Gas sensing properties of very thin TiO_2 films prepared by atomic layer deposition (ALD)

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Abstract. Very thin titanium dioxide (TiO_2) films of less than 10 nm were deposited by atomic layer deposition (ALD) in order to study their gas sensing properties. Applying the quartz crystal microbalance (QCM) method, prototype structures with the TiO_2 ALD deposited thin films were tested for sensitivity to NO_2. Although being very thin, the films were sensitive at room temperature and could register low concentrations as 50-100 ppm. The sorption is fully reversible and the films seem to be capable to detect for long term. These initial results for very thin ALD deposited TiO_2 films give a promising approach for producing gas sensors working at room temperature on a fast, simple and cost-effective technology.

1. Introduction

Nowadays TiO_2 in thin film form is one of the most extensively studied transition metal oxides. TiO_2 as n-type semiconductor is widely studied mainly for photocatalysis and gas sensing [1]. But it is also an excellent material for many solid-state devices including various optical applications [2], solar cells [3], corrosion-protective coating, gate insulator in MOSFETs and many others [1].

The gas sensing properties of TiO_2 thin films have been widely researched. Nevertheless, still there is lack of knowledge about the gas sensing of ultra thin films with thicknesses of a few nanometers.

ALD is a vapor phase deposition technique based on successive, alternating surface controlled and self-limiting reactions to produce highly conformal and uniform thin films with thickness control of sub-nanometer precision and capable of producing thin films of a variety of materials. ALD also offers exceptional thin film conformality on high-aspect ratio structures and tunable film composition. With these advantages, ALD has emerged as a powerful tool for many industrial and research applications [4-11].

A large number of techniques have been developed for environmental monitoring and control of the toxic gases. Semiconductor thin films such as TiO_2, SnO_2, WO_3, MoO_3 and ZnO have been widely investigated for sensing different toxic gases. These devices are usually not suited to make high precision measurements of gas concentrations but to detect the presence of target gases and give a warning if several threshold values are attained [11-19].

The quartz crystal microbalance (QCM) is a well-established tool for monitoring the adsorption of nano amounts of materials and for detecting physical properties of thin layers deposited on the crystal surface [20,21]. Compared with other sensors, the advantages of QCM sensors are the simple technological implementation, capability of operating at room temperature, good sensitivity and working process reversibility, low consumption and easy real-time monitoring. The QCM-based techniques attract particular interest due to their high sensitivity in the nanogram range and capability of detecting very small amounts. The analytical performance of such sensors strongly depends on the properties of the sensing coating deposited on the QCM electrodes.

Prototype QCM gas sensors with several transition metal oxide films were already made by our team and tested for sensitivity to NO_2 and NH_3 in a specially designed chamber. Among others, the sensing behavior of sputtered TiO_2 thin films towards NO_2 were investigated [22-24].

As a follow up of the previous studies, in the present research we focused on the sensing behavior of very thin TiO_2 films produced by atomic layer deposition (ALD). TiO_2 ALD films were grown 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 ALD grown films.

2. Experimental

The films were prepared using ALD deposition performed in a Picosun SUNALE R-100 reactor at 200^{o}C substrate temperature with titanium tetraisopropoxide (TTIP) and H_2O as precursors. The TTIP precursor was heated at 70^{o}C in order to reach sufficient partial pressure of its vapor. Nitrogen was used as carrier gas while the overall pressure in the reactor chamber was ~10 mbar. The precursor pulse times were 0.1 s for both TTIP and H_2O. The purge time was 3 s after the TTIP pulse and 4 s after the H_2O. TiO_2 thin films were deposited in 150 ALD cycles on both quartz resonators and Si wafers.

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

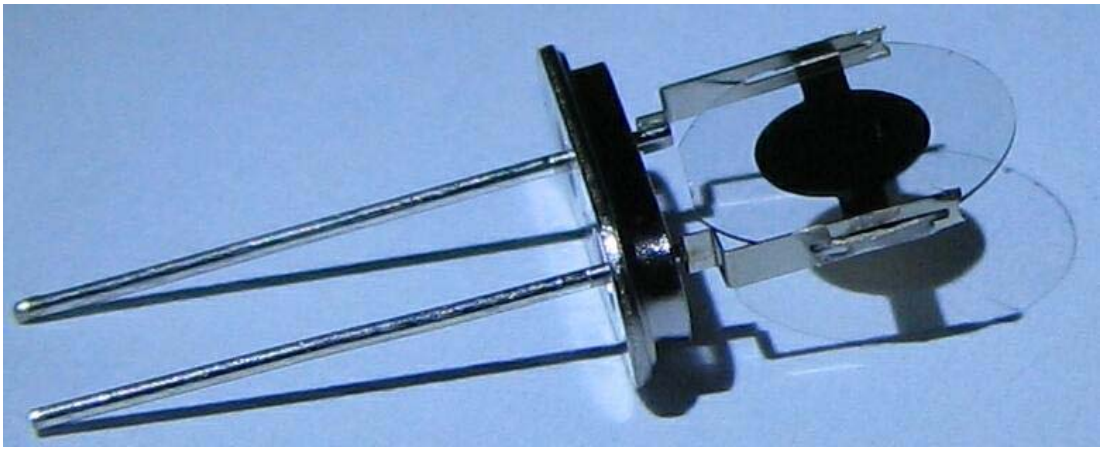

Figure 1. Image of the test sensor device based on QCM.

The sensing properties of the films were studied using quartz resonators and applying the QCM method. The tests were performed with resonators produced 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 (figure 1). Their working resonance frequency was around 16 MHz. The initial parameters of the resonator and its quality were evaluated by measuring the equivalent dynamic parameters: static capacitance C_0 and equivalent dynamic resistance Rq using a Selective Level Meter. The dynamic capacitance Cq, the dynamic inductance Lq, and the quality factor Q were obtained by calculation [25]. The sorption of NO_2 was tested in a special home-made measurement system, which was described in details previously [22].

The sorption properties of the TiO_2 films were evaluated by measuring the resonance frequency shift of the QCM structures covered with the TiO_2 thin films at different NO_2 concentrations. The main stages of the measurement consisted of (i) purging of the structures with dry air; (ii) creating a certain concentration of the measured gas in the chamber; (iii) reaching saturation of the frequency values; (iv) purging of the structures with dry air thus restoring the sensor and preparing it for new measurement. The NO_2 concentration in the test chamber was controlled by mass flow controllers (MFCs) for NO_2 and diluting gas flow. The experiments were carried out at constant room temperature. The QCM frequency was registered by frequency counter Hameg 8123 connected to the QCM and to a computer for data recording. The relative error for frequency measurement was ± 5.25×10^{-7}. The measurements were based on the correlation between the frequency shift and the additional mass loading the resonator. Sauerbrey [26] 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 resonance frequency, thus allowing the absorbed mass to be calculated. The desorption (recovery) time, t_d, was also measured.

3. Results and discussion

Very thin TiO_2 films with a thickness less than 10 nm were deposited by ALD on both QCMs and Si substrates. With 150 ALD cycles a thickness of ~ 8 nm was achieved, based on the UV-Vis reflectometry measurement of the reference TiO_2 thin films deposited on Si wafers.

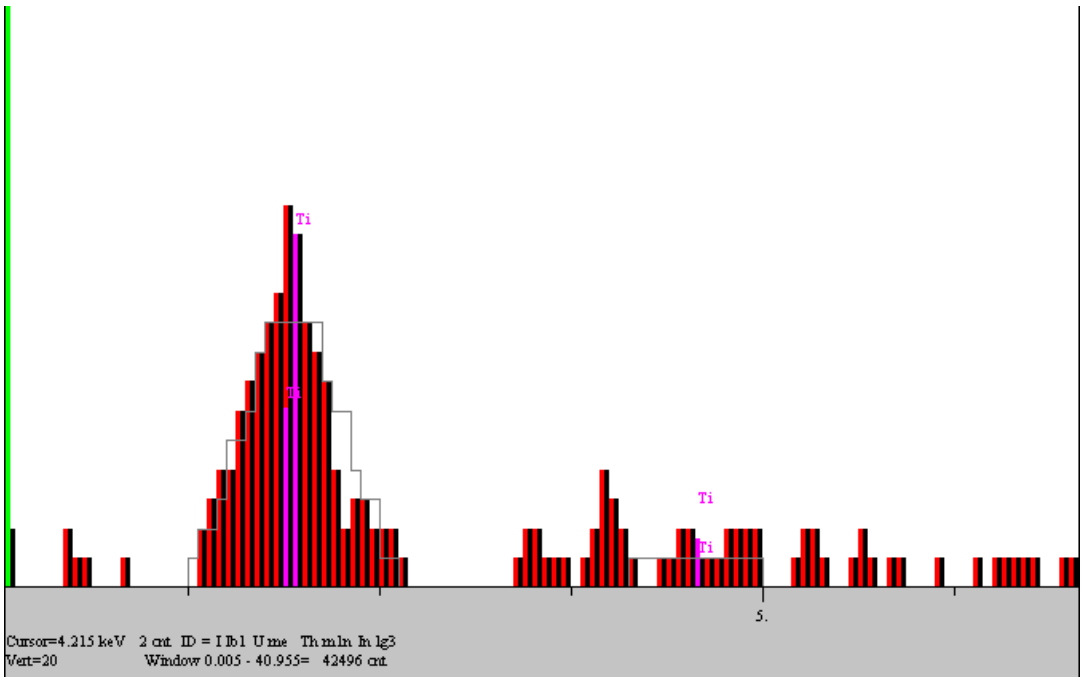

Figure 2. Ti peak in the enlarged EDX spectrum of the reference TiO_2 film grown by ALD on a Si wafer.

After the ALD deposition the film morphology was examined by SEM and their composition was studied by EDX. According to SEM images (not shown here), the films were of good quality,

homogeneous, uniform, and without cracks or defects. The successful deposition of TiO_2 was clearly shown by the presence of Ti in the EDX spectrum of the reference TiO_2 film grown by ALD on the Si wafer (figure 2). At this very small TiO_2 film thickness the EDX method had quite big inaccuracy of the oxygen detection, due to receiving signal mainly from the substrate covered by a native oxide layer, and also because adsorbed H_2O could be present on the surface of TiO_2. Thus, the EDX study had only qualitative character and was useful mainly to prove the successful deposition of the very thin TiO_2 films. Results from the EDX study of the reference 8 nm TiO_2 film deposited by ALD on the Si substrate are presented in table 1.

Table 1. EDX results for the ~8 nm thick reference TiO_2 film deposited by ALD on a Si wafer.

Element	**Atomic Wt %**	**Weight %**
O	2.68	1.54
Si	97.12	98.22
Ti	0.14	0.24

The gas sensing properties of the TiO_2 films were tested with concentrations in the interval between 10 ppm and 5000 ppm. The films were found to be sensitive even at 50-100 ppm, but at such concentrations their sensitivity was very week and the observed frequency change (Δf) was 3-4 Hz. Typical frequency-time characteristics (FTC) for a well-working sensor were observed at 1000 ppm (figure 3). The response of the sensor was fast (few s), and its sensitivity vs. concentration was close to linear. The recovery was also in a few s timescale. In addition, 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, shown by the full recovery of the sensor for comparably short time.

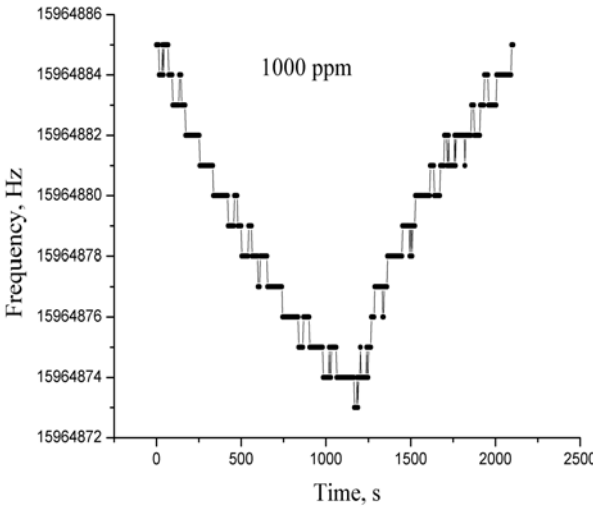

Figure 3. FTC of QCM with ~8 nm ALD deposited TiO_2 thin film during saturation and recovery at NO_2 concentration of 1000 ppm.

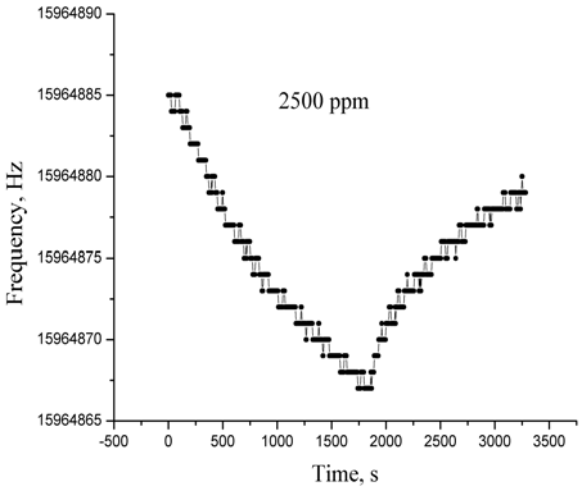

Figure 4. FTC of QCM with ~8 nm ALD deposited TiO_2 thin film during saturation and recovery at NO_2 concentration of 2500 ppm.

At higher concentrations the kinetics of the sorption process was even better expressed and faster. At concentration of 2500 ppm the change of frequency until reaching saturation was $\Delta f = 18$ Hz. The sorption was still physical and the resonator could be fully recovered but the recovery times were longer. The FTC at 2500 ppm is presented in figure 4.

In our previous studies similar results were observed for several times thicker TiO_2 films obtained by reactive sputtering and other methods [22-24]. Here, the results for the sensitivity to NO_2 of the very thin ALD TiO_2 films are very promising. They indicate that even ultra thin films can be implemented in such QCM gas sensors where only the surface properties of the TiO_2 films are used.

The present results are very promising, as they show that even ultra thin ALD TiO_2 films have the required sensitivity for NO_2 sensing. Therefore, these layers can be implemented in QCM gas sensors, because only the surface properties of the films are relevant for such applications.

4. Conclusion

Very thin (~8 nm) TiO_2 films were deposited by ALD and their sensitivity to NO_2 was studied applying the QCM method. Even these very thin ALD TiO_2 films showed good sensitivity to NO_2 at room temperature and capability to register as low concentrations as 50 ppm. The sorption was fully reversible. The ALD TiO_2 films were of good quality, stable and seemed capable for measurements for long terms. The ALD method was found to be suitable for fast and cost-effective deposition of TiO_2 thin films for QCM gas sensor applications.

The main conclusion based on the results obtained is that QCM structures covered with very thin ALD TiO_2 films are suitable for NO_2 detection. These promising results for sensitive films with thickness of less than 10 nm give a hope that, after a further study and development, ultra thin TiO_2 films could be used for gas sensing.

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