ULTRASONIC CHEMICAL SENSOR WITH ORGANIC MONOMOLECULAR LAYER

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In this work a structure of a ultrasonic chemical sensor with organic monomolecular layer as well as introductory measurement with the help of a set-up constructed in IFTR PAS are presented. Chemical composition of this layer is an equimolar mixture of 5-[[1,3-dioxo-3- [4-(1-oxooctadecyl) phenyl] propyl] amino] – 1,3 – benzenedicarboxylic acid (DA) and cetylamine (CA). The thickness of this layer is equal to dimension of one molecule. The sensor layer was deposited on one channel of the bi-channel sensor delay line (made from lithium niobiate) by means of the Langmuir–Blodgett method. The chemical sensitivity of this sensor to some mixtures of air with vapor of volatile organic compounds has been investigated.

Key words: ultrasonic chemical sensor, Langmuir–Blodgett layers, air-organic vapor mixtures, volatile organic compounds.

1. Introduction

There is a big demand of small, reliable and low-cost sensors in science, technology and industry. In last years ultrasonic sensors, where the ultrasonic waves are applied, become a great group of these kind of sensors [1]. The piezoelectric phenomenon is utilized in their construction and piezoelectric materials are used as substrates. Because of their material properties, mainly electromechanical coupling, the ultrasonic sensors are smaller, more reliable, more sensitive, more stable and cheaper than others.

Different physical and chemical parameters can be measured when the thin layer of a substance sensitive to a measured factor is placed on the piezoelectric substrate. During the physical or/and chemical interaction between this layer and the measured factor, the layer changes its acoustical, mechanical and electrical properties. Subsequently, these properties modify the ultrasonic field, which are converted into an electrical signal.

Parameters of these signal, especially frequency, voltage and current can be easily measured. Moreover, they are very convenient for data processing. Technology of sensor fabrication is compatible with that of integrated circuit.

In science and technology, volatile organic compounds (VOC) are used widely, and their application is essential. Leakage or another defect of installations that cause the air contamination by vapors of VOC are difficult to eliminate. On the other hand, in many cases, VOC are also harmful and flammable. A possibility of measurements of the vapor concentrations of VOC in the atmospheric air can affect on safety of a staff in places, where the organic solvents are used. In case of a failure of the installation containing VOC, the proper actions or procedures can be applied. These kind of possibilities are given by ultrasonic sensors with properly chosen sensor layer.

Langmuir–Blodgett (L–B) method allows to obtain layers with monomolecular thickness and deposit them on the substrate [2–4]. The total thickness of the sensor layer can be controlled very strictly. These layers (nanolayers) are highly ordered in the molecular sense due to interactions of deposited molecules with a water surface during the deposition process. This feature enables to expose the molecule moiety of the sensor layer on the influence of analyzed substance e.g. analite [5–7].

Generally, the sensor response i.e. frequency shift Δf and attenuation α of the ultrasonic wave can be written as:

$$\Delta f, \alpha = \left(\frac{\partial f, \alpha}{\partial m} \right) \cdot \Delta m + \left(\frac{\partial f, \alpha}{\partial c} \right) \cdot \Delta c + \left(\frac{\partial f, \alpha}{\partial \varepsilon} \right) \cdot \Delta \varepsilon$$
$$+ \left(\frac{\partial f, \alpha}{\partial \sigma} \right) \cdot \Delta \sigma + \left(\frac{\partial f, \alpha}{\partial T} \right) \cdot \Delta T + \left(\frac{\partial f, \alpha}{\partial P} \right) \cdot \Delta P, \qquad (1)$$

where Δm, Δc, $\Delta \varepsilon$, $\Delta \sigma$, ΔT and ΔP denote the changes of mass, visco-elasticity, dielectric constant, electrical conductivity, temperature and pressure, respectively. These changes influence ultrasonic wave propagation, and subsequently the frequency of the generator, in which the sensor delay line is an element of positive feedback. The frequency change can be expressed as:

$$\frac{\Delta f}{f_0} = \frac{\Delta \nu}{\nu_0}, \qquad (2)$$

where ν is velocity and subscript 0 denotes the initial state not disturbed by the interaction of the analite with the sensor layer. In most cases, the mass of the sensor layer is changed by bonding of the analite molecules with the sensor layer. This bonding can be caused by absorption, diffusion, saturation or condensation. In this case:

$$\Delta f = -k_m \cdot f_0^2 \cdot \frac{\Delta m}{A}, \qquad (3)$$

where k_m is a constant, $\Delta m/A$ – the mass of analite bonded with sensor layer per surface unit. The value of $\Delta m/A$ is connected with the analite concentration in the atmosphere near the sensor and, in the equilibrium, is determined by equilibrium equations of the proceeding physicochemical process.

2. Sensor with nanolayer and measuring setup

The setup consists the sensor delay line, chamber, electronic module, power supply, A/D converter and PC computer with specialized software [8]. Details of the setup are presented in Figs. 1 and 2.
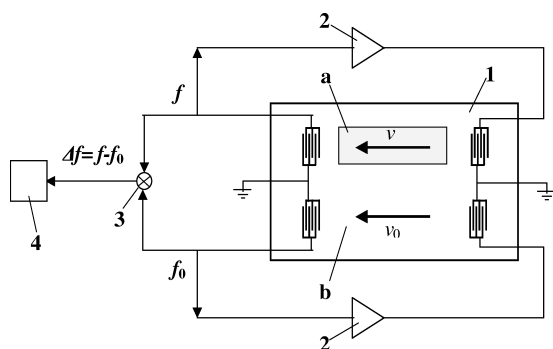

Fig. 1. The scheme of the measuring setup: 1 – sensor delay line (a – measuring channel, b – reference channel), 2 – high frequency amplifier, 3 – balanced mixer, 4 – difference frequency recorder.
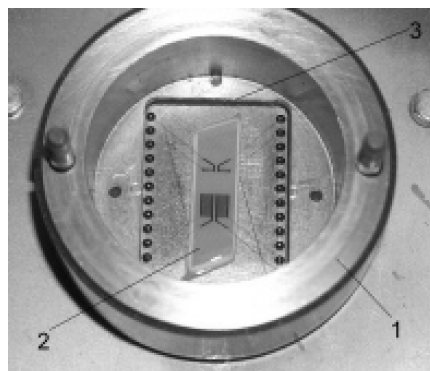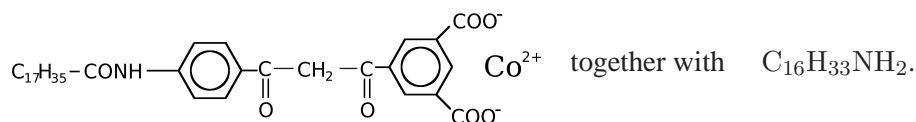

Fig. 2. The inside of the chamber: 1 – side wall of the chamber, 2 – sensor delay line, 3 – heater of the digital thermostate.

The sensor delay line has two independent emitting-receiving channels placed on the lithium niobiate substrate. One of them is covered by sensor layer. Second one is the reference channel for a temperature compensation. The work frequency of both channels equals 70 MHz.

The bicomponent nanolayer (thickness of it equals one molecule) was prepared by L–B method and deposited on a waveguide surface of one channel of the sensor delay line. The aqueous solution of cobalt bromide was applied as a subphase. The sensor monomolecular layer was deposited by lowering the subphase level, i.e. by horizontal method. The layer was fabricated from equimolar mixture of 5-[[1,3-dioxo-3-[4-(1-oxooctadecyl) phenyl] propyl] amino]-1,3-benzenedicarboxylic acid (DA) and cetylamine (CA).

In the presence of $CoBr_2$ in subphase, the subsequent compounds were deposited on the substrate:

$$C_{17}H_{35}-CONH-\!\!\bigcirc\!\!-\underset{O}{\overset{}{C}}-CH_2-\underset{O}{\overset{}{C}}-\!\!\bigcirc\!\!\overset{COO^-}{\underset{COO^-}{}}Co^{2+} \quad \text{together with} \quad C_{16}H_{33}NH_2.$$

The sensor is installed into the chamber, which has the thermostating setup, temperature sensor, inlet and outlet pipes. The constant temperature and controlled concentration of air-vapor of VOC atmosphere are kept in the chamber.

The role of electronic module is to generate ultrasonic waves in both channels and separate differential frequency, i.e. difference between the frequencies of the both channels. The sensor delay line is a part of the oscillator with positive feedback. The generation and stabilization circuits for both channels are identical.

The sensor delay line is thermally coupled with a heating element of the digital thermostat.

During measurement the differential frequency and temperature are recorded by the data acquisition setup. This setup consists of the two-channel A/D converter, personal computer and software.

3. Measurements

When the working conditions of the sensor delay line were stabilised, the air with the known concentration of the vapour of one VOC chosen for the measurement: methanol, isopropanol, n-butanol, acetone, chloroform and toluene, was pumped into the chamber. In the two-second intervals of time, the response of the delay line was recorded as the dependence of the differential frequency on time. Additionally, the temperature in the chamber is also recorded. In Fig. 3, the representative plots of the differential frequency are presented as the result of influence of the air containing 3.5% of VOC, on the sensor layer. Table 1 contains values of the response parameters of the sensor with DA + CA nanolayer on the presence of some VOC.

Table 1. Response parameters of the sensor with DA + CA nanolayer on the presence of some VOC.

Name of VOC	Decrease of differential frequency after contact with VOC [Hz]	Increase of differential frequency in time after contact with VOC [Hz/min]
Methanol	49	1.2
Isopropanol	83	1.2
n-Butanol	89	7.3
Chloroform	47	0.5
Acetone	38	0.8
Toluene	65	2.9

From Fig. 3 and Table 1, it can be noticed that the sensor layer reacts on the presence of VOC in different way. The decrease (jump) of differential frequency immediately after contact with VOC is highest for isopropanol and n-butanol, medium – for toluene, and lowest one – for methanol, chloroform and acetone. This observation means that at the beginning of the mutual contact, molecules of isopropanol and n-butanol interacts with DA + CA layer more intensively than molecules of methanol, chloroform and acetone.
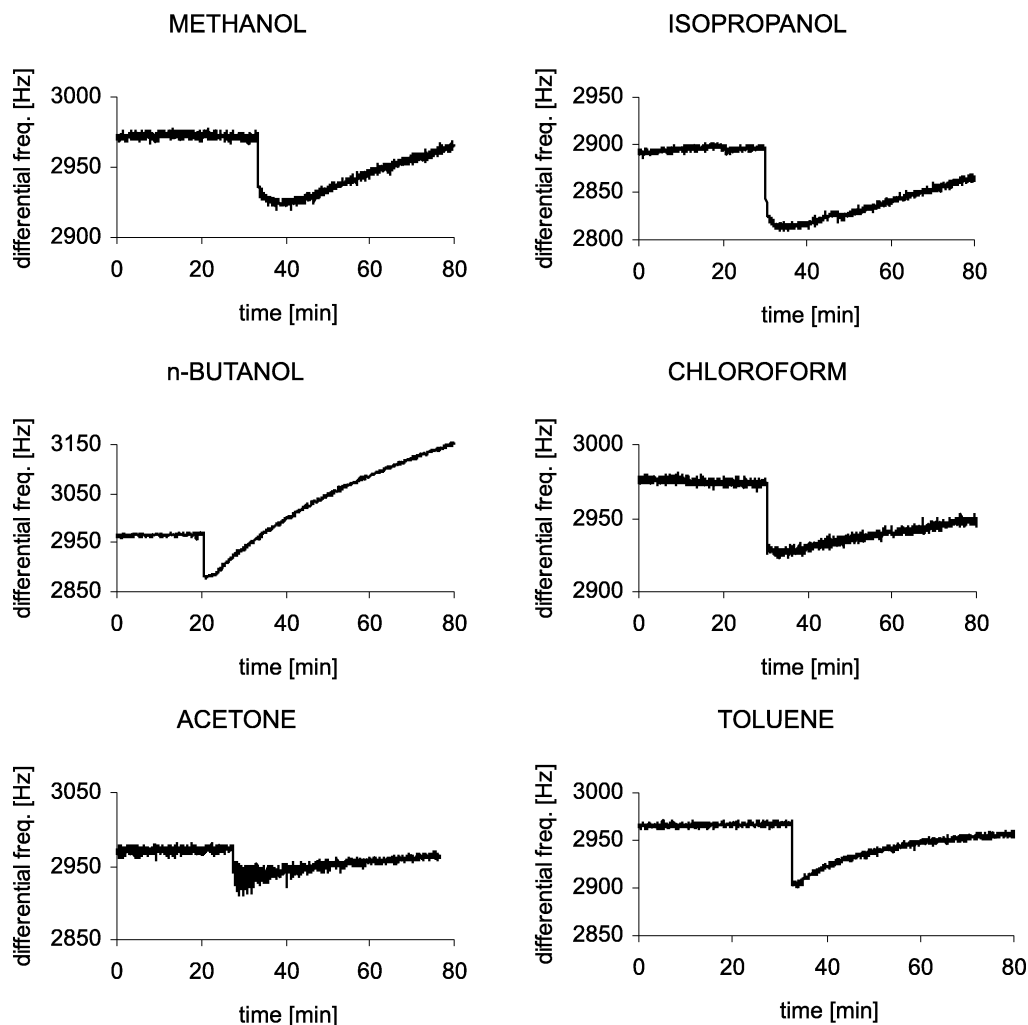
Fig. 3. Plot of the differential frequency vs. time for the sensor delay line with the layer of DA + CA in the air with 3.5% (mass) vapour of some VOC.

For n-butanol, the increase of differential frequency in time after contact with VOC is significantly greater than for other VOC. For methanol, isopropanol and acetone this increase has lowest values, and for toluene – medium one. This parameter reflect the long-term interactions between the molecules of analite and the layer.

For n-butanol and toluene, the dependencies of differential frequency on time rather fast go to saturation – Fig. 3.

In conclusion, the tested layer is the most sensitive to n-butanol and toluene, less – to isopropanol and methanol, and least – to chloroform and acetone.

These kind of measurements will be continued for other VOC. After that a removal of CA from the nanolayer is planned. This should cause its higher sensitivity to the

vapour of VOC, because of the formation of a skeletonized structure containing pores of the molecular dimensions. The investigations of that way prepared layer will be presented in a next paper.

4. Conclusion

In this work the results of the measurements are presented for the ultrasonic sensor with the layer made from equimolar mixture of 5-[[1,3-dioxo-3-[4-(1-oxooctadecyl) phenyl] propyl] amino]-1,3-benzenedicarboxylic acid (DA) and cetylamine (CA) by means of Langmuir–Blodgett method. The layer is sensitive at different degree to the vapours of some volatile organic compounds as methanol, isopropanol, n-butanol, acetone, chloroform and toluene in the air. The tested layer is the most sensitive to n-butanol and toluene, less – to isopropanol and methanol, and least – to chloroform and acetone. These results were obtained with the help of the setup constructed in IFTR PAS. This setup enables the automatic measurements of differential frequency between two channels of the sensor delay line and the temperature in the chamber.

The next measurements are planned for other volatile organic compounds and after the amine removal from this layer.

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