CHARACTERIZATION OF RF AND DC MAGNETRON REACTIVE SPUTTERED TiO$_2$ THIN FILMS FOR GAS SENSORS

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This study presents the technology for preparing and characterization of titanium oxide thin films with properties suitable for gas sensors. For preparing the samples the reactive radio frequency (RF) and direct current (DC) magnetron sputtering methods were used. The composition and microstructure of the films were studied by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and Raman spectroscopy, the surface of the films was observed applying high-resolution scanning electron microscopy (SEM). For measuring the thickness and identifying the refractive indices of the films laser ellipsometry was used. The research was focused on the sensing behavior of the sputtered titania thin films applying quartz crystal microbalance (QCM) method, which allows detection of mass changes in the nanogram range. Prototype QCM sensors with TiO$_2$ thin films were made by our team and tested for sensitivity to NH$_3$ and NO$_2$. These films even in as-deposited state and without heating the substrates show good sensitivity. Additional thermal treatment is not necessary, making manufacturing of QCM gas sensor simple and cost-effective, as it is fully compatible with the technology for producing the initial resonator. The sorption is fully reversible and the studied TiO$_2$ films are stable, which makes them capable for measurements for long terms.

1. Introduction

In the present research films with gas sensing properties were prepared by the methods of reactive RF and DC magnetron sputtering. Thus titanium oxide (TiO$_X$, TiO$_2$) thin films were deposited on different substrates. Titanium oxide has many unusual properties, which make it suitable for a variety of applications. Its excellent optical transmittance, high refractive index, and durability are attractive features for optical coating applications [1-3]. TiO$_2$ also shows good adsorption of ammonia, nitric oxides and many organic compounds as hydrocarbonic and aromatic gases, alcohol and many other [4-7], which makes it very suitable for gas sensor applications. Nowadays TiO$_2$ in thin film form is one of the most extensively studied transition-metal oxides. It is an excellent material for many solid-state devices, not only limited to sensors, but also bactericidal photocatalysts [8], solar cells [9], various optical devices [2] and many others.

In the past few decades, when new types of sensors appeared, a large number of techniques have been developed for environmental monitoring and control of the toxic gases. The QCM is a well-established tool for monitoring the adsorption of nano-amounts and for detecting physical properties of thin layers deposited on the crystal surface [10,11]. Compared with others

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sensors, the advantages of QCM sensors are the simple technological implementation, capability of operating at room temperature, good sensitivity and chemical process reversibility, low consumption and easy real-time monitoring.

The QCM-based techniques attract particular interest due to their high mass-sensitivity in the nanogram range. The analytical performance of such sensors strongly depends on the properties of the sensing coating deposited on the QCM electrodes. Semiconductor thin films such as SnO_2, WO_3, ZnO and MoO_3 have been widely investigated for sensing different toxic gases. Our research was focused on the sensing behaviour of the sputtered TiO_2 thin films towards NH_3 and NO_2. Prototype QCM sensors with other transition metal oxides sensitive films were made by our team and tested for sensitivity to NH_3 in specially designed chamber [12-15].

2. Experimental details

TiO_2 films of various thicknesses (30 nm – 100 nm) were deposited on resonators and silicon wafers with deposition times between 30 and 120 min. For both RF and DC sputtering depositions titanium targets in the presence of oxygen as reactive gas were used. Similar conditions were applied for better comparison of the methods for suitability of preparing TiO_2 films for sensor applications. The films were deposited on unheated substrates and were not thermally treated additionally.

The morphology of the films was observed by a 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 composition of the films as well as profile analyses on the structural changes were performed by an Ulvac-Phi "Scanning ESCA Microprobe Quantum2000" XPS system. It uses focused monochromatic Al Kα X-ray (1486,7 eV) source and a spherical section analyzer. The X-ray beam used was a 12,5 W, 50 μm diameter beam that was rastered over a rectangle on the sample with dimensions of about 1.5 mm by 0.1 mm. The X-ray beam is incident normal to the sample and the photoelectron detector was at 45° off-normal. Narrow scan with high energy resolution spectra of Ti2p, O1s, C1s and Si2p were collected using a pass energy of 23.50 eV. The thickness and refractive indices of the films were measured by multiangle four zone null ellipsometry. For further information about the RF sputtering deposition technology and conditions as well as the Raman spectroscopy and laser ellipsometry equipment, please refer to our previous publications [16,17].

To determine the sensing properties of the films the adsorption of NH_3 and NO_2 was tested using a special laboratory constructed system. Most of the test sensor devices were based on 8-mm polished AT-cut quartz plates with thermally evaporated golden electrodes (diameter 4 mm and thickness of about 120 nm with Cr underlayer) on both sides. QCM resonance frequency around 14 MHz was thus obtained.

The sorption properties of the TiO_2 films were determined by measuring the resonance frequency shift of the QCM structures covered with thin TiO_2 films at different NH_3 and NO_2 concentrations [17]. The measurements are based on the correlation between the frequency shift and the additional mass loading the resonator. Sauerbrey [18] developed an empirical equation for AT–cut quartz, describing the relation between the mass of the thin film deposited on the quartz crystal and the corresponding change in the resonant frequency, thus allowing the absorbed mass to be calculated. The equivalent dynamic parameters of the QCM needed for the calculations, including 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 [19]. The sorption properties of the TiO_2-QCM structure were measured at laboratory set up, which experimental unit, as well as the methodology of measurements, are described in details in our previous publications [12,13]. The main stages of the measurement consisted of: purging of the structures with dry air; creating a certain concentration of the measured gas in the chamber; measuring the sorption process until reaching saturation of the sorption and relatively constant frequency values; purging of the structures with

dry air thus restoring the sensor and preparing it for new measurement.

The NH_3 and NO_2 concentrations in the test chamber were controlled by mass flow controllers (MFCs) for NH_3, NO_2 and diluting gas flows. The experiments were carried out at 26 ^{o}C with an accuracy of $\pm$ 0.2 ^{o}C. The QCM frequency was registered by frequency counter Hameg 8123 connected to the QCM and a computer for data recording. The relative error for frequency measurement was $\pm$ 5.25.10^{-7}.

3. Results and discussion

The surface of the films is considered to be the most important region for the sorption properties of the films. To observe it we applied a high-resolution FE-SEM. The images are shown in fig. 1. The films are homogeneous and uniform. They are amorphous-like or with very small nano-sized grains of about a few nanometers or less. The defect on the surface shown in the images was only used to enable high-resolution focusing of the microscope.

S4800 15.0kV 8.0mm x50.0k SE(M) 1.00um   S4800 15.0kV 8.0mm x250k SE(M) 200nm

a)   b)
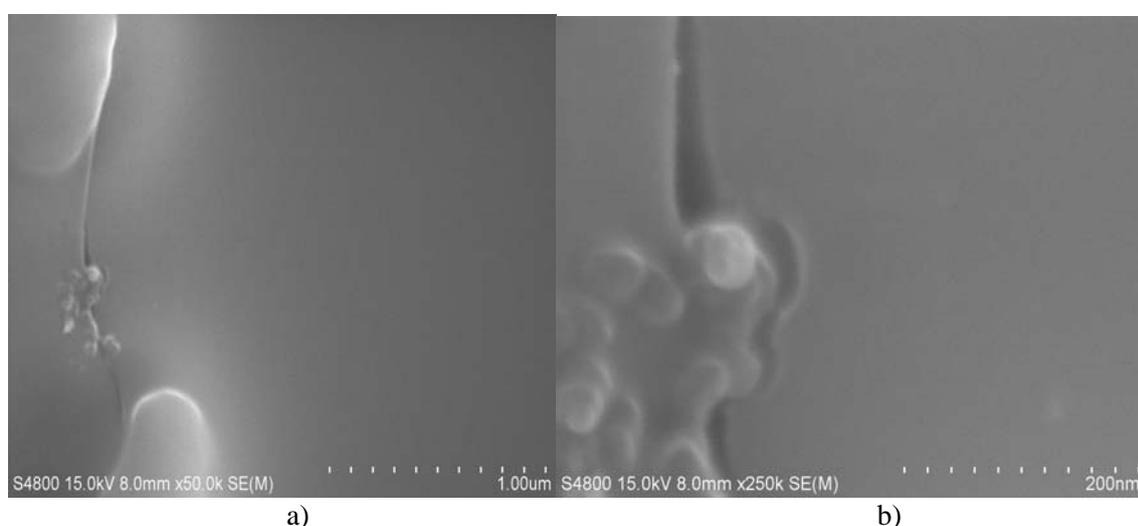
Fig. 1 - FE-SEM images of DC magnetron sputtered TiO$_2$ thin film with 50000x (a) and 250000x (b) magnification.

The XRD investigations showed that both RF and DC sputtered TiO$_2$ films are predominantly amorphous. These results were also supported by the Raman spectroscopy study. But the XPS profile analyses showed that the structure differentiates between the surface and the bulk of the film. In both DC and RF sputtered films profiles we observed close to the substrate very thin but significant metallic titanium phase followed by growth of amorphous-like titanium oxide, probably mixture of oxides of titanium in different oxidation states. However, on the surface we observed sharp peaks without shoulders with shape typical for TiO$_2$ [20,21,22]. The doublet separation between the 2p$_{1/2}$ and 2p$_{3/2}$ peaks of ~5.8eV [21,22,23] and the strong satellite at ~14 eV from the main peak are also characteristic for TiO$_2$ [24].

The results are shown in fig. 2 for DC and fig. 3 for RF sputtered films. Both profiles were made at sputtering energy 2 kV with 1 min sputtering intervals. The deposition conditions and film thickness are similar.
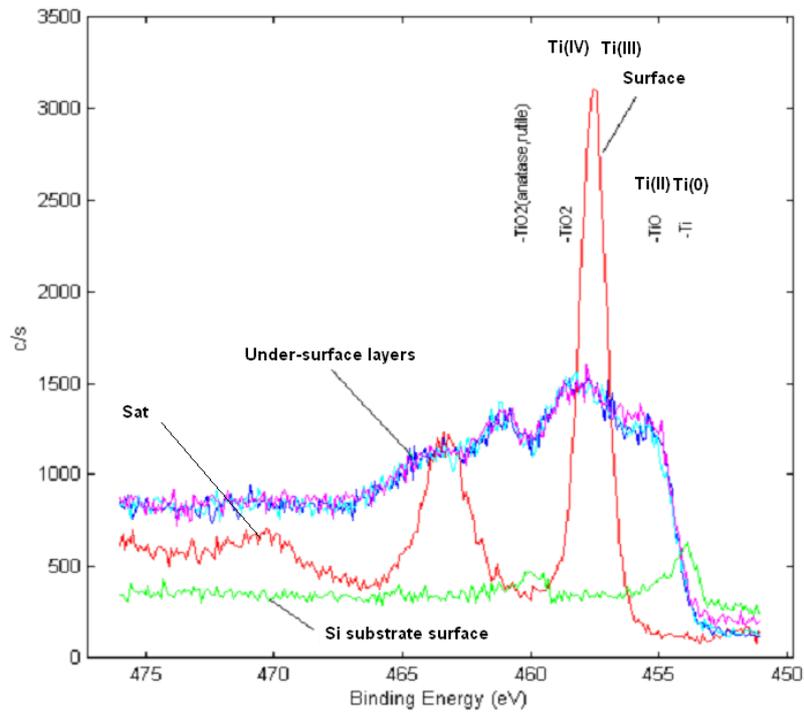
Fig. 2 - XPS spectra of Ti 2p core levels of ~ 65 nm thick DC magnetron sputtered TiO₂ thin film.
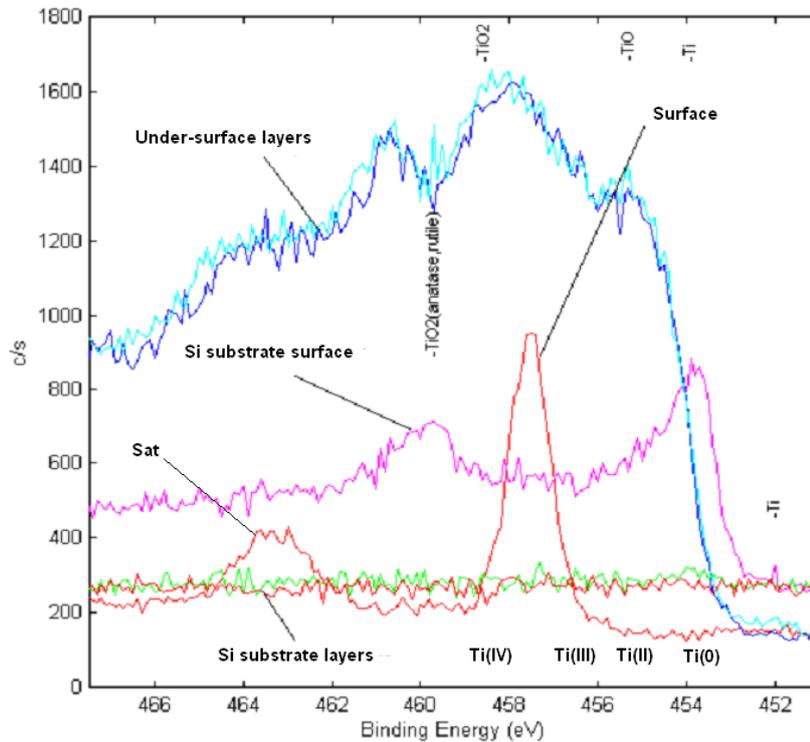
Fig. 3 - XPS spectra of Ti 2p core levels of ~ 50 nm thick RF sputtered TiO₂ thin film.

Although the Ti 2p picks for the surface study are not positioned exactly at the typical binding energies for Ti^{4+} state, but at a bit lower energy, they are sharp and without shoulders, and are not considered to be consisted of signals from Ti atoms in two different oxidation states. It is more probable that the binding energy deviation is caused by photocatalytic effects and Ti-C interactions from C-impurities on the surface (also detected in considerable amount during the XPS study) [25,26].

The results from the XPS study in the bulk, after etching the surface, are questionable because of the influence of the ion bombardment and the preferential sputtering effects [21,27]. Though the ion bombardment during the sputtering of the surface could influence changes in the structure of the film, it is doubtful that it brought any significant change during our study. According to our previous experience with XPS profiles of other transition metal oxides, made with the same sputtering power, there were not any changes observed between the surface and the bulk [28]. Other authors also report XPS profiles of TiO_2 films with same structure of the surface and the sub-surface layers after sputtering [29]. At the same time both profiles show that there is no any significant difference in the properties between layers of the film studied after different intervals of sputtering. That was observed not only for TiO_2 films in the present study, but also for MoO_3 films [30], which both demonstrated different properties between the bulk and the surface. In many of the reports of TiO_2 XPS profiles with difference between the surface and bulk properties, where conclusion is made that it is influenced from the sputtering with Ar, there are differences observed between the layers studied after different sputtering intervals and the structure changes proportionally with the sputtering time [31], which is not observed in our case.

The composition study for the DC magnetron deposited films showed very close to stoichiometric TiO_2 on the surface. The Ti:O ratio is 34:66 % on the surface and changes in depth slightly to ratio of around 36:64 % Ti:O. For RF deposited films the ratio is the same in the bulk but quite different on the surface, reaching 25:75 % Ti:O, which hardly could be explained with something else than catalytic effects or impurity of the surface, which can be concluded also from the lower intensity of the signal for the surface measurement in fig. 3.

The refractive indices of the films are around 2,32 (at wavelength 632.8 nm) and also prove composition close to stoichiometric TiO_2. However, our research was focused on the sensing behaviour of the sputtered TiO_2.thin films and the structure investigations of the films were limited only to the most necessary ones leading to the optimization of the deposition technology for obtaining films with better sorption.

Our prototype QCM sensors with TiO_2 thin films showed good sensitivity to NH_3 and NO_2. In fig. 4 are presented the frequency-time characteristics (FTCs) of TiO_2-QCM sensor produced by RF sputtering (together with the same TiO_2 film deposited on referent Si wafer, which results were shown on fig. 3) measured at different concentrations. FTC of the same sensor measured towards NH_3 sorption could be observed in our previous publication [32]. The working frequency after loading the resonator with the TiO_2 layers is about 13,8MHz, the equivalent dynamic impedance of the resonator is 7,9 Ohm.
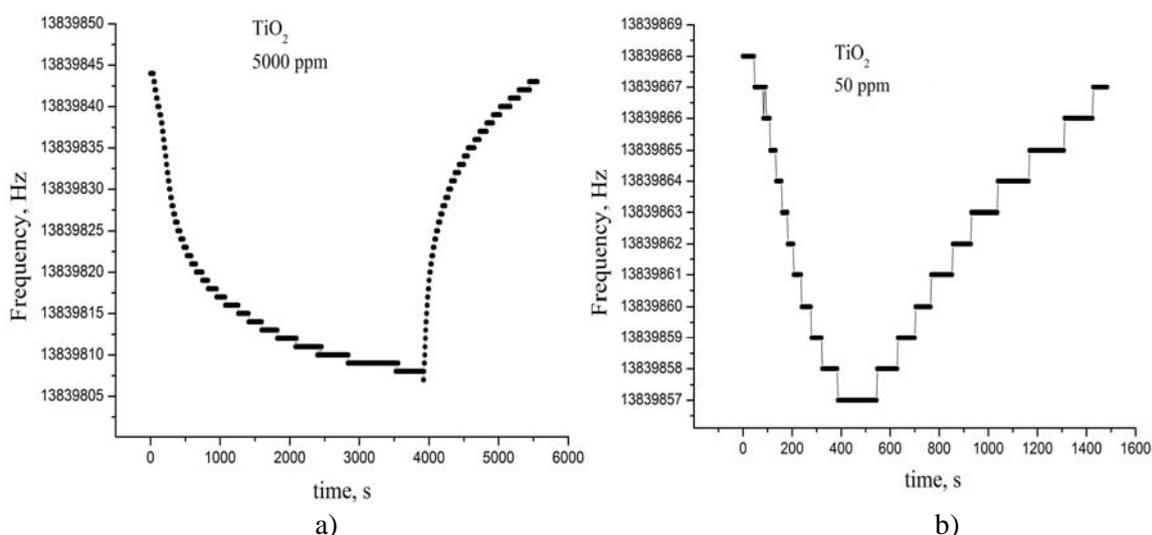
Fig. 4 - FTCs of QCM with RF sputtered TiO_2 thin films during saturation and recovery at NO_2 concentrations of 5000 ppm (a) and 50 ppm (b).

With both NH_3 and NO_2 measurements the behaviour of the sensors is very similar. At high concentration of about 500 ppm and over the process kinetics is well expressed. When the

measured gas is added in the gas flow, the sorption process starts and the frequency decreases fast and linearly during the first minute. The frequency change is almost linear and with 30-50 Hz for the first 1000s. This process is followed by a slower decrease of the frequency until a dynamic equilibrium between the sorbed and desorbed molecules is reached when the frequency remains constant. Similar FTC dependences are also observed for lower concentrations, with the main difference of the slower response (Fig. 4b), showing that the TiO_2-QCM system is also well-sensitive to smaller amounts of the polluting gas in the environment.

Turning off the measuring gas flow and blowing the sensor with 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 TiO_2-QCM sensor could be fully recovered without applying any additional energy.

Also, correlation was established between the measured gas mass that was sorbed on the QCM and its concentration. Fig. 5 illustrates the measured frequency shift and mass loading at different NO_2 concentrations – 50ppm, 100ppm, 500ppm, 1000ppm, 2500ppm and 5000ppm. The investigated TiO_2 films have higher sensitivity in the range from 50ppm to 1000ppm, afterwards it increases gradually. The values of the sorbed mass calculated according to the Sauerbrey equation [18] are also presented in fig. 5. The change is from 3 ng to 10,5 ng for NO_2 concentrations in the interval 50ppm to 5000ppm.
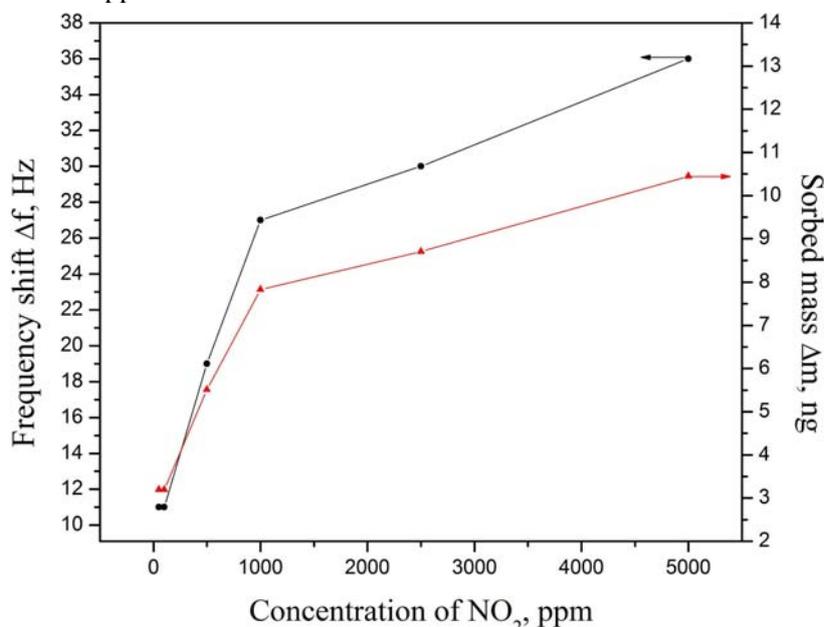
Fig. 5 - Frequency shift and sorbed mass of TiO₂-QCM sensor vs the NO₂ concentration.

Very important is the fact that the sensors produced according to the discussed technology are with stable parameters within long terms and could be used for many cycles. The first measurements with the presented RF sputtered sensor last from more than 6 years ago. Its parameters and sensitivity practically did not change at all during these years and it is expected that it could work for times more. This fact, as well as the promising results of the sorption, allows these TiO_2 films to be used as gas sensors for on-line monitoring of NH_3 and NO_2 concentrations.

Both the RF and DC sputtered films show similar sensing behaviour towards NH_3 and NO_2 and it is hard conclusion, which method is better, to be maid. Generally, better sorption properties were shown by films with higher porosity and defects, though this could lead to problems with the stability of the parameters of the sensors. Such problems with the stability of the films were observed mainly with other transition metal oxides, which grow faster even at not so high sputtering powers, like MoO_3, where cracks on the films could easily appear [30]. With TiO_2 we didn't observe such, as it grows generally much slower due to lower sputtering rates of the target caused by charging effects. High quality sensors with long term stability were obtained with depositions at comparably slow rates and in reactive atmosphere with excess of oxygen.

The main advantage of the described method is that the technology for producing the

sensitive films is fully compatible with the initial resonator preparation. Also, the films are able to detect 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. Still, there are remaining problems mainly regarding the selectivity of the structures and how they to be implemented in full-scale commercial sensing apparatus.

4. Conclusions

The properties of RF and DC-magnetron sputtered titanium oxide thin films were studied. The films were amorphous or nanocrystalline with very small grain size of several nanometres or less. Ununiformity between the surface and the bulk of the films was observed at the XPS profile study. The films are consisted of stoichiometric amorphous-like or nanocrystaline TiO_2 on the surface and amorphous mixture of titanium oxides in the bulk.

The reactive sputtering method was found to be suitable for deposition of TiO_2 films for sensor applications. The prototype QCM sensors with TiO_2 sensitive films showed good sensitivity to NH_3 and NO_2 at room temperature and capability to register well low concentrations as 50 ppm. The sorption is fully reversible, the TiO_2 films are stable and capable for measurements for long terms. The main conclusion based on the results obtained is that QCMs covered with RF and DC magnetron sputtered thin TiO_2 films are suitable for NH_3 and NO_2 detection.

Acknowledgements

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