Comparison of ALD-grown thin ZnO films with various thicknesses for NO₂ sensing

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Abstract. Thin zinc oxide (ZnO) films of various thicknesses were characterized and compared in terms of their suitability to gas sensor applications. Applying atomic layer deposition (ALD), very thin ZnO films were deposited on quartz resonators, and their gas sensing properties were studied using a quartz crystal microbalance (QCM). The ZnO thin films were prepared using diethyl zinc and water as precursors. The crystal structure of the films was studied by X-ray diffraction (XRD), and their surface was observed by scanning electron microscopy (SEM) coupled with energy dispersive X-ray analysis (EDX) used to study the films’ composition. Films of thickness of ~10 – 80 nm were deposited on quartz resonators with Au electrodes and the QCM method was used to build highly sensitive gas sensors. These were tested for sensitivity to various concentrations of NO₂. Although some of the films were very thin, they were sensitive to NO₂ already at room temperature and could register reliably as low concentrations as 50 ppm, while the sorption was fully reversible and the sensors could be fully recovered. With the technology presented, manufacturing of QCM gas sensors is simple, fast and cost-effective, and suitable for application in energy-effective portable equipment for real-time monitoring of NO₂ in the automotive industry or environmental protection.

1. Introduction

ZnO is one of the earliest and thus well-established gas sensing oxides, which has been extensively studied for detection of various gases, such as C₂H₅OH [1], NO₂ [2], NH₃ [3], H₂ [4], H₂S [5], CO [6] and many others. These sensors are usually not suited to measuring gas concentrations with a high precision, but rather to detecting the presence of target gases and giving a warning if threshold values are exceeded.

Most of the ZnO-based gas sensors usually operate at relatively high temperatures, generally within the range from 200 °C up to even 500 °C [2, 4, 6]. This requires heating of the sensing element, a

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drawback that can be overcome by using quartz crystal microbalance (QCM) sensors, which is one of their main advantages.

The QCM is a widely-used technique for detecting the mass of thin layers deposited on the crystal surface on a sub-nanogram level, but it could be also applied to monitoring the adsorption of nano-amounts of various toxic gases [7, 8]. The QCM sensors possess high sensitivity; 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 ability of very thin films. Since what is relevant to using QCM-based gas sensors are the surface properties of the films, such very thin films that could be prepared in a fast and cost-effective way are very promising for implementation in gas sensors.

ALD is a thin-film deposition technique based on successive alternating surface-controlled gas-phase reactions producing extremely conformal and uniform thin films with thickness precision at an atomic level [9, 10]. The self-limited growth of the films leads to the many advantages of ALD, as the film thickness can be programmed easily by the number of ALD cycles [11].

Previously, our team had fabricated prototype gas sensors based on ALD-grown thin ZnO films and tested them for sensitivity to NO$_2$ and NH$_3$ [12,13]; however, no comparative analysis was conducted, which was the aim of the present research.

2. Experimental

The films were grown by ALD in a Picosun SUNALE R-100 reactor at a substrate temperature of 200 °C with diethylzinc [(C$_2$H$_5$)$_2$Zn, DEZ] and H$_2$O as precursors. Nitrogen was used as a carrier gas, while the precursors were evaporated at room temperature. The overall pressure in the reactor chamber was ~10 mbar. The precursor pulse time was 0.1 s for both DEZ and H$_2$O. The purge time was 3 s after the DEZ pulse and 4 s after the H$_2$O. The thinnest ZnO films were deposited in 75 ALD cycles (sample ZnO$_{75}$), while the thickest ones were deposited using 600 ALD cycles (sample ZnO$_{600}$). The films were deposited both on quartz resonators, which were used for the gas sensing tests to NO$_2$, and on Si substrates, which were used as references for further characterization of the films. The relatively low deposition temperature of 200 °C was chosen because of the sensitivity of the very thin quartz resonators to high temperatures, as their quality factor might be affected when exposed to high temperatures (over 300 °C).

The films’ morphology was investigated by SEM; their 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 thin Cr underlayer) on both sides [12]. 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 properties were tested on a home-made measurement system, which, together with the methodology, was described in detail previously [12, 14, 15].

3. Results and discussion

ZnO thin films were deposited by ALD on both QCMs and Si substrates. Their thickness was varied by varying the ALD cycles – 75 cycles produced a thickness of ~10 nm (estimated by a UV-Vis reflectometry measurement of a reference ZnO thin film deposited on a Si wafer). Using 150 cycles resulted in a thickness of around 20 nm (sample ZnO$_{150}$), while with 600 cycles the thickness reached was ~80 nm.

SEM coupled with EDX was used to study the morphology and composition of the as-deposited films. As seen in the SEM images (inset of figure 1), the films were uniform and without cracks. The object shown is an atypical impurity used just for focusing. The successful deposition of ZnO was
clearly evidenced by the presence of Zn in the EDX spectrum of the reference ZnO films grown by ALD on the Si wafers (figure 1). The EDX is a simple, fast and cost-effective method (compared with alternative ones like XPS) to prove the successful deposition of very thin films [10, 15]. The results of the composition analysis of ZnO_{150} showed ~1 at % and ~3 wt % Zn. The EDX study has a qualitative character only, since its information depth is about 500 nm; thus, the majority of the EDX signal arises mainly from the substrate, and a small portion only originates from the ZnO film.

The XRD study showed that the ALD-grown ZnO films deposited at 200 °C were polycrystalline. Figure 2 shows part of the spectrum of sample ZnO_{600}. The three most typical peaks for crystalline ZnO are clearly seen. The film tended to grow preferentially in the (100) crystallographic orientation, while (002) was also clearly expressed. Crystal growth along (002) could explain the increased roughness at higher thicknesses, as in such morphology more voids are present between the crystallites [16]. For the thinner films, the noise was too high to allow reliable conclusions.

The gas sensing properties of the ALD-grown ZnO films to NO_{2} were tested with concentrations in the interval between 10 ppm and 5000 ppm. The films were found to be sensitive even at 50 ppm, but at such concentrations the sensitivity of the thinner films was very low and the frequency...
change ($\Delta f$) observed was just several Hz, while the sorption and desorption processes were quite dynamic. The sorption was considered to be a fully physical process, as the full recovery of the sensors took place rather quickly, even after detecting the comparably high concentration of 5000 ppm NO$_2$.

The typical frequency-time characteristic (FTC) for a well-working sensor was observed at somewhat higher concentrations, e.g., at 100 ppm (figure 3). At such a concentration, the response of the sensors was fast (few seconds), and their sensitivity vs. concentration was nearly linear. For ZnO$_{150}$, (figure 3a), a frequency shift was measured of just 10 Hz, compared with over 30 Hz for ZnO$_{600}$ (figure 3b). Thus, a four times as thick film produced a threefold higher frequency shift.

Usually, the sorption was fast and exponential in the first moments after introducing a certain NO$_2$ concentration; afterwards the sorption process slowed down until gradually reaching saturation. This is illustrated in figure 4, which presents the FTC of a ZnO$_{150}$ film detecting 500 ppm and 1000 ppm NO$_2$. Increasing the NO$_2$ concentration accelerated the sorption, but longer time was needed to reach saturation. Consequently, desorption also took longer until the entire mass was released from the sensing structure to fully recover it for the next measurement cycle. Both the times for reaching saturation and recovery of the sensor roughly doubled with the twofold increase of the NO$_2$ concentration.

Figure 3. FTC of QCM with a ~20 nm (a) and a ~80 nm (b) ALD-grown thin ZnO film detecting 100 ppm NO$_2$.

Figure 5 presents the frequency shifts measured for ZnO films with thicknesses from ~10 nm to ~80 nm for NO$_2$ concentrations from 50 ppm to 5000 ppm. The graphs presented are for ZnO$_{75}$, ZnO$_{150}$ and ZnO$_{600}$. One can clearly see the dependence of the sensitivity (proportional to the frequency shift and mass detected) on the films’ thickness. In our previous studies on different sensing films and detected gases we observed similar dependences [17, 18]. The dependence of $\Delta f/f$ on the film thickness is weekly expressed at low concentrations and is rather stronger for the higher ones. The rise of $\Delta f/f$ with the films’ thickness for

Figure 4. FTC of a QCM with ~20-nm ALD-grown ZnO film detecting 500 ppm and 1000 ppm NO$_2$. 
the same concentration was attributed to the existence of another sorption mechanism – diffusion of the gas to the depth of the film [17]. That study was conducted on films prepared by liquid-phase deposition (LPD), which are characterized by a lower quality and a higher porosity compared with the ALD-grown films. Therefore, for the diffusion to have a stronger effect on the sorption is more probable for LPD films. In other studies on ALD films, we found that the surface properties are predominant [12, 15], since in such cases the specific surface area is the most important parameter affecting the sorption. In some studies, the authors have found that thicker ALD-grown ZnO films exhibit a higher surface roughness [19, 20], supposedly due to having a higher specific surface area. Still, the increase in the sorption which we observed in the present study was not so large as to be explained by the increase of the film thickness. Also, although to a smaller extent in the ALD films, pores are present which in thicker films increase the specific surface area. Earlier we found that films with cracks possess an increased detection sensitivity due to the above mentioned effect [21]. Also, the diffusion of the detected gas into the pores and cracks is a comparably fast process and does not have a significant effect on the detection speed.

Most probably the results we observed in the present study are due to a combination of all the above-mentioned factors – increased roughness of the thicker films, diffusion into pores and bulk of the film. Which one is the predominant factor is hard to determine; however, for ALD-grown films, and bearing in mind the rate of the sorption and desorption processes – which are comparably fast – we suggest that the increased specific surface area of the thicker films due to higher roughness and deeper pores is more relevant, as the surface sorption (including in the pores and voids) is a much faster process than the sorption in the bulk of the film.

Sauerbrey’s equation [22] relates the concentration of NO₂, the measured frequency shift and the corresponding mass of the gas molecules sorbed on the QCM structure. The sorbed mass calculated using this equation is around 10 – 15 ng for NO₂ concentration of 50 ppm and reaches over 250 ng at 5000 ppm for ZnO₆₀₀. The thicker films are reaching saturation after sorbing higher amounts of NO₂, this dependence being proportional to the thickness.

Eliminating the influence of water vapor is of paramount importance for the operation of the NO₂ sensor, since the sorbed H₂O gives rise to errors in the NO₂ amount detected. This is why, together with measuring the sensors’ response to NO₂, we also tested their sensitivity to humidity. Figure 6a) illustrates the humidity detection of a QCM sensor with a very thin (about 10 nm) ALD-grown ZnO sensitive layer. The experiments were conducted at a temperature of 23 °C and a relative air humidity (RH) of 63%. The H₂O adsorption is a comparably fast process – saturation is reached in just a few seconds, while the frequency change is considerable, around 300 Hz. Figure 6b) visualizes the humidity detection of an ~80-nm-thick ZnO film (grown under equal other conditions). One can thus draw the conclusion that at around eight times higher thickness the frequency shift is ~2,5 times higher, while the response time to reaching saturation is almost the same. The humidity detection tests were performed immediately following the sensor’s full recovery from NO₂ detection.
4. Conclusions
ZnO films of various thicknesses (~10 – 80 nm) were grown on a QCM by ALD and their sensitivity to various concentrations of NO₂ was studied. The dependence was compared of the sensitivity, as proportional to the frequency shift and mass detected, on the thickness of the films. Even very thin ALD ZnO films showed a good sensitivity to NO₂ at room temperature and a capability to register as low concentrations as 50 ppm. Comparing the performance of films with various thicknesses showed that four times as thick films provide a threefold as large as a frequency shift while detecting 100 ppm NO₂. When comparing the detection of 500 ppm and 1000 ppm NO₂ by a ~20-nm thick ZnO film, we found that both the times for reaching saturation and recovery of the sensor roughly doubled as the concentration was increased twofold. Further, analyzing the frequency shifts for ZnO films with various thicknesses for various NO₂ concentrations allowed us to conclude that the dependence of Δf/f on the film thickness is weekly expressed at low concentrations and is rather stronger for the higher ones. We assume that this behavior is brought about by a combination of several effects – increased roughness of the thicker films and/or diffusion into voids, pores and bulk in the film.

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