conclusion that after the annealing at 500 °C a small quantity of MoO_3 phase is also formed.

Mainly in the center of the film, a colorless region was evident, which is typical of the SnO_2 phase. Indeed, the micro-Raman map (see Figure 5a) shows in this region a very high intensity of the A_{1g} band of this phase. Micro-Raman spectroscopy was used to map the sample surface and to see the distribution of the phases, even present in small quantity and therefore not detected by means of XRD analysis, as discussed before. In Figure 5 the maps of the characteristic bands of tin dioxide and molybdenum oxide for a $15 \times 15\,\mu$m area of the sample annealed at 500 °C are shown, respectively. In Figure 6 an optical image of the sample is shown, where the mapped area is evidenced by a circle. The Raman spectra of the samples annealed at 600 and 700 °C (not reported) showed only the characteristic band of the cassiterite phase. Thus, for these samples no molybdenum oxides were detected also by means of Raman spectroscopy.

Thus, after the annealing at 500 °C molybdenum oxides were detected, but for higher temperature treatments (600 and 700 °C) the Raman bands of these phases are absent. A possible explanation of these results is a sublimation of these molybdenum oxides for temperatures higher than 600 °C. This hypothesis is confirmed by the EDXS analysis that showed a significant reduction of the molybdenum signal after these thermal treatments (Table 1).

Conclusion

The oxidation process of a Sn/Mo system for sensing applications was explored, with particular attention paid to the tin oxides phases and molybdenum oxide formation. Indeed, the knowledge of structural properties is mandatory to improve the stability of the sensor device.

GIXRD and Raman spectra showed that, in the not annealed sample, a structure with a substoichiometry SnO_2 phase is present, probably stabilized by the presence of Mo. The existence of this phase was already reported.[17] GIXRD showed that at least two phases at 500 °C (SnO_2 and SnO) and at least three phases at 600 and 700 °C (SnO_2 and two tin monoxides) coexisted in the thin films. On the basis of micro-Raman spectroscopy maps, it was shown that in the film annealed at 500 °C the molybdenum segregated, and molybdenum oxides are present together with SnO_2 and SnO phases. The nonhomogeneity in these films may be due to the high temperature of the Mo deposition process, which promotes the segregation of molybdenum oxides.

Finally, for higher annealing temperatures (600 and 700 °C) molybdenum oxides probably evaporated, as confirmed by the absence of the characteristic Raman bands of the molybdenum oxide and by the decreasing of the molybdenum content as detected by EDXS analysis.

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