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Preparation and characterization of ALD deposited ZnO thin films studied for gas sensors

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Abstract. Applying atomic layer deposition (ALD) very thin zinc oxide (ZnO) films were deposited on quartz resonators, and their gas sensing properties were studied using the quartz crystal microbalance (QCM) method. The gas sensing of the ZnO films to NO₂ was tested in the concentration interval between 10 and 5000 ppm. On the basis of registered frequency change of the QCM, for each concentration the sorbed mass was calculated. Further characterization of the films was carried out by various techniques, i.e. by SEM-EDS, XRD, ellipsometry, and FTIR spectroscopy. Although being very thin, the films were gas sensitive to NO₂ already at room temperature and could register very well as low concentrations as 100 ppm, while the sorption was fully reversible. Our results for very thin ALD ZnO films show that the described fast, simple

and cost-effective technology could be implemented for producing gas sensors working at room temperature and being capable to register in real time low concentrations of NO₂.

Keywords: Atomic layer deposition; Gas sensor; Quartz crystal microbalance; Thin film; ZnO.

1. Introduction

Semiconductor thin films such as SnO₂, TiO₂, WO₃, MoO₃ and In₂O₃ have been widely investigated for sensing different toxic gases [1–5]. For that purpose a large number of techniques and devices have been developed. Many of 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. The quartz crystal microbalance (QCM) is a widely-used technique for detecting the mass of thin layers deposited on the crystal surface in the sub-nanogram level, but it could be also applied for monitoring the adsorption of nano amounts of various toxic gases. Compared with other sensors, the advantages of QCM gas sensors are the high sensitivity, capability of operating at room temperature, simple technological implementation and easy real-time monitoring, relative independence from electromagnetic fields and rapid temperature changes, durability, fast response even at low concentrations, portability, low energy consumption and cost [6–8].

Zinc oxide (ZnO) is a n-type semiconductor with a wide band gap of 3.4 eV at room temperature. Nowadays ZnO is one of the most widely studied materials, due to its promising optical, optoelectronic and piezoelectric properties [9,10]. Also, ZnO is one of the earliest-discovered and well-established gas sensing oxides, which has been extensively studied for detection of inflammable, hazardous and toxic gases, such as H₂ [11], C₂H₅OH [12], NO₂ [13], NH₃ [14], H₂S [15], CO [16] and many others. However, most of the ZnO gas sensors usually have to operate at relatively high temperatures over 200 °C [11,13,16]. The most-commonly used conductometric gas sensors quite often need comparably high operational temperatures and heating of the sensing element, a drawback that can be overcome by using QCM sensors, which is one of their main advantages. The QCM sensors possess high sensitivity and often certain gases can be well detected by high quality sensing layers even at room temperature. Also, although in the last decades the gas sensing properties of ZnO thin films have been widely researched, still there is a lack of knowledge about the

gas sensing of very thin and especially ultra thin films with thicknesses of several nanometers. Since only the surface properties of the films are relevant for gas sensors based on the QCM method, such very thin films, which can be prepared in fast and cost-effective way, are very promising for implementation in gas sensors.

ALD is a gas 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 great variety of materials. With these advantages, ALD became a powerful tool for many industrial and research applications [17–21].

Previously, prototype QCM gas sensors with several transition metal oxide films (e.g. MoO₃, TiO₂) were already made by our team and tested for sensitivity to NO₂ and NH₃ in a specially designed laboratory set-up. These films were mostly prepared by sputtering [22–25], and only in one case ALD was also used for film growth of TiO₂ [26]. As a follow up of the previous studies, in the present research we focused on the sensing behavior of very thin ZnO films produced by ALD. Hence, ZnO films were grown by ALD either on quartz resonators, which were used for the gas sensing tests to NO₂, or on Si substrates, which were applied for further characterization of the films.

Detection of NO₂ is quite important nowadays [13,27], since it is a spread pollutant in the atmosphere around big cities, mainly because of the increasing amounts exhausting combustion gases, and can cause respiratory irritation even in very small concentrations, as low as 15-25 ppm [27]. The described technology using QCM with ALD deposited very thin ZnO film suggests an effective way to detect NO₂ in the environment in real time.

2. Experimental

The films were prepared using ALD deposition performed in a Picosun SUNALE R-100 reactor at 200 °C substrate temperature with diethylzinc [(C₂H₅)₂Zn, DEZ] and H₂O as precursors. Nitrogen was used as carrier gas while the precursors were evaporated at room temperature. The overall pressure in the reactor chamber was ~10 mbar. The precursor pulse times were 0.1 s for both DEZ and H₂O. The purge time was 3 s after the DEZ pulse and 4 s after the H₂O. ZnO thin films were deposited in 150 ALD cycles on both quartz resonators and Si wafers. Thicker films with 600 ALD cycles were also deposited for reference. Not so high deposition temperature of 200 °C was chosen, because of the sensitivity of the very thin quartz resonators to

the high temperatures, and since their quality might be affected when exposed at high temperatures over 300 °C.

The film morphology was investigated by scanning electron microscopy (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 ellipsometry using a Woollam M-2000DI rotating compensator ellipsometer. The FTIR (Fourier transform infrared spectroscopy) spectra were recorded applying Shimadzu IR Prestige 21 spectrometer.

The sensing properties of the films were studied using quartz resonators by applying the QCM method. The tests were performed with resonators produced on 8-mm in diameter polished AT-cut quartz plates with thermally evaporated Au electrodes of diameter of 4 mm and thickness of about 60 nm (also with very thin Cr underlayer) on both sides. The scheme of the test device is presented in Fig. 1a) and its image in Fig. 1b).

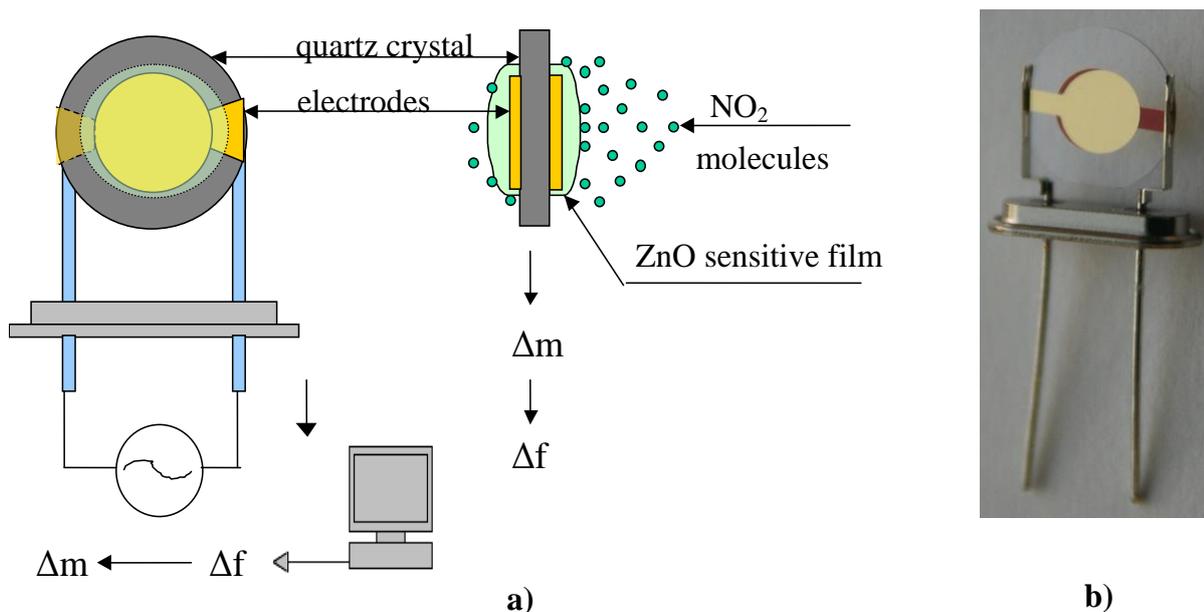


Figure 1. Scheme a) and image b) of the QCM based gas sensor device.

The working resonance frequency of these initial resonators is 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 obtained by calculation [28].

The gas sensing was tested in a special home-made measurement system, which was described in detail previously [22]. When the gas to be detected is introduced into the chamber, the sensing element starts to adsorb molecules from it and the frequency drops fast, in few seconds, thus allowing rapid detection even of very low concentrations. The sorption properties of the ALD ZnO films were evaluated by measuring the resonance frequency shift of the QCM structures covered with the ZnO thin films at various NO₂ concentrations between 10 ppm and 5000 ppm. The main stages of the measurement consisted of (i) purging the tested sensor with dry air; (ii) creating a certain concentration of the measured gas in the chamber; (iii) reaching saturation of the frequency values; (iv) purging the chamber with dry air to restore the sensor and prepare it for new measurement. The used chamber was with comparably small volume, in order the processes of mixing the gases and creating the needed concentration, as well as the purging, to be fast and precise. The NO₂ concentration in the test chamber was controlled by mass flow controllers for NO₂ 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 $\pm 5.25 \times 10^{-7}$. The measurements were based on the correlation between the frequency shift and the additional sorbed mass loading of the resonator. Sauerbrey [29] developed an empirical equation for AT-cut quartz, describing the relation between the mass of a thin film deposited on the quartz crystal and the corresponding change in the resonance frequency, thus allowing the absorbed mass to be calculated and the gas sensing to be quantitatively determined.

3. Results and discussion

Very thin ZnO films with a thickness of less than 20 nm were deposited by ALD on both QCMs and Si substrates. With 150 ALD cycles a thickness of ~16 nm was achieved, based on the ellipsometry measurement of the reference ZnO thin film deposited on Si wafer.

Scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) were used to study morphology and composition of deposited films. The successful deposition of ZnO was clearly shown by the presence of Zn in the EDS spectrum of the reference ZnO film grown by ALD on the Si wafer (Fig. 2). The results from the composition analysis are presented in the inset of Fig. 2. The EDS study had only qualitative character and was useful to prove the successful deposition of the very thin ZnO films. The information

depth of EDS is ca. 500 nm; thus the majority of the EDS signal came mainly from the substrate and only small portion of it originated from the ZnO film.

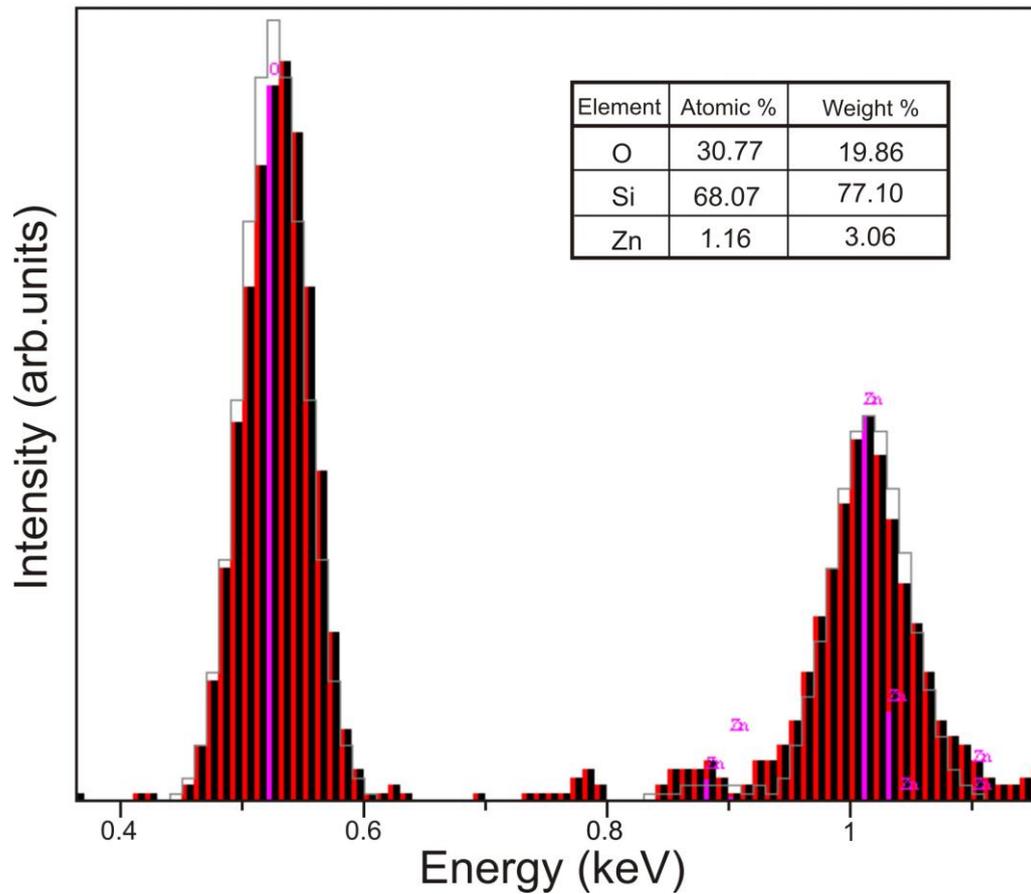


Figure 2. Zn and O peaks in the enlarged EDS spectrum, together with the concentration analysis results, of ~16 nm thick reference ZnO film grown by ALD on a Si wafer.

The XRD investigations showed that the ALD ZnO films deposited at 200 °C were polycrystalline (Fig. 3). The three most typical peaks for crystalline ZnO were observed at 31.7° (100), 34.4° (002) and 36.2° (101), corresponding to PDF 01-074-9940. The film tended to grow preferentially in the (100) crystallographic orientation.

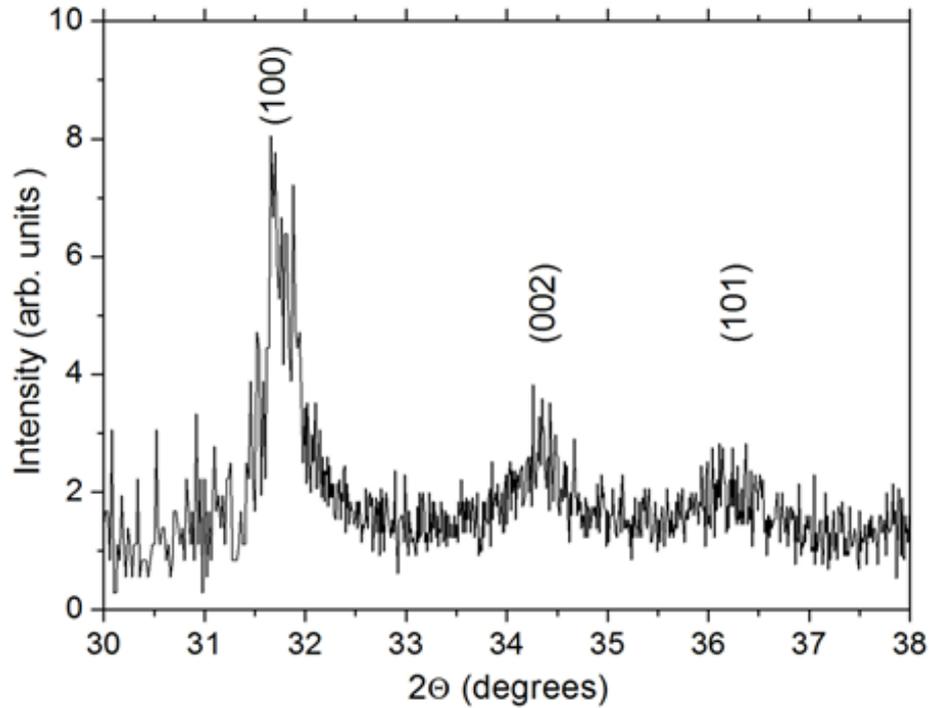


Figure 3. XRD pattern of reference ZnO film grown by ALD on a Si wafer.

The formation of ZnO thin film was also confirmed by FTIR study, as shown by the range typical for lattice vibrations of transition metal oxides (Fig. 4). The peaks (397 , 401 and 411 cm^{-1}) in the absorption band around $400\text{--}420\text{ cm}^{-1}$ correspond to Zn–O stretching vibrations for tetrahedral surrounding of zinc atoms [30,31]. The peaks at 719 and 1105 cm^{-1} can be attributed to bending and stretching vibrational mode of Si–O–Si [30]. The broad peak around 650 cm^{-1} also comes most probably from the Si substrate, as it can be attributed to Si–Si stretching vibration.

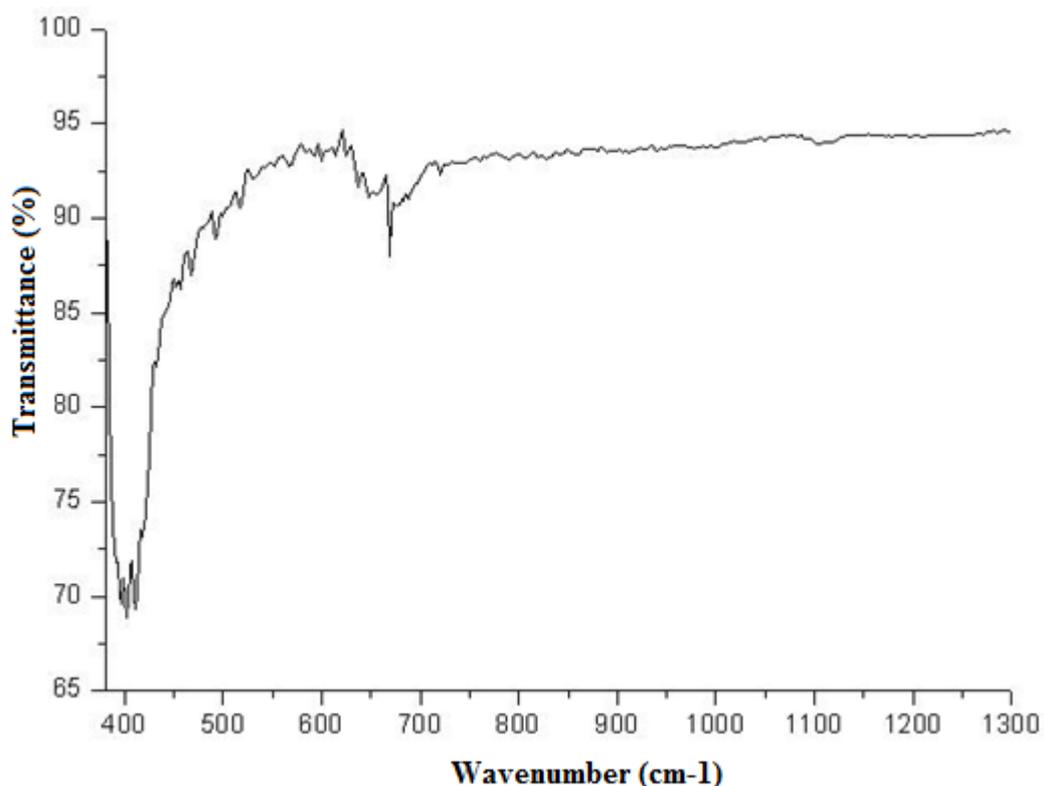


Figure 4. FTIR spectrum of ~16 nm thick reference ZnO film deposited by ALD on a Si wafer.

The gas sensing properties of the ZnO films to NO₂ were tested with various concentrations starting from 10 ppm. The films were found to be sensitive even at very low concentrations as 10-50 ppm, but at such concentrations their sensitivity was very weak and the observed frequency change (Δf) was just a few Hz. Typical frequency-time characteristic (FTC) for a well-working sensor was observed at 100 ppm (Fig. 5), and also for higher concentrations. The response of the sensor was fast (a few seconds), and its loading (proportional to the sorption of the detected gas) curve was close to linear. The desorption (recovery time, t_d) was also measured. The recovery of the sensor was complete and after removing the NO₂ gas from the chamber the initial values of the resonator were achieved. The sorption was considered to be a fully physical process, shown by the full recovery of the sensor for comparably short time.

At comparably low concentrations as 100 ppm, the sorption and desorption processes were quite dynamic. In Fig. 5 it can be observed that the loading and unloading of the resonator were comparably slow processes with similar speed. The overall observed frequency shift was only around 10 Hz but the processes were well-expressed.

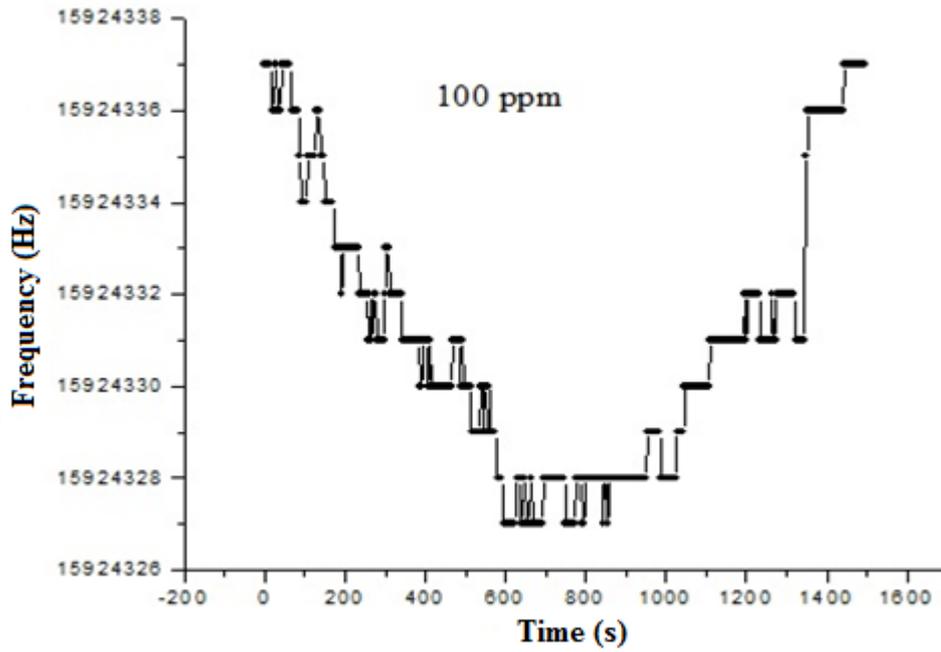


Figure 5. FTC of QCM with ~16 nm ALD deposited ZnO thin film during saturation and recovery at NO₂ concentration of 100 ppm.

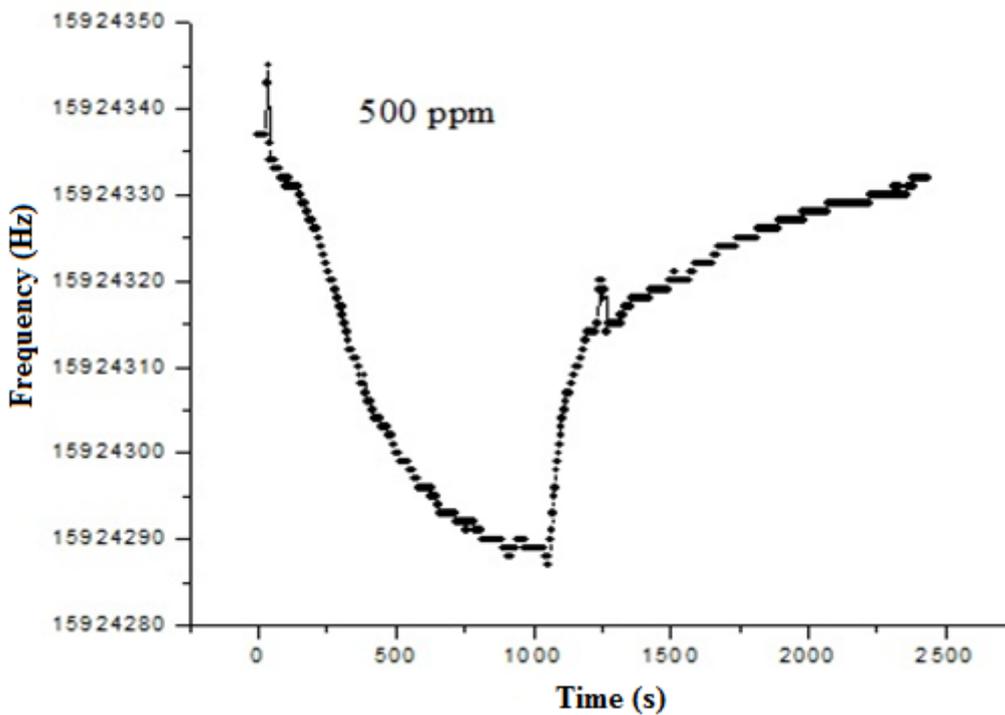


Figure 6. FTC of QCM with ~16 nm ALD deposited ZnO thin film during saturation and recovery at NO₂ concentration of 500 ppm.

At higher concentrations the sorption process was faster and better expressed. At concentration of 500 ppm the frequency change until reaching saturation was $\Delta f = 58$ Hz, while at 1000 ppm it was 105 Hz. The FTC for loading the QCM at 500 ppm is presented in Fig. 6. The time for reaching dynamic equilibrium was a bit longer, corresponding to the higher mass adsorbed on the film. The sorption was still physical and the resonator could be fully recovered, but the recovery times were considerably longer. Also the recovery process had two stages – fast and slow. At the first, for comparably short time, around half of the mass was released from the ZnO film surface, then for releasing the rest a considerably longer time was needed.

With increasing the NO₂ concentrations the sorption was faster, but longer times were needed for reaching saturation. Consequently, the desorption also took longer until all the mass is released from the sensing structure to fully recover for the next measurement cycle. In Fig. 7 is illustrated the gradual loading of the QCM with increasing concentrations from 1000 ppm, 2500 ppm and 5000 ppm. The loading processes with these 3 different concentrations were all measured for 2000 s. First the sensing structure was tested for the sorption of the first 2000 s after introducing 1000 ppm NO₂ in the chamber, afterwards the concentration was increased to 2500 ppm and measured for the next 2000 s, and then it 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 is faster and exponential in the first moments after introducing the certain NO₂ concentration, afterwards the sorption process speeds down until gradually reaching the saturation. But at very low and very high concentrations the process could be linear. This probably has different reasons. For the very low concentrations it can be attributed to the very dynamic processes of sorption and desorption, whose kinetic equilibrium is gradually changing. On the other hand, for the high concentrations it is most probable that the linearity is due to the highly saturated surface. In this term, for the middle concentrations the sorption process can be divided into two stages, i.e. (i) rapid sorption and (ii) slow saturation. From Fig. 7 it can be also concluded that with increasing the concentration the loading possibility of the sensing structure also increases, and it can still very well detect the higher concentrations.

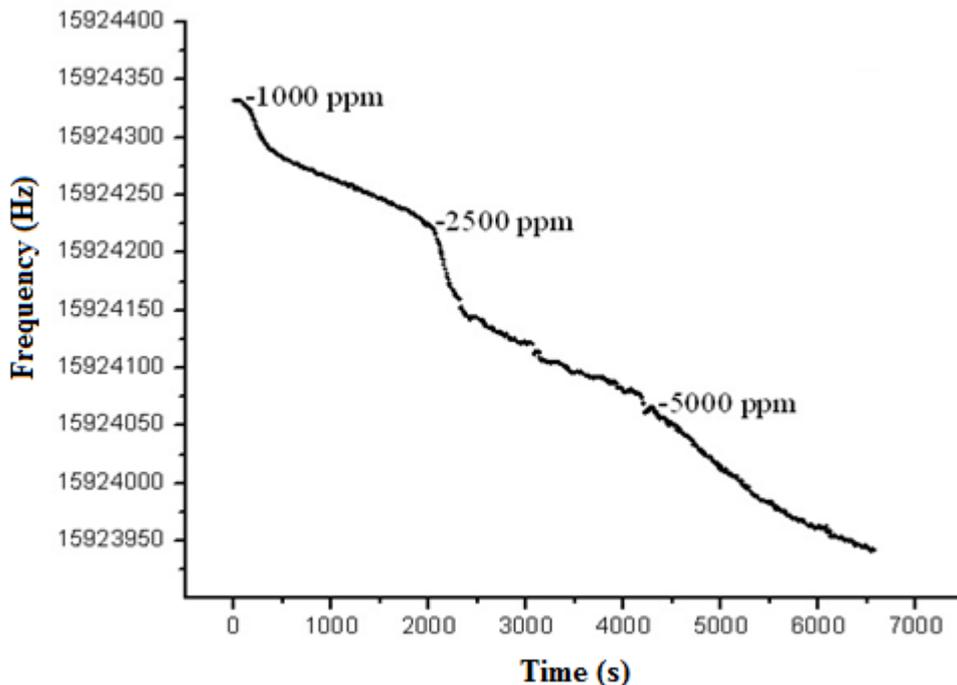


Figure 7. FTC of QCM with ~16 nm ALD deposited ZnO thin film during gradual loading at NO₂ concentration of 1000, 2500 and 5000 ppm.

Also, correlation was established between the concentration of NO₂, the measured frequency shift and the corresponding mass of the gas molecules, which were sorbed on the QCM structure. Fig. 8 presents the measured frequency shift and mass loading at different NO₂ concentrations, from 50 to 5000 ppm. The graph was built from the measurements for the gradual loading (presented on Fig. 7). The graph is with interpolations but it can be concluded that for the lower concentrations the frequency shift and the detected mass are linearly proportional to the measured concentrations. 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 values of the sorbed mass, calculated according to the Sauerbrey equation [29], are also shown in Fig. 8. The change is from around 10 ng to 86 ng for NO₂ concentrations in the interval 50 ppm to 5000 ppm.

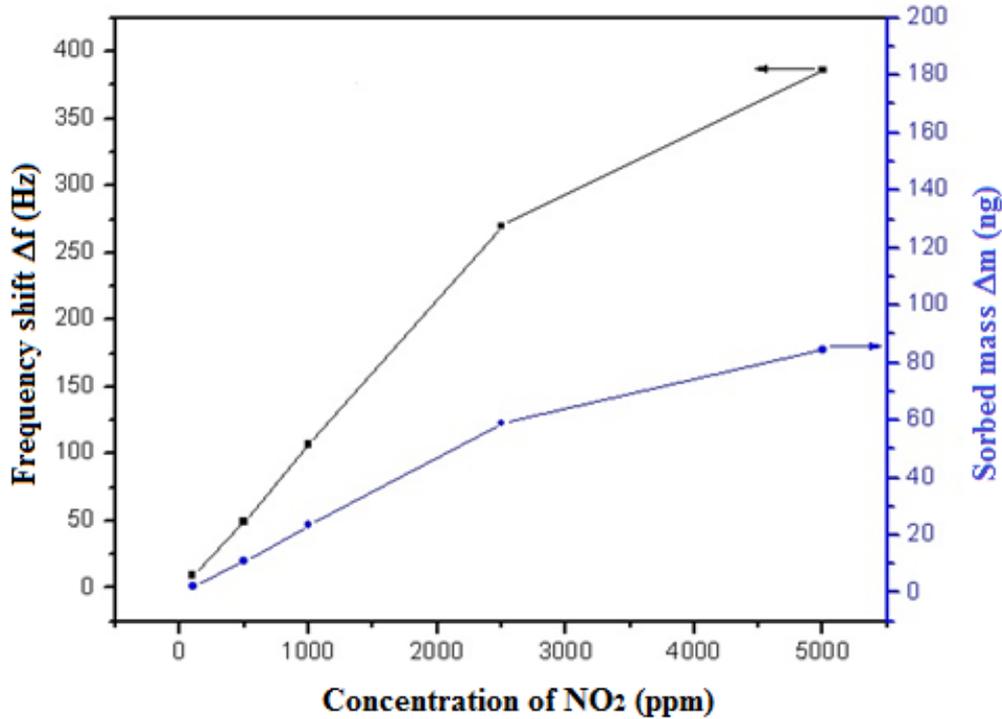


Figure 8. Measured frequency shift and calculated sorbed mass of ZnO-QCM sensor vs the NO₂ concentration.

In our previous studies similar results for sensitivity to NO₂ were observed for several times thicker films of MoO₃ and TiO₂ prepared by reactive sputtering [24,25]. When using QCM technology, 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 QCM working at high frequency, since high loads on the resonator decrease the sensitivity of the gas sensor, so using as thin as possible sensing layer is desirable. The present results are very promising, as they show that very thin ALD ZnO films possess high sensitivity to NO₂ and can be competitive to much thicker films obtained by other methods.

Also, since QCM sensors operate at room temperature, they do not have such problems with long term cycling as many conductometric sensors working at high operational temperatures. Similar QCM gas sensors were tested from our team after many years (some after even 7-8 years) and showed similar parameters, proving their ability to detect for long terms [24,25].

4. Conclusion

Very thin (~16 nm) ZnO films were deposited on quartz resonators by ALD and their sensitivity to various concentrations NO₂ was studied applying the QCM method. These very thin ALD ZnO films showed excellent sensitivity to NO₂ at room temperature and capability to very well register concentrations as low as 100 ppm. The sorption was fully reversible and the sensors were able to be recovered in considerably short time. The ALD method was found to be suitable for fast and cost-effective deposition of ZnO thin films for QCM gas sensor applications. These promising results for sensitive films with thickness of less than 20 nm give a hope that, after a further study and development, even ultra thin ALD ZnO films could be implemented in gas sensing devices.

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References

- [1] T. Oyabu, *J. Appl. Phys.* 53 (1982) 2785–2787.
- [2] P.K. Dutta, M. Frank, G.W. Hunter, M. George, *Sens. Actuat. B* 106 (2005) 810–815.
- [3] I.M. Szilágyi, S. Saukko, J. Mizsei, P. Király, G. Tárkányi, A.L. Tóth, A. Szabó, K. Varga-Josepovits, J. Madarász, G. Pokol, *Mater. Sci. Forum.* 589 (2008) 161–165.
- [4] M. Ferroni, V. Guidi, G. Martinelli, P. Nelli, M. Sacerdoti, G. Sberveglieri, *Thin Solid Films* 307 (1997) 148–151.
- [5] M. Ali, C.Y. Wang, C.-C. Röhlig, V. Cimalla, T. Stauden, O. Ambacher, *Sens. Actuat. B* 129 (2008) 467–472.
- [6] A. Cunningham, *Introduction to Bioanalytical Sensors*, Wiley, New York, 1998.
- [7] S.K. Vashist, P. Vashist, *J. Sens.* 2011 (2011) 571405.
- [8] A. Mirmohseni, K. Rostamizadeh, *Sensors* 6 (2006) 324–334.

- [9] Ü. Özgür, Y.I. Alivov, C. Liu, A. Teke, M.A. Reshchikov, S. Doğan, V. Avrutin, S.-J. Cho, H. Morkoç, *J. Appl. Phys.* 98 (2005) 041301.
- [10] S.M. Mihaiu, J. Madarasz, G. Pokol, I.M. Szilagy, T. Kaszas, O.C. Mocioiu, I. Atkinson, A. Toader, C. Munteanu, V.E. Marinescu, M. Zaharescu, *Rev. Roum. Chim.* 58 (2013) 335–345.
- [11] S. Basu, A. Dutta, *Sens. Actuat. B* 22 (1994) 83–87.
- [12] T.J. Hsueh, S.J. Chang, Y.R. Lin, I.C. Chen, C.L. Hsu, *J. Electrochem. Soc.* 155 (2008) K152–K155.
- [13] R. Ferro, J.A. Rodriguez, P. Bertrand, *Phys. Stat. Sol. (c)* 10 (2005) 3754–3757.
- [14] M.S. Wagh, G.H. Jain, D.R. Patil, S.A. Patil, L.A. Patil, *Sens. Actuat. B* 115 (2006) 128–133.
- [15] N. Zhang, K. Yu, Q. Li, Z.Q. Zhu, Q. Wan, *J. Appl. Phys.* 103 (2008) 104305.
- [16] C.Y. Liu, C.F. Chen, J.P. Leu, *J. Electrochem. Soc.* 156 (2009) J16–J19.
- [17] S.M. George, *Chem. Rev.* 110 (2009) 111–131.
- [18] I.M. Szilágyi, D. Nagy, *J. Phys.: Conf. Ser.* 559 (2014) 012010.
- [19] R.W. Johnson, A. Hultqvist, S.F. Bent, *Mater. Today* 17 (2014) 236–246.
- [20] I.M. Szilágyi, G. Teucher, E. Härkönen, E. Färm, T. Hatanpää, T. Nikitin, L. Khriachtchev, M. Räsänen, M. Ritala, M. Leskelä, *Nanotechnology* 24 (2013) 245701.
- [21] I.M. Szilágyi, E. Santala, M. Heikkilä, V. Pore, M. Kemell, T. Nikitin, G. Teucher; T. Firkala, L. Khriachtchev, M. Räsänen, M. Ritala, M. Leskelä, *Chem. Vapor Dep.* 19 (2013) 149–155.
- [22] V. Georgieva, P. Stefanov, L. Spassov, Z. Raicheva, M. Atanassov, T. Tincheva, E. Manolov, L. Vergov, *J. Optoelectr. Adv. Mater.* 11 (2009) 1363–1366.
- [23] S. Boyadzhiev, V. Georgieva, M. Rassovska, *J. Phys.: Conf. Ser.* 253 (2010) 012040.
- [24] R. Yordanov, S. Boyadjiev, V. Georgieva, L. Vergov, *J. Phys.: Conf. Ser.* 514 (2014) 012040.
- [25] R. Yordanov, S. Boyadjiev, V. Georgieva, *Digest J. Nanomat. Biostruct.* 9 (2014) 467–474.
- [26] S. Boyadjiev, V. Georgieva, L. Vergov, Z. Baji, F. Gáber, I.M. Szilágyi, *J. Phys.: Conf. Ser.* 559 (2014) 012013.
- [27] W. N. Rom, S. B. Markowitz, *Environmental and Occupational Medicine* (4th ed.), Wolters Kluwer, Philadelphia, PA, 2007.
- [28] S. Manolov, H. Tihchev, *Generators, Tehnika, Sofia*, 1982.
- [29] G.Z. Sauerbrey, *Physik* 155 (1959) 206–212.

- [30] A.K. Srivastava, Praveen, M. Arora, S.K. Gupta, B.R. Chakraborty, S. Chandra, S. Toyoda, H. Bahadur, *J. Mater. Sci. Technol.* 26 (2010) 986–990.
- [31] R. López, T. Díaz, E. Rosendo, G. García, A. Coyopol, H. Juárez, *Rev. LatinAm. Metal. Mater.* 31 (2011) 59–63.