Study of quartz crystal microbalance NO_2 sensor coated with sputtered indium tin oxide film

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Abstract. A study of NO_2 gas sorption ability of thin indium tin oxide (ITO) deposited on 16 MHz quartz crystal microbalance (QCM) is presented. ITO films are grown by RF sputtering of indium/tin target with weight proportion 95:5 in oxygen environment. The ITO films have been characterized by X-ray photoelectron spectroscopy measurements. The ITO surface composition in atomic % is defined to be: In-40.6%, Sn-4.3% and O-55%. The thickness and refractive index of the films are determined by ellipsometric method. The frequency shift of QCM-ITO is measured at different NO_2 concentrations. The QCM-ITO system becomes sensitive at NO_2 concentration $\geq$ 500 ppm. The sorbed mass for each concentration is calculated according the Sauerbrey equation. The results indicated that the 1.09 ng of the gas is sorbed into 150 nm thick ITO film at 500 ppm NO_2 concentration. When the NO_2 concentration increases 10 times the calculated loaded mass is 5.46 ng. The sorption process of the gas molecules is defined as reversible. The velocity of sorbtion /desorption processes are studied, too. The QCM coated with thin ITO films can be successfully used as gas sensors for detecting NO_2 in the air at room temperature.

1. Introduction

In the recent years one of the most important problems in the surrounding world is the increasing concentration of gas pollutants in the atmosphere. Among the hazardous gasses, the nitrogen dioxide (NO_2) can be extremely harmful for the human health, causing different senses irritations [1]. This is the reason, the researchers in this field to investigate intensively the possibilities for development of highly sensitive, fast, reversible, low temperature and low cost NO_2 detector.

It is well known that the quartz crystal microbalance (QCM) type sensors can react to the mass changes, respectively to the concentration changes, even in the nanogram range, in the case when suitable sensitive coating is deposited on the resonator electrodes [2,3]. Most typical application for this purpose have been found to be the metal oxide thin films, like WO_3, TiO_2, etc. [4,5]. Several papers have been reported in the literature, concerning deposition of different materials for effectively

detection of NO_2. $Ge_{33}Se_{67}$ chalcogenide glass was thermal evaporated and concentration of 1.48×10^{-10} mole of NO_2 molecules was detected [6]. Another used material is poly (3,4-ethylenedioxythiophene) (PEDOT) electrochemically deposited on the gold electrodes of the resonator, working at 35°C [7].

Indium tin oxide (ITO) also seems to be appropriate for gas detection. The available results show ITO films used for methanol, ethanol and ammonia vapors [8,9,10]. The principle of detection relies on the resistance change whit the vapors concentration changing and can be activated at optimum temperature in the range 150°C - 450°C. Hot wire semiconductor sensor with high surface area ITO film was prepared by the method of thermal oxidation for iso-butane detection at optimum temperature higher than 120°C [11]. Regarding NO_2 measurement, nanostructured Indium Tin Oxide (ITO) thin film has been produced by RF magnetron sputtering and concentrations lower than 50 ppm can be detected at high temperature of ~ 320°C. Again the sensor is resistive-type [12].

QCM principle in combination with ITO adsorbing film for NO and NO_x detection has been reported in [13,14]. It has been established that introduction of hydrogen during sputtering of ITO results in higher conductivity and more oxygen vacancies in the ITO films, which is ascribed as the key mechanism for sensing [13]. In [14] the acceptable mechanism of the NO_x adsorption in the deposited ITO film on QCM has not been established. By the authors' knowledge no available results about fabrication of reversible QCM sensor with sputtered ITO film from non-oxide target for application in nitrogen dioxide sensor working at room temperature are reported in the literature.

The aim of this work was to prepare and investigate the QCM-ITO structure for precision NO2 detection at different gas concentrations. The sensitive layers were deposited by RF sputtering of indium/tin target in oxygen environment.

2. Experimental

2.1. ITO films preparation and methods of characterization

ITO films were prepared by radio frequency sputtering in reactive atmosphere, using 3 inch non - oxidized target with In:Sn in a weight proportion of 90:5. The base pressure in the system was approximately 8.10^{-6} Torr. The partial pressure of the oxygen was set to 1.10^{-4} Torr and the total after introduction of the sputtering argon gas was adjusted to $1.5.10^{-2}$ Torr and was maintained constant during the process of deposition. The sputtering voltage was 0.85 kV and the plasma current of 0.16 A was measured (plasma power 136 W). The produced layers are neither thermally treated during deposition nor after that. In order to control the thickness and the composition of the film, together with the resonator, control pieces of glass and silicon were put on the holder, close to the target sample. The control samples were preliminary cleaned in detergent solution consisting of distilled water, ammonia and hydrogen peroxide in ratio 3:1:1. For the silicon piece additional treatment in water solution of hydrofluoric acid was performed for the native silicon dioxide removing. At this process' parameters a deposition rate of about 4 nm/min was achieved. The as-deposited ITO films were studied by ellipsometric methods and X-ray Photoemission Spectroscopy (XPS), in order to define their morphology, refractive index, thickness, surface state and composition. For this purpose a control silicon wafer, placed next to the resonator structure during sputtering. A Rudolph 435 ellipsometer at a wavelength of 632.8 nm was used. The XPS measurements are performed in ESCALAB Mk II (VG Scientific) electron spectrometer with aluminium radiation (hn = 1486.6 eV). X-Ray diffraction spectra are collected on Bruker D8 Advance diffractometer using CuK radiation and SoIX detector.

2.2. Sensor QCM – ITO structure

The ITO films were deposited on gold electrodes of quartz resonator by r.f. sputtering on both sides subsequently. An AT-cut approximately 16 MHz QCM with 8 mm diameter of the quartz plate and 4 mm gold electrodes was used as substrate. The ITO layer was deposited only on the gold electrode, using shadow stencil mask with low thermal capacity. The resonance frequency (f) and dynamic equivalent parameters of the QCM-ITO structure were measured during the investigation.

2.3. Sensing investigation of the QCM – ITO structure

The sensing properties of QCM-ITO were measured on home made laboratory set up. The methodology and the schematic diagram of the set up were described in detail in [15]. The test gas used in experiments was 1% NO_2 diluted in synthetic air. The synthetic air was used as carrier gas too. The flows of both the test and carrier gases were measured and controlled by mass flow controllers. By changing their ratio different concentration of the NO_2 in camera was created. The QCM was installed inside the camera on special holder. The temperature was measured by a Pt-thermosensor located next to the sample. All measurements were performed at room temperature (T) maintained with an accuracy of $\pm 0.2^oC$. A frequency counter connected to the QCM and joined to the computer for data recording the QCM frequency. Thereby, the frequency change as a function of time was measured. The measurement process can be conditionally divided into three stages:

- purging the camera with QCM-ITO structure with carrier gas until the frequency reaches a constant value (f_o),
- switching on the NO_2 gas flow and reaching the frequency saturation value (f),
- switching off the NO_2 gas flow and purging camera with carrier gas flow until reaching the f_o.

By measuring the time–frequency characteristics (FTCs) of the QCM-ITO at different NO_2 concentrations the sensitivity was determined. Experiments with NO_2 concentrations in the gas flow from 50ppm to 5000 ppm were carried out.

3. Results and discussion

3.1. Characterization of ITO thin films

The value of the refractive index is n=2.42 and the thickness is 150 nm as calculated from the ellipsometric measurements carried out at λ=632.8 nm. XPS measurements (figure 1) show that the surface composition of the ITO film is: O-55.1 at%, In–40.6 at% and Sn–4.3 at.%, which means that the film is indium rich. The O/In+Sn intensity ratio is 1.23 suggesting that the lower oxygen concentration probably results in more oxygen vacancies thus leading to creation of large number of active sites on the surface. The XPS spectra of the ITO film show In $3d_{5/2}$ and In $3d_{3/2}$ peaks at 444.4 and 452.0 eV, respectively. The binding energies of the photoelectron Sn $3d_{5/2}$, and Sn $3d_{3/2}$ peaks are 486.4 and 494.8 eV, respectively. These values reveal that the valence states of In and Sn are mainly +3 and +4, respectively, which is in consistent with the data for a $(In_2O_3)_{0.90}(SnO_2)_{0.1}$ phase of ITO oxide.

The 150nm thin films were deposited on both sides of the electrodes of the resonators. The QCM – ITO parameters of the structure were measured on every step of the experiments to ensure that the sensing response to NO_2 was the actual films' behaviour. The initial basic parameter such as motional resistance (R_s) was measured to be 9.74 ohm and quality factor (Q) of 40 323 was calculated. The parameters of the loaded QCM were suitable for gas sensing studies.

3.2. Gas sensing properties of ITO films to NO_2

The sorption ability of the ITO films was studied changing the NO_2 concentration in the range of 10 ppm - 5000 ppm. It was observed that QCM system became sensitive at NO_2 concentration $\geq$500 ppm. Response was detected at concentrations higher than 500 ppm up to 5000 ppm.

Frequency – time characteristics (FTCs) of the QCM-ITO structure under investigation were measured at 500 ppm, 1000ppm, 2500 ppm and 5000 ppm NO_2 concentrations. Figure 2 and figure 3 show the NO_2 response of ITO films for 1000ppm and 5000ppm respectively. At 1000 ppm the frequency change is linear for the sorption and desorption processes. The times for reaching saturation and recovering of the system are comparable (respectively 5.9 min. and 5.6 min.). Based on the sorption/desorption behaviour at this concentration, it is possible to suggest a mechanism of surface sorption. Increasing the NO_2 concentration leads to change in the mechanism of the sorption/desorption process.

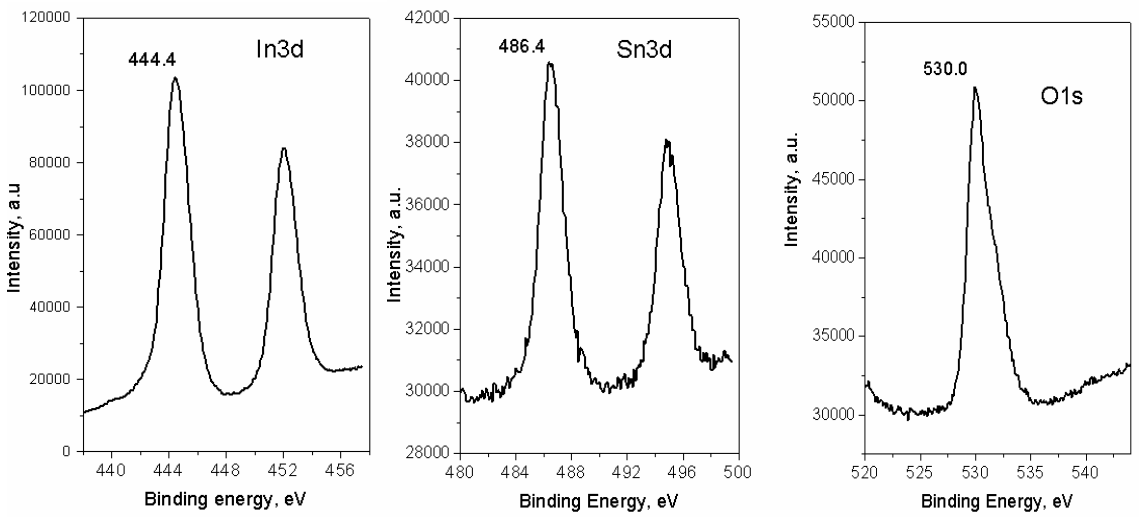

Figure 1. XPS spectra of an ITO film.

Typical FTC at high NO_2 concentration (5000 ppm) is shown in figure 3. Two stages can be observed during the change in the frequency of the FTC – a fast one and a slow one. The recovering (unloading) of the QCM goes off in the same manner. At the beginning of the sorption a sharp decreasing in the frequency was measured (f_{s1}), afterward slightly decrease of the frequency was detected until saturation was reached. This effect can be explained by sorption in depth of the film.

During the desorption process a similar effect was observed – a fast frequency recovering f_{d1} and slow reaching of the starting frequency f_{d2}. The comparison of the data shown in figures 2 and 3 demonstrates the resulting effect of the NO_2 concentration on the sorption and desorption processes.

The parameters of the described processes are summarized in table 1, where t_s and t_d are the total times for sorption and desorption at given constant NO_2 concentration, respectively. The times for

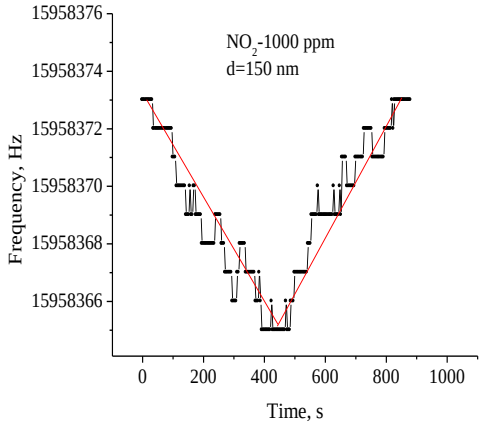

Figure 2. Frequency-time characteristic of ITO-QCM at 1000 ppm NO_2 concentration, thickness of ITO-150 nm.

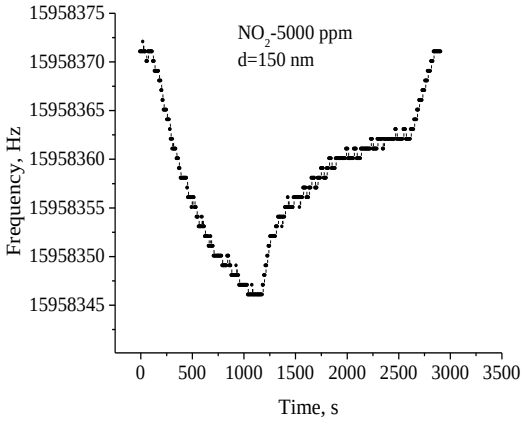

Figure 3. Frequency-time characteristic of ITO-QCM at 5000 ppm NO_2 concentration, thickness of ITO-150 nm.

reaching saturation of the system increase from 4.2 min to 14.9 min with NO_2 concentration increasing from 500 ppm to 5000 ppm. The same behaviour can be observed during the recovering process, where the increase is from 2.6 min to 23.4 min. The sorption and desorption rates (V_s and V_d respectively), defined as a frequency change with the time, shows an insignificantly increase of V_s from 1.2 Hz/min to 1.7 Hz/min and decreasing of the desorption rate V_d from 1.9 Hz/min to 0.9 Hz/min almost twice in the investigated concentration range.

Table 1. Sorption and desorption parameters of ITO (150nm) - QCM structure.

NO_2, ppm	t_s, min	t_d, min	V_s, H_z/min	V_d, H_z/min
500	4.2	2.6	1.2	1.9
1000	5.9	5.6	1.4	1.4
2500	8.9	14.5	1.7	1.0
5000	14.9	23.4	1.7	0.9

Based on the measured FTCs, the sorbed mass for each NO_2 concentration was calculated. The quantitative relationship between the change in frequency of an AT-cut piezoelectric crystal (f_o) and the mass change (Δm) caused by mass loading on the crystal surface was given by Sauerbrey equation [16]:

$$\Delta f = - 2.26.10^6 f^2_o \Delta m/s, \quad (1)$$

where f_o is the basic frequency of the unloaded piezoelectric crystal in MHz, Δm is the change of the mass on the surface in gram, and s is the surface area of the electrode in cm^2. The surface of the electrode in the experiment was 0.1256 cm^2. The resonant frequency shift (Δf) can be calculated as ($\Delta f = f-f_o$), where *f* is the frequency of the structure measured at saturation. Thereby using Sauerbrey's equation the sorbed mass on the resonator surface for each NO_2 concentration can be calculated. Figure 4 demonstrates the frequency shift and corresponding sorbed mass increase with increasing in NO_2 concentration. The obtained dependence for investigated structure QCM-ITO has almost linear characters. Tenfold increase in the concentration from 500ppm to 5000ppm leads to three times higher sorbed mass from 1.9 ng to 5.46 ng.

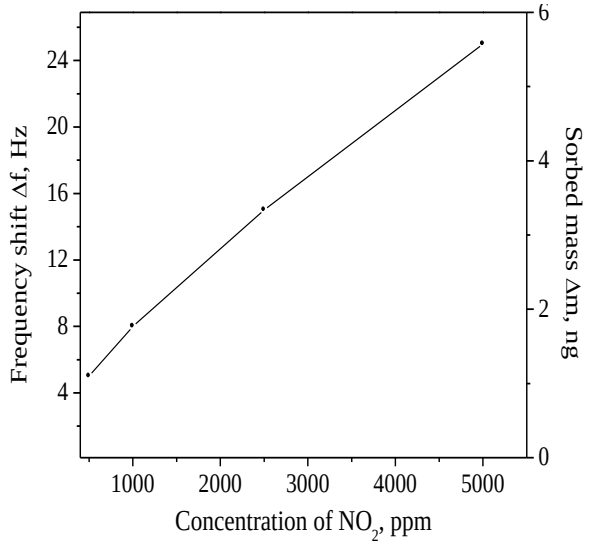

Figure 4. Dependence of the NO_2 concentration on the ITO-QCM frequency shift and mass loading. The thickness of ITO is 150 nm.

4. Conclusion

The QCM-ITO structure was realized. The ITO films were deposited by r.f. sputtering. The film properties such as: refractive index, morphology and composition were defined. The gas-sensing properties of the ITO to NO_2 in the air were studied. The ITO films were found to be sensitive to NO_2 concentrations above 500ppm. The sorption/desorption processes of NO_2 were estimated. The QCM-ITO structure is promising for NO_2 detection. The work demonstrated that the realized QCM-ITO structure could be used as gas sensor for NO_2 in the air. Further investigations were requires in aim of improving gas-sensing properties.

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