WO_3 THIN FILMS DEPOSITION ON QUARTZ CRYSTAL RESONATORS FOR APPLICATIONS IN GAS SENSORS

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The present research is focused on the preparation and properties of sputtered transition metal oxides thin films. WO3 films of various thickness were deposited on quartz resonators in order to use the quartz crystal microbalance method for studying their gas sensing properties. The influence of oxygen partial pressure and substrate temperature on the composition, crystal structure and optical properties of the films was investigated. The films' microstructure and physical properties were identified by Raman spectroscopy analysis. To study their optical properties the methods of infra-red spectrometry and laser ellipsometry were also used. The final objective of the research is the application of these thin films in gas sensors.

Keywords: gas sensor, quartz crystal microbalance, reactive sputtering, thin films, transition metal oxides

1. INTRODUCTION

Tungsten oxides have many unusual properties which make them suitable for a variety of applications. Their excellent optical transmittance, high refractive index, and durability are attractive features for optical coating applications. In thin film form has been under investigation as capacitors and as gas sensors [1]. They show good adsorption of ammonia, nitric oxides and many organic compounds as hydrocarbonic and aromatic gases, alcohol, gasoline, trimethylamine and many other. Besides, tungsten oxide films allow easy insertion of organic compounds in its crystal lattice and this leads to their use in electronic devices and heterogeneous catalysts [2]. They are particularly attractive technologically due their high electronic mobility and high lithium-ion mobility as well as a low-energy barrier for Li insertion and extraction reactions. Tungsten trioxide (WO_3) is an intriguing intercalated material for ambient temperature solid state Li batteries [3]. WO_3 films are also interesting with respect to their chromogenic properties as they possess electrochromic, thermochromic and photochromic effects [4], which make them an excellent material for electrochromic displays - a very perspective cost-effective technology for large-size displays [5]. Their 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 colored state. If applied in solar architectural building, such windows would control the energy of the solar flux entering the building.

Tungsten oxides in a thin film form are also widely investigated as a gas sensor. The operation of most gas sensors is based on the reversible changes of the resistivity of specific materials, caused by the presence of a gas in the environment. Tungsten trioxide (WO_3) has appreciable sensing capability for gases such as CO, NOx and NH_3. The possibility of nanostructured WO_3 films to build advanced chemical sensors, is very perspective.

Tungsten oxides thin films are produced by a number of deposition techniques, usually by chemical vapor deposition (CVD) and various forms of sputtering or evaporation. In the present research WO_3 films of various thickness were deposited by RF reactive sputtering on quartz resonators. The aim is to use the quartz crystal microbalance (QCM) method for studying gas sensing properties of these 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.

Test sensor devices were built. They are based on quartz resonators with Au electrodes and resonant frequency of about 14 MHz. These 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. EXPERIMENTAL

The film deposition was carried out using vacuum installation A-400VL. The method of reactive sputtering of molybdenum, tungsten and titanium targets (purity 99.99%) in the presence of oxygen as reactive gas is used. The main parameters of the RF reactive sputtering were 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 close to stoichiometric WO_3 films were used values of the oxygen partial pressure more than 1.10^{-4} Pa. 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, have also been studied. It was established that processing and microstructure play a key role in determining the sensing properties of these thin films.

WO_3 films of various thickness (300 nm – 1,5 μm) were deposited on quartz crystals with silver (Ag) and gold (Au) electrodes. First, the substrates were cleaned and dried in a high-purity nitrogen gas stream. Initial vacuum at 1.10^{-6} Pa was pumped in the chamber. The values of the oxygen partial pressure was between 1.10-4 - 1.10^{-3} Pa. Cathode voltages of 1 - 1,5 kV were applied for the RF sputtering process. The deposition time was between 30 – 120 min.

The structural properties of the films were characterized using Raman spectroscopy. Raman study was performed with SPEX 1403 Raman double spectrometer, equipped with a photomultiplier, working in photon counting mode. The 488 nm line of an Ar+ ion laser was used for excitation. The laser power on the samples was 50 mW in the spectral range 100 - 1200cm^{-1}. The measurements were taken with 2 cm^{-1} step for measuring a point the time was 5 s (for pure substrate Si - 2 s) and the spectral slit width was 4 cm^{-1}.

The optical properties of the films were investgated using UV-VIS spectrophotometry and multiangle four zone null ellipsometry. The ellipsometry wavelength was 632.8 nm. Variable angle four zone null ellipsometry method with angles 60, 65, 70 and 75 degrees was used. UV-VIS spectrophotometry was applied, employing Specord spectrophotometer.

3. Transition Metal Oxide Thin Films 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 transition metal oxide, can be build high sensitive gas sensor. QCM gas sensor construction is showed on fig. 1.

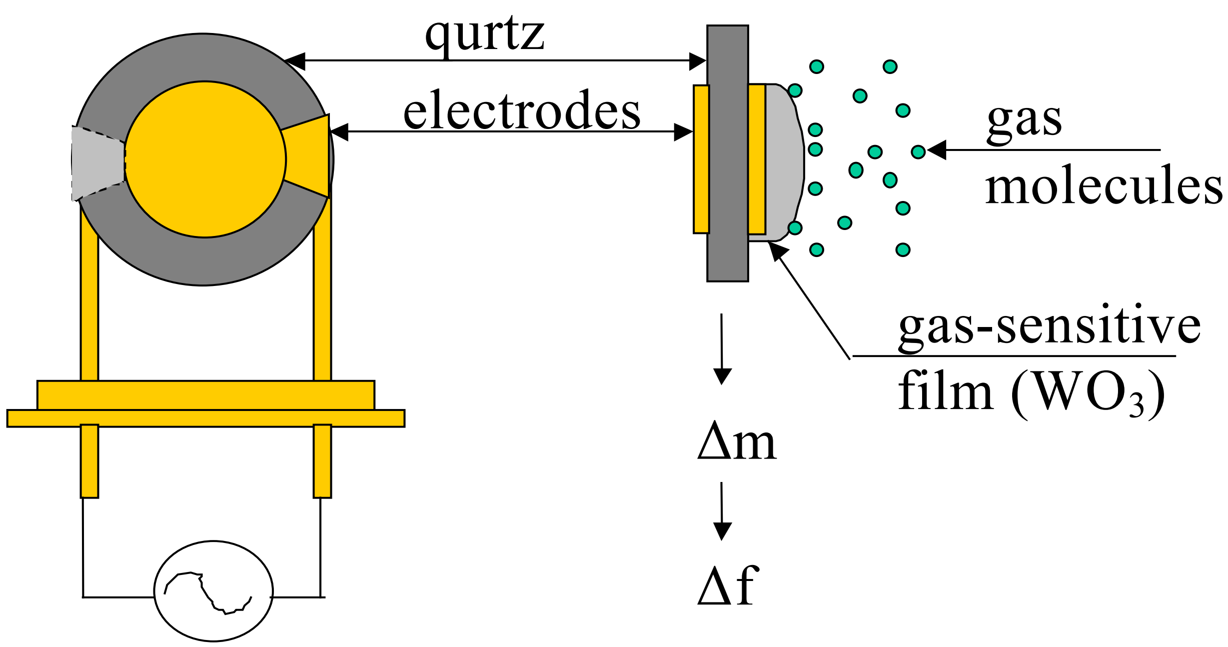

Fig.1. QCM gas sensor construction.

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) [6]. 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/cm^2),
A = piezo-electrically active area,
rq = density of quartz, 2.648 g/cm^3,
mq = shear modulus of quartz, 2.947´1011 g/cm´s^2.

In the present research are used quartz resonators with Ag and Au electrodes, working diameters 5mm and resonant frequency of about 14 MHz. When using Ag electrodes there appeared some problems – sometimes they oxidize during the process of reactive sputtering and there is bad adhesion between the electrode and the WO_3 thin film. For that reason the research continued using Au electrodes. Au has very good adhesion to WO_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 WO_3 sensitive films 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. CONCLUSION

In this paper, a brief review of RF sputtering technology for building a gas sensor with WO_3 sensitive films is represented. The technological conditions for depositing thin films with good quality and structure are described. Some technological difficulties are mentioned. A construction of QCM gas sensor, based WO_3 sensitive film is given. The follow-up of this study is aiming at the development of these gas sensors and testing the sensitivity to wide range of gases.

5. REFERENCES

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