SAW NO_2 SENSORS EMPLOYING COPPER PHTHALOCYANINE AS A SENSITIVE LAYER

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This paper presents some problems concerned with SAW NO_2 sensors employing copper phthalocyanine (PcCu) as the chemical interface. We have investigated the influence of crystalline structure of PcCu coating on the sensor sensitivity and on temperature stability of generated frequency. The experiments were carried out for SAW delay lines on STX-quartz and 128°YX lithium niobate.

1. Introduction

SAW gas sensors have been the subject of intensive research over the last years [1- 9].

SAW sensors are made by applying a thin chemically sensitive film onto the surface of the SAW delay line. In general the detection principle of the SAW gas sensor relies on the change of the SAW velocity upon absorption of the reactant by the sensor film. This velocity change can be brought about by three effects: the change in the mass density of the film, the change in its elastic constants or the change in its electrical conductivity.

This paper presents some problems concerned with SAW NO_2 sensors employing copper phthalocyanine (PcCu) as the chemical interface of SAW delay lines on STX-quartz and 128°YX lithium niobate.

The influence of piezoelectric substrate material, crystalline structure and morphology of the PcCu coatings on the sensors sensitivity, on the response time and on temperature stability of generated frequency is discussed.

2. Experimental procedure

We used polished single crystal STX-quartz and 128°YX $LiNbO_3$ wafers produced at ITME. Dual-delay lines on both these substrates have been designed.

The SAW sensing element consists of two identical delay lines. One of the lines is covered with PcCu as the chemical coating, while the other is used as a reference in order to compensate for the variation of such parameters as temperature, pressure, etc.

The geometrical and electrical characteristics of the delay lines were chosen to provide low insertion loss of about 17dB before and 20dB after coating with PcCu and appropriately large surface area to be coated. The parameters of delay lines on both substrates are shown in Table 1.

Thin films of PcCu were prepared in a two stage process. At the first stage the input material was purified by vacuum sublimation and at the second one vacuum deposited on piezoelectric substrates at a pressure of the order of 10^{-6} Tr.

The source temperature was 400°C, the distance between the source and the substrate was 40÷100 mm. The substrate temperature was varied between 100°C and 400° C.

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Table 1. The parameters of delay lines.

Parameters	LiNbO3	Quartz
center frequency	70.1 MHz	71.7 MHz
insertion loss	17 dB	17 dB
number of transducers	2	2
number of electrodes	41	201
transducer period	55.6 µm	44 µm
electrode width	7 µm	11 µm
acoustic aperture	2080 µm	6082 µm
spacing between IDTs	4000 µm	6000 µm
total chip area	15.0 × 10.2 mm	24.2 × 18.2 mm

The structure of the films was determined by X-ray diffraction measurements, while their morphology was examined using a scanning electron microscope. Film thickness was monitored *in situ* with a quartz crystal oscillator and later *ex situ* be an optical interferometer. The piezoelectric substrates were bonded to alumina ceramic plates by means of the special silicone adhesive, which proved to be an adequate material for the suppression of bulk modes and unwanted SAW edge reflections.

The experimental measurement system contains three modules: the gas mixing system (A), SAW device (B) and electronics circuits (C) (Fig.1).

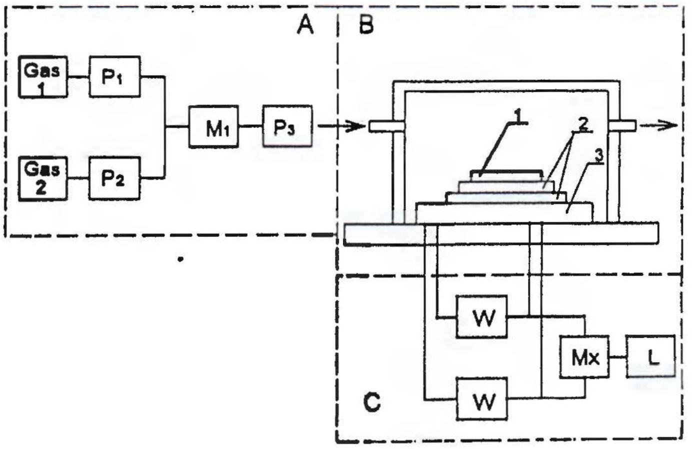

Fig. 1. Experimental measurement system.

A - gas mixing system
P_1,P_2,P_3-mass flowmeters
M - mixer of gases

C - electronics circuits
W - amplifier
M_x- frequency mixer
L - frequency counter.

B - SAW device
1 - piezoelectric substrates
2 - heater
3 - flatpack

The sensor was heated by a cermet thick film resistor deposited on the back side of the ceramic plate. The SAW device was mounted in the flatpack and introduced into the exposure chamber, containing the gas inlet and outlet. The surface of the SAW delay-lines was aligned in parallel with the gas stream line within the chamber.

The electronic system is connected to the delay lines by coaxial cables. This system includes amplifiers, mixer and frequency counter.

Oscillation is obtained using a wide band amplifier for each SAW delay line. The frequencies from these oscillators are mixed and the frequency difference is measured.

Nitrogen dioxide (NO_2) with nitrogen (N_2) was used as the test gas. The mass flowmeters were used to control the input gas flow and concentration.

3. Results

In our experiments we have obtained monocrystalline films of α-PcCu and β-PcCu structure, and also two phase α and β films. These types of PcCu film morphology are illustrated in Fig. 2 - 4.

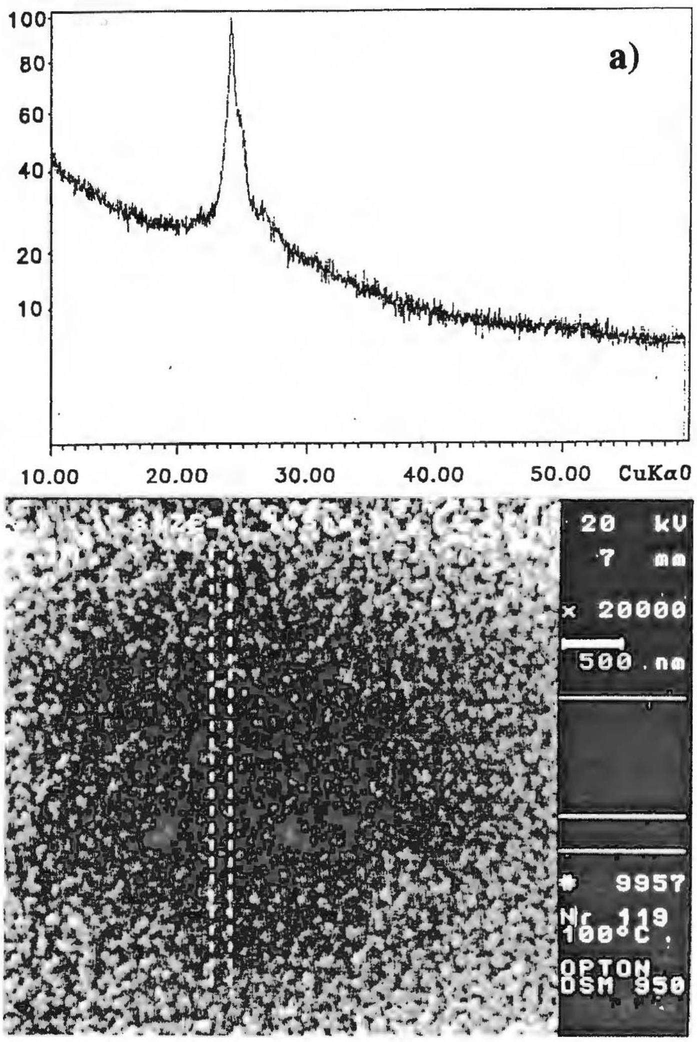

Fig. 2. α - PcCu diffraction spectrum and morphology:
a - diffraction spectrum (CuKα radiation),
b - film morphology.

We varied the coating layer thickness from 0.1 μm to 1.5 μm and it's density from 0.17 g/cm^3 to 1.6 g/cm^3.

In this paper we present as an example the results concerning only well ordered monocrystalline films of α and β-PcCu.

3.1 Temperature stability of generated frequency

The temperature stability of SAW delay line generated frequency was investigated in the temperature range from 20°C to 120°C.

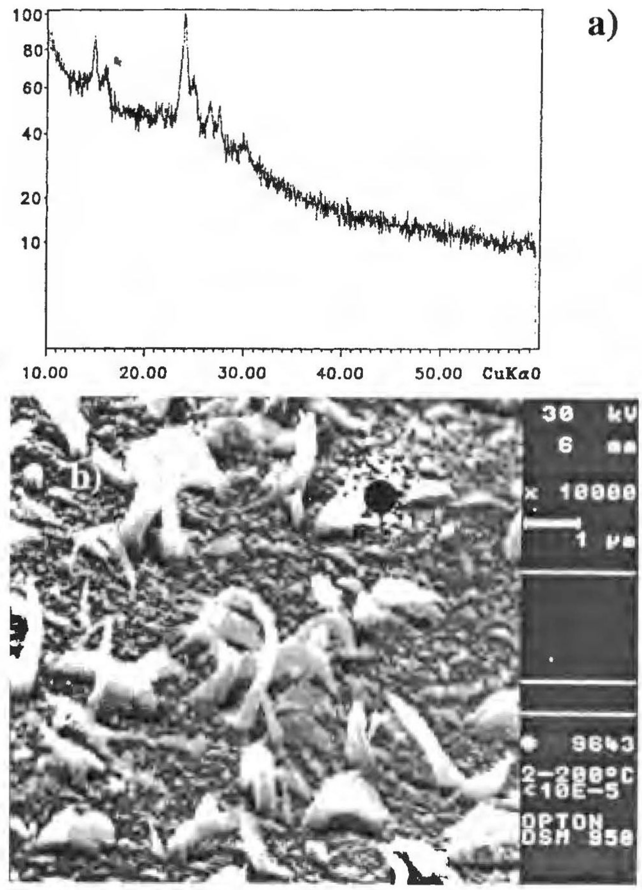

Fig. 3. α and β - PcCu diffraction spectrum and morphology:
a - diffraction spectrum (CuKα radiation),
b - film morphology.

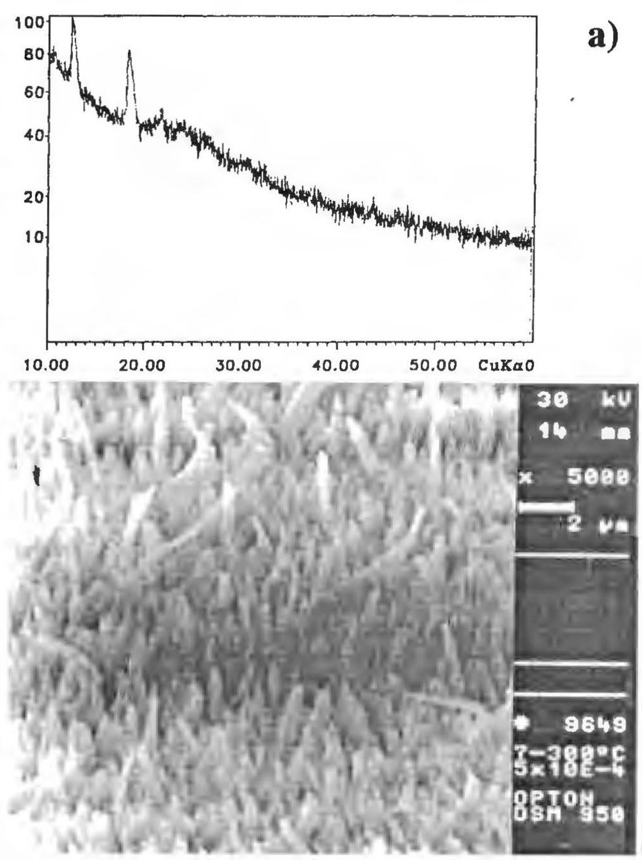

Fig. 4. β - PcCu diffraction spectrum and morphology:
a - diffraction spectrum (CuKα radiation),
b - film morphology.

The frequency of a single oscillator and the differential frequency were continuously measured during the heating process. The measurement was stopped approximately 1 hour after temperature stabilizing.

Typical plots are shown in Fig. 5-7.

The frequency versus time curves for the uncoated and PcCu-coated delay lines almost coincide for temperatures below 45°C. The discrepancy between the curves grows with the increase of temperature. The shape of the curves indicates that the differential frequency increases with the temperature (Fig. 5).

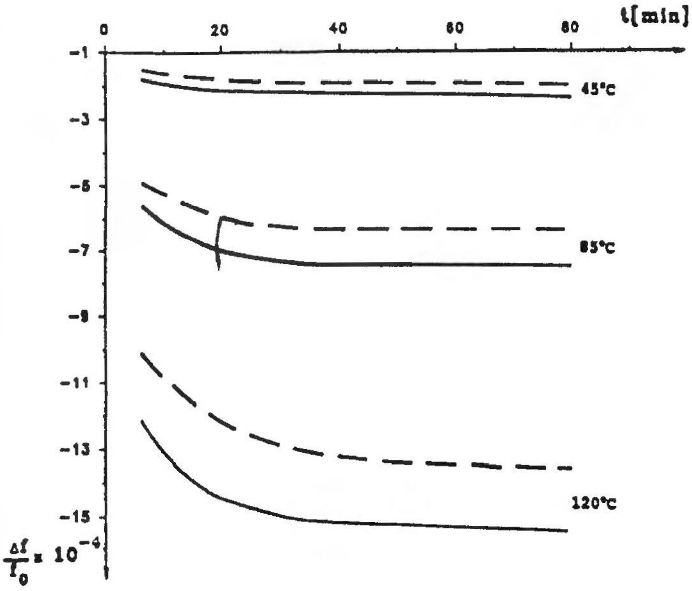

Fig. 5. The relative frequency shift of PcCu-coated and uncoated delay lines on quartz substrate during heating up to three different temperatures:

Δf - frequency shift,

f_0 - frequency of generation at room temperature,

- - - - uncoated delay line ,

—— - PcCu - delay line,

coating α - PcCu, mass - 3.2 × 10^{-6} g.

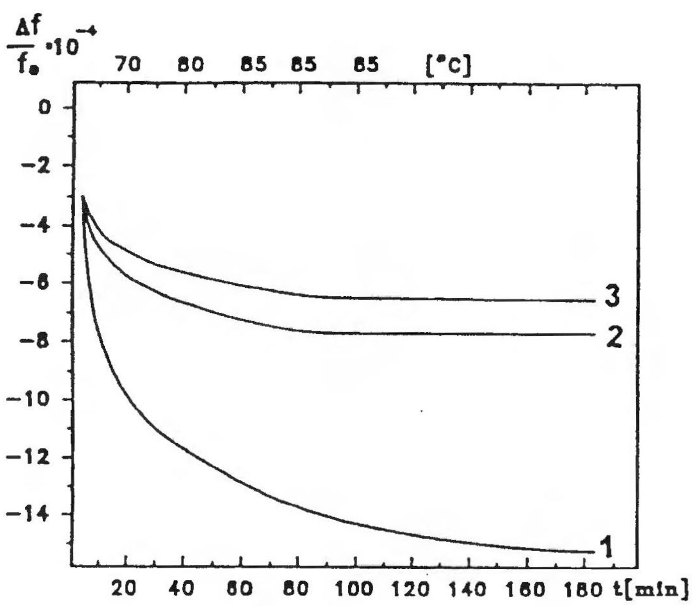

Fig. 6. The relative frequency shift of PcCu-coated delay line on quartz substrate during heating up to 85°C.

Δf - frequency shift,

f_0 - frequency of generation at room temperature,

1 - α - PcCu, coating mass - 4.8 × 10^{-6} g,

2 - α - PcCu, coating mass - 3.2 × 10^{-6} g,

3 - α - PcCu, coating mass - 4.8 × 10^{-6} g.

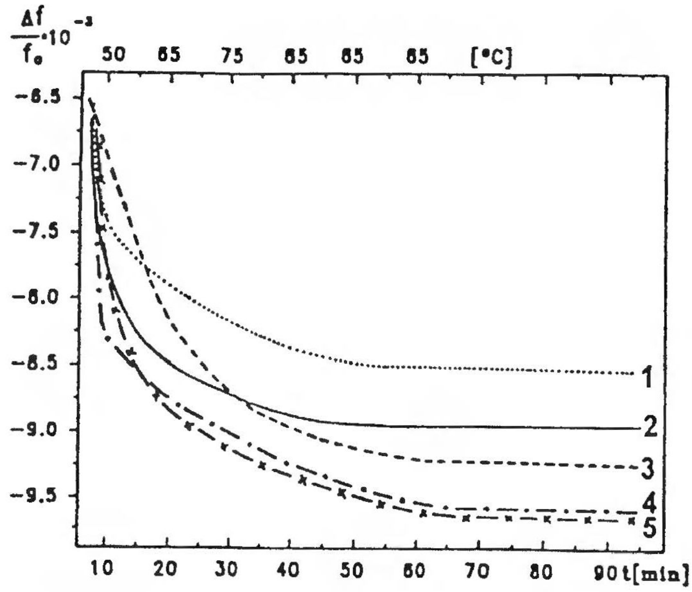

Fig. 7. The relative frequency shift of PcCu -coated delay line on $LiNbO_3$ substrate during heating up to 85 °C.

Δf - frequency shift

f_0 - frequency of generation at room temperature

1 - β - PcCu, coating mass - 5 × 10^{-7} g

2 - uncoated delay line

3 - α - PcCu, coating mass - 1 × 10^{-7} g

4 - α - PcCu, coating mass - 3 × 10^{-7} g

5 - α - PcCu, coating mass - 5 × 10^{-7} g.

Heating causes frequency decrease of a single oscillator. This is true regardless of the PcCu morphology and type of the substrate, however the value of frequency change depends on the structure of the layer.

From the graphs (Fig.6-7) it follows that the value of frequency change with temperature is greater for the delay line covered with α-PcCu film, than for the line employing the β-PcCu layer of the same mass.

At constant temperature the differential frequency drift is practically independent of the PcCu film parameters (Table 2).

Table 2. The differential frequency drift.

Temperature [°C]	Differential frequency drift	
	Delay line on quartz	Delay line on lithium niobiate
20•	≤ 1 Hz / min	≤ 2 Hz / min
45	≤ 2 Hz / min	≤ 6 Hz / min
120	≤ 3 Hz / min	≤ 7 Hz / min

3.2 Sensor sensitivity and response time

The sensor sensitivity was determined as the value of differential frequency shift during the film exposition on the reaction with NO_2, till saturation took place.

The frequency change as a function of time was measured for NO_2 concentration in the carrier gas equal to 10 ppm. The flow rate was 1 l/min. These measurements were taken at room temperature. Typical plots are shown in the Fig. 8-10.

The response time of SAW device designed on lithium niobate employing α-PcCu (Fig. 8), was about 5min, whereas that of β-PcCu was approximately 50 min (Fig.9). On the other hand the measured sensitivity of β-PcCu film was several times higher than the sensitivity of α-PcCu film.

In the case of SAW device based on quartz (Fig. 10) the frequency change is significantly smaller than in the case of lithium niobate with the similar response time (Fig.9).

For our experimental situation both mass loading and conductivity changes may cause a sensor response. In the case of low concentration of NO_2, the effect of change in mass was insignificant in comparison with the effect of conductivity change (therefore the sensitivity of SAW device on quartz was much smaller than on $LiNbO_3$), but if the concentration is greater than about 100ppm conductivity change will cease to be a function of NO_2 concentration.

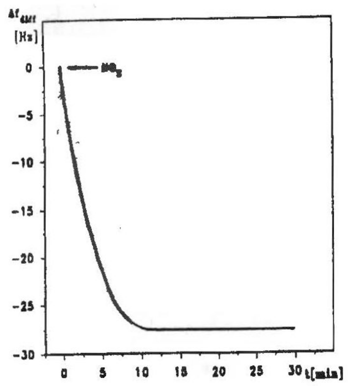

Fig. 8. The differential frequency change versus time for α-PcCu covered SAW device on lithium niobate (coating mass - 5 × 10^{-7} g).

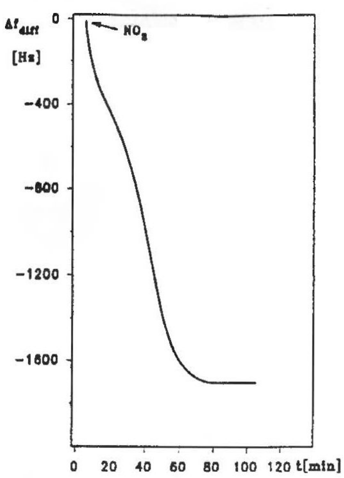

Fig. 9. The differential frequency change versus time for β - PcCu SAW device on lithium niobate (coating mass - 5 × 10^{-7} g).

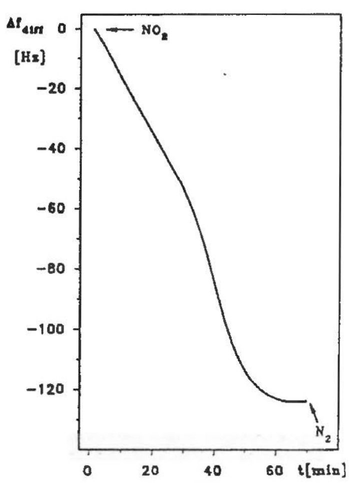

Fig. 10. The differential frequency change versus time for β-PcCu SAW device on quartz (coating mass - 3.2 × 10^{-6} g).

4. Conclusion

Our measurements show, that for the investigated range of parameters the β-PcCu layer provides several times better sensor sensitivity and temperature stability of SAW delay line generation frequency than α-PcCu layer of the same mass.

It seems interesting to try to optimize NO_2 detection by simultaneously using both lithium niobate and quartz sensors in the same detection system, utilizing β-PcCu as the chemically sensitive layer. This should make it possible to widen the measurement range of gas concentration and to increase the sensor sensitivity as well as selectivity.

Short biography note

Judyta HEČHNER received M.Sc. degree in chemistry from Warsaw University in 1973. From 1973 till 1989 she carried out research on picture tube technology at the Institute of Electronics in Warsaw, Poland. In 1989 she joined the Institute of Electronic Materials Technology, where she worked on TV SAW filters technology. Recently her research activities concerns technology of SAW gas sensors. She is a member of PSST.

Tadeusz WRÓBEL obtained his BS degree in electronic engineering from the Technical University of Warsaw in 1970 . From 1963 till 1992 he worked on technology filters, quartz devices and subsequently surface acoustic wave devices at Tele and Radio Research Institute in Warsaw, Poland. Since 1989 he has been working on SAW filters, resonators and sensors at the Institute of Electronic Materials Technology in Warsaw. He is a member of PSST.

5. References

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ON PROCESS SILICON MICRO EMITTERS WITH SHARP TIPS

Jan Dziuban
Anna Górecka-Drzazga

The most spectacular works of Micromechanics Group of Semiconductor Laboratory of the Technical University of Wrocław have been described. Varying pressure sensors micromachined in single-crystal silicon have been presented, including new version of self-compensenting piezoresistive pressure sensors, opto-devices with moving fiber, laboratory-scale models and masproduction devices have been pre-

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