Adsorption Properties of Porous Langmuir–Blodgett Layer Used in SAW Sensor for Vapors of Some Chlorinated Hydrocarbons

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The porous Langmuir–Blodgett film has been fabricated from an equimolar mixture of 5-[[1,3-dioxo-3- [4- (1-oxooctadecyl) phenyl] propyl] amino] – 1,3 – benzenedicarboxylic acid (DA) with cetylamine (CA) and subsequently removing of cetylamine after a layer deposition. This film has been investigated as the sensing layer of the surface acoustic waves (SAW) sensor of vapors of some chlorinated hydrocarbons in air. From the experimental results the values of the number of adsorbed molecules of chlorinated hydrocarbons per surface of sensing layer, N_M/A, for this porous Langmuir–Blodgett layer has been calculated. An attempt to explain the observed differences in the adsorption of chlorinated hydrocarbons has been undertaken.

Keywords: monomolecular Langmuir–Blodgett organic layers, chlorinated hydrocarbons, surface acoustic wave sensors

1. Introduction

Chlorinated hydrocarbons (CH) are simple hydrocarbons in which one or more of the hydrogen atoms have been replaced by the chlorine ones. Most chlorinated hydrocarbons of low molecular weight are useful as solvents. CH are used in many branches of industry and science as solvents and reagents. Their applications are essential. The possibility of detection of CH in air is very important for the safety of people and environment because CH are harmful, toxic and some of them are known as carcinogenic.

A high concentration of CH in air can be easily achieved since they have a high vapor pressure and low boiling temperature. Thus the monitoring of CH has become a serious task. Current monitoring methods (i.e. gas chromatography

and mass spectroscopy) requiring sample transportation and an off-site analysis are costly and time-consuming. An attractive alternative are real time sensors that can be placed in situ reducing the need for sample collection and an expensive off-site analysis. The widely used device is an surface acoustic wave (SAW) delay line covered by a chemosensitive layer, in which the increase of mass of this layer due to sorption of the analysed molecules produces a change of velocity of the surface acoustic wave [1]. Molecular imprinted polymers [2], carbon nanotubes [3], lipids [4], liquid crystals [5], supramolecular compounds from the groups of phtalocyanines [6], porphyrines [7], cyclodextrines [8], calixarenes [9] and cyclophanes [10] have been applied as materials for the chemosensitive layers.

The Langmuir–Blodgett (LB) method allows to obtain layers of monomolecular thickness and deposit them on the substrate in an extremely ordered manner in the molecular sense [11–16]. Because of its nanometer thickness, the LB layer causes only a small initial mass loading of the surface of the SAW delay line and a low attenuation of the surface acoustic wave.

In this work, the porous LB film has been investigated as the chemosensitive layer covering the SAW delay line system for the detection of vapors of some CH in air. The porous structure of the LB layer should change its sensing properties. The adsorption of this layer for the most frequently used CH such as dichloromethane (methylene chloride), trichloromethane (chloroform), tetrachloromethane (carbon tetrachloride), 1,1,1-trichloromethane (methyl chloroform), trichloroethene (trichloroethylene) and tetrachloroethene (tetrachloroethylene, perchloroethylene) has been studied.

2. Experimental

The experimental set-up consists of the SAW sensor delay line, the chamber, the electronic module, the power supply, the A/D converter and a PC computer with specialized software. This set-up is based on frequency changes in the acoustic surface wave dual delay line system, which is well known [1, 15–19]. The substrate is made of lithium niobiate and has interdigital transducers forming two independent and identical acoustic delay lines. A part of the surface of one of delay lines is covered by a monomolecular chemosensitive layer and forms the measurement line. The second delay line is the reference line for temperature and pressure compensations. The role of the electronic module is to generate ultrasonic waves in both the delay lines and to determine the difference frequency. The operating frequency of both lines equals 70.3 MHz. Both lines are parts of the positive feedback loop of oscillator circuits. The generation and stabilization circuits of both lines are identical. The response to the presence of vapor of a particular CH in air is detected and recorded as a change of the difference frequency between the two oscillator frequencies. The accuracy of the difference frequency measurements by the electronic module equals 1 Hz.

The chemosensitive layer is the nanolayer (the thickness of it equals one molecule), which was prepared by the LB method and deposited on a waveguide surface of the measurement line by lowering the subphase level, i.e. by the horizontal method [20].

The layer was fabricated from an 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 an aqueous 0.5 mM solution of cobalt bromide as a subphase. The presence of $CoBr_2$ causes a modification of the structure of the layer by the formation of salts and 1,3-diketonate complexes of DA with Co^{2+} [21], what makes this layer very stable due to intermolecular interactions between DA molecules. Subsequently, the cetylamnine was removed from the layer by washing in chloroform. This process caused the formation of a structure containing pores of molecular dimensions with diameter distribution from 16 nm up to the diameter of the hydrocarbon tail (0.2 nm), which modified the properties of the sensing layer. The atomic force microscopy (AFM) image of the porous DA layer in a tapping mode is presented in Fig. 1.
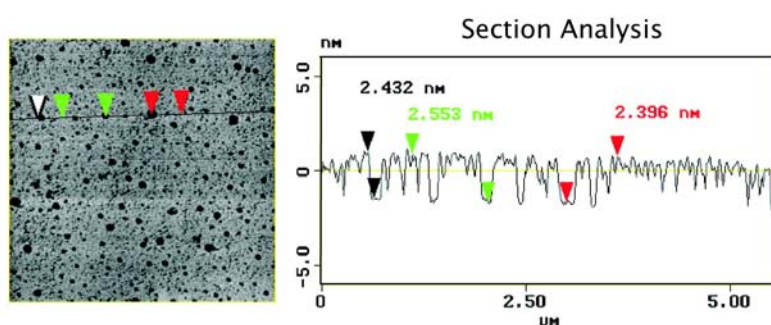

Fig. 1. The AFM image of a monolayer film obtained from an equimolar mixture of DA + CA molecules, transferred from $CoBr_2$ sub-phase at 35 mN/m of surface pressure and after removing of CA. The porous structure is visible.

The sensor was installed into a chamber. The chamber was filled by the mixture of air and a vapor of CH or by clean air. The difference frequency, i.e. the difference between the frequencies of the surface waves, which propagated in both lines (measurement and reference) was measured by the electronic setup. During the measurements, the temperature of the chamber and its interior containing the delay line system was kept constant (35.00 ± 0.05°C) by immersion into the bath of a thermostat. After the stabilization of the working conditions of the dual delay line system (a constant value of the difference frequency), the mixture of air and the CH vapors at 300 ppm concentration was pumped into the chamber. Dichloromethane, trichloromethane, tetrachloromethane, 1,1,1-trichloromethane, trichloroethene and tetrachloroethene have been chosen as tested CH. After 20 minutes the chamber was filled by clean air. In two-second intervals of time, the response of the sensor was recorded continuously by the data acquisition set-

up as the dependence of the difference frequency on time. Each measurement was repeated five times.

3. Results and discussion

In Fig. 2, plots of the difference frequency versus time are presented for different CH. These frequency shifts result from the interaction of the mixtures of air and the CH vapors with the sensing layer.
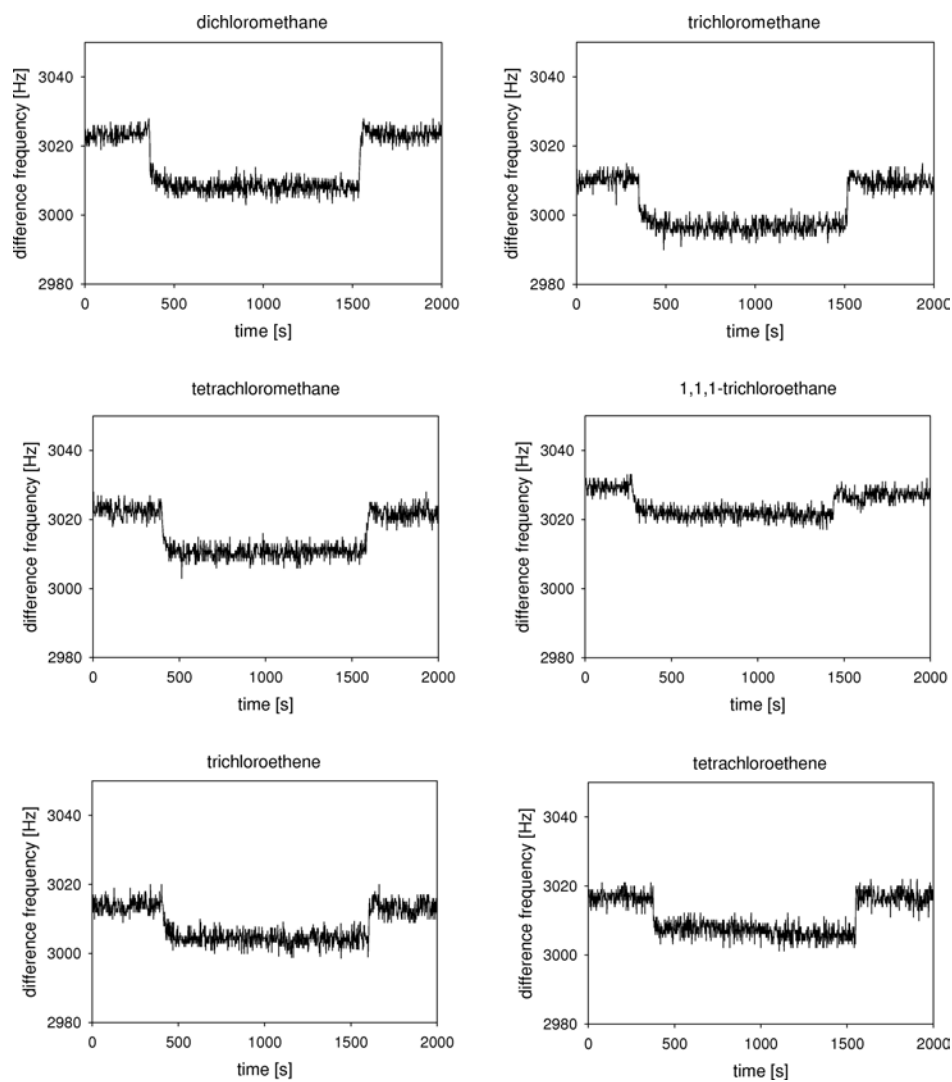

Fig. 2. Plots of the difference frequency vs. time as responses of the porous DA layer to the action of the mixture of chlorinated hydrocarbons and air. The chlorinated hydrocarbon vapour concentration equals 300 ppm.

The layer reacts on the vapors of the CH used in the testing. This reaction is reversible because the value of the difference frequency returns to the initial one when the chamber is filled by clean air. The reaction time, i.e. the time in which the difference frequency changes after the sensing layer contact with CH, is less than 2 seconds.

The analysis of the results allowed to determine the values of the response parameters of the sensor covered by the porous DA layer to the presence of CH, which are shown in Table 1. It should be noticed that decreases of the difference frequency after the contact with the vapor-air mixture and the diminution of this frequency in time depend on the kind of CH. It can be seen from Table 1 that there is a selectivity of the adsorption on the porous DA film for different CH. More information can be obtained taking into account the molecular mass of the CH.

Table 1. Mean values of the response parameters of the dual delay line covered by the porous DA layer on the presence of chlorinated hydrocarbons (CH). Each measurement was repeated five times. Standard deviations of the decrease of difference frequency after contact with CH and the diminution of difference frequency in time after contact with CH are not grater than 1.2 Hz and $3 \cdot 10^{-4}$ Hz/s, respectively.

Name of CH	Decrease of difference frequency after contact with CH [Hz]	Diminution of difference frequency in time after contact with CH [10^{-3} Hz/s]
dichloromethane	12.7	3.2
trichloromethane	10.6	2.6
tetrachloromethane	11.2	1.3
1,1,1-trichloroethane	5.8	1.7
trichloroethene	7.6	1.8
tertachloroethene	5.9	2.1

From the relationship between the change of difference frequency, Δf, of the delay line in an oscillator loop, which was measured as the response parameter of the dual delay line covered by the investigated layer, and the change of the mass bonded to the sensing layer, Δm (in grams), (neglecting the changes of a viscoelasticity, dielectric constant and electric conductivity of the layer):

$$\Delta f = K f_0^2 \frac{\Delta m}{A}, \qquad (1)$$

(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, s^{-1}, and A – surface of sensing layer in m^2) the number of adsorbed molecules of CH per surface of the sensing layer, N_M/A, have been calculated from the formula

$$\frac{N_M}{A} = \frac{\Delta f \cdot A_V}{K \cdot f_0^2 \cdot M} \qquad (2)$$

where A_V and M denote the Avogadro's constant and the molar mass of CH, respectively. The values of N_M/A are presented in Table 2.

Table 2. The numbers of adsorbed molecules of chlorinated hydrocarbons (CH) per surface of the sensing layer, N_M/A, for the porous DA layer.

Name of CH	Molar mass [g/mole]	N_M/A immediately after contact with layer [10^{17} m^{-2}]	N_M/A after 20 minutes contacting with layer [10^{17} m^{-2}]
dichloromethane	84.93	3.3	4.3
trichloromethane	119.38	2.0	2.5
tetrachloromethane	153.82	1.6	1.8
1,1,1-trichloroethane	133.40	1.0	1.3
trichloroethene	131.39	1.3	1.6
tetrachloroethene	165.83	1.1	1.5

In the group of chloromethane derivatives (di-, tri- and tetrachloromethane), the values of N_M/A decrease with the increasing number of the chlorine atoms in the molecule, which cause the molecule structure changes due to the large, in comparison with hydrogen, chlorine atom and the longer C-Cl bond length than that of C-H.

For trichloroethene, the values of N_M/A are slightly greater than for 1,1,1-trichloroethane. This observation can be explained by the existence of the double bond between the carbon atoms in the trichloroethene molecule and the lower number of hydrogen atoms, which make this molecule smaller than the 1,1,1-trichloroethane one. Tetrachloroethene has lower values of N_M/A than trichloroethene, since tetrachloroethene molecules possess the chlorine atom instead of the hydrogen one.

For the chlorinated methane derivatives the values of N_M/A are greater than for ethane and ethene ones due to the difference in the molecule dimensions.

Generally, it is noticeable that smaller molecules have larger values of N_M/A. That can be connected with the easier adsorption of smaller molecules on the porous DA layer . Selectivity of the process of CH adsorption becomes clear. The correlation of the amount of CH with the sizes of the molecules is visible. The differences in the N_M/A values can be used for the recognition of CH by the SAW method.

4. Conclusions

The porous Langmuir–Blodgett film reacts on the vapors of CH used in the tests even at low concentrations. This reaction is reversible. The reaction time is less than 2 seconds. The response parameters of the sensor, i.e. the decrease of the

difference frequency after contact with the vapor-air mixture and the diminution of this frequency in time, depend on the kind of the CH. From obtained the results and calculations it can be noticed that smaller molecules have larger of N_M/A values due to the easier adsorption in the porous DA layer by smaller molecules.

The results obtained confirm the utility of the LB chemosensing layers for developing SAW sensors for detection of vapors of chlorinated hydrocarbons.

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