ULTRASONIC CHEMICAL SENSOR FOR DETECTION OF ALIPHATIC AND AROMATIC HYDROCARBONS IN AIR

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The reaction of the organic monomolecular Langmuir–Blodgett layer, deposited on the sensor delay line using surface acoustic wave, on the presence of vapors of some aliphatic and aromatic hydrocarbons in air has been investigated. The 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). Time of sensor reaction is less than 2 seconds. Decrease of the differential frequency after contact with the vapor-air mixture and decrease of this frequency in time are different for various hydrocarbons; a length of the chain is important for aliphatic hydrocarbons and a presence or not of side chains – for aromatic ones. The reaction of the sensor on the hydrocarbon vapors in air is reversible.

Keywords: ultrasonic chemical sensor, monomolecular Langmuir–Blodgett organic layers, volatile organic compounds, hydrocarbons.

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].

Different physical and chemical parameters can be measured when the thin layer, also Langmuir–Blodgett type, of a substance sensitive to a measured factor is placed on the piezoelectric substrate.

In this work the ultrasonic sensor for detection of vapors of volatile organic compounds (VOC) from groups of aliphatic and aromatic hydrocarbons in air has been presented. VOC are used in many branches of industry and science as solvents and fuels.

The possibility of detection of VOC in air is very important for the safety of people and environment, because, in many cases, VOC are flammable and form explosive mixtures with air. They are also harmful, toxic and some of them are known as carcinogenic. A high concentration of VOC in air can be easily achieved since they have high vapor pressure and low boiling temperature.

Langmuir–Blodgett (L–B) method allows to obtain layers with monomolecular thickness and deposit them on the substrate [2–5]. 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 i.e. the analite.

2. Construction of the sensor

The sensor consists of piezoelectric substrate and thin, monomolecular chemosensitive layer, which covers a part of the substrate surface. The substrate is made from lithium niobiate and has interdigital transducers forming two independent emitting-receiving channels for surface acoustic waves (SAW). One channel covered by the chemosensitive layer is that for measurements. Second one is the reference channel for a temperature and pressure compensations. The operating frequency of both channels equals 70.3 MHz.

The chemosensitive layer is the bicomponent nanolayer (thickness of it equals one molecule), which was prepared by L–B method and deposited on a waveguide surface of one channel of the sensor delay line by lowering the subphase level, i.e. by horizontal method – Fig. 1.
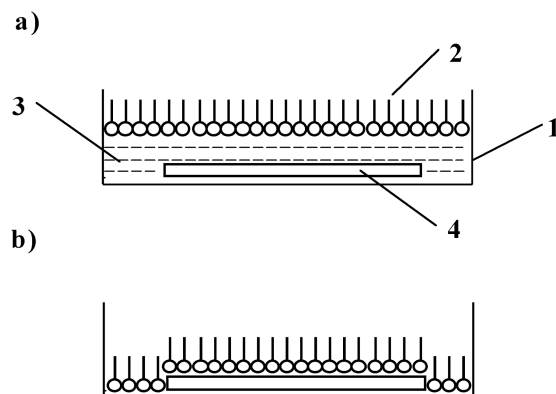

Fig. 1. Horizontal method of Langmuir–Blodgett layer deposition: a) before, b) after deposition. 1 – trough, 2 – deposited substance, 3 – subphase (water), 4 – substrate.

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)

with the help of a aqueous solution of cobalt bromide as a subphase. The presence of $CoBr_2$ causes a modification of the layer structure by the formations of salts and 1,3-diketonate complexes of DA with Co^{2+} [6], what makes this layer very stable. Atomic Force Microscopy (AFM) image of this layer in contact mode is presented in Fig. 2.
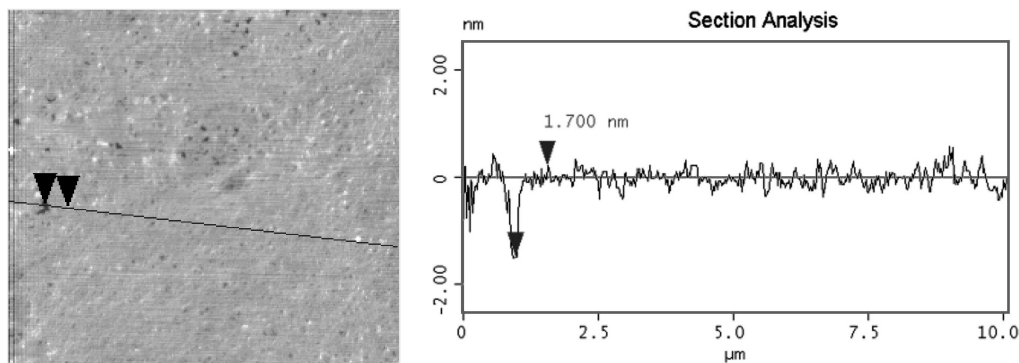

Fig. 2. The AFM image of DA+CA layer. According to section analysis, the layer quality is rather good.

The sensor was installed into a chamber. The chamber was filled by the mixture of air and a vapor of the hydrocarbon or clean air. The differential frequency i.e. the difference between the frequencies of the surface waves, which propagated in both channel was measured by the electronic setup [5].

3. Measurements and results

After stabilization of the working conditions of the sensor (a constant value of the differential frequency), the mixture of air and the vapors of the hydrocarbon at 300 ppm concentration was pumped into the chamber. Isopentane, n-hexane and n-heptane have been chosen as aliphatic hydrocarbons and benzene, toluene and o-xylene as aromatic ones. After 20 minutes the chamber was filled by clean air. In the two-second intervals of time, the response of the sensor was recorded continuously as the dependence of the differential frequency on time. More detailed description of the experimental setup and measurements are given in [5]. In Fig. 3, the representative plots of the differential frequency are presented as the result of interaction of the air containing the vapour of the hydrocarbon on the sensor layer.

The analysis of results allowed to determine values of the response parameters of the sensor with DA+CA nanolayer on the presence of the hydrocarbons – Table 1.

The sensor reacts on the vapors of the hydrocarbons used in testing. This reaction is reversible, because the sensor returns to the initial state when the chamber is filled by clean air. The reaction time i.e. a time when the differential frequency decreases after the sensor contact with the hydrocarbon, is less than 2 seconds. It can be noticed that decreases (jumps) of the differential frequency after contact with the vapor-air mixture

and decreases of this frequency in time are different for various hydrocarbons. The values of these decreases depend on a length of the chain for the aliphatic hydrocarbons and a presence or not of side chains – for the aromatic ones. The values of the decreases of the differential frequency in time after contact with the hydrocarbon vapor are bigger for the aromatic hydrocarbons than those for the aliphatic ones.

Table 1. Response parameters of the sensor on the presence of aliphatic and aromatic hydrocarbons.

Name of hydrocarbon	Decrease of differential frequency after contact with hydrocarbon [Hz]	Increase of differential frequency in time after contact with hydrocarbon [10^{-2} Hz/min]
isopentane	5.6	5.5
n-heksane	9.6	4.0
n-heptane	13.6	7.5
benzene	7.1	14.5
toluene	12.7	17.0
o-xylene	18.0	8.0

From the relationship between the change of frequency, Δf, of the sensor in an oscillator loop and the change of mass bonded to the sensor surface, Δm, (neglecting the changes of a viscoelasticity, dielectric constant and electric conductivity of the layer):

$$\Delta f = K f_0^2 \frac{\Delta m}{A}$$

(where K is a constant, for lithium niobate $K = 5.49 \cdot 10^{-11}$ sm^{2}g^{-1}, f_0 – operating frequency of the sensor and A – surface of chemosensitive layer) and the molar masses of the hydrocarbons, the ratio of a number of bonded hydrocarbon molecules to the number of molecules in the chemosensitive layer n/n_{L-B} were calculated and the values of these ratios are presented in Table 2.

Table 2. Values of $\Delta m/A$ and n/n_{L-B} for the aliphatic and aromatic hydrocarbons.

Name of hydrocarbon	Molar mass [g/mole]	$\Delta m/A$ immediately after contact with hydrocarbon [µg/m^2]	$\Delta m/A$ 20 minutes after contact with hydrocarbon [µg/m^2]	n/n_{L-B} immediately after contact with hydrocarbon $\cdot 10^3$	n/n_{L-B} 20 minutes after contact with hydrocarbon $\cdot 10^3$
isopentane	72.15	20.6	24.7	9.0	10.8
n-heksane	86.18	35.4	38.3	12.9	14.0
n-heptane	100.20	50.1	55.6	15.7	17.5
benzene	78.11	26.2	36.8	10.5	14.8
toluene	94.14	46.8	59.3	16.0	20.2
o-xylene	106.17	66.3	72.2	19.6	21.3

The ratios $n/n_{\text{L-B}}$ have low values. This observation and reversibility of the sensor layer indicates that the interactions between chemosensitive layer and hydrocarbons are weak – the nonpolar molecules of the hydrocarbon interact with nonpolar parts of molecules DA and CA. The values of the ratio $n/n_{\text{L-B}}$ increase when the molar mass increases for both group of the hydrocarbons. The increase of this ratio in time is the greatest one for benzene and the lowest one for isopentane.
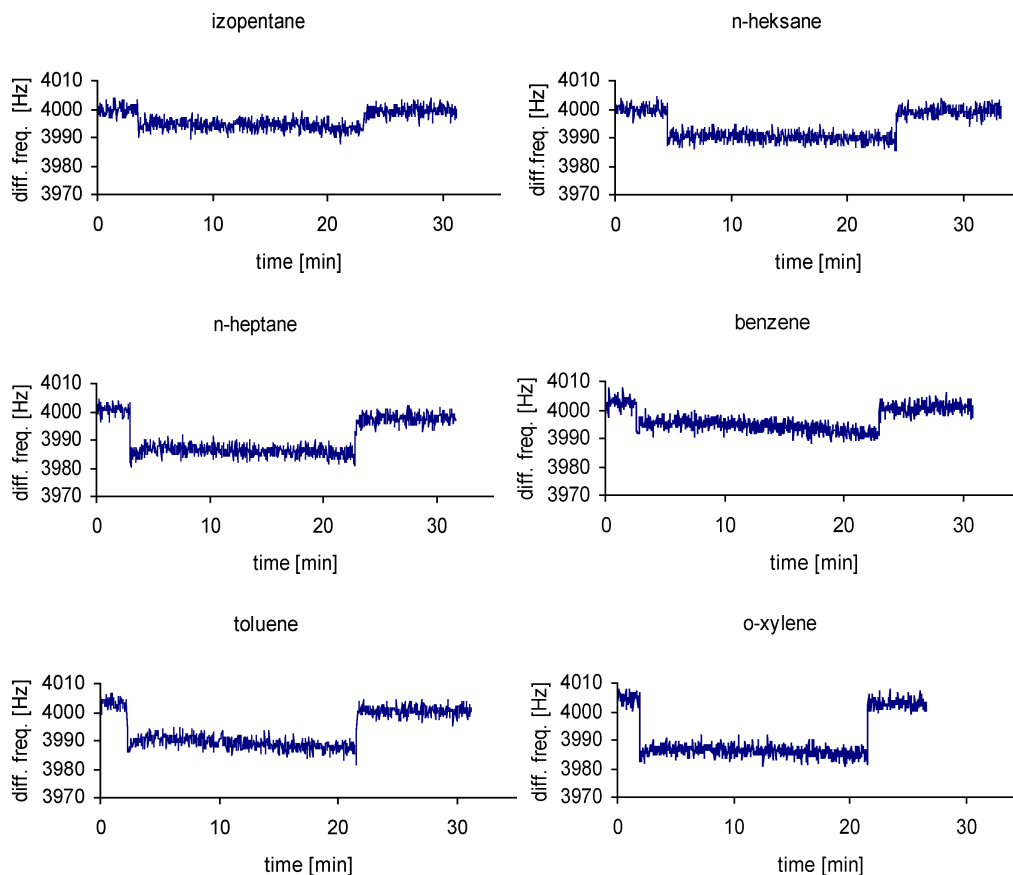

Fig. 3. Plot of the differential frequency vs. time as the sensor response for action of the mixture of the hydrocarbon and air. The hydrocarbon vapour concentration equals 300 ppm.

4. Conclusions

The sensor described in this work detects the presence of the vapours of the aliphatic and aromatic hydrocarbons at low concentrations. This sensor reacts quickly and its work is reversible. The response parameters of the sensor depend on the kind of the hydrocarbon.

Analogical 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 vapor of VOC, because of the formation of a skeletonized structure containing pores of the molecular dimensions – Fig. 4.
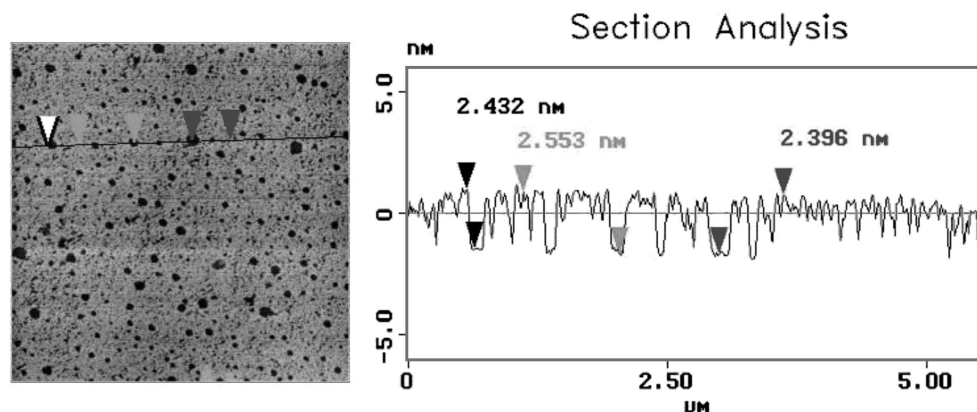

Fig. 4. The AFM image of DA+CA layer after removing of CA – skeletonized structure.

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