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DEVICES FOR MEASUREMENT OF THE NO_2 CONCENTRATION IN THE AIR BY MEANS OF SURFACE ACOUSTIC WAVES

M. URBAŃCZYK, W. JAKUBIK

Institute of Physics,
Silesian Technical University,
(44-100, Gliwice, ul. Krzywoustego 2)

E. ADAMCZYK

Institute of Fundamental Technological Research
Polish Academy of Sciences
(00-049 Warszawa, Świętokrzyska 21)

J. RZESZOTARSKA

Faculty of Chemistry, Warsaw University

The development of techniques concerning macromolecular compounds have made it possible to get thin layers which change their physico-chemical properties in result of their interaction with the ambient atmosphere. Changes of the physical properties of specially prepared chemically sensitive layers influence the conditions of the propagation of an acoustic surface wave arranged in the layered system piezoelectric waveguide – layer of the compound. Particularly, if the mass and electric conductivity of the chemically sensitive layer is changed, the velocity of the propagation of the acoustic wave changes too.

The presented paper include a short review of the SAW gas sensor field and some experimental results for detection a low concentration of NO_2 in air.

1. Introduction

The constantly growing pollution of the natural environment, particularly of the atmosphere, require a continuous monitoring of these contaminations. In recent years an intensive development of new method of diagnosing the state of our natural environment are to be observed. Among them acoustic methods deserve special attention; these are based on the propagation of surface acoustic wave (SAW) in layered structure, in which the chemical active layer is a macromolecular compound.

Literature [1] quotes the following types of sensors with a chemically sensitive layer:

a) chemiresistors, in which use is made of changes in the resistant layer due to the adsorption of gaseous particles from the environment,

b) piezoelectric quartz gauges with an acoustic bulk wave,

c) systems with surface acoustic waves.

Conducting macromolecular complexes are characterized by much more complex mechanism of conductivity than inorganic semiconductors; therefore acoustic methods may provide new information concerning the mechanism of conductivity, which is essential also from the viewpoint of the application of these compounds in indicators of gases.

Of much interest is the application of acoustic surface wave propagated in the layered system "piezoelectric waveguide – thin chemically sensitive layer" in the designing of indicators of gases. This results from the fact that a surface wave is extremely "sensitive" to all changes of the properties of the surface of the medium in which it is propagated. In the case of a piezoelectric medium changes in the velocity of the acoustic wave are to be observed which are caused by changes in the mass loaded with the chemically sensitive layer (due to the adsorption of gaseous particles), or by changes of the electric conductivity of this layer [2, 3]. The theoretical sensitivity of an oscillator with an acoustic surface wave at a frequency of about 100 MHz amounts according to [1] to about 17 Hz/ng/cm^2; for an active surface of the sensor amounting to 0.17 cm^2 this means a rather low level of detection of the changes of mass, i.e. 0.2 ng. At a frequency of about 3 GHz the sensitivity of the system amounts theoretically to about 3×10^{-15} g.

Analysers of gases applied so far, making use of electrochemical and photoacoustic phenomena, as well as gas chromatography do not warrant a satisfying accuracy, or they are only labour-consuming laboratory methods. The photoacoustic analysers advertised by BRUELL and KJAER [4] are very expensive. Therefore, various research centres all over the world try to design new kinds of gas sensors. Similar investigations have also been started at IFTR in Warsaw on the design of an apparatus for the SAW method [17] which is applied in the Institute of Physics at the Technical University of Silesia.

2. Layers applied for covering the SAW sensors

Compounds of metalphthalocyanines [2], known since the beginning of our century, have only recently attracted attention as thin active layers permitting a selective detection of vapours and gases. A modification of the interior structure of the macromolecule, consisting in the replacement of the metal ion and substituents in the aromatic rings, makes it possible to obtain metalphthalocyanines with various properties. At presence there are more than 70 varieties of them [1]. Phthalocyanines belong to the group of low-dimension organic semiconductors [2, 5]. Roentgenographic investigations of phthalocyanines have proved the existence of three polymorphic forms, viz. α, β and x [5]. The crystalline structure increases by sublimation at a temperature of 400 – 500° C in the presence of nitrogen (7Tr). Depending on the technological conditions of sublimation, phthalocyanine crystallises in the monoclinic or triclinic system. The metal atom included into the structure of the macromolecule affects essentially the physicochemical properties of phthalocyanine. Literature indicates that the most frequently investigated macromolecular

complexes of metalphthalocyanines are copper CuPc, lead PbPc and ferrous phthalocyanine FePc, as well without metal – H_2Pc.

CHANG *et al.* [6] have investigated monolayers of phosphateidylcholine obtained by means of Langmuir-Blodgett's method. O'DONNEL *et al.* [7] quote the results of investigations on the adsorption of NO_x by a layer of phthalocyanine. The achieved level of gas detection amounted to 5 – 200 ppm. Copper phthalocyanine CuPc was investigated, among others, as an active layer in a NO_2 – sensor by NIEUWENHUIZEN and his team [8]. The achieved sensitivity was within the range from 0.3 – 70 Hz/ppm, the time response/regeneration amounting from 1/6 to 107/156 minutes. At the same time a rather high sensitivity of such a type of layers to effects of NH_3, but no effect of CO_2, CO, CH_4, SO_2 could be detected, and neither of toluene vapours and water vapour.

A comprehensive publication dealing with investigations concerning the layers of the phthalocyanines H_2Pc, MgPc, FePc, CoPc, NiPc, CuPc and PbPc is [9], in which it has been attempted to evaluate the usability of these compounds for the purpose of detecting CO, CO_2, CH_4, NH_3, SO_2, water vapour and toluene vapours. Among others, the authors stress the fact that phthalocyanines, being semiconductive organic compounds of the type p, strongly interact with electronegative gases. This interaction involves a change in the conductivity of the macromolecular layer. It has been found that the tested layers do not interact so strongly with water vapour and oxygen.

Many papers inform about the application of the phthalocyanine H_2Pc, metalphthalocyanine as well as other complexes containing electronic systems of the type for the purpose of detecting the presence of NO_2 and chlorine.

The results of investigations on copper and iron phthalocyanines have been published in [10]. Among others, the influence of O_2 and strongly electronegative gases (NO_2, NO, Cl_2, Br_2 and I_2) on the properties of thin layers could be determined. These investigations confirmed that the sensitivity of these phthalocyanines to the aforesaid gases differs. The response time of the system amounted to 1–70 minutes. The sensitivity of the active layer depends on the carrier gas (air or nitrogen) forming the background of the investigated gas.

Attempts have also been made to construct a prototype of a microprocessor system of monitoring nitrogen dioxide. This was affected at the University of Kent (in the United Kingdom) in 1991, sponsored by British Gas [11]. The principle of detection was based on utilization of changes in the electric conductivity of thin layer of lead phthalocyanine exposed to the influence of electronegative NO_2. In this way a very high sensitivity of detection was achieved on the level of single ppb's as well as a comparatively short response time (about 30 s). With such parameters the sensor excels all the conventional commercial sensors.

Most publications on this subject matter come from the end of the 80's and the 90's of this century; they mainly deal with investigations concerning the sensory properties of these complexes. These publications prove that this problem is highly actual. The connection of the sensory properties of macromolecular compounds with investigations on the structure of thin chemically sensitive layers exposed to the interaction of gases has been deal with in these papers only incompletely or not taken into account at all. Extremely important is the correlation of such sensory parameters as sensitivity, the

dynamics of the sensor, the response time and the regeneration of the active layer, as well as the processes of ageing, including structural investigations of selected layers and taking into account the effect of the technological conditions of the process of sublimation on their structure and properties. In order to utilize the properties of phthalocyanine complexes fully it seems to be expedient to undertake the widest possible investigations on their electric properties (dependence of conductivity and energy of activation on the gaseous environment) and changes of their acoustic properties (absorption, dispersion).

As we know from literature, sensors of the type SAW may be divided into two categories, viz. sensors measuring physical quantities and sensors used to measure chemical quantities. The physical properties which can be measured by means of such sensors have been gathered in Table 1.

Table 1. Physical SAW sensor, after [18].

Measured quantity	Sensitivity/detecability
Temperature	0.0001°C
Pressure	0.1 ppm/atm
Force – acceleration	18 Hz/g
Electric field	15 – 30 ppm/kV/mm
Displacement	300 Hz/μm
Flow rate	11 Hz/sccm

If SAW is applied as a chemical sensor, a thin layer reacting with the analysed agent must be put on the surface of the piezoelectric substrate. The interaction of this agent must lead to changes of the properties of this layer, e.g. its density, viscosity, modulus of elasticity, dielectric constant or conductivity. In this way parameter of the propagation of the surface wave is changed. The sensitivity and selectivity of SAW sensors depends on the physicochemical properties of the covering layer. Most often two retarding lines are applied (discussed further on in this paper), forming two oscillating systems. One of these lines is covered with a layer reacting with the investigated medium, the other one remaining uncovered. The difference of frequencies between the generations of oscillators, resulting from physicochemical changes of the active layer amounts to several score of Hz up to several kHz, applying resonance frequencies of the oscillators within the range from several score to several hundred MHz.

Exemplary coverings of the retarding lines have been presented in Table 2.

The change of frequency oscillation in the generator system may result from two effects: the effect of conductivity, when in result of changes in the electric conductivity of the chemically sensitive covering due to the interaction of the ambient medium the conditions of propagation of the acoustic wave in piezoelectric waveguide are changed, and the mass effect, when due to changes in the mass of this layer the velocity of propagation of the acoustic wave is changed [3]. The operation of SAW sensors is based on the utilization of changes of the mass or electric conductivity of the chemically sensitive layer.

There are also other constructions of sensors which utilize Love's shear waves. Such sensors enable us to measure the properties of polymers and to determine their glassy

Table 2. Coverings applied in chemical SAW sensors.

Determined gas/vapour	Covering	Sensitivity/detecability
H_2	CuPc + Pd (doping)	50 ppm
NH_3	Zn0 + In	1 – 10 ppm
NO_x	PbPc, CuPc, H_2Pc	2 ppb – 500 ppm
H_2S	WO_3, SnO_2 + Pt	0.01 – 60 ppm
SO_2	Heteropolysiloxane, Triethanolamine, CeO_2	1 – 100 ppm
H_2O	Polyimide no film	1.1 kHz/% Rh dipole interactions

temperature, their melting point, the coefficient of expansion and the energy of thermal activation.

For several years now in the Institute of Physics at the Technical University of Silesia researches have been carried out in co-operation with the IFTR Polish Academy of Sciences on the application of thin layers of macromolecular complexes for the purpose of detecting the presence of gases. This year our researches concern mainly nitrogen dioxide.

3. Applied apparatus

For measurements of the NO_2 concentration the prototype of a device has been constructed, the block diagram of which is to be seen in Fig. 1. It consists of a cylindrical test chamber with the sensor plate inside – a system of the double line SAW on lithium niobate with a chemically sensitive layer in one path. The plate was fastened on a base with 14 feet, the dimensions of which were 20 × 17.3 mm. This base was mounted on a typical support as applied for the assembly of integrated circuits. The plate of laminated foil supports the other elements of the device – electronical elements and the numerical read – out. The acoustic waveguides have been denoted as $L1$ and $L2$. On one of the waveguides was padded with a thin chemically sensitive layer of lead phthalocyanine, serving as the sensory element. The other waveguide serves as a reference system. Each acoustic line operates in the feed-back loop of the wide-band amplifiers $A1$ and $A2$ as oscillators. The voltages of oscillation from the amplifiers of both lines are conveyed to the input of the mixing system M, at the output of which the signal of the beat frequency is given. The change of the beat frequency is a measure of the concentration of the monitored gas. In the monostable element F-FM1 the beat frequency is transformed into rectangular impulses with a constant width. The beat frequency is measured by summing up these impulses in some given time. The quartz-crystal oscillator at the output of the frequency dividers D1 and D2 generates one – second impulses, which at the gate G1 determine the summing – up time of the impulses of the differential signal in the counter COUNT. The four-decade read-out of the counter is decoded in the four-position LCD

display. The control system of the counter is set to zero, by the impulse R (reset) from the monostable element F-FM2, and next triggered from the divider D3 through the gate G2 by means of the impulses CLC (clock).

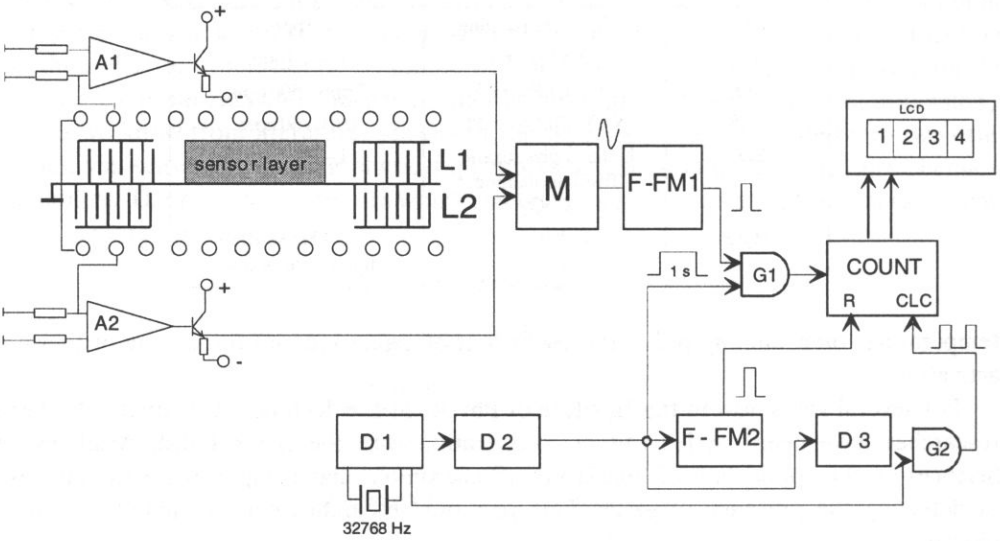

Fig. 1. Block diagram of the measuring instrument.

The deviders, the counter and the control system have been produced by means of the CMOS technique, the digital read-outs are liquid crystals. Such a system makes it possible to miniature the overall dimensions of the measuring instrument (to about 150×80 mm) and to save energy by applying batteries. Thus this device may be applied also as a portable one. It has been assumed that the measuring instrument will be used to detect and to measure the concentration of nitrogen dioxide in the air. The concentration of nitrogen dioxide admissible for a longer time amounts to $30 - 50\,mg/m^3$, the maximum one for 30 minutes being $150 - 500\,\mu g/m^3$.

4. The procedure of measurements

In order to get thin layers of the applied phthalocyanines their sublimation in a vacuum was applied. The initial material was powdered PbPc, FePc, CuPc, NiPc and H_2Pc produced by the firm SIGMA. Chemically sensitive layer were sublimed in a vacuum by a system of the type NA501P. As a source of vapours a quartz crucible was used, placed inside a tungsten spiral. Before its sublimation the initial material was degassed for 15 minutes in a vacuum 10^{-4} Tr at a temperature of 150° C to 200° C. Particularly intensive gassing was to observed in the case of iron phthalocyanine, the weakest when pure phthalocyanine was applied. The temperature of the source of vapours was controlled by means of a Cu – Konstantan thermocouple with the reference point placed in a container with melting ice. In the course of one cycle of sublimation the layers were placed on a

substrate consisting of lithium niobate with previously prepared (photholithographically) interdigital transducers, and on a glass substrate of the type Corning 7059 used to investigate the structure and to measure the thickness by means of the interferential method. The distance between the source of vapours and the substrate amounted to 25 cm. During the process of sublimation the thickness of the layer was controlled by means of a quartz thickness meter of the type MGS 100, and after evaporation had been completed, the thickness was measured optically. The thickness of the obtained layers to 0.08 – 0.35 μm and 1.3 – 1.4 μm.

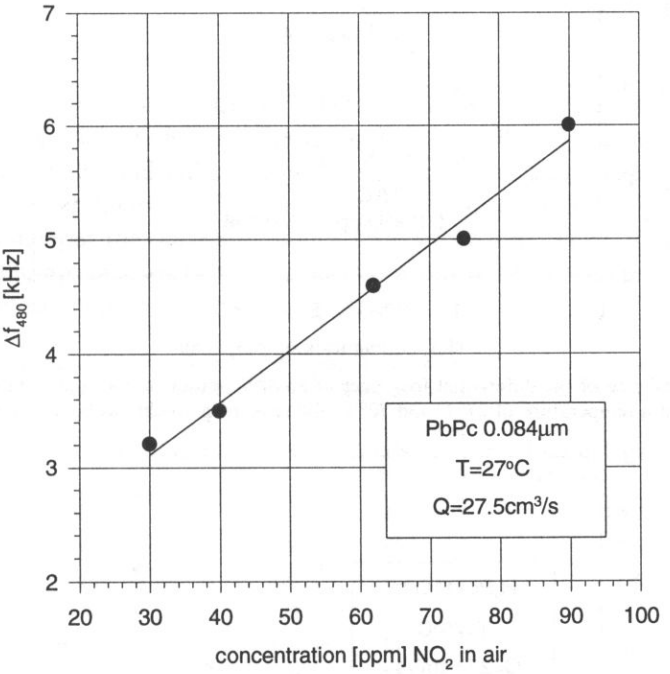

Fig. 2. The dependence of the differential frequency of an SAW sensor on the concentration of nitrogen dioxide in the air at a temperature of 27° C. The piezoelectric material was $LINbO_3$, the nitrogen dioxide was absorbed by a layer of lead phthalocyanine (PbPc), 83 nm thick.

The most essential part of the sensor is the differential system of two acoustic oscillators (active and compensating oscillator) eliminating the effect of the unsteadiness of temperature on the signal of the sensor. Each oscillator consists of two transducers of the surface wave (20 pairs of electrodes with a width of 12.5 μm and an aperture of 4 mm), produced photholithographically, and an exterior broadband amplifier. The mid-band frequency of the transducer amounted to about 43 MHz. The distance between the transducers amounted in the surface line to about 14 mm. Together with the acoustic retardation line and the transducers of the surface wave forms a closed electroacoustic loop. The system oscillates if the amplitude conditions for amplification of the signal in the loop is greater than 1, and the phasal condition (full phase shift in the loop equals a multiple of 2π) are satisfied. The measuring signal is a change of the differential frequency of the oscillators at the output of the mixer.

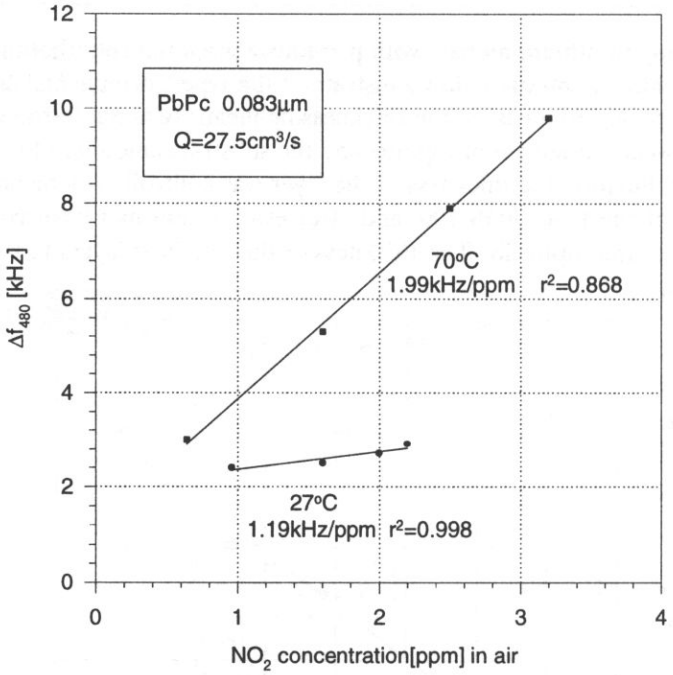

Fig. 3. The dependence of the differential frequency of an SAW sensor on the concentration of nitrogen dioxide in the air at a temperature of 27° C and 70° C, the remaining conditions being the same as in Fig. 2.

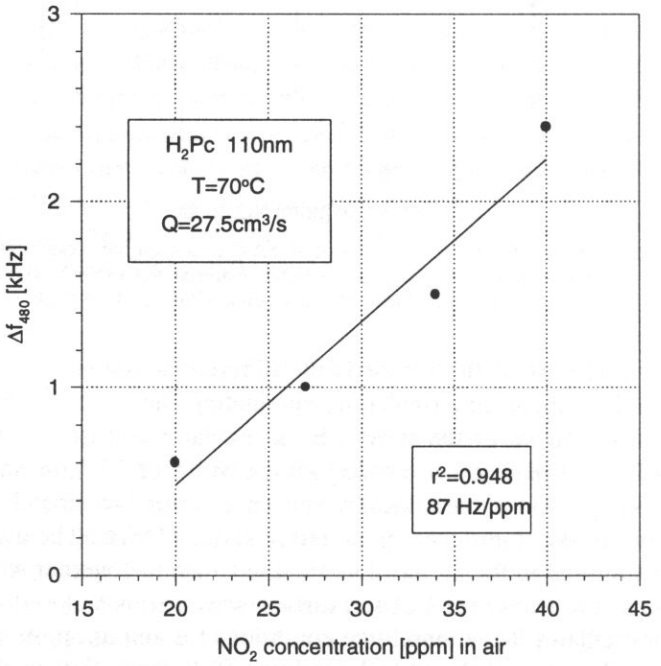

Fig. 4. The dependence of the differential frequency of an SAW sensor with an adsorbing layer of phthalocyanine (H_2Pc), 110 nm thick, on the concentration of nitrogen dioxide in the air at a temperature of 70° C.

The prolonged drift (30 minutes) of the temperature of the sensor amounted to about 50 Hz.

The time of filling, until a steady concentration of gas has been reached, amounts in the applied test chamber with a total volume of about 55 ccm at a flow rate of the gas equal to 55 ccm/s and 27.5 ccm/s to 7 and 14 seconds, respectively, being considerably shorter that the assumed time of exposure (480 s) of the investigated layer to the interaction of the given gas.

5. Results

The test results have been gathered in Table 3. The presented date indicate that most sensitive to the presence of nitrogen dioxide in the air are PbPc layers, followed by layers of CuPc, whereas FePc and NiPc practically do not adsorb NO_2. The influence of CO and CH_4 on the determination of NO_2 have been investigated too. The presence of these gases does not hamper the determination of nitrogen dioxide; FePc, on the other hand, is sensitive to the presence of methane and will in future be applied in the design of an SAW sensor determining the presence of methane.

Table 3. The influence of kind of phthalocyanine, its thickness and temperature on the sensitivity of an SAW sensor designed to determine the content of nitrogen dioxide in the air.

Layer type	Layer thickness [nm]	Temperature [°C]	Sensitivity to NO_2 [Hz/ppm]
PbPc	83	70	2000
PbPc	83	30	1200
CuPc	270	30	130
CuPc	720	30	18
H_2Pc	110	70	87
FePc	30	70	0
NiPc	230	70	0

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