RF REACTIVE SPUTTERING OF MoO_3 THIN FILMS FOR SENSOR APPLICATIONS

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The research was focused on the sensing behavior of sputtered thin films of molybdenum trioxide (MoO_3). Films of various thickness were deposited on quartz resonators. RF sputtering technology for deposition of MoO_3 thin films was elaborated on. The method of reactive sputtering of molybdenum target in the presence of oxygen as reactive gas was used. Technological parameters were optimized to obtain films with good quality on different substrates. The influence of technological conditions during deposition and the consequent thermal treatment in a different medium were studied. The films' structure was identified by TEM and Raman analysis. The ultimate purpose of the research is to apply MoO_3 thin films in gas sensors. Prototype sensor devices are made and they are an object of our present and extended study.

Keywords: thin films, MoO_3, reactive sputtering, gas sensor

1. INTRODUCTION

Molybdenum trioxide (MoO_3) is metal oxide that has excellent photochromic and electrochromic properties. As some other transition metal oxides, MoO_3 shows good adsorption of ammonia, carbon oxide, nitric oxides and hydrogen. It is also sensitive to many organic compounds such as hydrocarbonic and aromatic gases, ethanol, gasoline, trimethylamine and many other. However, MoO_3 has a low melting point of 795ºC. 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 and coworkers [1]. 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. The possibility of nanostructured MoO_3 films to build advanced chemical sensors, is very perspective.

MoO_3 films of various thickness (300 nm – 1,5 μm) were deposited by RF reactive sputtering on quartz resonators with silver (Ag) and gold (Au) electrodes. The aim is to use the quartz crystal microbalance (QCM) method for studying gas sensing properties of MoO_3 thin films. QCM is an extremely sensitive mass sensing method, capable of measuring mass changes in the nanogram range. This means that QCM sensors are capable of measuring mass changes as small as a fraction of a monolayer or a single layer of atoms. The high sensitivity and the real-time monitoring of mass changes on the sensor crystal make QCM a very attractive technique for gas sensors. Some difficulties in reactive sputtering deposition of MoO_3 on Ag, were established and the technology of deposition on resonators was optimized.

Test sensor devices were built. They are based on quartz resonators with Au electrodes and resonant frequency of about 14 MHz. These MoO_3 thin film gas sensors are being tested to find the feasibility of using this sensor type for on-line monitoring of the concentration of ammonia, carbon oxide, nitric oxides and other gases.

2. Molybdenum Trioxide Thin Films Deposition Technology and Properties

In the present research, in order to deposit MoO_3 thin films reactive sputtering of molybdenum target is used in the presence of oxygen as reactive gas. Technological parameters were optimized to obtain films with good quality on different substrates. The influence of technological conditions during deposition, such as the oxygen partial pressure and deposition time, on the molybdenum oxide structure and properties, have been studied. The optical properties were also examined by visual and infra-red spectroscopy and elipsometric analysis. The consequent thermal treatment in a different medium has also been studied.

Deposition of the films was carried out using vacuum installation A-400VL. The main parameters of the RF reactive sputtering was precisely tuned to get films with optimum properties. The thickness was controlled by the RF power (cathode voltage) and the deposition time. The oxide structure was controlled by the oxygen partial pressure. To obtain stoichiometric MoO_3 films were used values of the oxygen partial pressure more than 1.10^{-3} Pa. This means that the MoO_3 films are formed in excess of oxygen in the chamber. The films were deposited on unheated substrates. The structure was modified by consequent thermal treatment at temperatures 250-300ºC.

The films' structure is identified by Resonant Raman scattering analysis. Raman spectra showed that MoO_3 film structure strongly depends on the thickness. Raman spectra of MoO_3 films with three different values of thickness (0,9 µm – 1,4 µm) are showed on figure 1.

The Raman spectrum of as-deposited films of MoO_3 with thickness of 0.9 µm (N1) had very well expressed Raman peaks at positions, characteristic of the monoclinic modification. Some peaks of orthorhombic structure were also shown in thinner films spectrum. These films with orthorhombic structure that presupposes good sensitivity to many gases have been studied. Thicker films (N2, N3) are amorphous-like with large, low-intensity Raman peaks. Various sub-stoichiometric oxide species are also observed in different films.

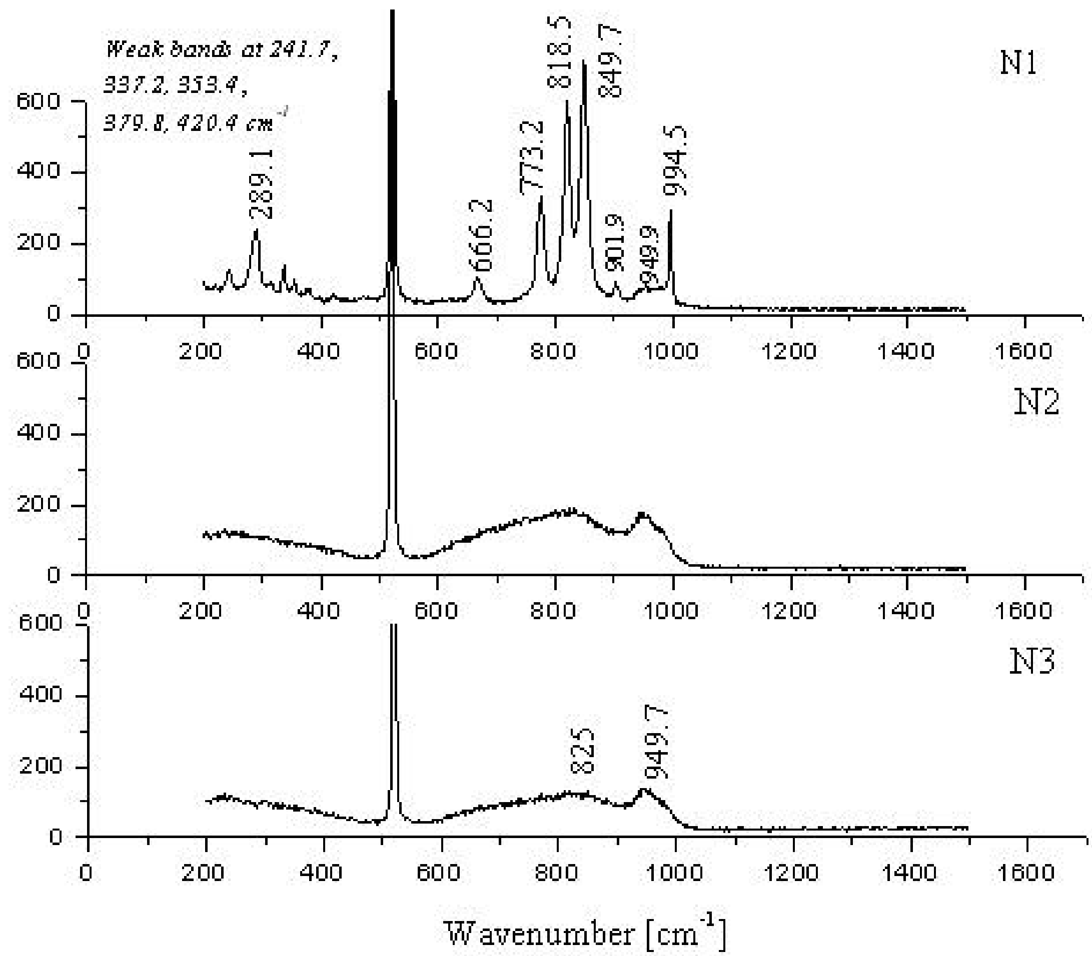

Fig. 1. Raman spectra of different thickness MoO_3 films

Processing and microstructure play a key role in determining the gas sensing behavior of the MoO_3 thin films. In order to be more sensitive the films should be porous and crystal, preferably with orthorhombic modification. As-deposited MoO_3 films with thickness more than 1,2 μm are almost amorphous. After heat treatment at temperatures higher than 250ºC MoO_3 crystallizes. However, processing the quartz resonators thermally causes problems. That is why, thinner films (0.5 – 1 μm) should be deposited on the resonators. Another reason for the films to be thinner is the necessity for less weight in order to obtain better selectivity of the QCM sensor. These thinner films, however, need special deposition technology to obtain good thickness uniformity. Some difficulties in RF sputtering deposition through aperture were established and the technology of deposition on resonators was optimized by using special masks.

3. MoO3 Thin Film Based QCM Gas Sensor

QCM crystals are used as sensors to determine mass changes as a result of frequency changes. Through deposition on the QCM crystal of gas sensing film, such as MoO_3, can be build high sensitive gas sensor. QCM gas sensor construction is showed on figure 2.

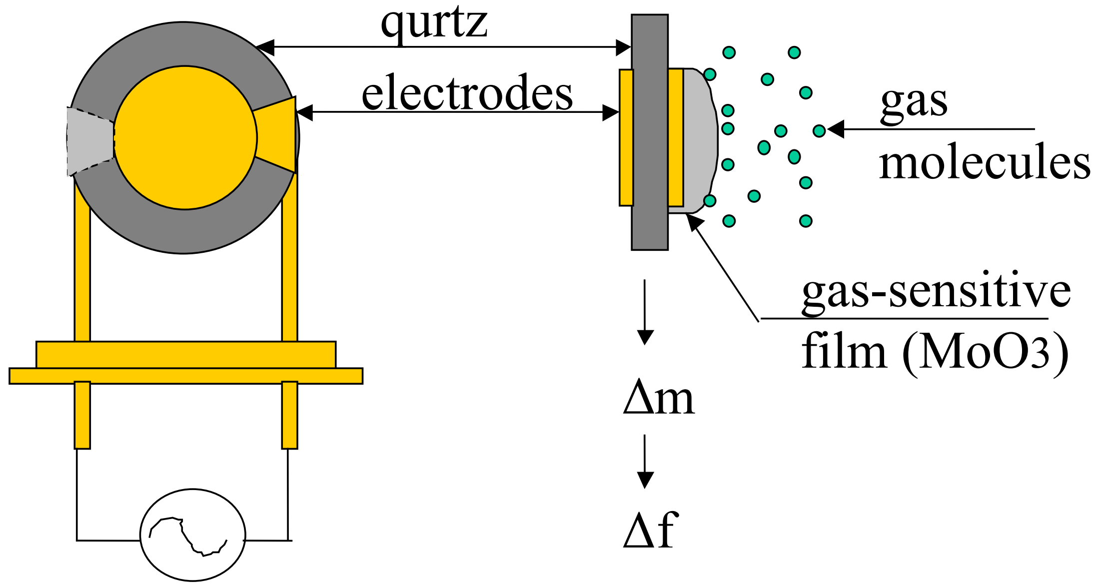

Fig. 2. QCM gas sensor construction

The heart of the QCM is the piezoelectric AT-cut quartz crystal sandwiched between a pair of electrodes. When the electrodes are connected to an oscillator and an AC voltage is applied over the electrodes the quartz crystal starts to oscillate at its resonance frequency due to the piezoelectric effect. This oscillation is generally very stable due to the high quality of the oscillation (high Q factor). If a rigid layer is evenly deposited on one or both of the electrodes the resonant frequency will decrease proportionally to the mass of the adsorbed layer according to the Sauerbrey equation:

$$Df = -[2.fo^2.Dm] / [A.(rq.mq)^{1/2}] \qquad (1)$$

where:
Df = measured frequency shift,
fo = resonant frequency of the fundamental mode of the crystal,
Dm = mass change per unit area (g/cm²),
A = piezo-electrically active area,
rq = density of quartz, 2.648 g/cm³,
mq = shear modulus of quartz, 2.947´1011 g/cm´s².

In the present research are used quartz resonators with Ag and Au electrodes, working diameters 5 mm and resonant frequency of about 14 MHz. When using Ag electrodes there appeared some problems – they oxidize during the process of reactive sputtering and there is bad adhesion between the electrode and the MoO_3 thin film. For that reason the research continued using Au electrodes. Au has very good adhesion to MoO_3 and high chemical stability to any of the studied gases, which makes it very suitable for this type of sensors.

Prototype QCM sensors with MoO_3 sensitive film have been made and showed good sensitivity to ammonia. They are being tested for sensitivity to other gases. The future development of these sensors can be successfully introduced into advanced chemical and biosensing devices.

4. Conclusions

In this paper, a brief review of RF sputtering technology for building a gas sensor with MoO_3 sensitive film is represented. The technological conditions for depositing high sensitive MoO_3 thin films are described. Some technological difficulties are mentioned. A construction of QCM gas sensor, based on MoO_3 sensitive film is given. The follow-up of this study is aiming at the development of these gas sensors and the usage of other transition metal oxides.

5. References

[1] Mutschall D., K. Holzner, and E. Obermeier, *Sputtered molybdenum oxide thin films for NH_3 detection*, Sensors and Actuators B-Chemical, 36(1-3): pp. 320-324, 1996.

[2] Ferroni M., V. Guidi, G. Martinelli, P. Nelli, M. Sacerdoti, and G. Sberveglieri, *Characterization of a molybdenum oxide sputtered thin film as a gas sensor*, Thin Solid Films, 307(1-2): pp. 148-151, 1997.

[3] Prasad A.K., P.I. Gouma, D.J. Kubinski, J.H. Visser, R.E. Soltis, and P.J. Schmith, *Reactively sputtered MoO3 films for ammonia sensing*, Thin Solid Films, 436(1): pp. 46-51, 2003.

[4] Cardona M., *Light Scatering in Solids*, Topics in Applied Physics, Vol. 8, 1975

[5] Pulker H. K. and J. P. Decosterd, *Applications of Piezoelectric Quartz Crystal Microbalances*, Elsevier, Amsterdam, The Netherlands, 1984