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SAW SENSOR FOR NO_2 DETECTION UTILIZING THE DYNAMIC CHARACTERISTIC OF THE DEVICE

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A surface acoustic wave (SAW) sensor for NO_2 detection with CuPc and PbPc layers, based on the dynamic characteristic of the lowest frequency mode has been developed. For the investigated concentrations range the changes in the device response, $\Delta f = f - f_0$, were very large (from a few kHz to even 10kHz), which resulted in a "jumping" of the generation system to the next frequency modes. Thus, we were not able to observe the saturation levels for the investigated concentrations and prepared phthalocyanine layers. Therefore, we decided to determine the NO_2 concentration after 480s from the moment when gas was allowed to flow through the measuring chamber. At a constant gas flow rate we have obtained a good linear dependence between the device output signal and the NO_2 concentration in pure air. In the case of CuPc films (0.27μm and 0.72 μm) the greatest sensitivity (130 Hz/ppm) has been obtained at a thinner layer and a higher gas flow rate. The sensitivity of the investigated PbPc layer (0.083 μm) was much higher (from 1200 Hz/ppm at 27°C to 2000 Hz/ppm at 70°C), thus was had to use a small concentration range (from 0.6 to 3.2 ppm NO_2) in order to maintain oscillations for at least 480s. Besides, the response of the device depends on temperature. At a higher temperature the magnitude of the response was greater and the response time shorter at this same gas concentration.

1. Introduction

Increasing pollution of the natural environment (especially of the atmosphere) stimulates research concerning new methods of monitoring the existing pollution. Gas detectors based on surface acoustic waves are now intensively investigated [1-5, 9, 10]. Adequately chosen active phthalocyanine layers in an acoustic dual delay line system have made it possible to design sensors with an especially high sensitivity, a small size and at a relatively low price. The basic principle of the measuring system, which is now well known, has been shown in Fig. 1.

Investigations carried out by many research teams in the past proved, that for the detection of NO_2 thin films of copper or lead phthalocyanines should be used [6-8]. Principally, any change in the physical properties of the thin active laver placed on a piezoelectric surface, can affect SAW propagation, However, from the practical

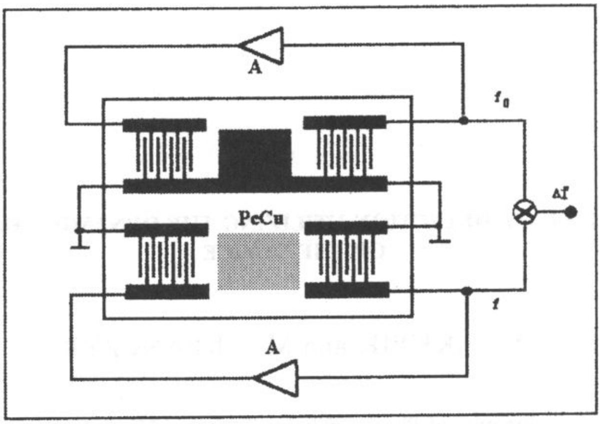

Fig. 1. The basic principle of the SAW dual delay-line oscillator system.

point of view only the two following effects have a potential meaning for phthalocyanines. Namely, a change in the mass density of the film, and a change in its electrical conductivity. Moreover, in the case of semiconducting layers the change in electrical conductivity is about three orders of magnitude bigger than that induced by mass loading [1, 5]. So, we can say, that as a result of changing the mass density and electrical conductivity of the thin phthalocyanine layer, the SAW velocity undergoes a change. These changes can be observed and measured as a frequency difference in dual acoustic delay lines – the delay line with an active thin layer and the reference delay line.

As a result of analysing the phase conditions of the generation system, the following formula defining the difference frequency has been derived [6, 12]:

$$\Delta f = f - f_0 = \frac{2\pi n - \Phi_e}{2\pi L}(v - v_0), \tag{1.1}$$

where n – integer, defining the number of frequency modes, f – frequency in the measuring path with the phthalocyanine layer, f_0 – frequency in the reference delay line, Φ_e – phase shift in the entire external circuit, v – propagation velocity of SAW in the measuring path, v_0 – velocity in the reference line, L – length of the acoustic path (distance between the central points of the transducers).

If we aasume, that Φ_e is constant (which is possible when the amplifier works in stable conditions) and the temperature is constant, then the relative change of the difference frequency is:

$$\frac{\Delta f}{f_0} = k\frac{\Delta v}{v_0}, \tag{1.2}$$

where k is the fraction of the centre- to-centre distance between the transducers affected by perturbation.

The change of the SAW velocity, v_0, can then be measured by means of precise measurements of the operating frequency, f, in the oscillator circuit of the device.

The only problem of the SAW sensor is caused by "jumping" of the generation system to higher operating frequencies during the interaction of the thin CuPc layers with NO_2 molecules. This problem is connected with the modal characteristic of the device and will be described in detail in the reference [11].

The best solution of this problem has been proposed in paper [1], where the authors made the transducers as long as the delay distance between the transducers. The oscillator operated only at one mode determinated by the fundamental resonant frequency.

2. Experimental

2.1. *Layer preparation*

CuPc layers with a thickness of about 0.27 μm and 0.72 μm and 0.083 μm for PbPc on a$LiNbO_3$ substrate, made by means of the vacuum sublimation method, have been prepared for investigations. The source of phthalocyanine vapour consisted of a quartz crucible placed in a properly formed tungsten spiral. Before the specific process of the sublimation, a copper phthalocyanine was initially out-gassed for 15 to 20 minutes at a temperature of 200⁰C, in a vacuum (10^{-4} Tr). The source temperature was about 600⁰C and the thickness was measured making use of the interference method.

2.2. *Acoustic paths*

Two identical delay lines were fabricated on the y-cut, z-propagating $LiNbO_3$ substrate.

We have obtained the fundamental resonant frequency $f_0 = 42$ MHz and the transducer bandwidth was about $\Delta f = 0.9$ MHz.

For investigations we utilized the lowest frequency modes of the device ($n = 1$). It was about 30 kHz for the 0.27 μm and 103 kHz for the 0.72 μm CuPc layer and 103 kHz for the 0.083 μm PbPc layer in the differential frequency of two acoustic oscillators. These modes were most sensitive for the studied film thicknesses and investigated NO_2 concentration range in pure air. The sensitivities of the higher frequency modes will be the subject of further researches.

3. Experimental system

All measurements were carried out with the use of a microprocessor system, which permitted the acquisition of difference frequencies, Δf. The main part of the setup was an aluminium vacuum chamber, wherein the prepared acoustic waveguides were placed. The temperature was measured on the crystal surface by a thermocouple which permitted its stabilization inside the chamber within 0.1⁰C. Almost all the measurements were carried out at this same temperature of 30^{0}C. Before measurements were taken, the chamber was initially evacuated to about 1 torr. Next, only pure air was allowed to flow through the chamber. It was then possible to determine the most stable working points of the oscillators at the required temperature. The maximal long-term (5h) temperature drift of the differential frequency, Δf, was about 20 Hz.

NO_2 gas and synthesised air were batched by means of simple system described in the reference [12]. The process of attaining the required homogeneous concentrations i the measuring chamber can be described by a simple equation (analogicaly to the charging of the condenser);

$$t(t) = c_0\left(1 - e^{\frac{-Q}{V_0}t}\right), \tag{3.1}$$

where: c_0 – is the demanded gas concentration defined by the dosing system, Q – the gas flow rate, V_0 – the cell and tubing volume.

For our experimental system we had the following magnitudes: cell volume – 30 cm^3 and tubing volume – 20 cm^3, thus V_0 is equal to 50 cm^3. The measurements were carried out for two values of the gas flow rates, namely for Q equal to 55 cm^3/s or 27.5 cm^3/s.

The time constants defined by $\tau = V_0/Q$ are then equal to about 1 or 2 seconds. A homogeneous concentration is obtained after flushing the chamber seven times for 7 or 14 seconds, respectively [2].

4. Results

In the case of the investigated thin phthalocyanine films and NO_2 concentrations we were not able to detect the saturation level of the difference frequencies. It was caused by too large frequency changes and "jumping" of the generation system to higher frequency modes. Thus, we have decided to utilize the dynamic characteristics of the device. They are shown in Figs. 2 and 3 for the 0.27 μm CuPc layer, for two different flow rates. The same characteristic has been obtained for 0.72 μm CuPc and 0.083 μm PbPc films. From the dynamic characteristic of this type it is possible to determine the device response, for example after 480s, from the moment when gas was allowed to flow through the measuring chamber.

The device response response signal, $\Delta f(480)$, for two investigated CuPc films, versus the NO_2 concentration in air is shown in Fig. 4. For the 0.27 μm layer two different flow rates have been studied. A good linear dependence, with correlation coefficients from 0.983 to 0.998, has been reached. For the 0.083 μm PbPc film the response was so high that we had to use much smaller concentrations (from 0.6 to 3.2 ppm in air) in order to maintain the oscillations for at least 480 s. The results are shown in Fig. 5 for two different temperatures.

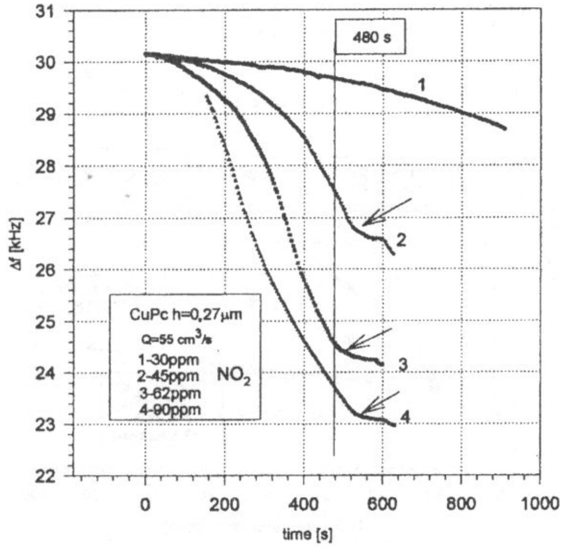

Fig. 2. Responses of the 0.27 μm CuPc layer to four NO_2 concentrations in air and for an entire gas flow rate of 27.5 cm³/s. The small arrows indicate the moments when the NO^2 flow is cut off.

The regeneration times of the investigated layers in the measuring temperature 30°C, were very long (~10 h). Practically, for other gas concentrations the measurements were possible on the next day. In higher temperature however, the recovery time becomes much shorter (~1h).

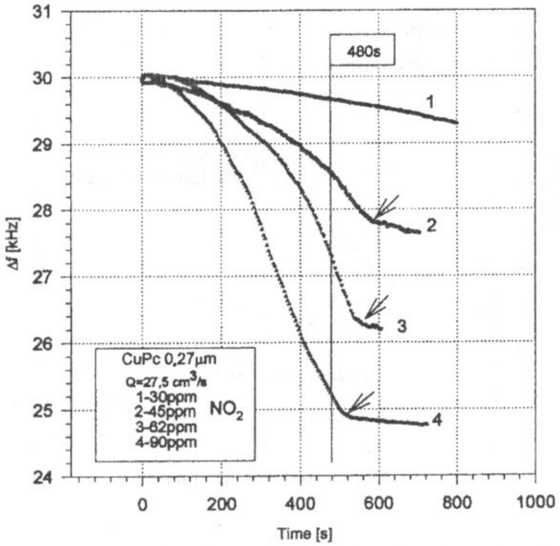

Fig. 3. Responses of the 0.27 μm CuPc layer to four NO_2 concentrations in air and for an entire gas flow rate of 27.5 cm³/s. The arrows indicate the same as in Fig. 2.

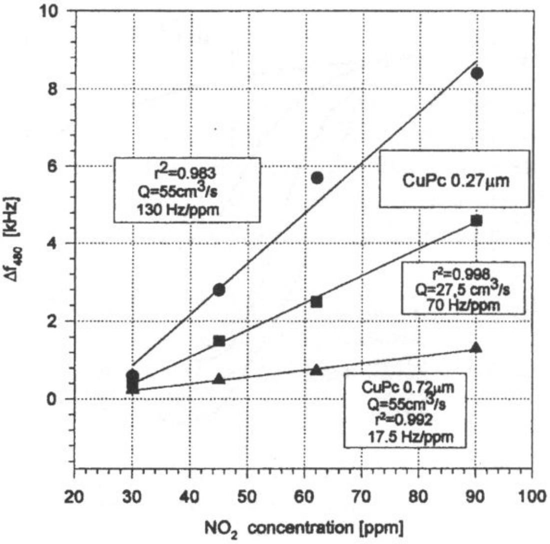

Fig. 4. Difference frequency atter 480s since the moment when the gas was allowed to flow through the measuring chamber in the case of CuPc layers, versus NO_2 concentrations in air, at a constant temperature of 27°C (300K). The device response is defined as, $\Delta f_{480} = \Delta f(0) - \Delta f(480)$, for the data in Figs. 2 and 3. For the 0.27 μm CuPc layer two gas flow rates have been studied.

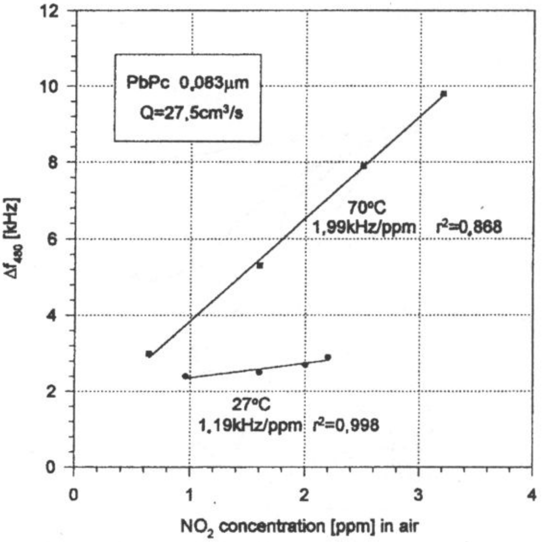

Fig. 5. Difference frequency after 480s since the moment when the gas was allowed to flow through the measuring chamber in the case of the PbPc film, versus NO_2 concentrations in air, at two different temperatures.

5. Conclusions

We are proposing a new way of determining the gas concentration basing on the dynamic characteristic of the device. In the case of our experimental system it was rather necessary, but we think that it can be a good method to determine the gas concentration for the layers with long response times (at room temperature). The determining time (480s in our case) should be much longer than the time constant of the experimental system.

For the investigated concentration range from 30 to 90 ppm of NO_2 in air for CuPc and 0.6 to 3.2 ppm for PbPc layer we have obtained a good linear dependence (Fig. 4 and 5).

The best sensitivity (130 Hz/ppm) was reached for the thinner (0.27 μm) CuPc layer and for higher (50 cm^3/s) gas flow rates. This is connected with the sheet conducitivity of the films (product of thickness and conductivity). For the thinner layer we have a smaller sheet conductivity and thus a greater change in the relative changes of velocity. The flow rate dependence of the response can be explained by the greater creating velocity of the ionised states at the surface [7], and thus in a faster change in the surface conductivity. The almost complete lack of reversibility of the NO_2 effect is undoubtedly connected with the temperature. At higher temperatures the recovery times become much shorter [8].

The sensitivity of the PbPc layer for the detection of NO_2 was much greater – from 1200 Hz/ppm at 27^{0}C to 2000 Hz/ppm at 70^{0}C (Fig. 5). The temperature dependence of the sensitivity can be related to the temperature dependence of the mobility of the charge carriers, and/or the easier charge exchange between interacting molecules.

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References

[1] M. von SCHICFUS, R. STANCEL, T. KAMMERECK, D. WEISKAT, W. DITTRICH and H. FUCHS, *Improving the SAW gas sensor: device, electronic and sensor layer*, Sensors and Actuators B, 18-19, 443-447, (1994).

[2] M. S. NIEUWENHUIZEN, J. L. N. HARTEVELD, *An automated SAW gas sensor testing system*, Sensors and Actuators A, 44, 219-229 (1994).

[3] V. I. Anisimkin and I. M. Kotelyaskii, *Operating characteristic of SAW gas detectors*, Sov. Phys. Tech. Phys. 37(2), February 1992.

[4] P. Banda, W. Włodarski and J. Scott, *Modelling aspects of surface acoustic wave gas sensors*, Sensors and Actuators A, 41-42, 638-642 (1994).

[5] A. J. Ricco, S. J. Martin and T. E. Zipperian, *Surface acoustic wave gas sensor based on film conductivity changes*, Sensors and Actuators, 8, 319-333 (1985).

[6] A. Venema, E. Nieuwkoop, M. Vellekoop, W. Ghijsen, A. Barendsz and M. Nieuvenhuizen, *NO_2 gas-concentration measurement with a SAW-chemosensor*, IEEE Trans. Ultrasonics, Ferroelectr. Freq. Control, **UFFC-34** (2) 148-155 (1987).

[7] R. Van Ewyk, A. Chadwick and J. Wright, *Electron donor – acceptor interactions and surface semiconductivity in molecular Crystals as a function of Ambient Gas*, J. C. S. Faraday I, 76, 2194-2205 (1980).

[8] B. Bott and T. A. Jones, *A highly sensitive NO_2 sensor based on electrical conductivity changes in phthalocyanine films*, Sensors and Actuators, 5, 43-54 (1984).

[9] R. M. Leć *et al.*, *Macroscopic theory of surface acoustic wave gas microsensors*, IEEE ultrasonic Symposium, Chicago 1988, 585-589.

[10] R. M. Leć, *Acoustic wave sensors*, Mat. Konf. COE'96. 31-43.

[11] M. Urbańczyk and W. Jakubik, *Optimal conditions for the generation system of a SAW gas sensor*, Archives of Acoustics, **21**, 1, 85-88 (1996).

[12] M. Urbańczyk, W. Jakubik and S. Kochowski, *Investigation of sensor properties of copper phthalocyanine with the use of surface acoustic waves*, Sensors and Acuators B 22, 133-137 (1994).