

Sol-gel TiO₂ films as NO₂ gas sensors

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Abstract. TiO₂ films were prepared by a sol-gel technique with commercial TiO₂ powder as a source material (P25 Degussa AG). After a special treatment, printing paste was prepared. The TiO₂ layers were formed by means of drop-coating on Si-control wafers and on the Au-electrodes of quartz resonators. The surface morphology of the films was examined by scanning electron microscopy (SEM). Their structure was studied by Raman spectroscopy and the surface composition was determined by X-ray photoelectron spectroscopy (XPS). The layers had a grain-like surface morphology and consisted mainly of anatase TiO₂ phase. The sensitivity of the TiO₂ films to NO₂ was assessed by the quartz crystal microbalance (QCM) technique. To this end, the films were deposited on both sides of a 16-MHz QCM. The sensing characteristic of the TiO₂-QCM structure was investigated by measuring the resonant frequency shift (ΔF) of the QCM due to the mass loading caused by NO₂ adsorption. The Sauerbrey equation was applied to establish the correlation between the QCM frequency changes measured after exposure to different NO₂ concentrations and the mass-loading of the QCM. The experiments were carried out in a dynamic mode on a special laboratory setup with complete control of the process parameters. The TiO₂ films were tested in the NO₂ concentration interval from 10 ppm to 5000 ppm. It was found that a TiO₂ loading of the QCM by 5.76 kHz corresponded to a system sensitive to NO₂ concentrations above 250 ppm. On the basis of the frequency-time characteristics (FTCs) measured, ΔF at different NO₂ concentrations was defined, the adsorption/desorption cycles were studied and the response and recovery times were estimated. The results obtained show that the process is reversible in the NO₂ interval investigated. The results further suggested that TiO₂ films prepared by a sol-gel method on a QCM can be used as a sensor element for NO₂ detection.

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1. Introduction

Titanium dioxide (TiO_2) is an extensively explored material because of its attractive properties, such as a high refractive index, a high dielectric constant, a high photocatalytic activity, good physical and chemical stability [1]. This is why TiO_2 has found wide applications in various gas sensors, optical coatings and antimicrobial materials [2]. Thin TiO_2 films have been prepared by various techniques: reactive sputtering and DC magnetron sputtering [3,4], electron-beam evaporation [5], vacuum arc plasma evaporation [6], chemical vapor deposition [7], chemical spray pyrolysis [8], and sol-gel methods [1-2,9-10]. The latter process has a number of advantages over the others, such as low processing temperature, easy control of the chemical composition, easy way of forming homogeneous thin layers.

In the study presented, by using a QCM we investigated the sorption ability to different NO_2 concentration of TiO_2 thin films prepared on the basis of commercial TiO_2 powder (P25 Degussa AG).

2. Experimental

The source material in our experiments was TiO_2 powder (P25 Degussa AG). Printing paste was prepared by mixing the powder with ethyl cellulose and α -terpineol and crushing in an agate mortar for about 20 minutes, as described in [11]. The paste was diluted by toluene in a weight ratio 1:1. The films were deposited on resonators by drop-coating and dried at 120 °C for 30 min.

The films prepared were analyzed by scanning electron microscopy (SEM), Raman Spectroscopy, X-ray photoelectron spectroscopy (XPS), and a gas-sensing test. The surface morphology of the samples was imaged by SEM after consecutive physical vapor deposition of 10 nm thick conductive films of amorphous carbon (C) and gold (Au). The sample observation was performed by a JEM T 200 device (Jeol) in secondary electron imaging mode. The Raman spectra were recorded by a Horiba Jobin Yvon Lab RAM HR800 spectrometer using a 600 l/mm grating and a HeNe laser for excitation. The samples were placed under the 100 \times achromatic objective of a BX41 microscope and measured in back scattering configuration. The XPS measurements were performed by an ESCALAB Mk II (VG Scientific) electron spectrometer with aluminum radiation ($h\nu = 1486,6$ eV). The X-Ray diffraction spectra were collected on a Bruker D8 Advance diffractometer using CuK radiation and a SoIX detector.

The gas sensing properties of the films TiO_2 were studied using 16-MHz QCMs covered with thin TiO_2 films on both sides by drop-coating. The QCMs were fabricated on AT-cut quartz plates with a diameter of 8 mm. Au-electrodes with a diameter of 4 mm and a thickness of 60 nm were evaporated on both sides of the quartz plates thus implementing QCM- TiO_2 systems. The performance of the QCMs and the QCM- TiO_2 systems were evaluated by measuring the motional resistance (R_s) and calculating the quality factor (Q). The sensing properties of QCM- TiO_2 systems were defined by measuring on a laboratory setup; the measurement methodology and the setup were described in detail in [12]. The test gas used in the experiments was 1 % NO_2 . The different NO_2 concentrations in the camera were obtained by altering the ratio of the NO_2 gas and diluting the air flow measured by MFCs. The temperature in the camera was maintained at 24 ± 0.2 °C. The frequency change was registered by a counter connected to the QCM and to a computer. The measurement process involved three stages: purging the camera with the QCM- TiO_2 structure with dry air until the frequency reaches a constant value (F_0); switching on the NO_2 gas flow with a certain concentration and reaching the saturation frequency value (F); purging the camera with dry air to reach the initial value of the QCM- TiO_2 system frequency (F_0). The sensitivity was defined by measuring the time-frequency characteristics (FTCs) of the QCM- TiO_2 system at different NO_2 concentrations (10 ppm-5000 ppm).

3. Results and discussion

3.1. Characterization of TiO_2 thin films and of TiO_2 -QCM system

Figure 1 shows typical SEM images of as-deposited TiO_2 films at a magnification of 20 000. All films fabricated were found to have a grain-like structure. The average grain size was in the interval from 67 nm to 160 nm. Agglomerates of a size of approximately 250 nm were also observed.

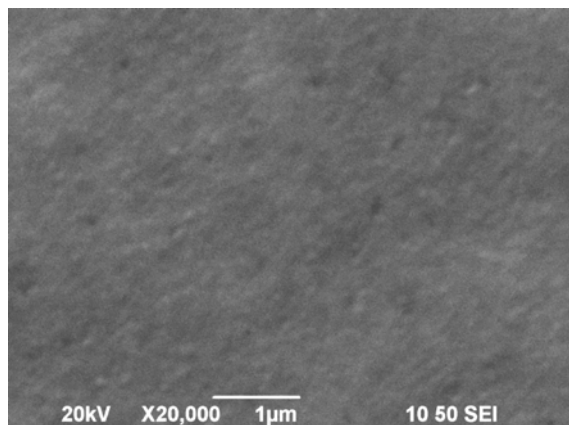


Figure 1. SEM image of TiO_2 films as-deposited on a Au resonator's electrode.

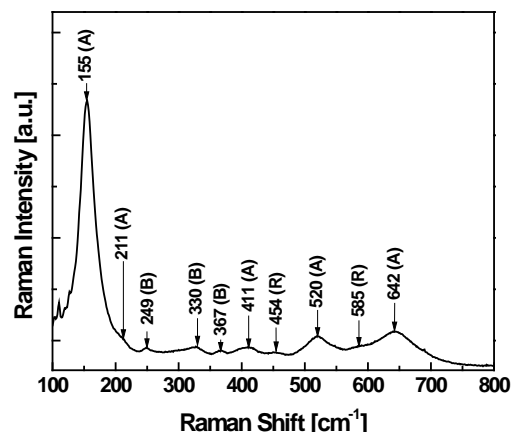


Figure 2. Raman spectrum of a TiO_2 layer; A-anatase, B-brookite, R-rutile.

Figure 2 presents a typical Raman spectrum of the layers measured directly on the resonator. As cited in [13], the starting material (Degussa P25) for the preparation of the printing paste is a mixture of TiO_2 phases, namely, about 80 % anatase, some rutile and an amorphous phase. In the film studied, the anatase is prevalent again as demonstrated by the characteristic peaks in the Raman spectrum [14]. The fact that the intensive low-energy band is shifted from 144 cm^{-1} to 155 cm^{-1} and its width exceeds 30 cm^{-1} shows that the film contains very small anatase crystallites (with a size of less than 10 nm) [15]. The spectrum also exhibits the characteristic rutile bands [15] and the strongest Raman bands of brookite [16]. This demonstrates that the film contains these two phases in smaller amounts.

The $\text{Ti}2\text{p}$ photoelectron spectrum (figure 3) shows a $\text{Ti}2\text{p}_{3/2}$ peak at 459,0 eV. The peak position observed and the doublet separation between the $2\text{p}_{1/2}$ and $2\text{p}_{3/2}$ peaks of $\sim 5.7\text{ eV}$ are characteristic of TiO_2 . The $\text{O}1\text{s}$ spectrum shows a main peak at 530,3 eV, attributed to lattice oxygen, and a shoulder at $\sim 532,2\text{ eV}$, assigned to hydroxyl groups. The valence band spectrum shows a typical TiO_2 structure with two peaks due to $\text{O}2\text{p}$ states. The surface concentrations of O and Ti are 71,3 at. % and 28,7 at. %. The inexact stoichiometry is attributed to the presence of adsorbed oxygen species.

The QCM parameters before and after loading were measured to ensure that the sensing response to NO_2 was the actual films' behavior. The QCM basic parameters, R_s and Q , were in the ranges

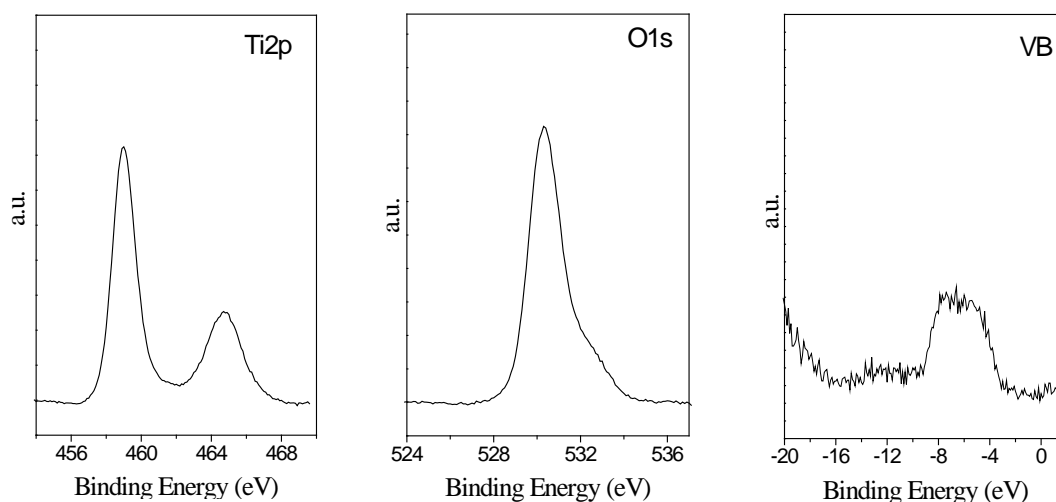


Figure 3. XPS spectra of a sol-gel prepared TiO_2 film.

12 – 20 Ω and 30 000 – 50 000, respectively. The negligible loading (5,76 kHz) of the QCM led to a change in the R_s from 24.95 Ω to 32.24 Ω .

3.2. TiO_2 films' sensing properties to NO_2

All measurement were based on Sauerbrey' formula, who was the first to derive the quantitative relationship between the change in the frequency of an AT-cut piezoelectric crystal (F_0) and the mass change (Δm) caused by mass loading on the piezoelectric crystal surface [17].

$$\Delta F = (2.3 \cdot 10^6 F_0^2 / A) \Delta m, \quad (1)$$

where F_0 (106 Hz) is the basic frequency of the unloaded piezoelectric crystal, Δm (g) is the change in the mass on the surface of the crystal, and A (cm^2) is the surface area of the electrode [18]. In our experiments $A = 0,1256 \text{ cm}^2$. Thus, using eq. (1) one can calculate the mass (Δm) of the adsorbed gas by measuring the resonant frequency shift ($\Delta F = F - F_0$).

In the NO_2 range measured (10 ppm-5000 ppm), the system's minimal sensitivity was found to be 250 ppm. Figure 4 presents typical FTCs for a TiO_2 -QCM structure at two NO_2 concentrations. In a chamber containing a test gas, the TiO_2 film adsorbs NO_2 molecules on its surface, thus mass-loading the QCM and lowering its resonance frequency. The sorption process continues until a dynamic equilibrium is reached. As the test gas flow is switched off, the opposite process begins – NO_2 molecules desorption leading to a diminished mass load and an increased resonance frequency. The two curves in figure 4 have similar behavior in spite of the different concentrations. The FTCs curves obtained proved that the adsorption/desorption process is reversible and typical for physisorption. The frequency shift rises from 18 Hz to 30 Hz as the NO_2 concentration is raised from 1000 to 5000 ppm.

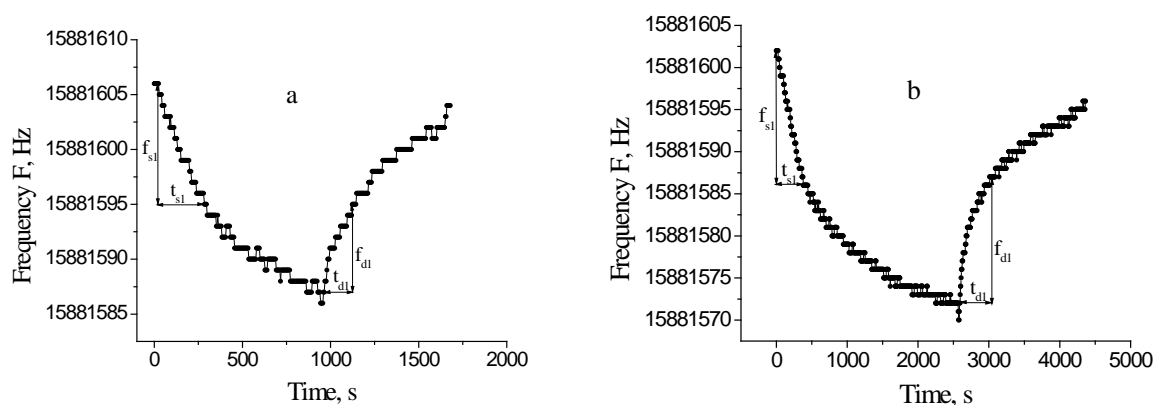


Figure 4. FTC of TiO_2 -QCM structure at NO_2 concentration: a)-1000 ppm, b)-5000 ppm.

One can clearly see the existence of a two-step (a fast one and a slower one) sorption-desorption process. In figure 5, the response-time (t_{s1}) variation in the fast sorption step is illustrated as a function of the NO_2 concentration. As the NO_2 concentration is raised, t_{s1} rises from 3 minutes at 250 ppm to 5,6 minutes at 5000 ppm NO_2 . The calculated sorption rate during the first step (v_{s1}) of the response time increases from 0,82 Hz/min to 2,85 Hz/min as a function of the NO_2 concentration. We also measured the desorption times and calculated the desorption rates during the first step of the structure's recovery (t_{d1} , v_{d1}). We established insignificant rises in t_{d1} and v_{d1} – from 4,5 to 5,66 minutes and from 1,77 to 2,47 Hz/min for all NO_2 concentrations.

Figure 6 shows the response of the TiO_2 -QCM structure versus the NO_2 concentration. Using the FTCs, and in accordance with Sauerbrey's equation, the total $\Delta F = F - F_0$ was calculated for each concentration, together with the corresponding sorbed mass increases for each ΔF . Thus, figure 6 illustrates that the frequency shift increases from 7 Hz to 30 Hz as the sorbed mass increases (with the NO_2 concentration) from 1.54 ng to 6.53 ng, respectively.

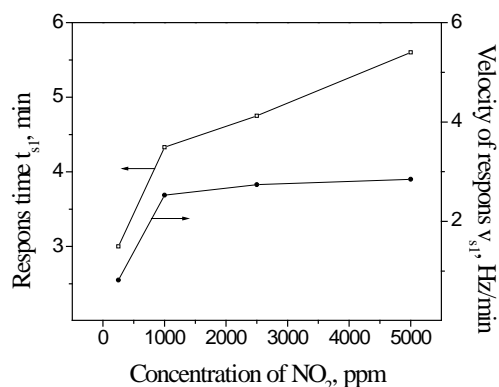


Figure 5. The TiO₂-QCM response and rate of response versus the NO₂ concentration.

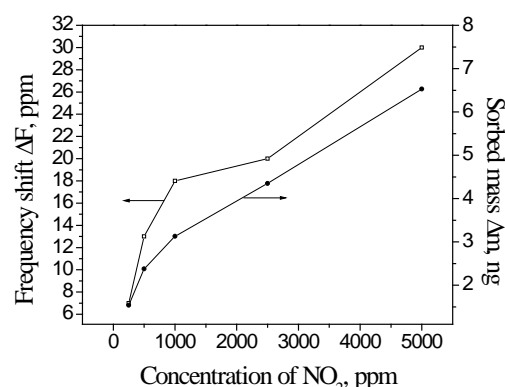


Figure 6. Dependence of the TiO₂-QCM frequency shift and sorbed mass versus the NO₂ concentration.

4. Conclusions

TiO₂ films prepared by a sol-gel technique on QCMs were investigated in view of application as NO₂ sensors. The films had a grain-like structure and contained predominantly an anatase phase. The adsorption/desorption process of NO₂ was studied and was found to be reversible and typical for physisorption. The lower sensitivity limit of the TiO₂ films was determined to 250 ppm. A TiO₂ loading (5,76 kHz) of a QCM is sufficient to implement a NO₂ sensitive system. The results obtained are very promising, but it is necessary to optimize the preparation conditions, the structure of the films, and to define the higher loading of the QCM in order to improve the TiO₂ sensitivity.

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