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Characterization of thin MoO₃ films formed by RF and DC-magnetron reactive sputtering for gas sensor applications

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Abstract. The present work discusses a technology for deposition and characterization of thin molybdenum oxide (MoO_x, MoO₃) films studied for gas sensor applications. The samples were produced by reactive radio-frequency (RF) and direct current (DC) magnetron sputtering. The composition and microstructure of the films were studied by XPS, XRD and Raman spectroscopy, the morphology, using high resolution SEM. The research was focused on the sensing properties of the sputtered thin MoO₃ films. Highly sensitive gas sensors were implemented by depositing films of various thicknesses on quartz resonators. Making use of the quartz crystal microbalance (QCM) method, these sensors were capable of detecting changes in the molecular range. Prototype QCM structures with thin MoO₃ films were tested for sensitivity to NH₃ and NO₂. Even in as-deposited state and without heating the substrates, these films showed good sensitivity. Moreover, no additional thermal treatment is necessary, which makes the production of such QCM gas sensors simple and cost-effective, as it is fully compatible with the technology for producing the initial resonator. The films are sensitive at room temperature and can register concentrations as low as 50 ppm. The sorption is fully reversible, the films are stable and capable of long-term measurements.

1. Introduction

MoO₃ is one of the most promising inorganic materials with a wide potential for technological applications as large-area electrochromic devices (displays and smart windows), optical switching coatings and high-density memory devices [1]. Thin MoO_x films can also be used for many other applications, such as catalysts [2], lubricants [3], solid-state microbatteries [4]. And, last but not least, MoO₃ was shown to be sensitive to NO₂ [5,6], NH₃ [7], CO [8], H₂ [9], volatile organic compounds (VOC) [10] and some other gasses. The aim of the present work was to study the gas sensing properties of films prepared by RF and DC-magnetron sputtering. To this end, thin MoO_x and MoO₃ films were deposited on different substrates.

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The quartz crystal microbalance (QCM) is a well-established technique for detecting physical properties of thin layers deposited on the crystal surface on the sub-nanogram level [11]. It could also be applied to monitoring the adsorption of nano-amounts of various toxic gases [10,11]. Compared with others sensors, the advantages of the QCM sensors are simple technological implementation, capability of operating at room temperature, good sensitivity and chemical process reversibility, low consumption and easy real-time monitoring.

The performance of the QCM sensors strongly depends on the properties of the sensing coating deposited on the QCM electrodes. Thin transition metal oxides films, such as SnO_2 , WO_3 , TiO_2 and ZnO , have been widely investigated for sensing different toxic gases. Our present research was focused on the sensing behavior of the sputtered thin MoO_3 films with respect to NH_3 and NO_2 . Prototype QCM sensors with other sensitive transition metal oxides films were also fabricated by our team and tested for sensitivity to NH_3 in especially designed laboratory set-up [12,13]. Even in as-deposited state and without heating the substrates, these films, as well as the MoO_3 films investigated in the present work, show good sensitivity without an additional thermal treatment, so that manufacturing QCM gas sensors becomes simple and cost-effective, as their preparation is fully compatible with the technology for producing the initial resonator.

The thin MoO_3 films studied were characterized by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and Raman spectroscopy. The morphology of the films was studied by a high-resolution scanning electron microscopy (SEM). Thorough profile analyses on the structure were performed applying XPS, allowing interactions with the substrate and different modifications of the structure to be investigated. Laser ellipsometry was used to measure the thickness and to determine the refractive index of the films. The as-prepared gas sensors were then tested for sensing NH_3 in our laboratory-constructed system.

2. Experimental

MoO_3 films of various thicknesses (50 nm – 300 nm) were deposited on quartz resonators and silicon wafers. The deposition time varied between 10 and 60 minutes. For both RF and DC sputtering depositions, molybdenum targets were used and the sputtering was performed in the presence of oxygen as a reactive gas. Similar conditions were applied to allow for a better comparison of the methods. The films were deposited on unheated substrates and were not annealed.

The surface of the films was observed by a Hitachi S-4800 high-resolution field-emission SEM (FE-SEM) device. The structural properties of the films were characterized using a Philips X-Pert-MRD XRD system, and Raman spectroscopy was performed by an SPEX 1403 Raman double spectrometer. The composition of the films, accompanied by thorough profile analyses of the structure, was performed by an Ulvac-Phi Scanning ESCA Microprobe Quantum2000 XPS system, using a focused monochromatic $\text{Al K}\alpha$ X-ray (1486,7 eV) source and a spherical section analyzer. The thickness and the refractive index of the films were measured by multi-angle four-zone null ellipsometry. Further information on the RF sputtering deposition technology and conditions, as well as on the Raman spectroscopy and laser ellipsometry equipment, can be found in our previous publications [14,15].

The sensing properties of the films were studied as the adsorption of NH_3 and NO_2 was tested. Most of the sensor structures were based on 8-mm polished AT-cut quartz plates with thermally evaporated golden electrodes (a diameter of 4 mm and a thickness of about 120 nm with a Cr underlayer) on both sides. A QCM resonance frequency around 14 MHz was thus obtained. The measurements are based on the correlation between the frequency shift and the additional mass loading of the resonator.

Sauerbrey [16] developed an empirical equation for AT-cut quartz describing the relation between the mass of a film deposited on the quartz crystal and the corresponding change in the resonance frequency, thus allowing the sorbed mass to be calculated. Other parameters of the QCM needed for the calculations, including the static capacitance, C_0 , and the equivalent dynamic resistance, R_q , were measured by a selective level meter. Further, some parameters, as the dynamic capacitance, C_q , the

dynamic inductance, L_q , and the quality factor, Q , were calculated [17].

The sorption properties of the MoO_3 films were determined by measuring the resonance frequency shift of the QCM structures covered with thin MoO_3 films at different NH_3 and NO_2 concentrations. This was carried out on a laboratory-constructed system, whose experimental unit, as well as the methodology of measurements, were described in detail in [12,13].

The main stages of the measurement consisted of: purging the QCM structure by dry air; creating a certain concentration of the gas measured; reaching saturation of the frequency values; purging the structure with dry air to recover the initial parameters of the sensor and prepare it for a new measurement. The NH_3 and NO_2 concentrations were controlled by mass flow controllers (MFCs) for the NH_3 , NO_2 and diluting gas flows. The QCM frequency was registered by a Hameg 8123 frequency counter connected to the QCM and to a computer for data recording. The relative error in the frequency measurement was $\pm 5.25 \times 10^{-7}$. The experiments were carried out at $26 \pm 0.2^\circ\text{C}$.

3. Results and discussion

To observe the surface, whose quality is considered to be the most important factor determining the sorption properties of the films, we applied ultra-high resolution FE-SEM (figure 1). The films are uniform and homogeneous. They are amorphous-like and, in general, no grains with size larger than a few nanometers are observed. The object on the surface shown in the image was only used to enable high-resolution focusing of the microscope.

Our XRD research showed that both the RF and DC sputtered MoO_3 films are predominantly amorphous. These results were also supported by the Raman spectroscopy study. The results, as well as these from ellipsometry measurements, can be seen in our previous publications [14,15,18]. However, the XPS profile analyses showed that the structure changes between the surface and the bulk. In both the DC and RF sputtered film profiles, we observed close to stoichiometric MoO_2 throughout the film, almost without any significant changes in the composition. Yet, on the surface our investigations revealed a typical MoO_3 film. The Mo 3d core levels spectra are shown in figure 2. We observed sharp peaks without shoulders with shapes typical for MoO_3 [19,20]. The labels on the figure are for the $3d_{5/2}$ peaks. The doublet separation between the $3d_{3/2}$ and $3d_{5/2}$

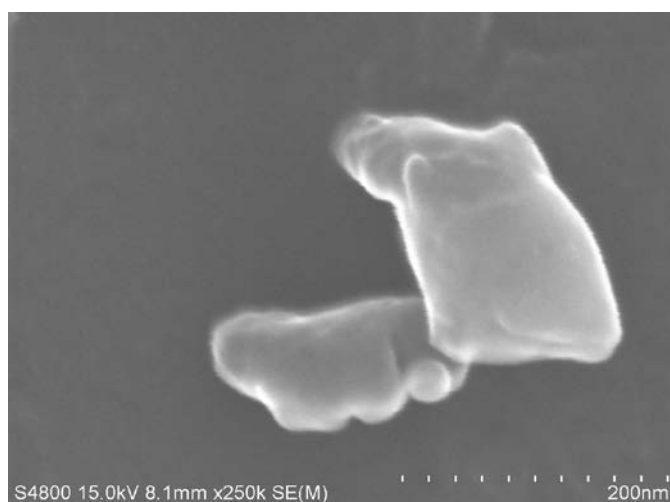


Figure 1. FE-SEM image of a DC-magnetron sputtered thin MoO_3 film at magnification 250 000 \times .

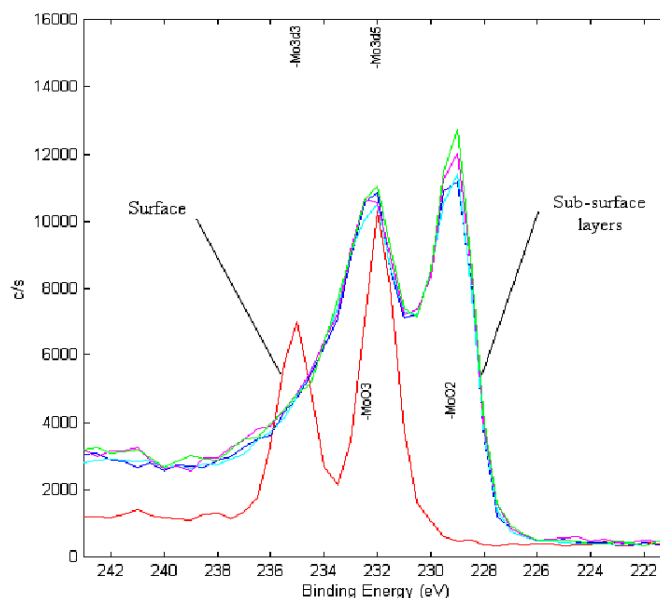


Figure 2. XPS spectra of Mo 3d core levels of a ~ 200 -nm RF-sputtered thin MoO_3 film.

peaks of $\sim 3,1$ eV – $3,2$ eV is also characteristic for MoO_3 [19-21]. The results from the compositional study of the same film are presented in figure 3. The profile was made at a sputtering energy of 2 kV with 2-minute sputtering intervals.

The Mo 3d peaks in the surface study are not positioned exactly at the most typical binding energies for the Mo^{6+} state, but at a slightly lower energy. They cannot be considered as being consistent with signals from Mo atoms in two different oxidation states, since they are sharp and without shoulders. It is more probable that the binding energy deviation of $\sim 0,5$ eV is caused by Mo interacting with C-impurities on the surface [19] (also detected in a considerable amount during the XPS study).

Although the sputtering during the etching of the surface could affect the structure, it is doubtful that it brought any significant changes. According to our previous experience with XPS profiles of other transition metal oxides, made at the same sputtering power, no changes are observed between the surface and the bulk [22].

Our prototype QCM sensors with MoO_3 thin films showed good sensitivity to NH_3 and NO_2 . Figure 4 shows a frequency-time characteristic (FTC) of a MoO_3 -QCM sensor produced by RF sputtering (together with the same MoO_3 film deposited on a referent Si wafer, whose characteristics are shown in figures 2 and 3). The FTC of the same sensor with respect to NH_3 sorption can be found in our previous publication [18]. The working frequency after loading the resonator with the MoO_3 film is about 13,87 MHz.

Both the NH_3 and NO_2 measurements reveal a very similar behavior of the sensors. When the measured gas is added to the gas flow, the sorption process starts and the frequency decreases quickly and almost linearly during the first several minutes. This process is followed by a slower decrease of the frequency until a dynamic equilibrium between the sorbed and desorbed molecules is reached, when the frequency remains constant. Turning off the measured gas flow and purging the sensor with dry air leads to a desorption process and unloading the sensor until the initial frequency is reached, thus proving the physical nature of the sorption process. This experiments show that the sorption process is reversible and the MoO_3 -QCM sensor can be fully recovered without applying any additional energy.

The fact is very important that the sensors produced following the technology described exhibit a

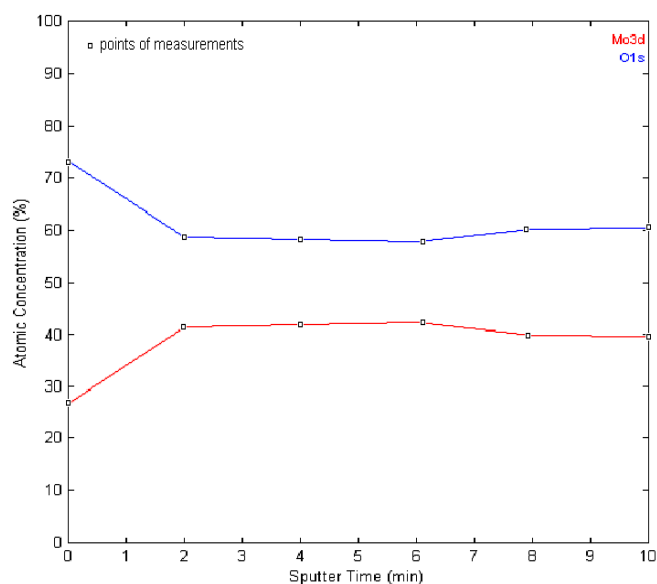


Figure 3. XPS compositional study of a ~ 200 -nm RF-sputtered thin MoO_3 film.

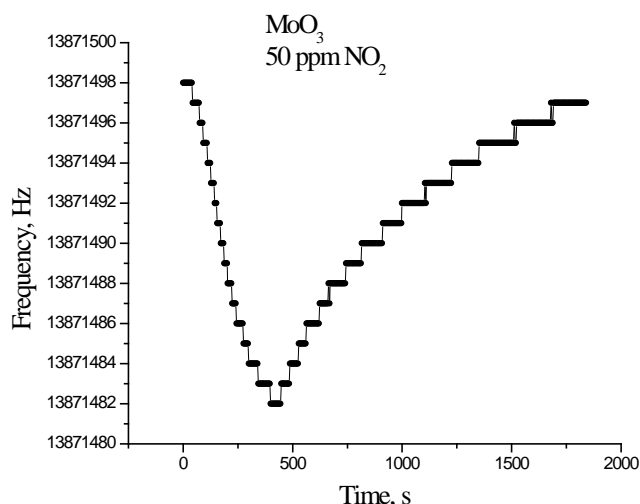


Figure 4. FTC of the MoO_3 -QCM structure at 50 ppm NO_2 concentration.

long-term parameters stability and can be used for a large number cycles. The first measurements with the RF sputtered sensor presented here were carried out more than five years ago. Its parameters and sensitivity practically have not changed during these years; we expect that it will continue operating for a long time. This fact, as well as the promising results concerning the sorption, allows these MoO₃ films to be used as gas sensors for on-line monitoring of NH₃ and NO₂ concentrations. The main advantage of the method described is that the technology for producing the sensitive films is fully compatible with the initial resonator preparation. Also, the films are able to detect even in as-deposited state and without heating the substrates. Additional thermal treatment is not necessary, which makes the manufacturing of QCM gas sensors easy and cost-effective. Further, they can be used at room temperature, which makes them suitable for portable systems for environmental control. Still, there remain problems mainly regarding the selectivity and the way to implement a large-scale manufacturing of commercial devices.

4. Conclusions

The properties of RF- and DC-magnetron sputtered thin molybdenum oxide films were studied. The films were amorphous or possibly nanocrystalline with grain size of several nanometres or less. Non-uniformity between the surface and sub-surface layers of the films was observed by XPS profiling. The films consist of stoichiometric MoO₃ with nano-size structure on the surface and amorphous nearly stoichiometric MoO₂ in the bulk.

The reactive sputtering method was found to be suitable for deposition of MoO₃ films for sensor applications. The prototype QCM sensors with MoO₃ sensitive films showed good sensitivity to NH₃ and NO₂ at room temperature and capability to register concentrations as low as 50 ppm. The sorption is fully reversible, the MoO₃ films are stable and capable of long-term measurements. The main conclusion based on the results obtained is that QCM structures covered with RF- and DC-magnetron sputtered thin MoO₃ films are suitable for NH₃ and NO₂ detection.

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