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Thin MoO_3 films for sensor applications♣

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This paper reports on the preparation, surface, structural and sorption characterization of as-deposited MoO_3 thin films elaborated by r.f. magnetron sputtering. Characterization of the films was carried out by different techniques. The surface analysis of MoO_3 was performed using X-ray Photoemission Spectroscopy and Scanning Electron Microscopy. X-ray Diffraction was used to study the structure. The refractive index and thickness were determined from ellipsometric measurements. The layers were studied with the objective of developing an NH_3 sensor. The MoO_3 sensitivity to NH_3 was estimated using a Quartz Crystal Microbalance (QCM) with thin MoO_3 films sputtered on it. Deposition took place at a deposition rate of 20 nm/min. The sorption property of a QCM with a thin MoO_3 layer was defined as of function of the mass-loading, resulting in a frequency change of the QCM Δf after exposure to different NH_3 concentrations. In our experiments, the NH_3 concentrations was changed in the range 50 to 1000 ppm and frequency changes from 96 to 312 Hz were registered. On the basise of the measured Δf for each concentration, the actual sorbed mass was calculated. The obtained results on the MoO_3 sorption properties can be successfully applied in the development of a NH_3 sensor.

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Keywords: MoO_3 thin films, QCM sensor, NH_3 gas adsorption

1. Introduction

Molybdenum trioxide MoO_3 is one of the most promising inorganic materials, with wide potential technological application in the fields of: large area display devices, high-density memory devices and gas sensors [1]. Thin films of MoO_3 can be prepared by various techniques such as: thermal evaporation, chemical-vapor deposition, flash evaporation, electron beam and ion beam evaporation, magnetron sputtering etc. The films produced by the evaporation technique are always non-stoichiometric [2]. The magnetron sputtering method presents more potential for MoO_3 film preparation. The films produced by r.f. magnetron sputtering have many advantages: low porosity, high film adhesion to the substrate and a constant chemical composition. It is reported that the optimum stoichiometery and morphology are the main factors that define the performance of such films in chemical devices [3]. In the present investigation, MoO_3 thin films were prepared by r.f. magnetron sputtering. The purpose of the study was to evaluate the feasibility of using the MoO_3 coated quartz crystal monitor (QCM) as a sensor for detecting gaseous pollutants such as NH_3.

2. Experimental

An AT-cut 16 MHz QCM with 4 mm gold electrodes on both sides was used as a substratum. The MoO_3 layers were then subsequently deposited onto each side of the QCM by r.f. magnetron sputtering of the Mo target. The process of sputtering was carried out under the following conditions: a frequency of 13.56 MHz, applied power of 500W, total pressure of 30 mTorr and partial pressure ratio between oxygen and argon R=p(O2)/p(Ar)=1. For these process parameters, a deposition rate of about 20 nm/min was achieved.

The as-deposited MoO_3 films were studied by X-ray Photoemission Spectroscopy (XPS), Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD) and ellipsometric methods, in order to define their surface state, structure, morphology, refractive index and thickness.

The XPS measurements were performed in an ESCALAB Mk II (VG Scientific) electron spectrometer with aluminum radiation (hv = 1486.6 eV). X-Ray

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♣ Paper presented at the International School on Condensed Matter Physics, Varna, Bulgaria, September 2008 diffraction spectra were collected on Bruker D8 Advance diffractometer using CuK_α radiation and a SoIX detector.

SEM investigations were carried out with a 515 Philips, with a magnification of 30.10^3; the sample being coated with C and Au thin layers in order to increase the resolution.

A schematic diagram of the experimental setup is presented in Fig. 1.

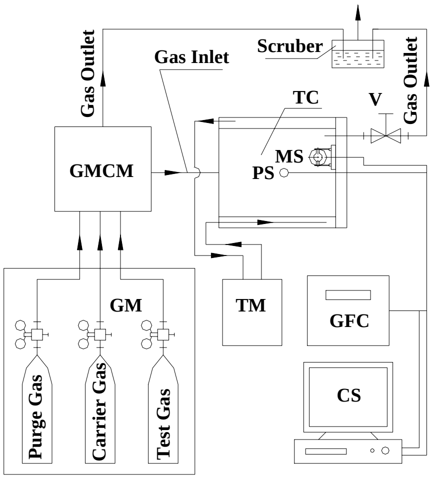

Fig. 1. The experimental set up.

The set up contained the following basic modules: a gas module (GM) – bottles with carrier gas, purge gas and test gas; a gas mix and control module (GMCM) – which included two mass flow controllers (FC-260 and FC-280) and a mixing camera; a test chamber (TC) with a Pt-thermosensor (PS) and a mass sensitive sensor (MS); a thermostat module (TM); a generator and frequency counter (GFC) and a computer system (CS).

The QCM was installed on a special holder inside the test chamber. The temperature of the sample was measured by a Pt-thermosensor positioned near the QCM. Firstly, the chamber was air-scavenged, and then test gas with a certain concentration was released as a permanent flow. The velocities of both the carrier and test gases were measured and controlled by mass flow controllers, their ratio being defined by the desired concentration.

A frequency counter (Hameg 8123) connected to the QCM as well as to the computer for data recording registered the QCM frequency. In this way, the frequency change as a function of time was identified. As an initial frequency value, we took the measured one in the carrier gas flow, under saturation conditions. The gas to be tested came from certified bottles diluted with nitrogen. The test gas was added to the carrier gas continuously for obtaining the desired composition. After adding the mixtures of gases into the system, the frequency started to decrease, and after certain period of time it reached a constant value, when a dynamic equilibrium at certain gas concentration was established and the temperature in the chamber was achieved. A temperature of 28.6°C was maintained in the test camera. During the experiments, if the pollutant flow was terminated, the frequency started to increase as a result of desorption of mass from the QCM. The frequency returned to its initial value. At that stage the measurement was finished.

Experiments with NH_3 concentrations in the gas flow from 50 to 1000 ppm were carried out.

3. Results and discussion

The received SEM data demonstrated that the r.f. sputtered MoO_3 films were homogeneous and uniform. They consisted of spherical clusters with different sizes from 70 to 140 nm. The XRD spectra of MoO_3 were used to define the crystallinity of the films. The diffractograms showed that they are amorphous, and no peak due to MoO_3 is observed. The structure of films was confirmed by the ellipsometric measurements - the refractive index was n=2.06 at a thickness of 221 nm. The measurements were carried out at λ=632.8 nm.

The composition and the electronic properties of the MoO_3 films were investigated by XPS.

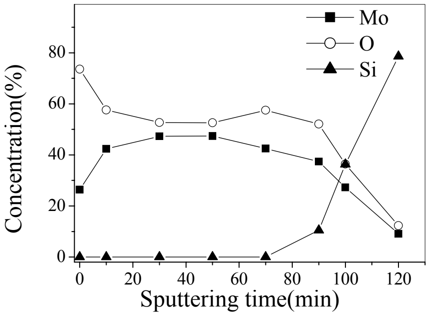

Fig. 2. XPS depth profile of MoO_3 film.

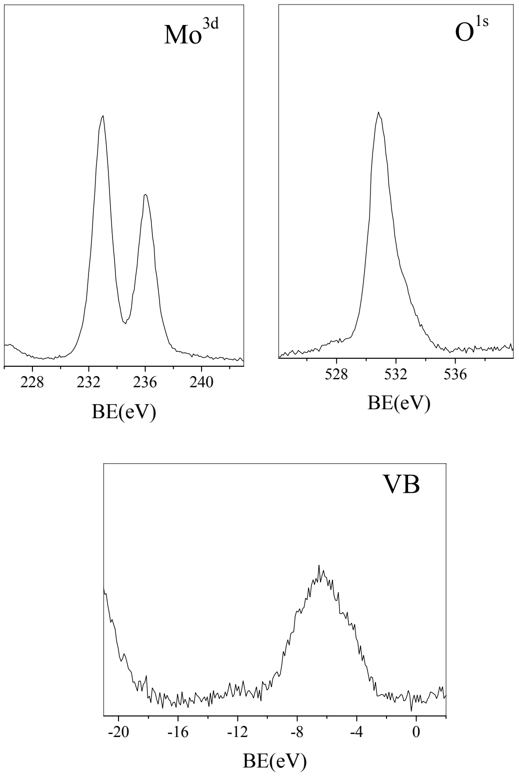

Fig.3. Mo^{3d}, O^{1s} core level spectra and valence band spectrum of the surface of a MoO_3 film

The XPS depth profile in Fig.2 provided information for film`s homogeneity. The O and Mo atomic concentrations were almost constant from the subsurface layers to the film/substrate interface, indicating a homogeneous composition. Compared to the surface, the O/Mo intensity ratio was lower (~1.3) in the inner layers. This phenomenon could be ascribed to preferential sputtering of oxygen, leading to a partial reduction of MoO_3.

Fig. 3 shows the Mo^{3d} and O^{1s} spectra of the film surface. The observed peak positions, and the doublet separation between the $3d^{5/2}$ and $3d^{3/2}$ lines of 3.1 eV are characteristic of MoO_3. The O^{1s} spectrum shows a main peak at 530.8 eV with a slight shoulder at ~532.4 eV. These were identified as oxygen coordinated to molybdenum atoms and as oxygen in adsorbed hydroxyl groups, respectively.

The photoemission spectrum of the MoO_3 film revealed the valence band structure with a peak at 6.3 eV and a shoulder at 4.5 eV (Fig. 3.). The width of the valence band was about 7.5 eV, which is typical for MoO_3. The dominant contribution was due to oxygen (O^{sp} states), while the molybdenum contribution was smaller (Mo^{4d} states) and mainly due to the lower part of the valence band [4]. The valence band did not exhibit a peak at 1.1 eV below the Fermi level, which is attributed to 4d emission from reduced Mo centers [4]. However, the higher intensity of the peak at 6.3 eV compared to that at 4.5 eV is evidence for an increased degree of reduction of the oxide layers.

The estimated sensing properties of thin MoO_3 layers by QCM show that the NH_3 gas concentration varied from 50 to 1000 ppm.

The response of MoO_3 to ammonia is shown on Fig. 4. The frequency change *(Δf)* was measured at a NH_3 concentration in the gas flow of 500 ppm.

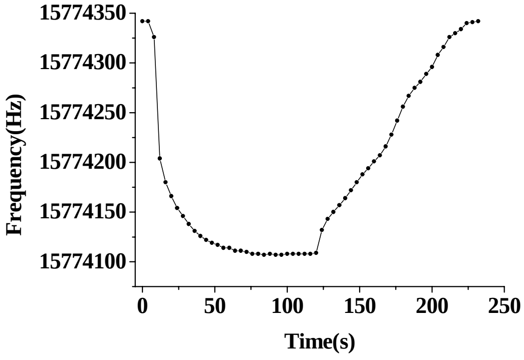

Fig. 4. Response of $Mo0_3$ to ammonia.

During dry air scavenging of the chamber in the first measurement stage, the frequency increased as a result of cleaning of the sample surface. As an initial frequency (f_o) we took the measured *f* value in the carrier gas flow, under conditions where f_o= 15774342 Hz – Fig. 4, after which the sorption process was continuously registered. Including NH_3 in the gas flow lead to an abrupt leap fall in the measured frequency (Δf), - by 162 Hz in only 16 s. A period of 84 s followed, when a slight drop in the frequency was measured (72 Hz). Over the next 16 s, the saturation gas fraction was fixed, giving a constant frequency value. The dynamic equilibrium between the sorbed and desorbed NH_3 molecules of the MoO_3 surface is defined by this fraction. When the NH_3 flow in the gas system was stopped, the processes of desorption and the tendency to recover the initial frequency f_o was observed over 112 s. Comparing the sorption velocity (10.12 Hz/s) in the first fraction of Fig. 4 to the desorption one (2.09 Hz/s), shows that the last is five times lower. The overall dependence indicates the physical character of the sorption process and its reversibility.

The QCM frequency change vs. time for various concentrations of ammonia is plotted in Fig. 5. It is obvious that regardless of the NH_3 concentration, the curves have the same character.

The frequency change velocity, when f changed fastest - in the first 12 seconds of the sorption process - was evaluated. The time necessary to obtain dynamic equilibrium for each concentration was evaluated, and the maximal frequency change for every NH_3 concentration was calculated. The obtained results show that, when the NH_3 concentration increases in the gas phase, the velocity of the frequency change rises from 3.17 Hz/s at 50 ppm to 9.25 Hz/s at 250 ppm. This means that the concentration increases by five times, when the sorption velocity rises by three times, and reaches 18.75 Hz/s at 1000 ppm. At the higher NH_3 concentrations, more rapid response times were observed. The curves obtained (Fig. 5) clearly show the different periods necessary for saturation at the different NH_3 concentrations. At low concentrations (50 – 500 ppm NH_3), the time to reach dynamic equilibrium was 52 – 84 seconds, while it rose to 104 seconds for a concentration of 1000 ppm. This dependence can be explained with the sorption in the layer's depth at higher NH_3 concentrations. The maximal frequency changes, Δf were calculated as the difference between the initial frequency f_o and the one achieved at saturation f_s. Values of Δf from 96 to 312 Hz for the investigated concentration interval (50 - 1000 ppm NH_3) were obtained.

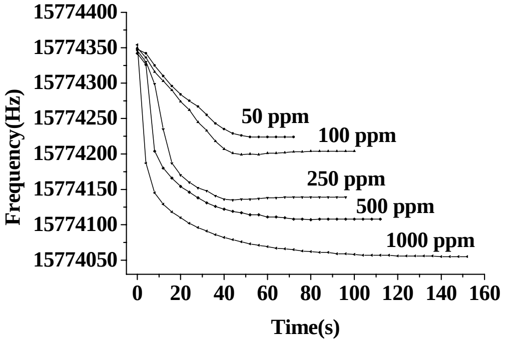

Fig.5. QCM frequency change at various NH_3 concentrations.

The mass of the sorbed molecules was calculated on the basis of the experimentally obtained Δf for each concentration. It is known that, as the gas molecules are adsorbed on a coated QCM, its mass (m) increases as a result of the additional mass loading, and its frequency (f) decreases. The correlation between f and m for a QCM created on AT-cut quartz was given by Sauerbrey [5]. The frequency change Δf is proportional to the mass change Δm at a fixed vibration frequency:

$$\Delta f = - 2.26\ 10^6 f_0^2\ \Delta m\ /s \qquad (1)$$

where Δf and f are in Hz and MHz, Δm is in g and s in cm^2 is the area of the QCM electrode.

In our experiments Δf for every NH_3 concentration was calculated with the extracted value from Fig. 5. The sorbed mass was evaluated at s = 0.1256 cm^2. The tendency of the sorbed molecules' mass to rise when NH_3 increases in the gas flow is very well expressed (Fig. 6). It rises from 21.44 to 69.69 ng in the studied range.

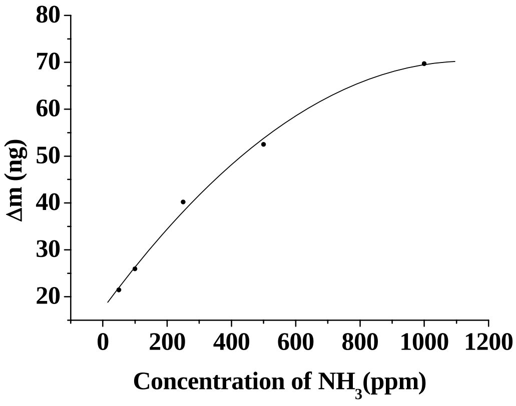

Fig.6. Sorbed mass vs NH_3 concentration

This dependence can be described very accurately with a polynomial of the second degree: $y = A + B_1x + B_2x^2$, where A = 17.41387; B = 0.09331; $B_2 = -4.1213.10^{-5}$.

4. Conclusions

The sensing properties of r.f. magnetron sputtered MoO_3 were studied in order to establish the applicability of these films deposited on QCM for environmental gas monitoring. The films were found to be sensitive to ammonia in the range 50 to 1000 ppm NH_3. It was found that the response signals Δf to ammonia, the response time and the time for saturation were functions of the gas concentration. The process of NH_3 adsorption on the surface of the MoO_3 was reversible. The system MoO_3-QCM could be used as a sensor element for NH_3 detection.

Acknowledgements

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