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Characterization of reactive sputtered TiO$_2$ thin films for gas sensor applications

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Abstract. The technology for preparing and characterisation of titanium dioxide (TiO$_2$) thin films with properties appropriate for usage as gas sensors are discussed. For preparing the samples the methods of reactive radio frequency (RF) and direct current (DC) magnetron sputtering were used. The composition and microstructure of the films were studied by XPS, EPMA, XRD and Raman spectroscopy and the surface of the films was observed by high resolution SEM. Thorough profile analyses on the structure changes were performed by XPS. Interactions with the substrate and changes between the different modifications of the crystal structure also were investigated. For measuring the thickness and to identify the refractive indices of the films laser ellipsometry was used. The research was focused on the sensing behaviour of the sputtered TiO$_2$ thin films. Films of various thickness were deposited on quartz resonators and the quartz crystal microbalance (QCM) method was used. This enables highly sensitive gas sensor capable of detecting changes in the molecular range to be constructed. Prototype QCM sensors with TiO$_2$ sensitive films made in our laboratory, showed good sensitivity to ammonia at room temperature, and are currently being tested for sensitivity to other gasses.

1. Introduction
Titanium dioxide attracts attention due to its remarkable chemical, electrical and optical properties such as large energy gap, high refractive index and dielectric constant, excellent chemical stability, nontoxicity, good mechanical hardness and high transparency in the visible and near infra-red range. [1,2] Additionally TiO$_2$ exhibits excellent photocatalytic and superhydrophilic properties [3-5] and is a promising material for humidity, chemical and gas sensors, as it shows good adsorption of nitric oxides, ammonia, CO, H$_2$S and many organic compounds including alcohols, hydrocarbonic and aromatic gases and many other [6-11].

Various techniques are employed for deposition of TiO$_2$ thin films, such as electron beam evaporation [1], various forms of sputtering [1-2,7,9,11], sol–gel [4], chemical vapor deposition (CVD) [5], pulsed laser deposition (PLD) [12] and others [1,8]. Wide variations were found in the films’ properties, even among films produced under nominally the same deposition conditions [1]. Among these techniques, reactive sputtering has gained significant importance because it enables control of the structure, composition and properties of TiO$_2$ films by adjusting the deposition conditions. This results in high quality thin films with thickness uniformity over large areas and well
controlled stoichiometry. Moreover, sputtering methods are widely used in industrial processes because high quality films can be obtained at low substrate temperatures. These advantages, as well as the possibility of building QCM sensors with TiO₂ thin films with only one additional operation encouraged us to use this method in the present research. The technological parameters were tuned to obtain films with optimal properties at different substrates – silicon and quartz and PZT resonators with gold and silver electrodes. The control silicon samples were used for XPS, XRD, EPMA, Raman and ellipsometry analysis. The resonators were used for preparing sensors based on the QCM method. QCM is a well-established tool for monitoring the adsorption of nano-amounts. 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. Compared with others sensors, the advantages of QCM are: simple technological implementation, capability of operating at room temperature, good sensitivity and chemical process reversibility [13].

2. Experimental

For both RF and DC sputtering depositions titanium targets (purity 99.99%) in the presence of oxygen as reactive gas were used. 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. TiO₂ films of various thickness (30 nm – 120nm) were deposited on resonators and silicon wafers. The deposition time was between 30 and 120 min.

The composition of the films as well as thorough profile analyses on the structure changes 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”. The surface of the films was observed by a high resolution FE-SEM (Field Emission 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 and refractive indices of the films were measured by multiangle four zone null ellipsometry. More detailed information about the RF sputtering deposition technology and conditions as well as the Raman spectroscopy and laser ellipsometry apparatus can be found in our previous publication [14].

To determine films’ sensing properties first adsorption of ammonia was tested using a special laboratory constructed measurement system. Most of the test sensor devices were based on 8-mm polished AT-cut quartz plates with gold electrodes (diameter 4 mm and thickness 120 nm) evaporated on both sides. QCM resonance frequency around 14 MHz was thus obtained. The piezoelements thus prepared were covered with TiO₂ thin films on both sides. Equivalent dynamic parameters of the QCM, including the static capacitance, C₀, 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 [15]. The sorption properties of TiO₂ were defined from the frequency-time characteristics (FTC) when saturation over aqueous ammonia solutions for each concentration investigated was achieved. To eliminate the influence of H₂O molecules on the NH₃ sorption, each sample was first saturated with water vapor preceding the measurement over the ammonia solution. This frequency 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 temperature influence on the resonant QCM frequency, f, the piezoelements were prepared on thermostable AT-cut quartz plates. The temperature was maintained at 25 °C ± 0.5 °C during the experiments. The QCM resonant frequency shift, Δf, was measured and the sorbed mass was calculated by Sauerbery’s equation, which gives a linear relationship between the Δf and the mass adsorbed on the electrode surface [16].

\[
\Delta f = \frac{-2.26 \times 10^6 \times f^2 \times \Delta m}{S_1}
\]
According to the Sauerbery’s equation developed for an AT-cut quartz crystal (1), for each value measured of $\Delta f$, the NH$_3$ mass sorbed ($\Delta m$) can be calculated when one knows the initial frequency $f$ in MHz, the measured $\Delta f$ in Hz and the area of the electrodes ($S_\perp$) in cm$^2$. For our experiments $S_\perp = 0.1256$ cm$^2$. The experimental system and the methodology of the measurement are described in detail in [17].

3. Results and discussion
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 changes between the surface and the bulk. In both RF and DC sputtered film profiles we observed close to the substrate very thin but significant metallic titanium phase followed by growth of close to stoichiometric amorphous titanium dioxide. The films are predominantly amorphous, with weak lines showing crystalline structure (both TiO$_2$ and TiO) throughout the film, almost without any significant changes in composition. However on the surface we observed clear crystalline structure. The results are shown in figures 1 and 2. Both profiles were made at sputtering energy 2 kV with 1 min sputtering intervals. The sputtering conditions and film thickness are similar. We observed slightly better expressed crystalline phase in the bulk for the RF sputtered films but there is no significant difference.

![Figure 1. XPS profile of 50nm thick RF sputtered TiO$_2$ thin film.](image-url)
Figure 2. XPS profile of 50nm thick DC magnetron sputtered TiO₂ thin film.

The composition study results for the same films are presented in table 1.

Table 1. XPS composition study of RF and DC magnetron sputtered TiO₂ thin films

| Sputtering | RF sputtered film | DC magnetron sputtered film |
|------------|-------------------|----------------------------|
|            | Ti [at. %]        | O [at. %]                  |
| 0 (surface)| 24.2              | 75.8                       |
| 1          | 35.8              | 64.2                       |
| 2          | 36.0              | 64.0                       |
| 3          | 29.6              | 70.4                       |

It was not possible to corroborate the 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 SiO₂ film of the substrate surface. The refractive indices of the films are around 2.32 (at wavelength 632.8 nm) and also support a composition close to stoichiometric TiO₂. To investigate the surface, which is considered to be the most important region for the sorption properties of the films, we applied an ultra-high resolution FE-SEM. The images are shown in figure 3. The films are homogeneous and uniform. They are amorphous or with very small nano-sized grains of a few nanometers. The object shown in the images was only used to enable improved focusing of the microscope.
The present research was focused on the sensing behavior of the sputtered TiO$_2$ thin films. Prototype QCM sensors with other transition metal oxides sensitive films were also made by our team [18] and showed good sensitivity to ammonia. Similar results for good sensitivity to NH$_3$ of the TiO$_2$ thin films were observed. Figure 4 shows the sorption properties of a QCM coated on both sides with 50 nm TiO$_2$ thin film when exposed to water vapour.

The behavior of the curve indicates that during the first 30 s the structure is abruptly loaded, which results in a rapid frequency decrease. During the following 150 s the curve falls more smoothly and
after 200 s a dynamic equilibrium is gradually established between the number of sorbed and desorbed water molecules, which corresponds to a state of saturation. Once being saturated over H₂O, the sample was placed above aqueous solutions of NH₃ with 1000 ppm concentration. Again in the first 35 s there is fast sorption leading to rapid frequency changes, followed by smooth curve during the next 300 - 350 s. After 400 s the system reaches saturation. The results are presented in figure 5. Once the experiments were completed, the samples were placed in a neutral environment, which resulted in recovering the initial frequency of the samples, thus proving the reversible nature of the sorption process.

4. Conclusions
The properties of RF and DC magnetron sputtered titanium oxide thin films were studied. The films were predominantly amorphous and nanocrystalline with grain size of a few nanometers. Non-uniformity between the surface and sub-surface layers of the films was observed at the XPS profile study. The films consist of stoichiometric TiO₂ on the surface and amorphous-like, including many phases like TiO, TiO₂-x, in the bulk.

The reactive sputtering method is found to be suitable for deposition of TiO₂ thin films for sensor applications. Prototype QCM sensors with TiO₂ sensitive films were made and showed good sensitivity to ammonia. These films even in as-deposited state and without heating the substrates show good sensing properties and 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 future development of these sensors as NH₃ detection devices is therefore possible.

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References
[1] Bennett J M, Pelletier E, Albrand G, Borgogno J P, Lazarides B, Carniglia C K, Schmell R A, Allen T H, Tuttle-Hart T, Guenther K H and Saxer A 1989 Appl. Opt. 28 3303
[2] Karunagaran B, Kim K, Mangalaraj D, Yi J and Velumani S 2005 Sol. Energy Mater. Sol. Cells 88 199
[3] Fujishima A and Honda K 1972 Nature 238 37
[4] Yu J, Zhao X and Zhao Q 2000 Thin Solid Films 379 7
[5] Brevet A, Fabreguette F, Imhoff L, Marco de Lucas M C, Heintz O, Saviot L, Sacilotti M and Bourgeois S 2002 Surf. Coat. Technol. 151-152 36
[6] Madou M J and Morrison S R 1989 Chemical Sensing with Solid State Devices (Boston: Academic Press)
[7] Tang H, Prasad K, Sanjines R and Lévy F 1995 Sens. Actuators B 26 71
[8] Zhang Y, Fu W, Yang H, Qi Q, Zeng Y, Zhang T, Ge R and Zou G 2008 Appl. Surf. Sci. 254 5545
[9] Guidi V, Carotta M C, Ferroni M, Martinelli G, Pognalonga L, Comini E and Sberveglieri G 1999 Sens. Actuators B 57 197
[10] Idriss H and Seebauer E G 2000 J. Mol. Catal. A: Chem. 152 201
[11] Chow L L W, Yuen M M F, Chan P C H and Cheung A T 2001 Sens. Actuators B 76 310
[12] Syarif D G, Miyashita A, Yamaki T, Sumita T, Choi Y and Itoh H 2002 Appl. Surf. Sci. 193 287
[13] Cunningham A 1998 Introduction to Bioanalytical Sensors (New York: Wiley)
[14] Bojadziev S I, Dobrikov G H and Rassovska M 2007 Thin Solid Films 515 8465
[15] Manolov S and Titechev H 1982 Generators (Sofia: Tehnika) 128 (in Bulgarian)
[16] Sauerbery G 1959 Z. Phys. 155 206
[17] Lazarova V, Spassov L, Andreev S, Manolov E and Popova L 1996 Vacuum 47 1423
[18] Boyadjiev S and Rassovska M 2007 Proceedings of the 16-th Scientific and Applied Science Conference Electronics ET’2007 vol 4 p 121