Characterization of Reactive Sputtered Molybdenum Oxide Thin Films for Gas Sensors

Stefan Boyadzhiev*
Technical University of Sofia, 8 Kl. Ohridski Blvd, Sofia 1756, Bulgaria and Department of Applied Science, School of Engineering, Tokai University, 1117 Kitakaname, Hiratsuka, Kanagawa 259-1292, Japan

Velichka Lazarova
Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee Blvd, Sofia 1784, Bulgaria

Koji Makita and Yuta Kotani
Department of Applied Science, Graduate School of Engineering, Tokai University, 1117 Kitakaname, Hiratsuka, Kanagawa 259-1292, Japan

Irena Yordanova
Technical University of Sofia, 8 Kl. Ohridski Blvd, Sofia 1756, Bulgaria

Yoshihito Matsumura
Department of Applied Science, School of Engineering, Tokai University, 1117 Kitakaname, Hiratsuka, Kanagawa 259-1292, Japan.

Milka Rassovska
Technical University of Sofia, 8 Kl. Ohridski Blvd, Sofia 1756, Bulgaria.
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Molybdenum oxide (MoO$_x$) thin films were deposited by two different techniques of reactive sputtering and their properties were characterized in order to determine their usage in gas sensors. For preparing the samples, the methods of radio frequency (RF) and direct current (DC) magnetron reactive sputtering were used. The composition and microstructure of the films were studied by X-ray photoelectron spectroscopy (XPS), electron probe microanalyzer (EPMA), X-ray diffraction (XRD) and Raman spectroscopy. The films' surface was observed by Scanning electron microscopy (SEM) and EPMA. The research was focused on the sensing behavior of the MoO$_3$ thin films. In order to do that, films of various thickness were deposited on quartz resonators and the quartz crystal microbalance (QCM) method was used. Applying it can be build high sensitive gas sensor capable to detect changes in the molecular range. These prototype QCM sensing structures with MoO$_3$ sensitive films in as-deposited state and without heating the substrates 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 chemical sensing devices. [DOI: 10.1380/ejssnt.2009.796]

Keywords: Molybdenum oxides; Amorphous thin films; Sputter deposition; Gas sensor; Quartz crystal microbalance

I. INTRODUCTION

Molybdenum oxides have attracted great interest of the researchers in recent years due to their intriguing structural, chemical, optical and electronic properties [1–7]. Indeed, as many other transition metal oxides, MoO$_3$ can be switched between two different optical states defined as photochromic [1, 3, 8–10], electrochromic [1, 3, 6, 9], gasochromic [5] and thermochromic [10] effect. The substoichiometric films MoO$_{3-x}$ with oxygen deficient contain excess metal atoms which act as doping centers, which control the electrical and optical properties of the films [1, 3]. These properties determine the major applications of the molybdenum oxide thin films in electrochromic display devices (ECDs), optical switching coatings and smart windows [1, 11]. But the MoO$_2$ thin films can be used in many other applications such as catalysis [12], lubricants [13], solid state microbatteries [2, 14], memory devices [9] and last but not least gas sensors [15–18]. Relatively small amount of studies was made to examine MoO$_3$ sensing properties compared to investigations carried out to evaluate the sensing properties of SnO$_2$, ZnO$_2$, TiO$_2$, In$_2$O$_3$ and WO$_3$. MoO$_3$ has shown to be sensitive to NO$_2$ [17], CO [16], H$_2$ [18], NH$_3$ [15] and some other gases.

Molybdenum oxide thin films are prepared by different methods, such as thermal evaporation [3, 6, 10], sputtering [5, 9, 15, 18], chemical vapor deposition [7], spray pyrolysis [19], flash evaporation [14] and some others [4]. In the present research we used two different reactive sputtering techniques to fabricate 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 QCM method. QCM is a well-established tool for monitoring the adsorption of nano-amounts, capable to detect mass changes as small as a fraction of a monolayer or a single layer of atoms. The high sensitivity and the possibility for real-time monitoring make QCM a very attractive technique for gas sensors. Compared with others sensors, the

*Corresponding author: stefan_b@mail.bg
advantages of QCM are: simple technological implementation, good sensitivity, chemical process reversibility and capability of operating at room temperature [20].

II. EXPERIMENTAL

The films’ deposition 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 (purity 99.99 %) 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 used for some measurements. First, the substrates were cleaned and dried in a high-purity nitrogen gas stream. Initial vacuum at $1 \times 10^{-5}$ Pa was pumped in the chamber. The values of the oxygen partial pressure were between $1 \times 10^{-3}$-1×$10^{-2}$ Pa for the RF sputtered films and 2×$10^{-2}$-3.5×$10^{-2}$ Pa 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 composition of the films was studied also by Shimadzu “Electron Probe Microanalyzer EPMA-1610”, applied as well as for surface observation. The films were also observed by Ultra-High Resolution 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 Veeco Dektak 3 profilometer and laser ellipsometry. For more detailed information about the RF sputtering deposition technology and conditions as well as the Raman spectroscopy and laser ellipsometry apparatus, please refer to [21].

To determine films’ sensing properties the adsorption to ammonia was tested using 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 molybdenum oxide thin films on both sides. Schematic construction of the sensor is presented in Fig. 1.

Some equivalent dynamic parameters of the QCM, as the static capacitance, $C_0$, and the equivalent dynamic resistance, $R_q$, were measured by a Selective Level Meter. Other parameters, such as the dynamic capacitance, $C_q$, the dynamic inductance, $L_q$, and the quality factor, $Q$, were calculated [22]. The sorption properties of the molybdenum oxide films were defined from the frequency-time characteristics (FTC) when saturation over aqueous ammonia solutions was achieved. To eliminate the influence of H$_2$O molecules on the NH$_3$ sorption, each sample was first saturated with water vapors preceding the measurement over the ammonia solution. The frequency defined over the water was taken as an initial value for subsequent measurements. Besides being highly sensitive to mass changes, the QCM frequency is also sensitive to temperature variations. To eliminate the temperature influence
ence to the resonant QCM frequency, \( f \), the piezoelements were prepared on thermostable AT-cut quartz plates. The temperature was maintained at 25±0.5 °C during the experiments. 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 [23]. The experimental system and the methodology of the measurements are described in [24] in detail.

III. RESULTS AND DISCUSSIONS

The XRD investigations showed that the as-deposited DC-magnetron sputtered molybdenum oxide films are predominantly amorphous (Fig. 2) while some of the RF sputtered films showed a certain degree of crystalline structure. These results were also proved by the Raman spectroscopy study. The thinner RF sputtered films and those obtained with enriched oxygen content showed a higher degree of crystallization predominantly in the monoclinic modification. Detailed information about the Raman study of RF sputtered MoO\(_3\) thin films can be found in our previous publication [21]. 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 crystallinity is not considered important for the present research, as we observed that the sorption process and 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 crystal structure as far as this.

The composition study performed by XPS revealed interesting ununiformity between the films’ surface and the sub-surface layers in depth. The results are shown in Fig. 3. The profile was made at sputtering energy 2 kV with various sputtering intervals. The surface layer composition shows stoichiometric MoO$_3$. 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 barely any significant changes of the composition were observed and the ratios slightly vary around 40:60 %.

It can be reckoned that in almost its’ entire depth the films are closer to MoO$_2$ (or more accurately Mo$_4$O$_6$). We cross-proved these results with the core level spectra of the same film that can be seen in Figs. 4 and 5. In Fig. 4(a) the core level Mo 3$d$ spectra can be observed clearly showing the difference between the surface MoO$_3$ layer and the rest of the film. The labels there concern to the higher pick of Mo 3$d^5$. All sub-surface layers have identical energy referring to MoO$_2$. The surface layer’s energy shows MoO$_3$. In Fig. 4(b) the XPS profile can be traced in better way in the films’ depth. In Fig. 5 the oxygen core level spectra for O 1$s$ are presented. These again explain the difference in composition ratio between the surface and in depth.

It was not possible to cross-prove the findings measured by XPS composition with EPMA because the films are too thin and there is an inaccuracy in the oxygen concentration caused by additionally detected oxygen from the SiO$_2$ film of the substrate surface. But we also used it to observe the films’ surface (Fig. 6). The films are homogeneous and uniform but when higher power during deposition is applied we observed many cracks. Even though these cracks are positive when considering the larger surface which improves the sorption ability and sensing properties, they decrease the films’ stability. These results lead to a decreasing of the deposition rates that we used.

For studying the surface properties of the films, as its structure was not clear from the other techniques, we observed them by high-resolution FE-SEM applying magnifications up to one million. The images are presented in Fig. 7. The films are very smooth and homogeneous. They are amorphous-like or with very small nano-sized

![FIG. 6: EPMA images of DC-magnetron sputtered MoO$_3$ thin film with (a) 3000 and (b) 30000 magnification.](http://www.sssj.org/ejssnt)

![FIG. 7: FE-SEM images of DC-magnetron sputtered MoO$_3$ thin film with (a) 10000, (b) 50000, (c) 150000 and (d) 800000 magnification.](http://www.sssj.org/ejssnt)

![FIG. 8: FTC of QCM with molybdenum oxide thin film during saturation at 1000 ppm NH$_3$.](http://www.sssj.org/ejssnt)
grains of about a few nanometers.

The research was focused on the sensing behavior of the sputtered molybdenum oxide thin films. The prototype QCM sensors with other transition metal oxides sensitive films were made by our team and showed good sensitivity to ammonia [25]. Similar results for good sensitivity to NH$_3$ of the MoO$_3$ thin films also were observed. Figure 8 presents the FTC of a QCM coated on both sides with molybdenum oxide thin film. First, before measuring the NH$_3$ sorption the film was saturated with water vapors. The behavior of the curve indicates that during the first 10 s the structure is abruptly loaded, which results in a fast frequency decrease. During the following the first 10 s a smooth loading followed by a dynamic equilibrium to ammonia [25]. Similar results for good sensitivity to ammonia films were made by our team and showed good sensitivity to ammonia [25]. Similar results for good sensitivity to ammonia [25].

Deorption allows 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 apparatuses.

IV. CONCLUSIONS

The properties of RF and DC-magnetron sputtered molybdenum oxide thin films were studied. Interesting ununiformity between the surface and sub-surface layers of the films was found during the XPS profile analyses. 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 good sensitivity to ammonia at room temperature. The future development of these sensors can be successfully introduced into advanced chemical and biosensing devices.

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