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QCM gas sensor characterization of ALD-grown very thin TiO₂ films

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Abstract. The paper presents a technology for preparation and characterization of titanium dioxide (TiO₂) thin films suitable for gas sensor applications. Applying atomic layer deposition (ALD), very thin TiO₂ films were deposited on quartz resonators, and their gas sensing properties were studied using the quartz crystal microbalance (QCM) method. The TiO₂ thin films were grown using Ti(iOPr)₄ and water as precursors. The surface of the films was observed by scanning electron microscopy (SEM), coupled with energy dispersive X-ray analysis (EDX) used for a composition study. The research was focused on the gas-sensing properties of the films. Films of 10-nm thickness were deposited on quartz resonators with Au electrodes and the QCMs were used to build highly sensitive gas sensors, which were tested for detecting NO₂. Although very thin, these ALD-grown TiO₂ films were sensitive to NO₂ already at room temperature and could register as low concentrations as 50 ppm, while the sorption was fully reversible, and the sensors could be fully recovered. With the technology presented, the manufacturing of gas sensors is simple, fast and cost-effective, and suitable for energy-effective portable equipment for real-time environmental monitoring of NO₂.

1. Introduction

TiO₂ is one of the most extensively studied transition metal oxides. Nowadays, TiO₂, as an n-type semiconductor, is widely explored for photocatalysis, gas sensing and various optical applications [1,2]. Although in the last decades the gas sensing properties of TiO₂ thin films have been thoroughly researched, still knowledge is lacking on the gas sensing of very and ultra-thin films with thicknesses of several nanometers.

The quartz crystal microbalance (QCM) is a popular technique of detecting the mass of thin layers deposited on the crystal surface on a sub-nanogram level, but it could also be applied for monitoring the adsorption of nano amounts of various toxic gases [3,4]. Since only the surface properties of the films are relevant to gas sensors based on the QCM method, ALD-grown very thin films are very promising for implementation of gas sensors.

ALD is based on successive, alternating surface-controlled reactions from gas phase to produce highly conformal and uniform thin films, with thickness control of sub-nanometer precision [5,6]. In ALD, the adsorption of reactants is self-limited and the various precursors meet only on the surface of

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the substrate. This self-limiting growth leads to the many advantages of ALD. ALD can provide thickness control at an atomic level, as the film thickness can be programmed easily by the number of ALD cycles. Not only the thickness, but also the composition of the film can be controlled precisely. With these advantages, ALD has emerged as a powerful tool in many research and industrial applications [7,8].

A large number of techniques have been developed for environmental monitoring and control of the toxic gases. Gas sensors based on wide-band gap semiconductors, as SnO_2 , TiO_2 , WO_3 , MoO_3 , ZnO , In_2O_3 etc. have been widely investigated for sensing different toxic gases [9–15]. Many of these devices often require high operation temperatures, generally within the range from 200 °C up to even 500 °C [16]. Also, they are usually not suited to performing high-precision measurements of gas concentrations, but only to detecting the presence of target gases and issuing a warning if certain threshold values are attained.

Detection of NO_2 has lately become a very important task, since it is a pollutant abundant in the atmosphere over large cities, mainly because of the increasing amounts of combustion exhaust gases that can cause respiratory irritation even in very small concentrations, as low as 15-25 ppm [17]. The technology described here, namely, using a QCM with an ALD-grown very thin TiO_2 film presents an effective way for real time detection of NO_2 in the environment.

Previously, prototype QCM gas sensors with several transition metal oxide films (e.g. MoO_3 , TiO_2 , WO_3) were already prepared by our team and tested for sensitivity to NO_2 and NH_3 in a specially designed laboratory set-up [11,14,18–22]. Among others, the sensing capability was explored of PVD and ALD grown TiO_2 thin films to NO_2 . These films were mostly prepared by sputtering [19,21], and only in one case ALD was also used for TiO_2 film growth [22]. As a follow up of the previous studies, in the research presented we focused our effort on the sensing behavior of very thin TiO_2 films grown by ALD.

2. Experimental

The films were grown by ALD in a Picosun SUNALE R-100 reactor at a 200-°C substrate temperature with titanium tetraisopropoxide ($\text{Ti}(\text{iOPr})_4$, TTIP) and H_2O as precursors. The precursor pulse times were 0.1 s for both TTIP and H_2O . The TTIP precursor was heated at 70 °C in order to reach a sufficient partial pressure of its vapor. The purge time was 3 s after the TTIP pulse and 4 s after the H_2O . Nitrogen was used as a carrier gas, while the overall pressure in the reactor chamber was ~10 mbar. TiO_2 thin films were deposited either on quartz resonators, which were used for the gas sensing tests to NO_2 , or on Si substrates, which were used for further characterization of the films.

The film morphology was investigated by SEM and the composition was studied by energy dispersive X-ray analysis (EDX) on a JEOL JSM-5500LV scanning electron microscope. The thickness of the films was measured by UV-Vis reflectometry using an Avaspec-2048 spectrophotometer.

The sensing tests were performed using quartz resonators produced on 8-mm polished AT-cut quartz plates with thermally evaporated gold electrodes (diameter of 4 mm and thickness of about 120 nm with a Cr underlayer) on both sides [14,22]. Their working resonance frequency was around 16 MHz. The initial parameters of the resonators and their quality were evaluated by measuring the equivalent dynamic parameters, static capacitance C_0 and equivalent dynamic resistance R_q using a selective level meter. The dynamic capacitance C_q , the dynamic inductance L_q , and the quality factor Q were calculated. The gas sensing was tested in a home-made measurement system, which was described in detail previously [18].

The sorption properties of the TiO_2 films were evaluated by measuring the resonance frequency shift of the QCM structures covered by the TiO_2 thin films at various NO_2 concentrations. The measurement was performed in the following way: first, purging the structures by dry air, then creating a certain concentration of the measured gas in the chamber until reaching saturation of the frequency values; after that, again purging by dry air thus restoring the sensor and preparing it for a new measurement. The NO_2 concentration in the test chamber was controlled by mass flow controllers (MFCs) for NO_2 and diluting gas flow (synthetic air). The QCM frequency was registered by a Hameg

8123 frequency counter connected to the QCM and to a computer for data recording. The relative error of the frequency measurement was $\pm 5.25 \times 10^{-7}$. The measurements were based on the correlation between the frequency shift and the additional mass loading the resonator, namely, Sauerbrey's equation for AT-cut quartz [23] describing the relation between the mass of the thin film deposited on the quartz crystal and the corresponding change in the resonance frequency; the absorbed mass was thus calculated [11,14,23].

3. Results and discussion

Very thin TiO_2 films were deposited by ALD on both QCMs and Si substrates. With 200 ALD cycles, films with a thickness of ~ 10 nm were grown; the thickness was evaluated based on the UV-Vis reflectometry measurement of the reference TiO_2 thin films deposited on Si wafers.

SEM coupled with EDX was used to study the morphology and composition of the as-deposited films. According to the SEM images (inset of figure 1), the films were of good quality, homogeneous, uniform, and without cracks or defects. We have to note that the object shown is an untypical impurity used just for focusing. The successful deposition of TiO_2 was clearly proved by the presence of Ti in the EDX spectrum of the reference TiO_2 film grown by ALD on the Si wafer (figure 1). The results from the composition analysis are presented in the inset. The EDX is simple, fast and cost-effective method (compared with alternative ones like XPS) to prove a successful deposition of very thin TiO_2 films [6, 22]. The EDX study had only qualitative character, since the information depth of EDX is ca. 500 nm; thus, the majority of the EDX signal comes mainly from the substrate and only a small portion originates from the TiO_2 film.

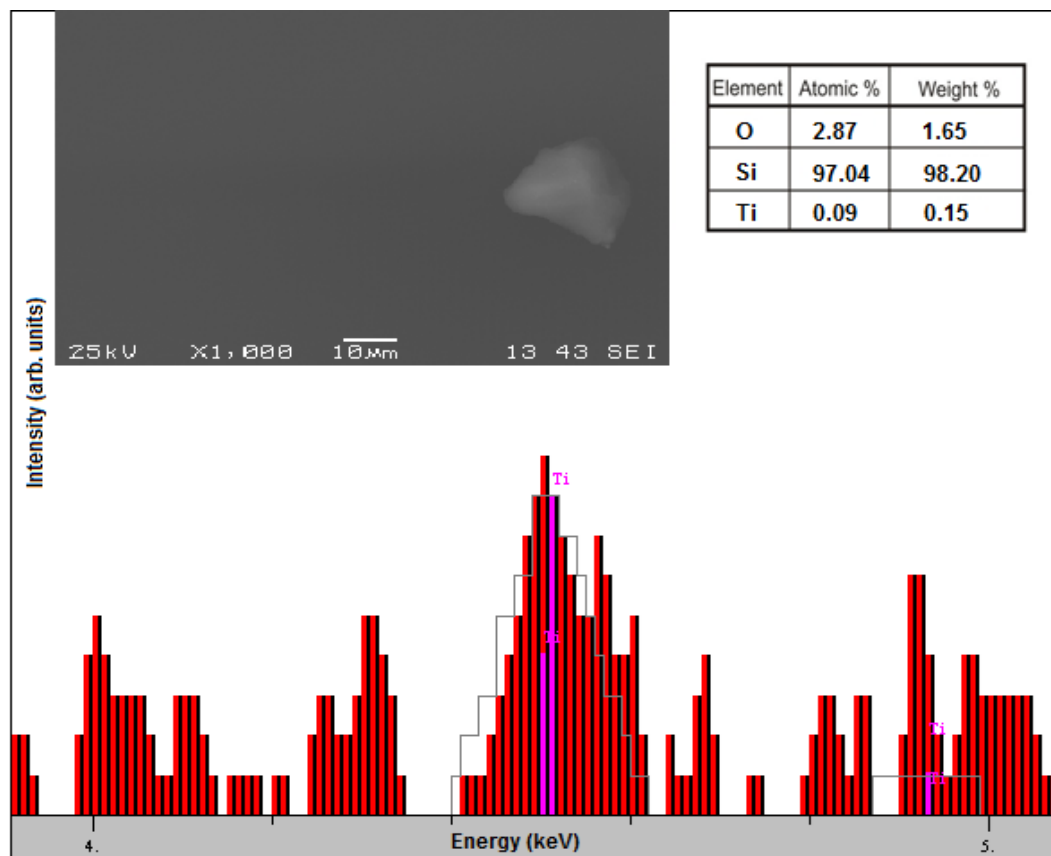
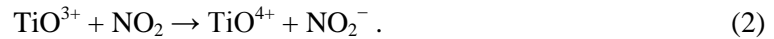
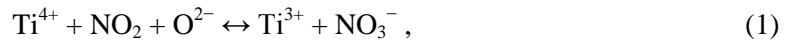
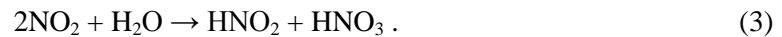


Figure 1. Ti peak in the enlarged EDX spectrum, together with a SEM image of the studied area (the center of the clean film area), and concentration analysis results of the reference TiO_2 film grown by ALD on a Si wafer.

At room temperature in the presence of oxygen and under anhydrous conditions, NO₂ is adsorbed on the surface of TiO₂ according to the following reactions [16, 24]:



In fact, the mechanism of NO₂ adsorption on TiO₂ is much more complicated, and includes also catalytic reactions. Also, under actual sensor operation conditions, a complete elimination of humidity is practically impossible. In the presence of humidity, co-adsorption of water molecules occurs on the TiO₂ surface, which leads also to the formation of nitric acids [16, 25]:



This leads us to the paramount importance of detecting and eliminating the influence of water vapor on the NO₂ sensor operation, as it will result in errors in evaluating the amounts of NO₂ detected. Thus, as a first step of the test measurements of NO₂ concentration, a saturation of the sensor to water vapor was performed and its influence was eliminated from the calculations of the detected NO₂ mass. Figure 2 presents the sorption ability of the QCM sensor with an ALD-grown TiO₂ layer sensitive to H₂O vapor. The sensing was tested at a temperature of 24 °C and relative humidity of air (RH) of 63%. It can be seen that the H₂O adsorption is a relatively fast process and the saturation is reached in less than a minute (~50 s), while the frequency change is ~40 Hz. The study was performed after the TiO₂–QCM structure was tested to NO₂ (and restored) several times.

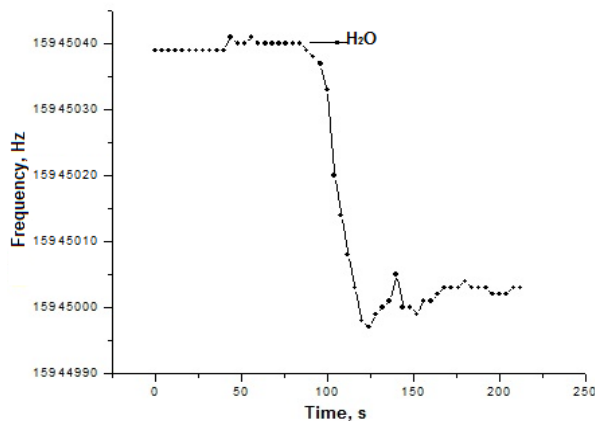


Figure 2. FTC of a QCM with ~10-nm ALD-grown TiO₂ thin film during saturation by water vapor.

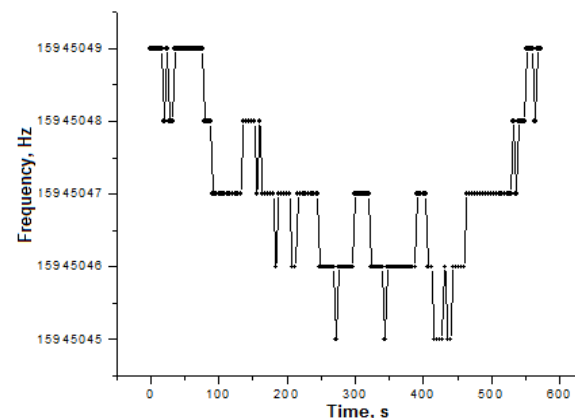


Figure 3. FTC of a QCM with ~10-nm ALD-grown TiO₂ thin film during saturation and recovery at NO₂ concentration of 100 ppm.

The gas sensing properties of the TiO₂ films to NO₂ were tested with concentrations in the interval between 10 ppm and 5000 ppm. The films were found to be sensitive even at 50 ppm (figure 3), but at such concentrations their sensitivity was very weak and the frequency change (Δf) observed was just 4-5 Hz, while the sorption and desorption processes were quite dynamic.

Typical FTCs for a well-working sensor were observed at slightly higher concentrations, for example at 500 ppm. At such a concentration, the response of the sensor was fast (few s), and its sensitivity vs. concentration was close to linear. Figure 4 illustrates the gradual loading of the QCM by increasing concentrations of 500 ppm, 1000 ppm and 5000 ppm. The loading processes with these three different concentrations were all measured for 7 min (420 s) with 3-min (180 s) desorption time. First, the sensing structure was tested for the sorption of the first 7 min after introducing 500 ppm NO₂ in the chamber, afterwards three minutes were allowed for desorption, and then the concentration was increased to 1000 ppm and measured for the next 7 min; then, similarly, the concentration was

increased to 5000 ppm. The graph is stepwise and represents the non-linearity of the sorption process, and that it differs at different concentrations. Usually, the sorption was faster and exponential in the first moments after introducing a certain NO_2 concentration; afterwards the sorption process decelerated until gradually reaching saturation. As the NO_2 concentrations was increased, the sorption accelerated, but longer times were needed to reach saturation. Consequently, the desorption also took longer until all the mass was released from the sensing structure to fully recover for the next measurement cycle. It has to be stressed that the recovery was complete, and the initial values of the resonator were achieved after removing the NO_2 gas from the chamber. The sorption was considered to be a fully physical process, as shown by the full recovery of the sensor for a relatively short time, even after having detected the high concentration of 5000 ppm of NO_2 . Figure 4 leads us to the conclusion that the loading ability of the sensing structure increases with the concentration, so that it can successfully detect higher concentrations.

Sauerbrey's equation [23] allows one to study the correlation between the concentration of NO_2 , the frequency shift measured and the corresponding mass of gas molecules sorbed on the QCM structure. Figure 5 presents the frequency shift measured by the mass loading (proportional) at different NO_2 concentrations, from 50 ppm to 5000 ppm. The graph was built using the measurements for the gradual loading (presented in figure 4). The graph is interpolated, but allows us to conclude that for the lower concentrations the frequency shift and, consequently, the detected mass are linearly proportional to the concentrations measured. The films have higher sensitivity for lower concentrations; afterwards the sorption increases gradually, but it is also slower because of the gradual saturation of the sensing surface. The sorbed mass, calculated according to the Sauerbrey equation [23], was around 9 ng for a NO_2 concentration of 50 ppm, and reached 49 ng for 5000 ppm.

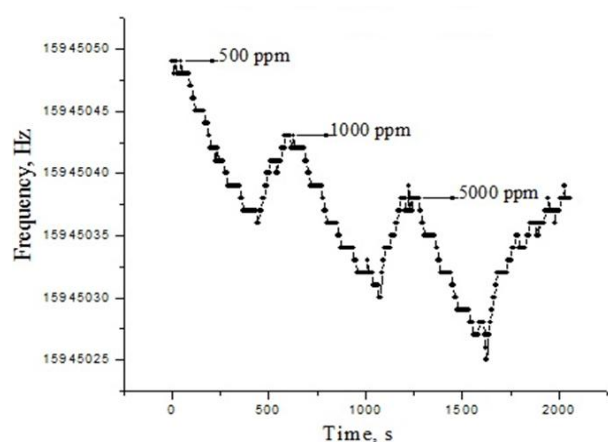


Figure 4. FTC of QCM with ~10-nm ALD-grown TiO_2 during gradual loading by NO_2 concentrations of 500, 1000 and 5000 ppm.

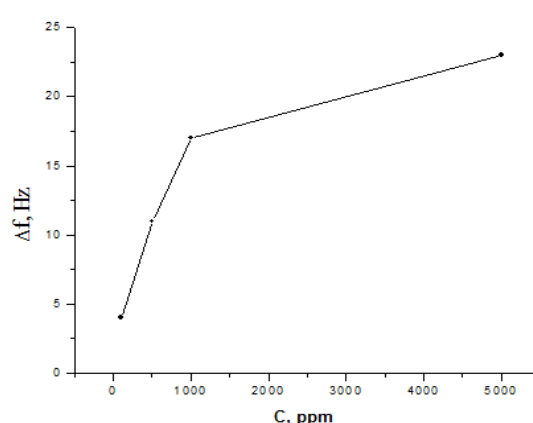


Figure 5. Measured frequency shift of a QCM sensor with an ALD TiO_2 film vs. the NO_2 concentration.

In our previous study, similar results for the sensitivity to NO_2 were obtained for several times thicker TiO_2 films deposited by reactive sputtering [21]. When using the QCM method, which allows high sensitivity while detecting very small concentrations, the thickness of the sensing layer and, consecutively, its load on the resonator is of importance, especially for a QCM working at a high frequency, since the higher loads on the resonator decrease the sensitivity of the gas sensor; thus, using as thin as possible sensing layer is desirable. The results presented here are very promising, as they show that very thin ALD-grown TiO_2 films possess good sensitivity to NO_2 and can be competitive with much thicker films obtained by other techniques.

However, even though our results show that very and ultra-thin ALD TiO_2 films have the required sensitivity for NO_2 sensing, still their sensitivity need to be improved to detect very low

concentrations, as it is required of the modern gas sensors. One approach to increasing further the sensitivity of such sensors is by preparing a nanostructured sensing surface to increase the surface area or/and to combine sensitive materials by preparing nanocomposites [16,26]. But here many new problems arise, connected with the preparation of the QCM sensors with nanostructured surface and their stability, long-term usage and cost-effectiveness. Also, the nanocomposites used for gas sensing at room temperature may have a higher sensitivity, but their selectivity is lower. As a follow-up of the present study, the new challenge should be not only implementing ultra-thin films for gas sensing, but also combining such nanolaminates and nanocomposites of various materials, creating nanostructured morphology on the sensing electrodes, while at the same time making steps towards improving the selectivity of the sensors.

4. Conclusions

Very thin (~10 nm) TiO₂ films were grown on QCM by ALD and their sensitivity to various concentrations NO₂ was studied. These very thin ALD TiO₂ films showed good sensitivity to NO₂ at room temperature and a capability to register as low concentrations as 50 ppm. The sorption was fully reversible, and the sensors were able to recover in a short time. The ALD method was found to be suitable for fast and cost-effective deposition of TiO₂ thin films for QCM gas sensor applications. These promising results for sensitive films with thickness of less than 10 nm raise the hope that, after a further study and development, even ultra-thin ALD TiO₂ films of a few nm could be implemented in gas sensing devices for NO₂ monitoring.

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