Detection of NH₃ by quartz crystal microbalance coated with TiO₂

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Abstract. A quartz resonator with a thin TiO₂ film is investigated in view of possible applications as a sensor for detecting the presence of ammonia in the ambient. A study of the sorption properties of thin TiO₂ films to NH₃ vapors is also presented. The films are deposited using electron beam evaporation. In order to determine the sorption ability of TiO₂ to NH₃, a quartz crystal microbalance (QCM) with a thin TiO₂ film is used, the latter serving as a receptor for the NH₃ gas. The AT-cut 16-MHz quartz resonator allows conversion of the additional mass load that occurs as a result of sorption into a frequency shift. The experiments are carried out by measuring the QCM resonant frequency shift due to the absorption of vapors from an aqueous solution of NH₃ with different concentration ranging from 100 to 1000 ppm. The experimental results obtained indicate that the variation of the resonant frequency is a function of the ammonia concentration. This demonstrates that a QCM covered with a thin TiO₂ layer is sensitive to ammonia vapors at room temperature and is capable of detecting NH₃ concentrations in the range investigated (100-1000 ppm).

1. Introduction
The quartz crystal microbalance (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 [1,2]. Compared with others sensors, the advantages of QCM are: simple technological implementation, capability of operating at room temperature, good sensitivity and chemical process reversibility. Different types of metallic oxide films have been studied in view of improving the sensing properties of the QCM [3, 4]. In this paper we present results on the performance of a QCM covered with e-beam evaporated TiO₂ when measuring ammonia vapor concentrations at room temperature.

2. Experimental
The possibility of e-beam evaporated TiO₂ to sorb NH₃ was estimated using a QCM method. An AT-cut quartz crystal microbalance was constructed using an 8-mm polished quartz plate with golden electrodes (diameter 4mm and thickness 60 nm) evaporated on both sides. QCM resonance frequency of 16 MHz was thus obtained. The piezoelements thus prepared were covered with a thin TiO₂ layer on both sides.
The electron beam evaporator shown in figure 1 consists of a heated tungsten filament $F$ apertured with a screen $W$ surrounding the filament. Both the apertured anode $A$ and the crucible are at ground potential. Accelerating voltage $U_a$ is applied to the filament and to the screen. The magnetic field $B$ is created by an electromagnet. The evaporation power $P_{ev}$ needed to heat the crucible containing TiO$_2$-powder (the evaporated material) is controlled. The process was carried out at initial vacuum of $7 \times 10^{-4}$ Pa and operational-mode vacuum of $3 \times 10^{-3}$ Pa. The deposition rate at those conditions was 50 nm/min.

The refractive index and thickness of the TiO$_2$ layers were determined by ellipsometric measurements on a control silicon wafer. A Rudolph 435 ellipsometer at wavelength of 632.8 nm was used.

![Figure 1. Electron beam evaporator:](image)

1 – control unit, 2 – pulse time modulator, 3 – ramp generator and final control element (FCE).

Using a SEM-Philips 515, we determined the surface morphology of the TiO$_2$ layers deposited on the resonators. Some equivalent dynamic parameters of the QCM, as the static capacitance, $C_0$, and the equivalent dynamic resistance, $R_q$, were measured by a Selective Level Meter. Other parameters, as the dynamic capacitance, $C_q$, the dynamic inductance, $L_q$, and the quality factor, $Q$, were calculated [5].

The sorption properties of TiO$_2$ 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 H$_2$O molecules on the NH$_3$ sorption, each sample was saturated with water vapor preceding the measurement over the ammonia solution. The frequency defined over the water was taken as an initial value for the subsequent measurements. Besides being highly sensitive to mass changes, the QCM frequency is also sensitive to temperature variations. To eliminate the 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, $\Delta f$, was measured and the sorbed mass was calculated by the Sauerbery’s equation, which gives a linear relationship between the $\Delta f$ and the mass adsorbed on the electrode.
surface [6]. This equation and its various refinements generally assume that the mass is uniform and fully attached to the QCM surfaces – in many cases this is a good approximation [7]. According to the Sauerbery’s equation developed for an AT-cut quartz crystal ($\Delta f = -2.26 \times 10^6 \times f^2 \times \Delta m/S_\perp$), for each value measured of $\Delta f$; the NH$_3$ mass sorbed ($\Delta m$) can be calculated when one knows the initial $f$ 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 were described in detail in [8].

3. Results and discussion
The TiO$_2$ films were characterized by SEM and ellipsometric measurements. The films are smooth and amorphous. The negligible difference observed between the morphology of the TiO$_2$ films can be attributed to the different substrates. The absence of crystal formations is due to the fact that the deposition process was not accompanied by an additional heating of the samples. The value measured of the refractive index $n=2.136$ confirm the films’ amorphousness. TiO$_2$ films with $n$ between 2.2 and 2.3 at $\lambda = 633$ nm also exhibit an amorphous structure. The films produced at 300 °C are characterized by the formation of an “anatase” phase, which explains the relatively high values of $n$, up to 2.65. The results from our previous studies of TiO$_2$ films deposited by reactive sputtering of Ti targets in oxygen ambient also revealed (by means of Raman analysis) an amorphous TiO$_2$ structure [9].

Regardless of the technique used, the films deposited at low temperatures are amorphous. The QCM prepared with $f = 16$ MHz were coated on both sides with TiO$_2$ films with thickness of 99.5 nm.

Table 1 presents the QCM parameters for each stage of the experiments performed. Based on the values measured of the in-series, $F_s$, and in-parallel, $F_p$, frequencies, we calculated the remaining dynamic parameters ($R_q$, $C_q$, $L_q$, $Q$). Immediately after preparation, the resonator structures had good $R_q = 8.36 \Omega$ and $Q = 47520$. After loading the structures with the oxide film, we observed an increase of the $R_q$ value to 10.30 $\Omega$ and a decrease of $Q$ to 39553. The values of these two parameters point to a partial decrease of the structure’s parameters, due both to the e-beam evaporation process and to the mass loading. Treatment over H$_2$O and over 100 ppm and 1000 ppm NH$_3$ water solutions tended to improve the structure’s parameters ($Q$ grew to 50659 for an initial value of 47520). This changes can be explained by the improvement of the electrodes’ quality due to the sorption and desorption processes, which lead to a reduction of the acoustic losses. Thus, regardless, of the mass loading by a gas-sensitive film, the QCMs parameters improved after samples treatment. A similar trend was established when studying QCMs coated with Ta$_2$O$_5$ and treated over NH$_3$ solutions for longer periods of time and for wider concentration intervals of the solutions, from 10 ppm NH$_3$ to 10000 ppm NH$_3$. The improvement of the parameters was accompanied by an increase in the sorbing films’ density [10].

### Table 1. QCM-parameters.

| $F_s$/Hz | $F_p$/Hz | $R_q/\Omega$ | $C_q/pF$ | $C_q/F$ | $L_q/mH$ | $Q$ | REMARKS |
|----------|----------|--------------|-------|--------|-------|------|---------|
| 15888392 | 15920561 | 8.36         | 5.57  | 2.52.10$^{-14}$ | 3.981 | 47520 | Initial QCM parameters |
| 15851386 | 15882841 | 10.30        | 5.55  | 2.46.10$^{-14}$ | 4.093 | 39553 | After TiO$_2$ deposition |
| 15851143 | 15882299 | 8.11         | 5.56  | 2.44.10$^{-14}$ | 4.127 | 50659 | After treatment |

3.1 Sorption properties of the QCM
Figure 2 illustrates the sorption ability of a QCM coated with a TiO$_2$ film to water vapor. The behavior of the curve indicates that during the first 30 s the structure is abruptly loaded, which results in a frequency decrease $\Delta f = 84$ Hz. During the following 70 s, one observes a smooth loading resulting in a $\Delta f$ of 12 Hz. After 150 s, a dynamic equilibrium is established between the number of sorbed and desorbed water molecules at $f=15855520$ Hz, which corresponds to a state of saturation. The overall frequency shift during the entire measurement interval is $\Delta f = 102$ Hz, corresponding to 22.55 ng.
Once being saturated over H₂O, the sample was placed above water solutions of NH₃ with different concentrations. Figure 3 presents the QCM saturation curve above a 100 ppm NH₃ solution. During the first 500 s, the frequency is reduced by 30 Hz; this is followed by ∆f = 22 Hz after five times as long a period. The dynamic equilibrium in this case occurs only after 3000 s. The overall frequency shift is 52 Hz, corresponding to 11.50 ng. The behavior of the FTC of the sample saturated above 1000 ppm NH₃ water solution is similar, as seen on figure 4. Following an initial frequency drop of 30 Hz during 120 s, one observes a monotonic decrease of the frequency for 700 s. The overall mass sorbed for the entire interval as calculated in comparison with saturation over H₂O is 38.47 ng, corresponding to the frequency shift measured of ∆f = 174 Hz. Thus, a tenfold rise in the NH₃ concentration resulted in a three-fold rise in the mass sorbed. Once the experiments were completed, the samples were placed in a neutral medium, which resulted in the samples’ recovering their initial f., thus proving the physical nature of the sorption process. The studies reported here concerning the capability of QCMs with thin TiO₂ films to detect low NH₃ concentrations confirm the results published earlier related to the properties of TiO₂ films produced by reactive sputtering and liquid phase deposition [9, 11]. The Ta₂O₅ films studied previously and prepared by the same technique as TiO₂ had thickness of 86 nm; they exhibited a stronger sorption ability over 100 ppm and 1000 ppm NH₃, with frequency change as follows: ∆f = 102 Hz and ∆f = 216 Hz, as compared with ∆f = 52 Hz and ∆f = 174 Hz for e-beam evaporated TiO₂, while 100 nm rf-sputtered TiO₂ [9] possess lower sorption ability, close to ∆f = 65 Hz. In spite of the fact that the TiO₂ films produced by the various technologies exhibit different properties in what concerns their stoichiometry, density, and surface morphology, the trends of the FTC measured over NH₃ solutions are analogous. This is a proof of the potential applications of TiO₂ as sensitive layers in QCM regardless of the technique of synthesis.
4. Conclusions
The ability of thin TiO$_2$ films to sorb NH$_3$ vapor is analyzed. Detection of NH$_3$ by 16 MHz AT-cut QCM covered with TiO$_2$ is investigated. The e-beam evaporated thin TiO$_2$ films deposited at room temperature show capability to register low NH$_3$ concentrations (100 ppm – 1000 ppm) over aqueous ammonia solutions. A correlation was established between the NH$_3$ mass sorbed on the QCM and the NH$_3$ concentration. The main conclusion based on the results obtained is that QCMs covered with e-beam evaporated thin TiO$_2$ films are suitable for NH$_3$ detection.

Acknowledgements
This study was supported by Grant No: NT3-03/2006 of the Ministry of Education and Science of Republic of Bulgaria.

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