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THE INFLUENCE OF TEMPERATURE ON THE SENSITIVITY OF A SAW GAS SENSOR WITH A THIN LAYER OF LEAD PHTHALOCYANINE

M. URBAŃCZYK

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

The paper deals with experimental investigations concerning the influence of temperature on the sensitivity of a SAW sensor with a thin layer of lead phthalocyanine (PbPc) to NO_2 molecules in the air. Measurements have been carried out with a dual delay line system providing simultaneously a survey of the differential frequency, Δf, and the measuring frequency, f. In all cases the measured frequency, f, was increased, whereas the changes in the difference of frequency, Δf, were negative as a result of the interaction with NO_2 molecules. All the experiments have been made at the same conditions, i.e., with the same PbPc layer of a 310 nm thickness, at 40 ppm NO_2 in air and at a constant gas flow rate of 100 ml/min. In the range 30 – 60° C, the sensitivity increased almost linearly with temperature a constant rate of 0.13 – 0.15 kHz/° C.

1. Introduction

Systems with Rayleigh's acoustic surface waves have been applied in the construction of detectors of toxic gases for a long time [1–4, 9, 10]. The basic system of SAW gas sensors is a generator in which an acoustic delay line works in the positive feedback loop of the amplifier. The acoustic delay line assures the phase condition for generation whilst the amplifier assures the amplitude condition. The amplifier gain should be higher than the delay line insertion losses. For this purpose, two identical circuits are formed on a piezoelectric substrate (e.g. $LiNbO_3$) to facilitate the propagation of a surface wave excited by means of interdigital transducers. Next, a thin layer of an organic semiconductor of metalophthlocyanine type (MPc) is formed in one of the paths by sublimation in vacuum, the thickness of the layer not exceeding 1% of the length of the propagating surface wave. The free path of a crystal serves as a reference. As a result of the interaction of the thin metalophthlocyanine layer with gas, the SAW velocity undergoes a change. This change can be observed and measured as a frequency of the single acoustic delay line or as a difference frequency of the dual acoustic delay lines, i.e. between the delay line with an active thin layer and the reference one.

An essential feature of a surface wave is the concentration of the whole energy just near the surface within a layer of thickness not exceeding two wavelengths (2λ), so that it becomes possible for the wave to affect easily and effectively the medium placed on the crystal surface. In this way the propagation of waves along the path in which the layer has been placed is slightly disturbed (depending on the thickness of the layer, h, its density, ϱ, and the electric conductivity, σ). Physically this disturbance consists in a reduction of the velocity and an increase of the attenuation of the propagating wave.

The reduction of the velocity of propagation is mainly caused by two phenomena [5, 6]:

a) the mass load on the crystal surface and

b) the electric "load" resulting from the effect of interaction of the electric potential associated with the surface wave with mobile charge carriers in the layer.

The interaction of the thin phthalocyanine layer with active gas molecules can be shown in the form of a diagram [7, 8].

Diagram of the interaction: gas – chemical active layer – SAW – electronic system

Interaction of the thin MPc layer with gas particles
Adsorption resulting from the formation of ionised states at the layer surface due to the exchange of electrical charges
Criterion: – electron affinity of the gas
– the kind of metal in the MPc particle
– **temperature of the reaction**

↓

Change of the surface mass of the layer as well as changes in the electrical conductivity
(generation of additional charge carriers)

↓

Interaction of the disturbed layer with the propagating SAW:
– mass effect
– conductivity effect

↓

Changes of the velocity of the wave propagation, and hence an additional change in the frequency of generation, f, (wavelength is constant; determined by the geometry of the transducer)
Changes of the amplitude due to changes in the wave attenuation

↓

Detection of the frequency difference $\Delta f = f - f_0$

This article is aimed mainly at the study of the influence of the temperature on the aforesaid interaction.

2. Experimental and results

The measurements have been carried out with a dual delay line system providing simultaneously a survey of the differential frequency, Δf, and the measuring frequency, f. The temperature was stabilized inside the measuring chamber on the balance principle by means of a power transistor (Fig. 1). The stabilization was within the range $\pm 0.1°$ C.

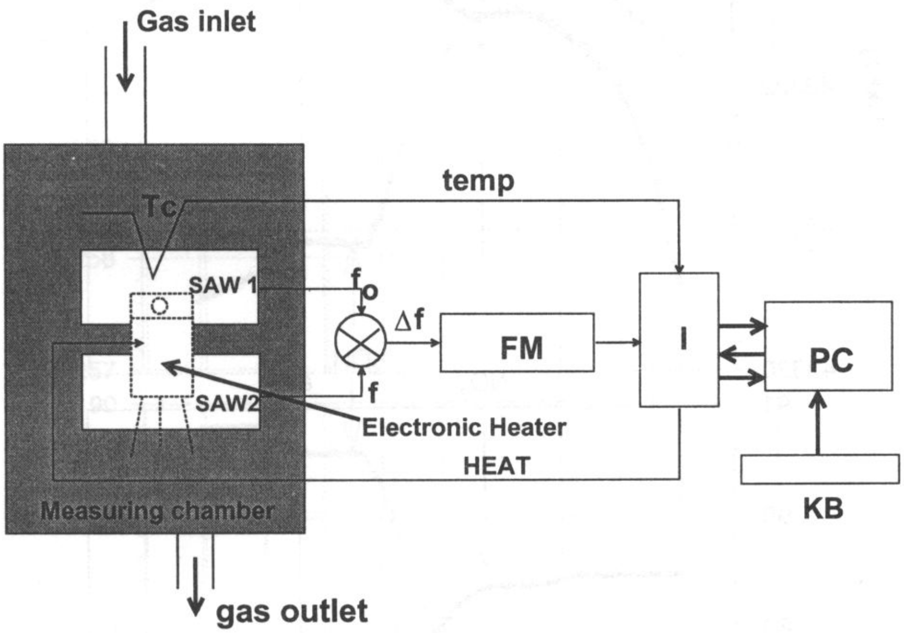

Fig. 1. Schematic representation of the experimental set-up. The measuring frequency, f, was measured directly by means of a probe. Symbols: I – interface, PC – personal computer, KB – keyboard, FM – frequency meter., Tc – thermocouple (Cu – const), SAW 1, 2 – surface acoustic wave lines.

Each measurement was carried out after the stabilization of temperature. The long time frequency drift was compensated in the dual delay line system as can be seen in Figs. 2–5. These diagrams show the interaction of a thin PbPc layer with NO_2 molecules in air. Basing on these results, a final diagram was drawn showing the difference and measuring frequency versus temperature of interaction (Fig. 6).

3. Conclusions

In all cases the change of the measuring frequency, f, was positive, whereas the change in the difference frequency, Δf, was negative as a result of the interaction with NO_2 molecules. This is connected with the configuration of the frequency modes f and f_0; since in the normal configuration $f < f_0$, the increase of the measuring frequency f causes a decrease in the difference frequency Δf. The main conclusion is that the sensitivity is increased (a larger change in the frequency) with the increase of the interaction

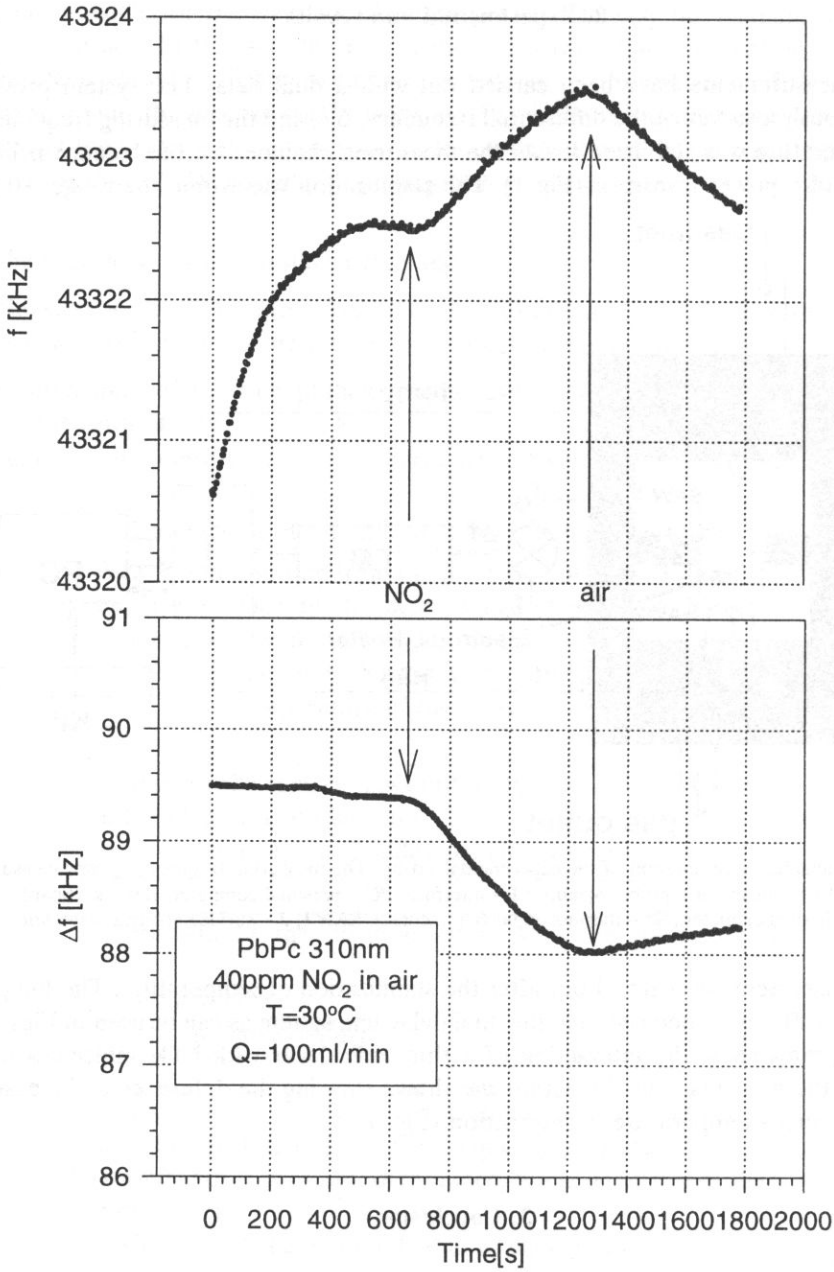

Fig. 2. Interaction of a 310 nm PbPc layer with NO_2 molecules of concentration of 40 ppm in air at 30° C and at a constant gas flow rate of 100 ml/min.

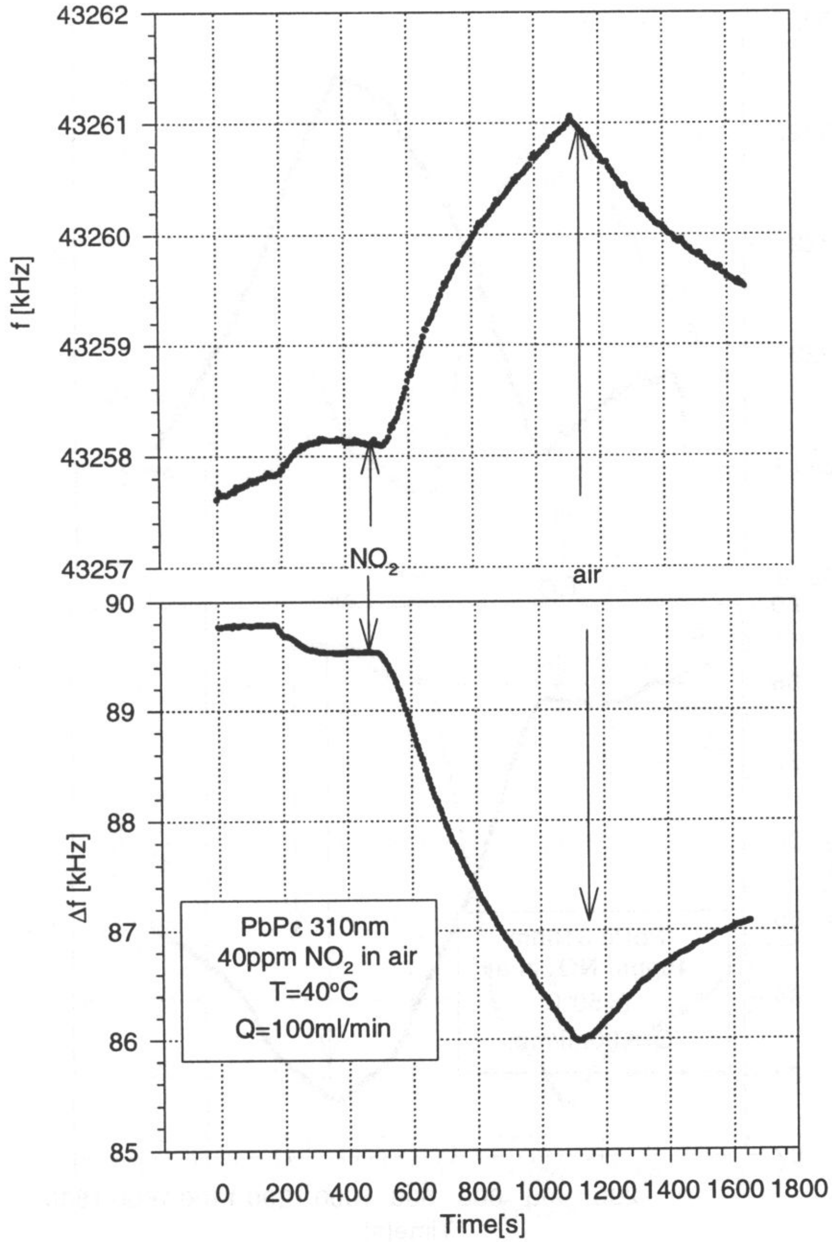

Fig. 3. Interaction of a 310 nm PbPc layer with NO_2 molecules of concentration of 40 ppm in air at 40° C and at a constant gas flow rate of 100 ml/min.

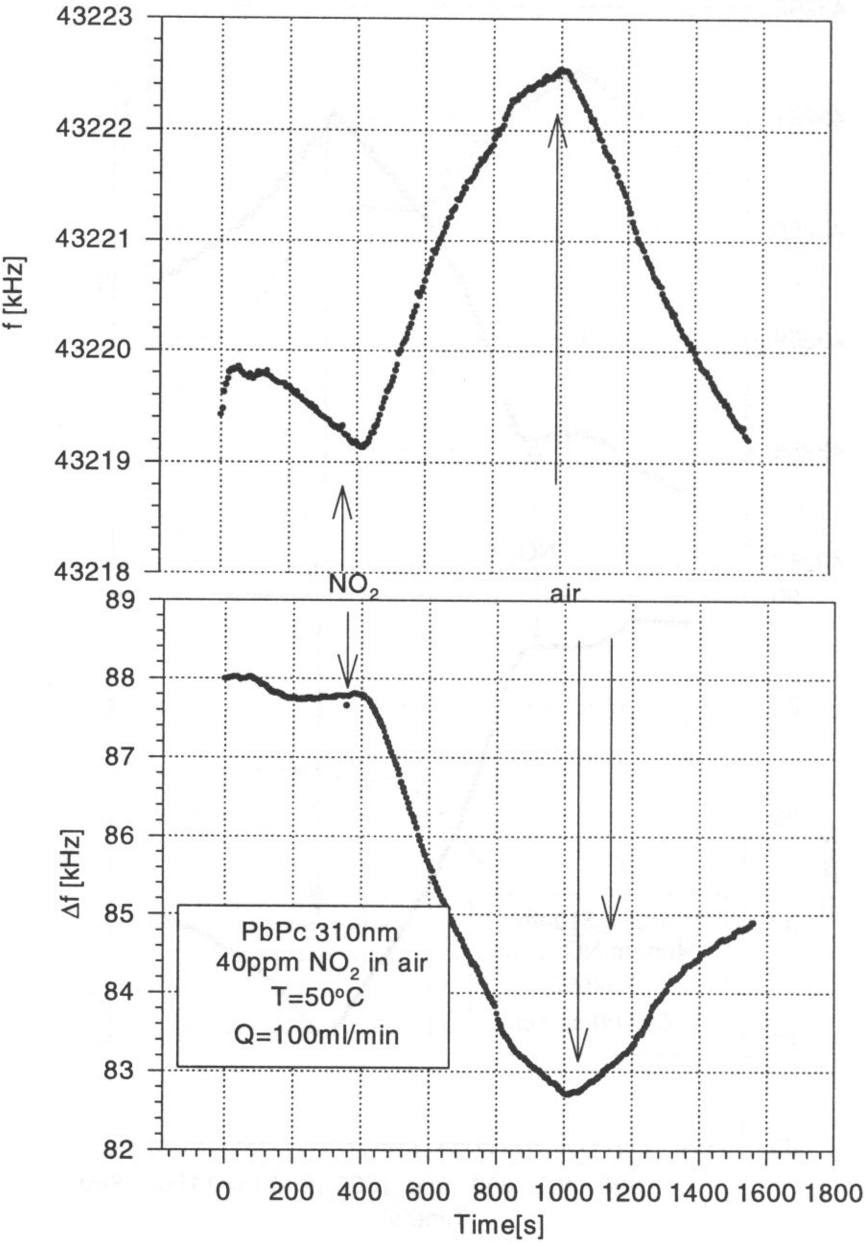

Fig. 4. Interaction of a 310 nm PbPc layer with NO_2 molecules of concentration of 40 ppm in air at 50° C and at a constant gas flow rate of 100 ml/min.

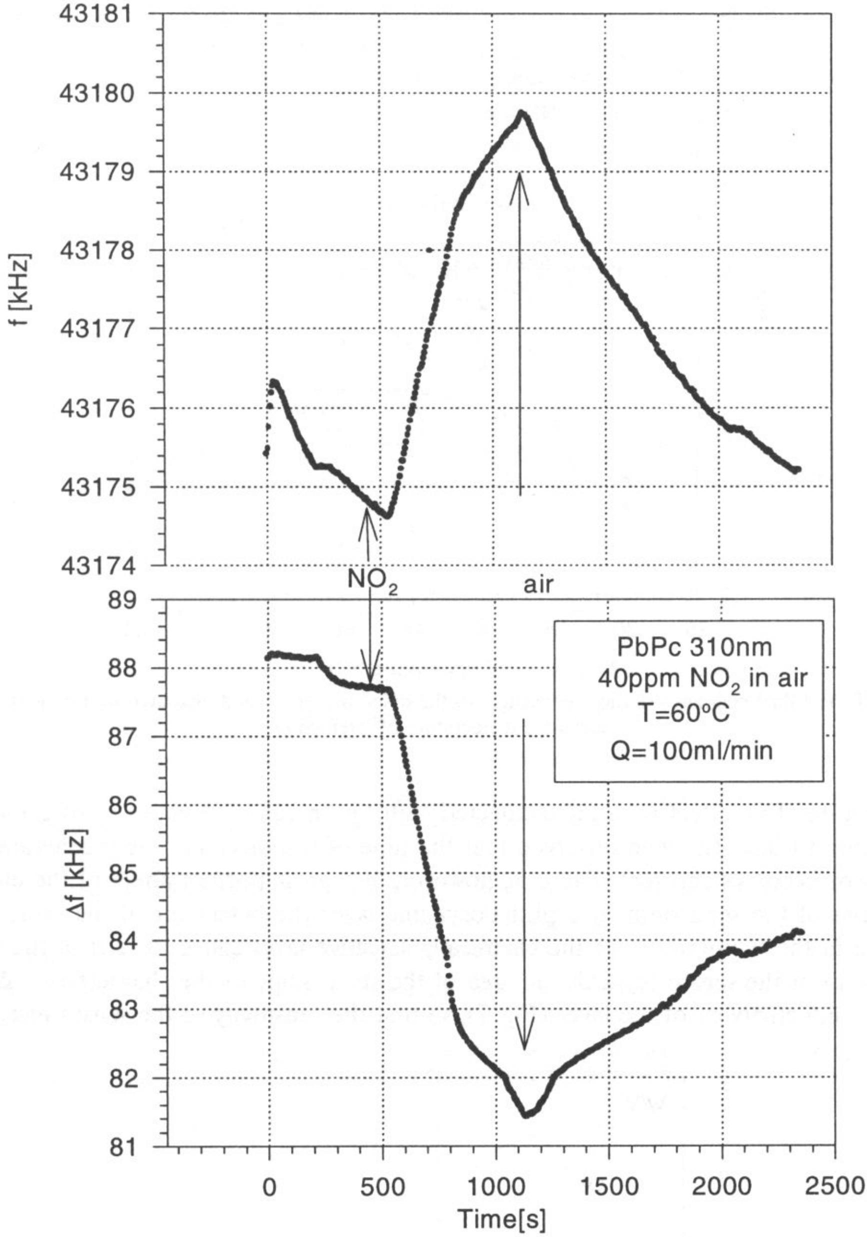

Fig. 5. Interaction of a 310 nm PbPc layer with NO_2 molecules of concentration of 40 ppm in air at 60° C and at a constant gas flow rate of 100 ml/min.

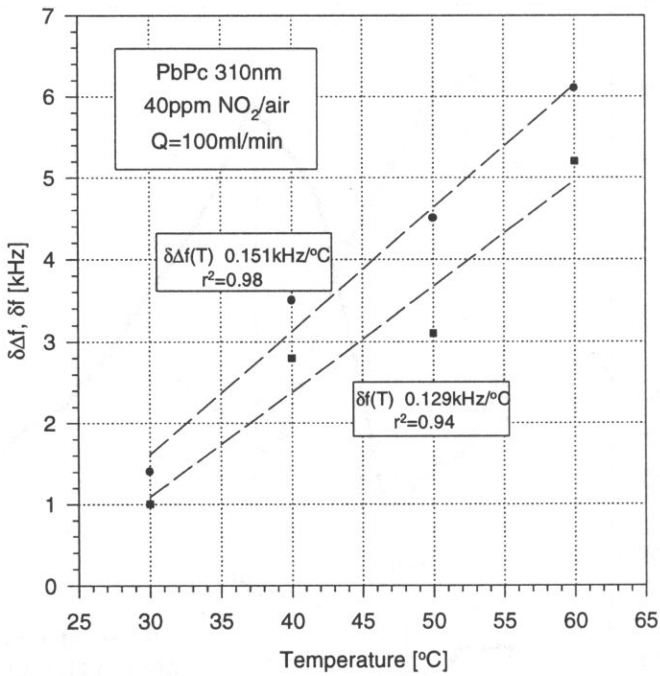

Fig. 6. The final diagram showing the changes of the difference $\delta(\Delta f)$ and measured δf frequencies versus the temperature of interaction.

temperature. This effect is surely connected with the increased kinetics of sorption and desorption (it has also been observed that the time of response and the regeneration of the sensor becomes shorter). There is, however, also an important affect of the electric properties of the semiconductive phthalocyanine layer the behaviour of the sensor. An increase in the temperature of the chemically sensitive layer causes a shift of the operating point of the sensor towards the area of the steep slope of the characteristic $\Delta v / v_0$ versus conductivity σ_s of the layer (Fig. 7), so that the sensitivity of the sensor increases.

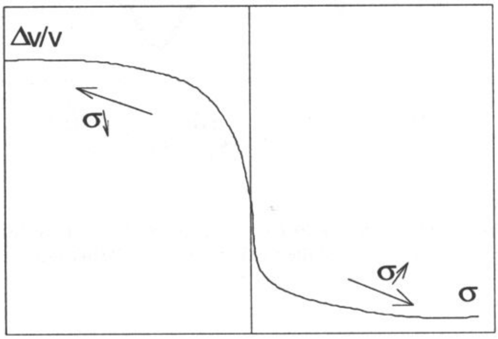

Fig. 7. Velocity of the SAW wave propagation versus electrical conductivity of the sensor layer.

It results also from the diagrams that there is some difference between the change in the frequency difference Δf and that in the measuring frequency f. This can be due to the dipole interaction of polar molecules with the electric field associated with the SAW in the reference acoustic path. This will be the subject of feature research.

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