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# Comparison between RF and DC magnetron reactive sputtered molybdenum oxide thin films for gas sensors

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This paper reports about the preparation, surface, structural and sorption characterization of as-deposited molybdenum oxide ($MoO_3$) thin films prepared by two different techniques of reactive sputtering. The methods of radio frequency (RF) and direct current (DC) magnetron reactive sputtering were used for deposition of the films. The composition and microstructure of these thin films were studied by X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and X-ray diffraction (XRD). The films' surface was observed by a high-resolution scanning electron microscopy (HRSEM). To determine the thickness of the films as well as their refractive indices laser ellipsometry was applied. In order to study the sensing properties, films of various thickness and at different deposition rates were deposited on quartz resonators, and the quartz crystal microbalance (QCM) method was used. Applying it we built prototype QCM sensors with $MoO_3$ sensitive films. Even in as-deposited state and without heating the substrates these thin films showed good sensitivity to ammonia at room temperature. They are also being tested for sensitivity to other gases and with future development can be successfully introduced into advanced environment monitoring devices.

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## 1. Introduction

Molybdenum oxide ($MoO_3$) is a transition metal oxide with intriguing structural, chemical, optical and electronic properties [1]. Molybdenum oxides are particularly attractive technologically due to their high electronic mobility and high lithium-ion mobility as well as a low-energy barrier for Li insertion and extraction reactions. $MoO_3$ also has excellent photochromic and electrochromic properties, which make it a suitable material for electrochromic displays - a very perspective cost-effective technology for large-size displays [2]. Another significant application is the so-called "smart windows", which are capable to switch between two basic modes - a mode of fully transparent state to a mode of coloured state. If applied in solar architectural building, such windows would control the energy of the solar flux entering the building. $MoO_3$ in thin film form has been under investigation as capacitor [3]. Besides, $MoO_3$ films allow easy insertion of organic compounds in its crystal lattice and this leads to their usage in electronic devices and heterogeneous catalysts [4]. $MoO_3$ is an intriguing intercalated material solid state Li batteries [5].

However, there has been limited research on $MoO_3$ for gas sensing applications. The sensing behavior of sputtered $MoO_3$ thin films was first studied by Mutschall et al. [6]. Thin films of $MoO_3$ were prepared by RF sputtering. These films were found to be highly sensitive to ammonia in the temperature range of 400-450°C. $MoO_3$ has also shown to be sensitive to $NO_2$ [7], CO [8], $H_2$ [9] and to many organic compounds such as hydrocarbonic and aromatic gases, ethanol, gasoline, trimethylamine and many other. The possibility of introducing nanostructured $MoO_3$ films into gas sensors is very perspective. In the present research we used two different reactive sputtering techniques to deposit molybdenum oxide thin films – RF and DC-magnetron sputtering. Quartz resonators were used for preparing sensors based on the sorption properties of molybdenum oxide films using the quartz crystal microbalance (QCM) method. QCM is an extremely sensitive mass sensing method, capable of measuring mass changes in the nanogram range. The high sensitivity and the possibility for real-time monitoring make QCM a very attractive technique for gas sensors. Compared with others sensors, the advantages of QCM are: simple technological implementation, good sensitivity, chemical process reversibility and capability of operating at room temperature [10]. The sensors that we prepared are based on quartz resonators with Au electrodes and resonant frequency of about 16 MHz.

## 2. Experimental

The deposition of the films was carried out using a RF (13.56 MHz) Leybold A-400VL and a DC-magnetron Hitachi-based laboratory-made vacuum installations. For both RF and DC depositions, sputtering of molybdenum targets in the presence of oxygen as reactive gas was made. The films were deposited on unheated substrates. The influence of technological conditions during deposition, such as the oxygen partial pressure and deposition time, on the films' structure and properties was studied. Molybdenum oxide films of various thickness (50

– 500 nm) were deposited on quartz resonators with gold electrodes as well as control silicon wafers were used for some measurements. First, the substrates were cleaned and dried in a high-purity nitrogen gas stream. Initial vacuum at $1.10^{-6}$ Torr was pumped in the chamber. The values of the oxygen partial pressure were between $1.10^{-4}$ - $1.10^{-3}$ Torr for the RF sputtered films and $2.10^{-3}$ – $3{,}5.10^{-3}$ for the DC sputtered. Cathode voltages of 750 - 1500 V were applied for the RF sputtering process. The power of the DC-magnetron sputtering process was between 25 and 50 W. The deposition time was between 5 and 45 min.

The composition of the films as well as thorough profile analyses were performed by Ulvac-Phi "Scanning ESCA Microprobe Quantum2000" XPS system. The surface of the films was observed by a Ultra-high resolution Field Emission SEM (FE-SEM) Hitachi S-4800. The structural properties of the films were characterized using Philips "X-Pert-MRD" XRD system and Raman spectroscopy study performed by "SPEX 1403" Raman double spectrometer. The thickness of the films was measured by a profilometer and laser ellipsometry. More detailed information about the RF sputtering deposition technology and conditions as well as the Raman spectroscopy and laser ellipsometry apparatus could be found in [11].

To determine films' sensing properties was tested the adsorption to ammonia on a special laboratory constructed measurement system. Most of the test sensor structures were based on 8-mm polished AT-cut quartz plates with golden electrodes (diameter 4 mm and thickness 120 nm) evaporated on both sides. The piezoelements thus prepared were covered with $MoO_3$ thin films on both sides. Some equivalent dynamic parameters of the QCM, as the static capacitance, $C_0$, and the equivalent dynamic resistance, *Rq*, were measured by a Selective Level Meter. Other parameters, as the dynamic capacitance, *Cq*, the dynamic inductance, *Lq*, and the quality factor, *Q*, were calculated [12]. The sorption properties of the $MoO_3$ films were defined from the frequency-time characteristics (FTC) when saturation over ammonia was achieved. The $NH_3$ concentration in the test chamber is controlled by MFCs for $NH_3$ and the diluting gas flows. The QCM frequency is registered by frequency counter Hameg 8123 connected to the QCM and a computer for data recording. Thus frequency change is fixed with accuracy of $\pm$ $5.25.10^{-7}$ Hz. The sorption ability of the QCM sensor is evaluated on the basis of the measured FTCs at different $NH_3$ concentrations. The QCM resonant frequency shift, $\Delta f$, was measured. The mass of the deposited sensitive layer, as well as the sorbed mass ($\Delta m$) were calculated from the measurements of QCM resonant frequency shift ($\Delta f$), according to the Sauerbery's equation [13]. Besides being highly sensitive to mass changes, the QCM frequency is also sensitive to temperature variations. To eliminate the temperature influence to the resonant QCM frequency, *f*, the piezoelements were prepared on thermostable AT-cut quartz plates. The temperature was maintained at 25 $^{o}$C $\pm$ 0.5 $^{o}$C during the experiments. For more information about the experimental system and the methodology of the measurements please refer to [14].

## 3. Results and discussion

The XRD study showed that the as-deposited DC-magnetron sputtered molybdenum oxide films are predominantly amorphous or nanocrystalline with a very small grain size (Fig. 1), while some of the RF sputtered films showed degree of crystalline structure. These results were also proved by the Raman spectroscopy study. The thinner RF sputtered films and these obtained with enriched oxygen content showed higher degree of crystallization predominantly in the monoclinic modification. Some Raman peaks of orthorhombic modification were also found. Detailed information about the Raman study of RF sputtered $MoO_3$ thin films can be found in our previous publication [11].

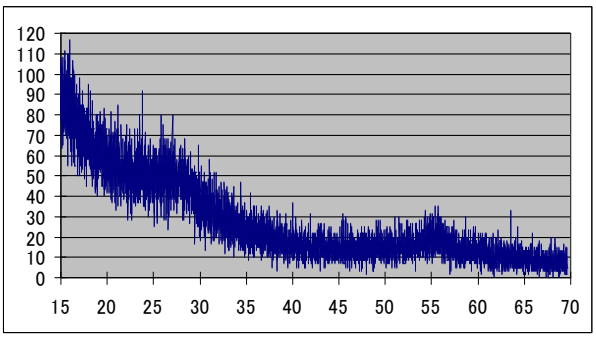


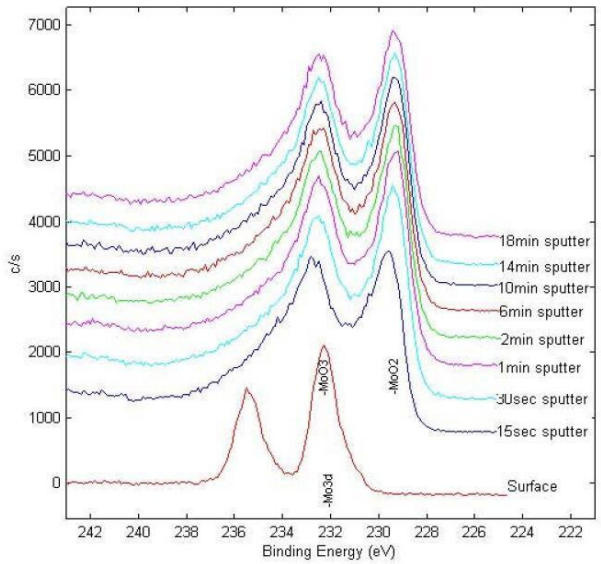

*Fig. 1. XRD analysis of DC-magnetron sputtered $MoO_3$ thin film.*

The fact that we observed a certain degree crystalline structure and the crystallinity is slightly improving at higher oxygen partial pressures in the RF-sputtered process could be explained by the decrease in the rate of deposition due to a lesser amount of argon in the system. We did not notice the same with the DC-sputtered films as the deposition rates we used were higher, so the decreasing of these rates due to the mentioned reason was probably not enough to influence the films' crystal properties. We observed crystal films only when very slow film growth was made and in very thin films of about 100 nm or less. But since the sensing properties are not closely related with the crystal structure of the film as a whole but only with its surface properties, we limited the study of the films' crystal structure.

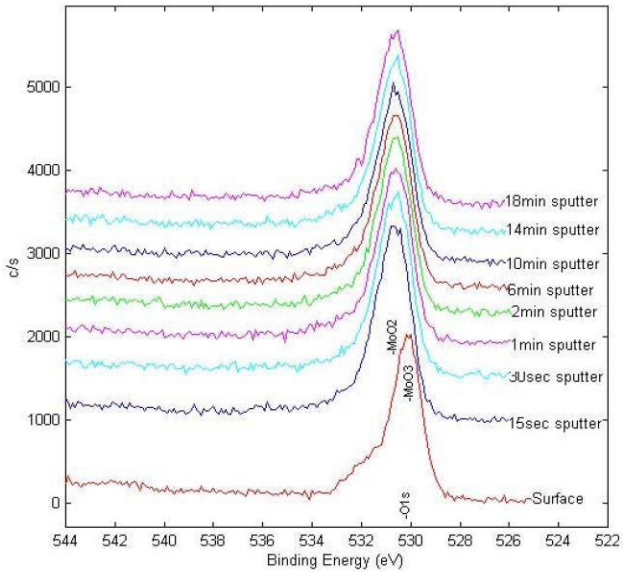
The XPS composition study showed interesting ununiformity between the surface and the sub-surface layers in depth of the films. The surface layer composition shows stoichiometric MoO3. The Mo:O ratio is 25:75 % on the surface but decreases radically in depth immediately after the surface to ratios about 40:60 % Mo:O. The first sputtering was made only for 15 sec (that means around 10 nm from the surface) and showed drastic change of the composition to ratios 37:63 % Mo:O. In the sub-surface layers were not observed almost any significant changes of the composition and the ratio slightly vary around 40:60. It can be reckoned that in almost whole its depth the films are closer to $MoO_2$ (or more accurately $Mo_4O_6$). We cross-proved these results

with the core level spectra and the profile analyses of the same film that can be seen in Fig. 2.

The depth profile was made at sputtering energy 2 kV with various sputtering intervals. The $Mo^{3d}$ spectra clearly show the difference between the surface $MoO_3$ layer and the rest of the film. The labels in the figure concern to the higher pick of $Mo^{3d5}$. All sub-surface layers have identical energy referring to $MoO_2$. The surface layer's energy shows $MoO_3$. The oxygen core level spectra for $O^{1s}$ showed in Fig. 2b) analogically show the difference in composition ratio between the surface and in depth.



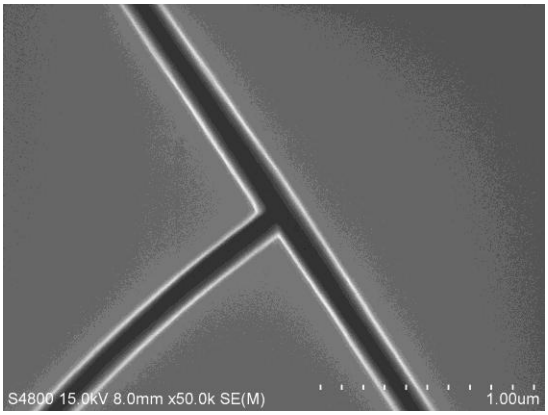

a)



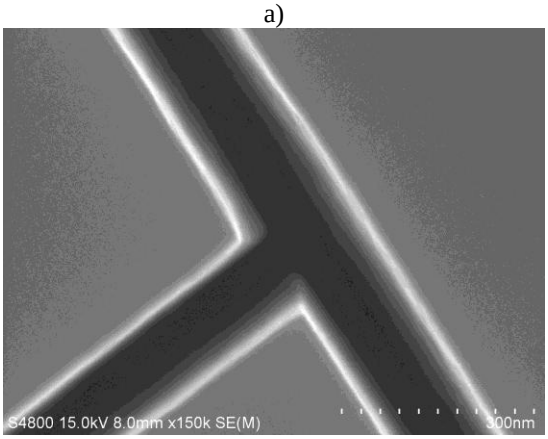

b)

*Fig. 2. XPS profile of $MoO_3$ thin film - $Mo^{3d}$ core level spectra (a) and $O^{1s}$ core level spectra (b).*

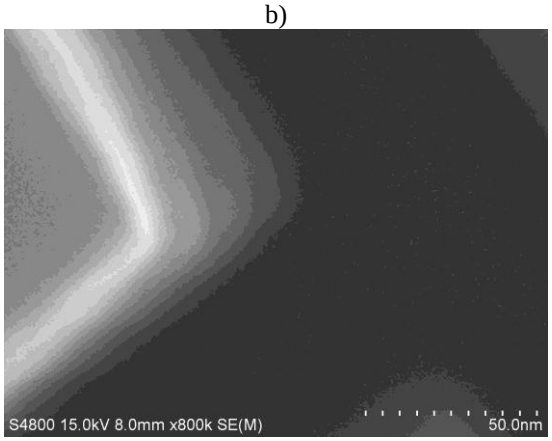
As the films' structure was not clear from the other investigations, we decided to observe them by a high-resolution FE-SEM applying magnifications up to one million. Images are presented in Fig. 3.




a)




b)

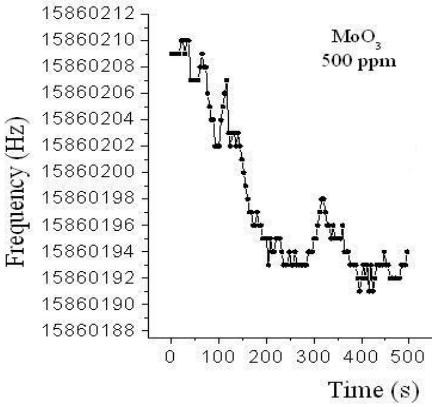



c)

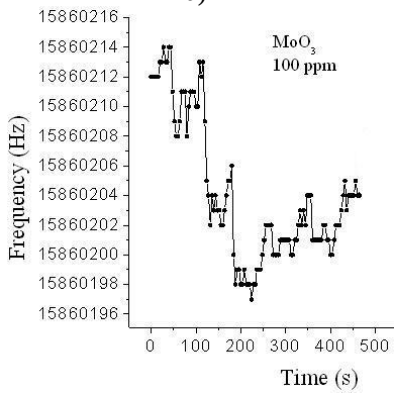
*Fig. 3. FE-SEM images of DC-magnetron sputtered $MoO_3$ thin film magnified 50000 (a), 150000 (b) and 800000 (c) times.*

The films are homogeneous and uniform. They are amorphous-like or with very small nano-sized grains of about a few nanometers. When higher power during deposition is applied we observed many cracks. Even these cracks are positive concerning the larger surface which improves the sorption ability and sensing properties, they decrease the films' stability. These results leaded to decreasing of the deposition rates that we used.

The research was focused on the sensing behavior of the sputtered molybdenum oxide thin films. The prototype QCM sensors with $MoO_3$ thin films showed sensitivity to $NH_3$. In Fig. 4 are presented typical frequency-time characteristics (FTCs) of $MoO_3$-QCM sensor.




a)




b)

*Fig. 4. FTCs of QCM with RF sputtered molybdenum oxide thin films during saturation to $NH_3$ at concentrations of 500 ppm (a) and 100 ppm (b).*

At $NH_3$ concentration of 500 ppm the process kinetics is well expressed. When $NH_3$ is added in the gas flow, the sorption process starts and the frequency decreases with 18 Hz for response time 180s. This process is followed by a dynamic equilibrium between the sorbed and desorbed molecules when the frequency remains constant. The same FTC dependence are also observed for the 100 ppm $NH_3$ concentration (Fig. 4b), showing that the $MoO_3$-QCM system is also well-sensitive to smaller amounts of ammonia in the environment.

Turning off the $NH_3$ flow and blowing the $MoO_3$-QCM sensor through dry air leads to 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 could be fully recovered without applying any additional energy. This fact, as well as the promising results of the sorption allow these molybdenum oxide films to be used in chemical sensors for on-line monitoring of $NH_3$ concentration. The main advantage of the method is that the technology for producing the initial resonator is fully compatible with the sensitive films' preparation. Also the films are able to adsorb $NH_3$ even in as-deposited state and without heating the substrates. Additional thermal treatment is not necessary which makes the manufacturing of QCM gas sensor easy and cost-effective. Also they can be used at room temperature which makes them suitable for portable systems for environment control.

## 4. Conclusions

The properties of RF and DC-magnetron sputtered molybdenum oxide thin films were studied. The films were predominantly amorphous and nonocrystalline with grain size of several nanometres. Ununiformity between the surface and sub-surface layers of the films was observed at the XPS profile study. The films are consisted of stoichiometric $MoO_3$ on the surface and amorphous $MoO_{2-x}$ in their depth. At high deposition rates appearance of cracks was observed.

The reactive sputtering method was found to be suitable for deposition of molybdenum oxide films for sensor applications. The prototype QCM sensors with $MoO_3$ sensitive films showed sensitivity to ammonia at room temperature. The process of sorption is determined as reversible. The initial results of the sorption properties of the studied $MoO_3$ thin films showed that the $MoO_3$-QCM sensor, with some future development, is suitable for $NH_3$ detection devices.

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