JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS, Vol. 11, No. 9, September 2009, p. 1367 - 1370

Sorptive properties of thin TiO_2 and humic acid layers to NH_3, estimated by a QCM[♣]

V. GEORGIEVA[*], L. SPASSOV, A. MOGILEVSKY[a], A. GRECHNOKOV[a], N. DONKOV[b], TS. YORDANOV, V. GADJANOVA
Georgi Nadjakov Institute of Solid State Physics, Bulgarian Academy of Sciences, 1784 Sofia, Bulgaria.
[a]*Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, 119991 Moscow, Russia*
[b]*Academician Emil Djakov Institute of Electronics, Bulgarian Academy of Sciences, 1784 Sofia, Bulgaria.*

A Quartz Crystal Microbalance (QCM) coated with two different sensitive layers has been investigated for the determination of NH_3 concentrations. For this purpose, AT-cut 16 MHz resonators were constructed and investigated. In this work, we report results on the gas-sensing characteristics for NH_3 of two kinds of thin layers: TiO_2 and humic acids. The first studied layer was electron-beam evaporated thin TiO_2 deposited on both sides of a QCM. The sensing characteristics of TiO_2 were measured in the concentration range of NH_3 from 100 to 1000 ppm. All studied TiO_2 layers were found to possess good sensitivity and reversibility in the examined range of NH_3 concentrations. The second layer was humic acid, extracted from soil and deposited on a QCM by a drop-coating method. The main analytical parameters of such sensors, including the sensitivity, selectivity and reproducibility were evaluated. It was found that a QCM with humic acid is characterized by a higher sensitivity but a lower stability compared to metal oxides. Good linearity of the concentration dependence was obtained in the concentration range 2 to 100 ppm. The presented results demonstrate that both studied types of sensitive layer can be used for ammonia detection.

(Received November 5, 2008; accepted December 15, 2008)

Keywords: TiO_2 thin films, QCM sensor, NH_3

1. Introduction

A Quartz Crystal Microbalance (QCM) is a very stable device, which can measure an extremely small mass change on the nanogram scale [1]. The use of a QCM coated with a sensitive material has become an alternative approach for the detection of low concentrations of poison gases in the environment. One high priority atmospheric pollutant is ammonia, so the determination of NH_3 concentrations in the air is an important and topical problem for ambient monitoring.

The analytic signal of QCM sensors is formed due to the effect of mass loading, i.e., when the sensitive layer adsorbs the tested gas. Therefore the sensor sensitivity and selectivity strongly depend on the sorptive properties of the QCM coating. Also, other properties such as a high modulus of elasticity, high adhesion to the QCM electrodes and stability are important.

In this work, we present further results of our investigation of the TiO_2 sorptive properties for NH_3. Also, a novel sensitive material for QCM, based on humic acids, is offered and investigated with respect to their ability to sorb ammonia.

2. Experimental

The sorption properties of both investigated layers to NH_3 were studied using the QCM. It was created on a polished quartz AT-cut plate with a diameter of 8 mm. Au electrodes with diameters of 5 mm and thicknesses of 60 nm were evaporated on both sides of the quartz plate. Thus, a QCM with a resonance frequency of 16 MHz was fabricated. The QCM's quality was evaluated by measuring some equivalent dynamic parameters, such as the static capacitance C_0 and the equivalent dynamic resistance Rq by a Selective Level Meter. Other parameters, namely the dynamic capacitance Cq, the dynamic inductance Lq, and the quality factor-Q, were calculated [2]. The created structures were divided into two groups. The first one was coated with a TiO_2 layer, and the second one with a humic acid layer.

The mass of the deposited sensitive layer, as well as the sorbed mass (Δm), was calculated from measurements

---

[♣] Paper presented at the International School on Condensed Matter Physics, Varna, Bulgaria, September 2008 of the QCM resonant frequency shift, according to the Sauerbery equation [3]. The experimental system and the methodology of the measurements were described in detail in [4].

2.1. A QCM covered with an e-beam evaporated TiO_2 layer

The thin TiO_2 layers were prepared by e-beam evaporation of a TiO_2 powder source. The process was carried out at initial vacuum of $7x10^{-4}$ Pa and an operational-mode vacuum of $3x10^{-3}$ Pa, without additional heating of the quartz plate. A deposition rate of 50 nm/min was obtained under these conditions. Similar schemes of the experimental set-up and the conditions for e-beam evaporation of TiO_2 are presented in [5].

The refractive index and thickness of the TiO_2 layers were determined by ellipsometric measurements on a control silicon wafer, placed next to the resonator structure during evaporation. A Rudolph 435 ellipsometer at a wavelength of 632.8 nm was used. The surface morphology of the TiO_2 layers deposited on the resonators was determined using a SEM-Philips 515. The sorption abilities of the TiO_2 were determined by measuring the resonance frequency shift of the QCM over aqueous solutions of NH_3 with different concentrations. The frequency-time characteristics (FTCs) for each investigated concentration were measured. The influence of H_2O molecules on the NH_3 sorption was eliminated by saturation with water vapor prior to measuring over the ammonia solution. The frequency obtained over the water was taken as an initial value for the subsequent measurements. The temperature of the solution during the experiments was maintained at $25^oC \pm 0.5^oC$, in order to eliminate its influence on the sorption process.

2.2. A QCM covered with a humic acid layer.

The humic acids were preliminarily extracted from soil, using a NaOH solution. Then the supernatant was acidified with HCl and separated by centrifugation, and finally, the humic acid fraction was re-dissolved by adding a NaOH solution. The obtained solution was coated on both sides of a QCM. A drop-coating method was used to form the thin films.

The sorptive properties of humic acids were studied using a closed gas-testing unit, including a 5 L vessel, a peristaltic pump and a chamber with the sensor. The aliquot part of the vapours over 27% aqueous solutions of NH_3 was sampled with a microsyringe and injected into the vessel. Within 3-5 min (needed for a homogeneous distribution) a carrier gas (air or nitrogen) was pumped through the vessel and the chamber with the sensor. The flow rate was 100 ml/min. The flow was switched to the atmosphere for desorption. The FTCs were measured for 9 different concentrations of NH_3 in the range 2 to 100 ppm.

3. Results and discussion

3.1. A QCM covered with an e-beam evaporated TiO_2 layer

The investigations on the TiO_2 surface in the area of the metal electrode and quartz plate showed insignificant differences, caused by the plate. The layers were amorphous. The measured refractive index n=2.167 confirmed this. No “anatase” phases were observed, which are typical of layers deposited at temperatures of about 300^oC and characterized with relatively high values of n - up to 2.65.

The quality of the samples obtained, and the changes appearing in them on each stage of the investigations, were evaluated by measuring the in-series - F_s, and in-parallel - F_p, frequencies, and calculating the dynamic parameters (*Rq, Cq, Lq, Q*). The obtained data for each stage are presented in Table 1.

Table 1. QCM Parameters

#	F_s, Hz	R_q, Ω	C_q, fF	L_q, mH	Q
1	15867811	5.0	35.99	2.798	55544
2	15794789	6.7	34.34	2.960	43818
3	15794409	4.4	34.03	2.987	67329

1 - Initial QCM parameters, 2 - After TiO_2 deposition, 3 - After treatment

Table 1 shows that the initial parameters (Rq =5.0 Ω and Q = 55 544) of the prepared QCM structures were very good. The process of TiO_2 film evaporation worsened the QCM parameters.

Loading the electrodes with additional mass increased this process. This leads to an insignificant increase in the Rq value – from 5.0 to 6.7, and Q decreased by approximately 20%. Despite the changes appearing in the QCM parameters, they were characterized with good values, i.e. the process of dielectric layer deposition is absolutely compatible with the QCM technology. After treatment over ammonia water solutions, a considerable improvement of the parameters was observed (Table 1).

3.2. Sorption properties of a QCM with a TiO_2 layer

Fig. 1 presents the sorption properties of a QCM coated on both sides with a 249 nm TiO_2 layer, with respect to water vapor.

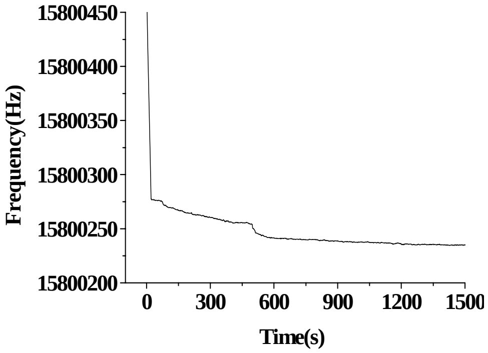

Fig. 1. FTC of a QCM with a TiO_2 film during water saturation.

The FTC show that in the first 20 seconds the frequency rapidly decreased at 540 Hz/min. In the second fragment of the curve, which is in the range 20 to 700 s, it decreased to 3.35 Hz/min, after which saturation appeared. The measured frequency change in the whole interval was 225 Hz. After the saturation process over the water in the FTC of the samples positioned over a 100 ppm NH_3 solution, a leap of 78 Hz/min was measured again in the first 20 seconds. During the next 460 seconds the velocity decreased (at 3.78 Hz/min), and saturation appeared (Fig. 2).

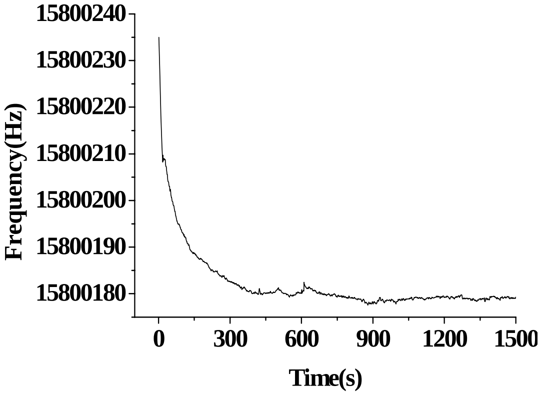

Fig. 2. FTC of a QCM with a TiO_2 film during saturation over a 100 ppm aqueous NH_3 solution.

Analogical FTC was also measured for the samples positioned over a ten times more concentrated solution. There was a difference only in the measured values and temporary interval. The measured velocity of 36 Hz/min for the first 20 seconds was followed by the second fragment of velocity, almost 10 times lower (3.50 Hz/min) in the next 460 seconds, and reached saturation with a velocity of 1.05 Hz/min. The measured maximum difference in the frequency was 166 Hz.

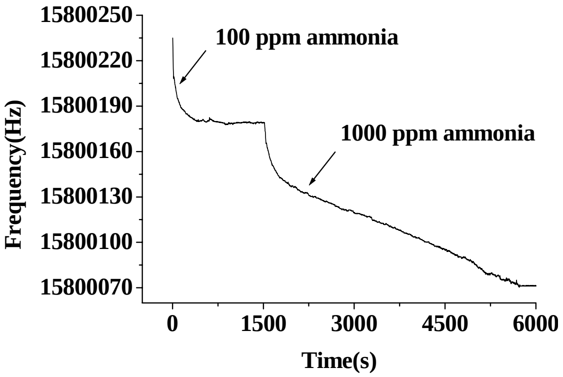

Fig. 3. FTC of a QCM with a TiO_2 film during subsequently saturation over 100 ppm and 1000 ppm aqueous NH_3 solutions.

Fig. 3 shows the frequency change dependence when the NH_3 concentration was changed from 100 to 1000 ppm. The frequency drop is very clear when the concentration increases tenfold. The NH_3 sorption in the layer's depth can explain the slow decrease of the FTC over the NH_3 solution with high concentration.

Based on the obtained maximal differences of the initial frequency and its saturation above every solution used, the maximum quantity of sorbed mass was calculated respectively: 78.26 ng above the water solution and 19.83 ng and 57.74 ng over 100 and 1000 ppm NH_3.

The obtained results based on the SEM and ellipsometric measurements for e-beam evaporated TiO_2 films were similar to those previously obtained for rf TiO_2 films, where an amorphous TiO_2 structure was also revealed by means of Raman analysis [6].

The dynamic parameters of a QCM prepared with f = 16MHz and coated on both sides with TiO_2 films (249 nm) showed changes in every stage of the sample's investigation.

These changes can be explained by an improvement in the electrodes' quality, due to the sorption and desorption processes, which results in a reduction in the acoustic losses. The obtained values of the dynamic parameters were better than the initial ones. A similar tendency was established when studying QCMs coated with Ta_2O_5 and treated over NH_3 solutions for longer periods of time and in wider concentration intervals of the solutions - from 10 to 10000 ppm NH_3.

The improvement of the parameters was explained by an increase in the sorbing films' density [7].

The obtained results of the NH_3 sorption from 249 nm TiO_2 layers have been compared to those earlier published for 99.5 nm TiO_2 [5]. It was established that the FTC's character is analogous too. A three times increase in the sorbed water vapors' mass was observed - from 22.55 ng (99.5 nm TiO_2) to 78.26 ng (249 nm TiO_2). The same effect was revealed over NH_3 solutions – from 11.5 to 19.83 ng at 100 ppm and from 38.47 ng to 57.74 ng at 1000 ppm. These results represent the influence of the sensitive layer's thickness on the sorption process, which is a potential opportunity for its increase when using TiO_2 layers in sensor elements. The main advantages of QCMs covered with TiO_2 consist of their high stability and reproducibility during repeated measurements.

3.3 A QCM covered with a humic acid layer

For determination of the optimal conditions of NH_3 detection, the effect of the sensitive layer mass on the sorptive properties was studied. It was found that in the range 2-12 μg, the sorbed ammonia mass was proportional to the mass of the humic acid layer. Above 12 μg, the dependence was transformed to a non-linear one, and at masses of 22-25 μg the suppression of oscillations was observed. Increasing the sensitive layer mass resulted not only in an increased sensitivity, but also in frequency noise. Evidently, this was due to the internal losses raising the vibration energy in the bulk of layer. Therefore, for every deposited mass we measured the signal-to-noise ratio. According to the obtained data, the optimal mass of the humic acid layer, corresponding to the maximum of signal-to-noise ratio, was 15 μg.

Fig. 4 presents typical FTC of a QCM coated with a 15.2 μg humic acid layer, sensitive to 10 and 50 ppm vapor phase NH_3. It is seen that adsorption equilibrium was established within about 3 min. The total frequency shifts during sorption process were 45 Hz for 10 ppm and 218 Hz for a five times higher concentration of NH_3. These values correspond respectively to 17.4 ng and 88.3 ng of sorbed NH_3. The presented data, as well as the results of experiments with other concentrations, showed good linearity of the concentration dependence in the range 2 to 100 ppm NH_3. The results demonstrate that the sensitivity of the sensor with humic acid is more than one order of magnitude higher than that for the TiO_2 layers, probably due to higher bonding energy of ammonia molecules with the carboxylic groups of humic acid. However, a QCM with humic acid possesses a lower long-term stability compared to metal oxides.

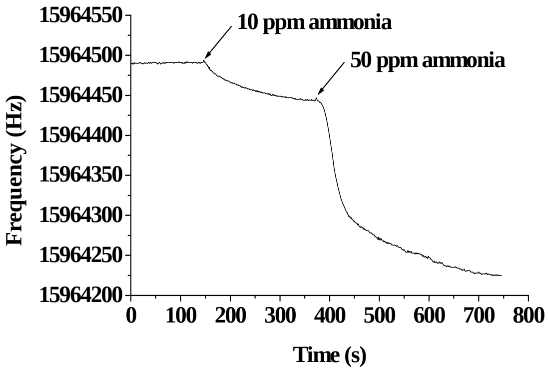

Fig. 4. FTC of a QCM coated with a 15.2 μg humic acids layer to10 and 50 ppm NH_3.

4. Conclusions

The sorption property of thin TiO_2 layers and humic acid to NH_3 was evaluated. It was shown that they can successfully be used as sensitive layers for sensor applications in different concentration intervals.

QCMs coated with humic acid are suitable for NH_3 detection in the range 1 to 100 ppm, while TiO_2 is appropriate for the detection of NH_3 in the investigated concentration interval of 100 to 1000 ppm.

Acknowledgements

This study was partly supported by Grant № NT3/2006 from the Ministry of Education and Science of Bulgaria

References

[1] A. Cunningham, Introduction to Bioanalytical Sensors, Wiley, New York (1998).

[2] S. Manolov, H. Tihchev, Generators, Sofia Tehnika, (1982).

[3] G. Sauerbery, Z. Phys. **155,** 206 (1959).

[4] V. Lazarova, L. Spassov, S. Andreev, E. Manolov, L. Popova, Vacuum **47,** 1423 (1996).

[5] V. Georgieva, L. Spassov, N. Donkov, V. Gadjanova, J. Phys. Conf. Ser. **113,** 012003 (2008).

[6] S. Boiadjiev, V. Lazarova, M. Rassovska, Proc. 6th Int. Conf. of BPU, AIP, 2007, p. 765.

[7] V. Georgieva, L. Spassov, N. Donkov, M. Atanassov, Plasma Proc. Polym. **3**, 209 (2006).

---

[*] Corresponding author: lazarova@issp.bas.bg