

Detection of NH₃ by quartz crystal microbalance with Sn_xNi_y coating

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In this paper, the gas-sensing properties of bimetallic structures of Sn and Ni to NH₃ are investigated using Quartz Crystal Microbalance (QCM). The 16 MHz QCM are created on AT-cut quartz with gold electrodes (4mm diameter). The bimetallic layers are prepared by cathode electro-deposition on QCM. Special electro-chemical cells are constructed to investigate the electro deposition process. Nickel is used as anode and the optimal current density is 3 A/dm². After electro deposition the coatings are treated at 200°C for one hour in air environment. The coatings are investigated by Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS) methods. SEM micrographs of the coatings show that they consist of a highly branching layer of bimetallic needles. The structure investigation of coatings indicate dendrite ones consisting of different Sn_xNi_y crystalline phases and Sn. The sorption properties of Sn_xNi_y coatings to NH₃ are studied in dynamic regime. The frequency-time characteristics (FTC_S) of the system QCM-Sn_xNi_y are measured. The changes of the frequency from 5Hz to 77Hz are defined for 10ppm and 1000ppm respectively. The maximum frequency shift and mass-loading are determined. It is obtained that Sn_xNi_y coatings possess sorption ability to NH₃ and can be successful used as sensor element for NH₃.

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1. Introduction

Quartz Crystal Microbalances (QCMs) are intensively studied in aim of their use as sensors. QCM posses many advantages compared to other sensors such as micromechanical and surface acoustic wave, cantilever and semiconductor [1-2].

The main priorities of QCM are high sensitivity, durability, fast response and recovery times. Their low cost and low energy consumption presumed wide application. The sensing properties of QCM can be improved by deposition of different coatings on QCM electrodes. The choice of appropriate material is important for QCM realization. Metal oxide such as SnO₂, TiO₂, WO₃ are used extensively for gas sensors [3]. In the last years different nanostructured thin films as nanowires, nanobelts, nanorods, nanotubes are good candidate for gas sensing applications due to its specific area [4-5]. Because QCM is sensitive to mass change, adsorption of very small quality of analyte can be detect through frequency change.

The aim of the current work is to study Sn_xNi_y layer as NH₃ sensor element by QCM; to define the properties of the coatings and to obtain the response and recovery times, the frequency shift and the sorbed mass in the NH₃ concentration interval from 10ppm to 1000ppm.

2. Experimental

2.1. Preparation of coating and QCM

The coating is fabricated by cathode electro-chemical deposition from water solution containing: 0,4M NiCl₂·6H₂O, 0,03M SnCl₂·2H₂O and NH₄HF₂-0,50M at pH=7,0 and temperature 20°C. Electrochemical cells are constructed to investigate the electro-deposition process. Nickel is used as anode and optimal current density is 3 A/dm². Polished copper plates are utilized as substrates for XRD and SEM investigation of coatings. The QCM (16 MHz) are created on AT-cut quartz crystal with 4 mm gold electrodes. For the experiments the QCM are covered by cathode electro-deposited Sn_xNi_y layer and treated at 200°C for one hour.

2.2. Methods of Sn_xNi_y and QCM estimation

The coatings are investigated by Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD) and X-ray Photoemission Spectroscopy (XPS) methods in order to define their morphology, structure and surface state.

The SEM investigation is carried out by a 515 Philips. The samples are coated additionally with C and Au thin layers in order to resolution increasing. X-ray diffraction analysis is carried out on specimens in powder form. For

this purpose, the coating is scrubbed off from the substrate and the powder was subjected to thermal treatment at 200 °C in air for 1 hour for a complete removal of the water absorbed. XRD spectra are collected at room temperature on a Bruker D8 Advance with CuK α radiation and SoIX detector at 2-theta range from 10° to 80° with a step of 0.05° and counting time of 1s/step.

The XPS measurements are performed in ESCALAB Mk II (VG Scientific) electron spectrometer with Al-radiation ($h\nu = 1486.6\text{eV}$). X-Ray diffraction spectra are collected on Bruker D8 Advance diffractometer using CuK α radiation and SoIX detector. The coatings for XPS investigation are prepared on QCM.

The QCM's quality is evaluated by measuring the equivalent dynamic parameters: static capacitance C_0 and equivalent dynamic resistance R_q by a Selective Level Meter. The dynamic capacitance C_q , the dynamic inductance L_q , and the quality factor Q are calculated [6].

The sorption properties of the created system to NH_3 are measured in laboratory set up. The experimental unit and the methodology of measurements are described in details [7]. The basic stages of the measurement process are: a) purging of the structures with dry air, reaching saturation and fixing the initial frequency F ; b) creating a certain NH_3 concentration; c) reaching saturation of the frequency values - ΔF (frequency of saturation for response time t_s); 4) purging of the structures with dry air, which restores to the initial frequency. The desorption (recovery) time, t_d is also measured. The NH_3 concentration in the test chamber is controlled by MFCs for NH_3 and the diluting gas flows. The temperature of measurements is maintained 26°C with an accuracy of $\pm 0.2^\circ\text{C}$. The QCM frequency is registered by frequency counter Hameg 8123 connected to the QCM and joined to the computer for data recording. Thus frequency change is fixed with accuracy of $\pm 5.25 \cdot 10^{-7}\text{Hz}$. The sorption ability of QCM - Sn_xNi_y system is evaluated on the basis of the measured FTCs at different NH_3 . Correlation between total frequency shift (ΔF) and sorbed mass (Δm) for AT-cut quartz is given by Sauerbrey equation [8].

3. Results and discussion

3.1. Morphology, structure and surface composition of Sn_xNi_y coatings

The coating has a dendrite structure, the dendrites growing from the substrate to the outer surface. SEM micrographs reveal a highly branching dendrite layer (Fig. 1). Big dendrites are observed with an average diameter of about 1 μm , which are built from smaller dendrites with an average diameter of about 0.17 μm .

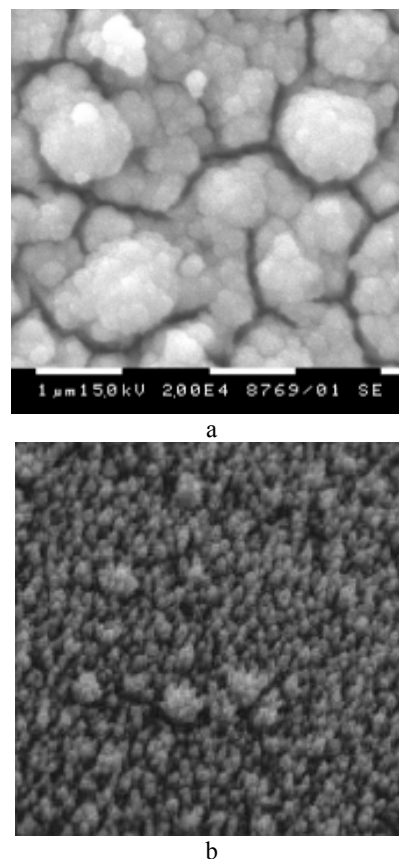


Fig. 1. SEM images of Sn_xNi_y at magnification: (a) 20000, Tilt = 90°; (b) 12000, Tilt = 45°

Fig. 2 shows a XRD spectrum. The coating is a mixture of crystalline phases: Sn_2Ni_3 (31°, 43°, 44°), SnNi_3 (28°, 45°) and Sn (32°). The phase Sn_4Ni_3 is unstable and during growth and after the thermal treatment it is transformed into a thermodynamically stable Sn_2Ni_3 [9]. The resulting structures can be explained with the close normal potentials of Sn and Ni, as well as with diffusion control on Sn deposition.

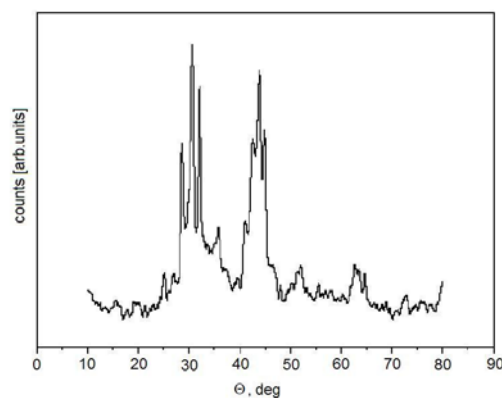


Fig. 2. XRD spectrum of a Sn_xNi_y coatings.

The surface composition of the Sn_xNi_y sorption layer obtained from the XPS data is 12.9% Sn, 10.0% Ni and 77.1% O (Fig. 3). The stoichiometry of the intermetallic layer is close to SnNi. The detected oxygen is due to formation of an oxide layer on the surface of the film, which is thin to screen the photoemission from the film underlayers. The photoelectron Sn3d peaks are broad and for instance the Sn3d_{5/2} peak can be resolved into two components with maxima at 485.1 eV and 486.6 eV, respectively. The low binding energy peak is attributed to tin in the SnNi alloy, while the peak with a higher binding energy is attributed to tin coordinated with oxygen atoms, probably in SnO or SnO₂. The Ni2p_{3/2} spectrum also contains two peaks - the first one at 853.1 eV is due to nickel in the alloy and the second one at 856.5 eV is connected with Ni²⁺ ions in NiO.

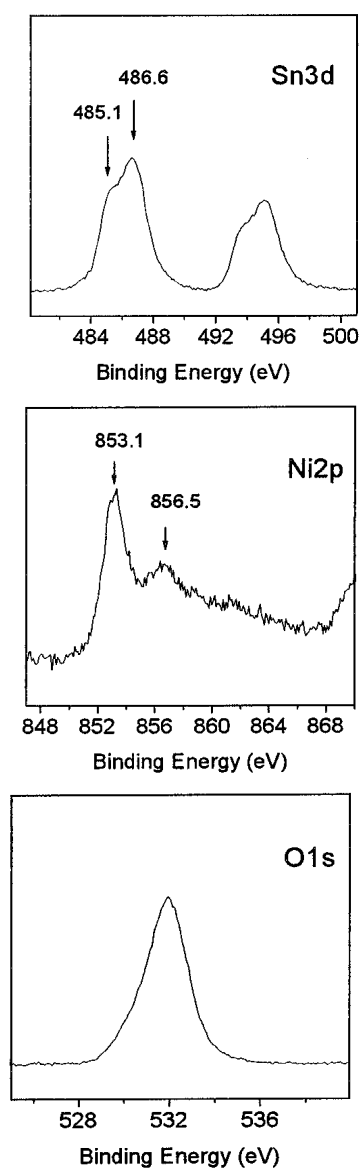


Fig. 3. Binding Energy (eV) of a Sn_xNi_y films

3.2. QCM - Sn_xNi_y equivalent parameters and gas sensing properties

The values of initial QCM parameters as R_q and Q are defined as 9,14Ω and 42 251 respectively. The process of Si_xNi_y film deposition worsened the QCM parameters as result of mass loading, but they remain appropriate (R_q=24.4Ω and Q=18 900) for sorption measurement. Insignificant improvement of the parameters (R_q= 22.5Ω and Q=20 675) is observed after ammonia treatment. The changes of the parameters probably are due to the decreasing of the acoustic losses as a result of the increased layer density.

In Fig. 4 are shown typical frequency - time characteristics (FTCs) of QCM-Sn_xNi_y at 100ppm NH₃ concentration where the process kinetics is well expressed. When NH₃ is added in the gas flow the sorption process starts and the frequency decreases with $\Delta f^s = 10\text{Hz}$ for response time $t^s = 28\text{s}$. This process is followed by a dynamic equilibrium between the sorbed and desorbed molecules when the frequency remains constant. Turning off the NH₃ flow and blowing the QCM-Sn_xNi_y structure through dry air leads to unloading for recovery time $t^d = 28\text{s}$ in which the frequency at the beginning is reached.

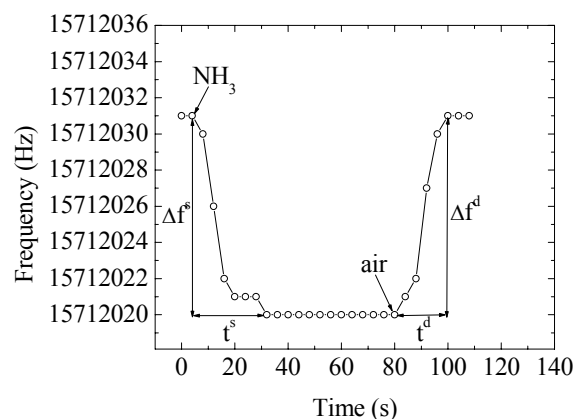


Fig.4. Kinetic of NH₃ adsorption and desorption for QCM - Sn_xNi_y sensor at 100ppm NH₃

Analogous kinetic process is observed for NH₃ concentration range from 10ppm - 100ppm. For concentrations higher than 100ppm, in the studied range 250ppm -1000ppm, FTCs change (Fig. 5). The sorption and desorption processes have two stages - fast and slow. During the first stage, for the response time $t_1^s = 28\text{s}$ the frequency Δf_1^s changes with 21 Hz at rate 0,75 Hz/s, while during the second for the response time $t_2^s = 176\text{s}$ the frequency Δf_2^s changes with 27Hz at rate 0,15 Hz/s, i.e. the speed decreased 5 times. The total frequency shift at NH₃ concentration of 250ppm is 48 Hz for 204s at average rate 0,23Hz/s.

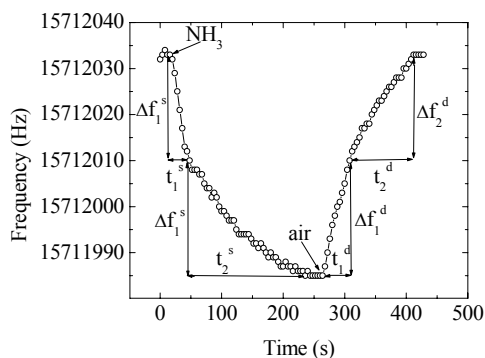


Fig. 5. Kinetic of NH_3 adsorption and desorption for QCM - Sn_xNi_y sensor at 250ppm NH_3

During the desorption process the two stages are in the same order as at sorption. First for $t_1^d=48\text{s}$ the frequency Δf_1^d is recovering with 25Hz at rate 0,57 Hz/s, then for $t_2^d=104\text{s}$, Δf_2^d is rising with 23Hz at rate 0,22Hz/s. The average sorption rate of 0,23Hz/s is significantly slower than the desorption rate of 0,31Hz/s.

The same changes of FTC dependence are observed for the 1000 ppm NH_3 concentration (Fig. 6). Comparing Fig. 5 and 6 finds only quantitative differences. The sorption times at higher concentrations increase significantly during both stages - from 28s to 72s during the first and from 176s to 284s during the second, while Δf increases from 48Hz to 77Hz respectively for concentrations 250ppm and 1000ppm. During the recovery process the dependence is similar.

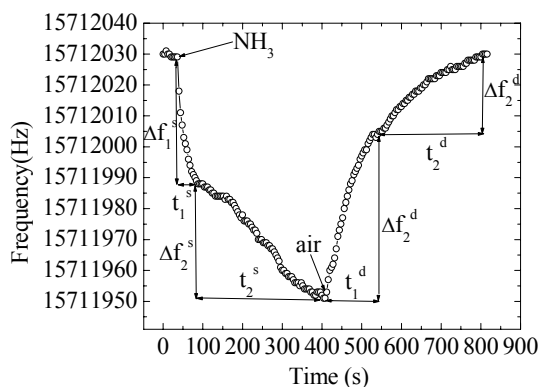


Fig. 6. Kinetic of NH_3 adsorption and desorption for QCM - Sn_xNi_y sensor at 1000ppm NH_3

The experiments show that the sorption process is reversible. The QCM- Sn_xNi_y system could be fully recovered without applying any additional energy, i.e. the sorption is physical. The response and recovery times are short and in function of the NH_3 concentration. For evaluation the sorption ability of the films by QCM method is necessary to measure only the fast stage of FTC.

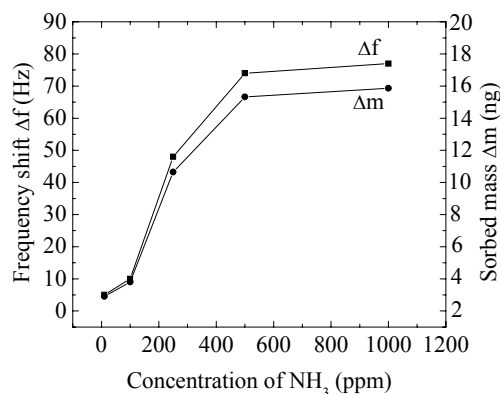


Fig. 7. Frequency shift and mass-loading of QCM - Sn_xNi_y sensor vs NH_3 concentration.

Fig. 7 illustrates measured frequency shift and mass-loading at different NH_3 concentrations. The investigated Sn_xNi_y coatings have higher sensitivity in the range 10ppm - 500ppm, afterwards it increases slowly. Value of the sorbed mass calculated with Sauerbrey equation is shown in Fig. 7 too. It changes is from 1,13ng to 17,33ng for NH_3 concentrations of 10ppm to 1000ppm.

4. Conclusions

The Sn_xNi_y coatings are prepared by electro deposition. The SEM images show a highly branching layer of bimetallic needles. XRD spectrum confirms the presence of a mixture of crystalline phases (Sn_2Ni_3 , SnNi_3 and Sn).

From XPS analysis of the structure QCM - Sn_xNi_y follows that the stoichiometry of the Sn_xNi_y is close to SnNi . The sorption ability of the coating deposited on QCM to NH_3 is investigated. The obtained results show two kinds mechanisms of sorption and desorption process: one step and two-steps for (10ppm NH_3 - 100ppm NH_3) and (250ppm NH_3 - 1000ppm NH_3) respectively. The process of sorption is determined as reversible. The frequency shift from 5Hz to 77Hz is registered and sorption mass from 1.13ng to 17.33ng is calculated for the NH_3 investigated interval. The initial results of the Sn_xNi_y sorption properties showed that QCM - Sn_xNi_y is suitable as a sensitive element for NH_3 detection.

Acknowledgments

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References

- [1] Y. Zhao, J. He, M. Yang, S. Gao, G. Zuo, *Analytica Chimica Acta*, **654**, 120 (2009).

- [2] S. Ichinohe, H. Tanaka, Y. Kanno, *Sens. Actuators* **B123**, 306 (2007).
- [3] C. Kim, R. Lad, C. Tripp, *Sensor and Actuators* **B76**, 442 (2001).
- [4] X. Wang, J. Zhang, Z. Zhu, *Applied Surface Science* **252**, 2404 (2006).
- [5] G. Mor, M. Carvalho, O. Varghese, M. Pishko, C. Grimes. *J. Mater. Res.*, **19**, 628 (2004).
- [6] S. Manolov, H. Tihchev, *Generators, Sofia Tehnika*, (1982).
- [7] V. Georgieva, P. Stefanov, Z. Raicheva, *J. Optoelectron. Adv. Mater.*, **11**, 1363 (2009).
- [8] G. Sauerbrey, *J. Physik* **155**, 206 (1959).
- [9] H. Qina, X. Zhaoa, N. Jianga, Z. Li, *Journal of Power Sources*, **171**, 948 (2007).

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