SENSOR PROPERTIES OF BILAYER STRUCTURES WITH PALLADIUM, LEAD AND COBALT PHTHALOCYANINES IN SURFACE ACOUSTIC WAVE AND ELECTRIC SYSTEMS

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Presented here are the results concerning a hydrogen sensor based on a novel bilayer structure with lead and cobalt phthalocyanines in a Surface Acoustic Wave dual-delay line and electric systems. The sensor material consists of two layers produced in two different vapour deposition processes. The first one is a lead or cobalt phthalocyanine (~310nm PbPc or 200nm CoPc) layer, whereas the second is a ~20 nm thin palladium (Pd) film. This structure was simultaneously formed in a one of the SAW dual delay lines and on the interdigital electrodes of the glass substrate for electric measurements. These sensor structures have been investigated from the point of view their sensitivity towards: hydrogen, nitrogen dioxide and sulphur dioxide gases with different concentrations in dry air. Preliminary measurements of this two bilayer structures have been performed simultaneously in the same chamber for this same measurement conditions.

Keywords: *bilayer sensor, palladium, lead phthalocyanine, cobalt phthalocyanine, surface acoustic wave, electric method*

1. INTRODUCTION

Surface Acoustic Wave (SAW) gas sensors are very attractive due to their remarkable sensitivity in a specific configuration of the bilayer structure, as well as their small size, low power consumption and frequency measurements. The bilayer structure (semiconductor and metal) on a piezoelectric substrate creates new possibilities for detecting gas in a SAW sensor system by using an acoustoelectric coupling between the surface wave and the sensor structure in a high sensitivity region. In a bilayer sensor structure we can use the much stronger acoustoelectric effect in the SAW sensor system as the main detection mechanism [1-3]. This effect can be many times greater than the mass effect which can be dominant in

nonconductive polymer films and simple metal and dielectric films in SAW gas systems [4-9].

Any change of the physical or chemical properties of a thin active structure placed on a piezoelectric surface, can affect SAW propagation. However, from the practical point of view, only the following two effects are potentially significant, namely a change in the mass of the sensor structure and a change of its electrical conductivity cause a significant change of the velocity and attenuation of SAW [5]. These two effects occur simultaneously in the interaction time of an active sensor structure with specific gas concentrations and their contribution in the entire sensor response depends mainly on the kind of sensor material and also on the physical properties of the substrate and active sensor structure. For instance, in non-conductive polymer films only the mass effect exists, whereas in thin phthalocyanine films as organic semiconductors both do exist, but the electric effect can be greater (several times, depending on the gas concentrations) [10,11].

It is well known that a palladium film easily absorbs hydrogen molecules [12,13]. However, when only a metal (palladium) layer is used on a piezoelectric substrate (like $LiNbO_3$ Y-Z) [1,14], the metal layer shortens the electric field associated with the surface wave. Consequently, the sensor can detect only the mass loading. When only a CuPc layer is used, the sensitivity of this compound is too weak to detect hydrogen molecules; besides, the conductivity of the layer at room temperature is too high and this sensor must be temperature-activated [1]. Nowadays it is well established that, in the case of phthalocyanine compounds in a SAW system the electric effect is much greater than the mass loading [5,10,11]. Thus, in order to take full advantage of the high sensitivity offered by the SAW sensor, the sensor structure conductivity must be contained within some particular range. For instance, the resultant electrical conductivity of the bilayer structure (CuPc 720nm + 20nm Pd) on a $LiNbO_3$ Y-Z substrate is well fitted to the high sensitivity range of the SAW device and can detect hydrogen molecules even at room temperature [1].

In Fig.1 a block scheme is shown for a SAW gas sensor on a piezoelectric substrate. These sensors can be now divided into two groups: with a single sensor layer and bilayer or even multilayer sensor structure. In the second group a new class of SAW gas sensor – Acoustoelectronic Gas Sensor- can be introduced, where the detection mechanism is based on an acoustoelectronic interaction. Besides two various detection methods: frequency amplitude changes and interaction speed are shown as a new one as well.

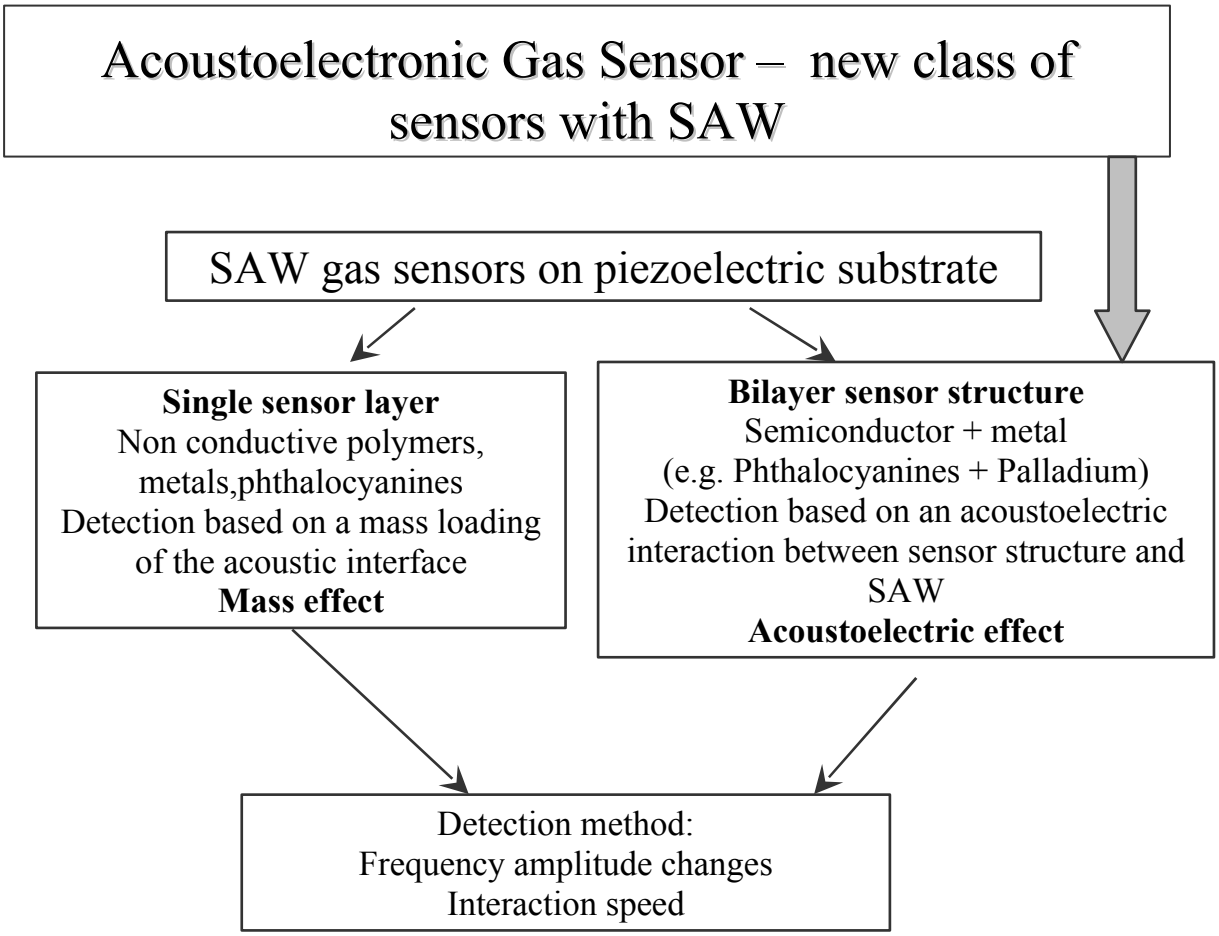

Fig.1. Two groups of gas sensors with SAW

The sensor structure - Fig.2 - consists of two layers, usually obtained in two different vapor deposition processes or any other thin film deposition technology. The first one is a semiconductor layer and the second one – a thin metal film. The preliminary results for 720nm CuPc (organic semiconductor) and 20nm Pd were really very promising [1].

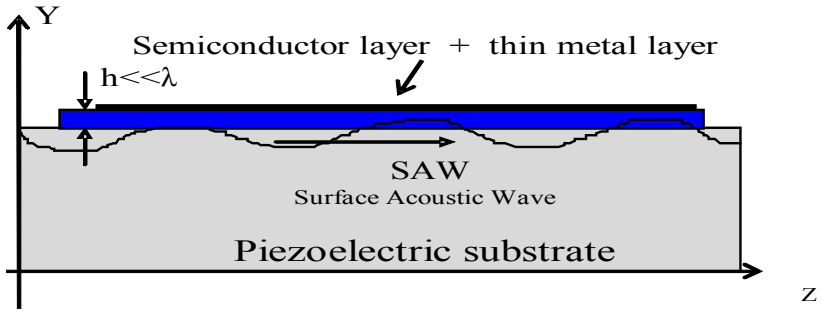

Fig.2. The bilayer structure (semiconductor + metal) creates new possibilities of gas sensing in a SAW sensor system with the use of an acoustoelectric coupling between the surface wave and the sensor structure in a high sensitivity region.

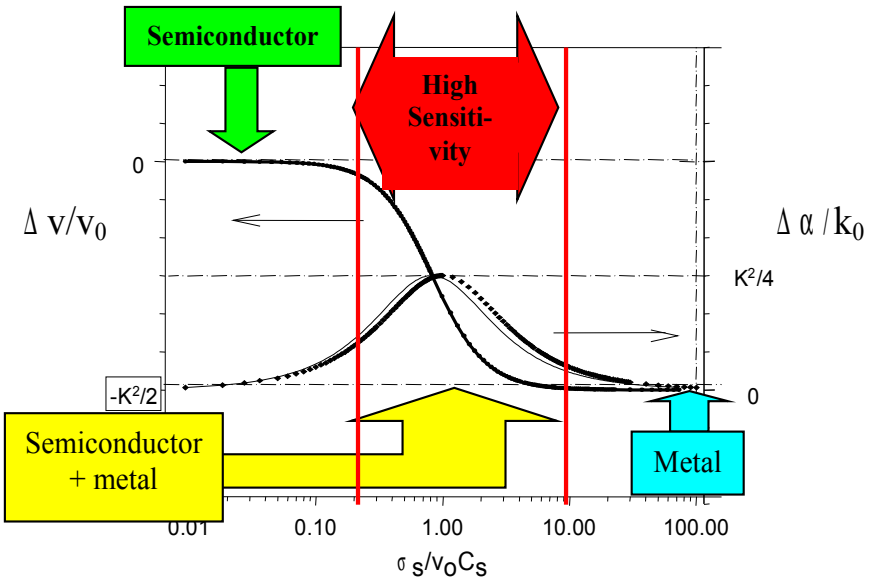

Fig.3. The theoretical dependence of relative changes of the SAW velocity (left axis) and attenuation (right axis) vs. the normalised surface conductivity σ_s of the structure placed on the piezoelectric substrate. For $LiNbO_3$ Y – Z, $\sigma_s = v_0 Cs = 1.6 \times 10^{-6}$ [Ω^{-1}] (v_0 is unperturbed SAW velocity, C_s is the sum of the piezoelectric substrate and environment permittivities)

The acoustoelectric effect has one very interesting feature, namely it causes significant changes in the case of propagation of the SAW only in some particular range of surface conductivity of the thin film structure of the sensor. Thus, in order to take full advantage of the high sensitivity offered by the SAW sensor with an acoustoelectric effect, the resultant conductivity of a thin film must be in this particular range, which depends only on the properties of the piezoelectric substrate [1,2]. When only a metal layer is used (for instance palladium as a well-known material for hydrogen detection) on a strong piezoelectric substrate (like $LiNbO_3$ Y-Z), the metal layer shortens the electric field associated with the surface wave. Consequently, the sensor can detect only the mass loading, which is rather very small in thin films (~20 nm of Pd) [14]. The acoustoelectric effect is not effective in the case of a simple metal film because even in spite of substantial changes of the conductivity it does not cause any significant changes in the wave velocity – it is the "Metal" region in Fig.3. We have almost the same situation in the case of a simple semiconductor (like metallophthalocyanine compounds); this time the „work point" is rather at the beginning of the characteristics – the "Semiconductor" region in Fig.3.

Because of the assumptions described above a bilayer structure consisting of a semiconductor buffer layer and a thin metal layer on the top as an active film should have its

resultant electrical conductivity much better fitted to the high sensitivity range – the "Semiconductor + metal" region in Fig.3.

Such a bilayer structure creates new possibilities of gas sensing in a SAW sensor with the use of an acoustoelectric coupling between the surface wave and the sensor structure.
A simple interaction model of the bilayer structure (phthalocyanine and palladium) with hydrogen molecules is shown in Fig.4. The described physical and chemical base was proposed first by Lundstroem long ago [15]. Molecular hydrogen dissociates to atomic hydrogen on the outer palladium surface, then the atomic hydrogen diffuses into the palladium film and some of it is adsorbed at the inner palladium surface. Adsorbed hydrogen atoms then act as electrical dipoles at the metal-semiconductor interface and create alterations in the work function of the palladium at the interface and in the surface conductivity of the phthalocyanine layer. These variations in the surface conductivity can cause a considerable fluxuation in the velocity of the acoustic surface wave, which finally leads to a modification in the measuring frequency and differential frequency Δf as well. However, as has been mentioned above (Fig.3), significant changes in the SAW velocity under surface conductivity variations are possible only when the resulting conductivity of the bilayer structure is properly fitted to an active range of the acoustoelectric effect. This active range depends mainly on velocity of the substrate SAW and the dielectric properties of the substrate and environment.

In the previous papers [1,2] the idea of a new two-layered structure (20nm palladium thin film on cooper phthalocyanine 720 nm and nickel phthalocyanine 230 nm as a buffer layers) for hydrogen detection in a SAW system was introduced. The results were really very promising and in this paper the measurements are performed with other phthalocyanine as buffer layers, i.e. lead phthalocyanine 310 nm (PbPc), cobalt phthalocyanine ~200nm (CoPc) and ~ 20 nm thick palladium films. The thickness of the buffer layer was chosen arbitrarily. The structure was produced in two different vapour deposition processes on the two substrates simultaneously – for SAW sensor and for the electric one. In this paper, the first preliminary measurements of these bilayer structures are showed and discussed from the point of view of hydrogen detection in a medium concentration range (from 3% to 4% in air) and also their cross sensitivity towards NO_2 and SO_2 in dry air.

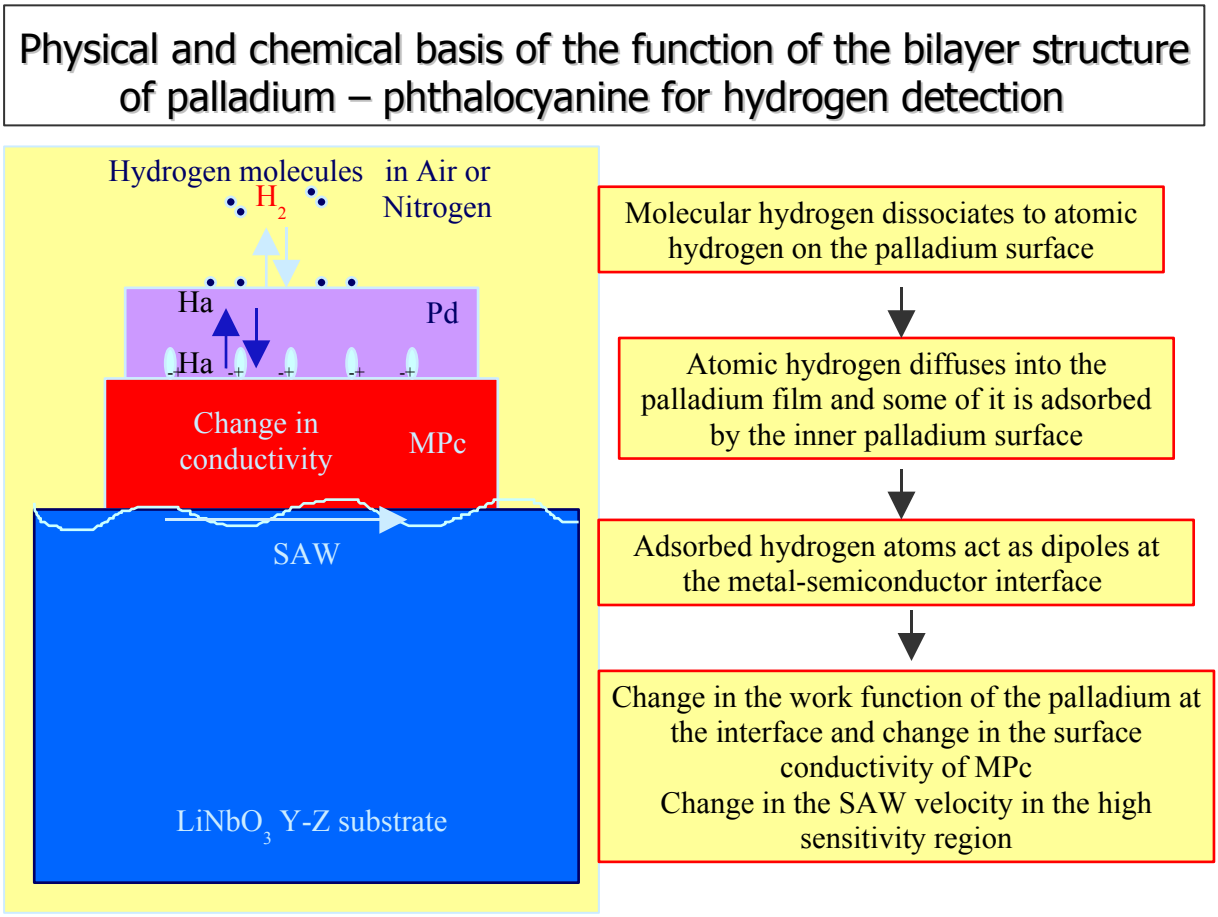

Fig.4. Physical and chemical basis of the function of the bilayer structure on the example of a bilayer structure: organic semiconductor (metallophthalocyanine) and palladium (Pd) for hydrogen detection – based on the I.K Lundstroem [15].

2. EXPERIMENTAL

The experimental set-up for acoustic sensor is based on frequency changes in a surface acoustic wave dual delay line system, which is nowadays well known [5,7,11]. On a piezoelectric $LiNbO_3$ substrate, two identical acoustic paths are formed, using interdigital transducers. Next, a bilayer active structure is formed in the measuring line in two different vacuum deposition processes. The second path serves as a reference and can compensate small variations of temperature and pressure. Both delay lines are placed in the feedback loop of oscillator circuits and the response to the particular gas of the active bilayer is detected as a change of the differential frequency Δf, i.e. the difference between the two oscillator frequencies f and f_0.

The structure for electrical measurements was made in these same technological processes like the structure for SAW sensor. As a consequence the investigated structures

were identical. For electrical measurements a planar method with interdigital electrodes was applied [9]. The investigated lead phthalocyanine layer with thickness of about 310 nm, was made by means of the vacuum-sublimation method, using a special aluminium mask. The source temperature was about 600 ^{o}C and the thickness was measured by the interference method. A copper-constantan thermocouple was used to control the temperature. The thin (~20 nm) palladium layer was made separately by means of vapour deposition in high vacuum and after the deposition of a phthalocyanine film in a new process [16-18]. The total flow rate of 1000ml/min was used during all the measurements. The volume of the measuring chamber was about 30cm^3. The sensor was tested in a computer-controlled system. Gases of 99.999% pure hydrogen and 99.998% pure nitrogen were mixed using mass flow controllers (Bronkhorst Hi-Tech). The temperature was measured using a thermocouple adjacent to the bilayer structure. The experimental set-up is shown in Fig.5

Fig.5. Experimental set-up: measuring chamber with top-cover and gas dosing system.

3. RESULTS

An example of interaction of single palladium layer in SAW system is shown in Fig.6. We can see very small changes of the differential frequency under hydrogen gas.

An example of preliminary acoustic and electrical measurements for PbPc+Pd structures is shown in Fig.7. The structures were made in the same technological processes, and were placed in the same measuring chamber. Measurements were performed simultaneously in these same conditions of gas concentrations and temperature. In all the measurements, depending on the hydrogen concentration, a repeatable decrease and increase of the frequency Δf is to be observed.

In Fig.8 an interactiom of bilayer sensor structure CoPc+Pd with the same concentration (25 ppm) of SO_2 in air at room temperature is shown. We can see only a big interaction under the first concentration. So the answer of the structure is not repeateable.

In the case of the novel bilayer structures the obtained preliminary results were very promising, although in the first interaction cycle some problems in stability of the response have been observed and the response was very weak – Fig.7.

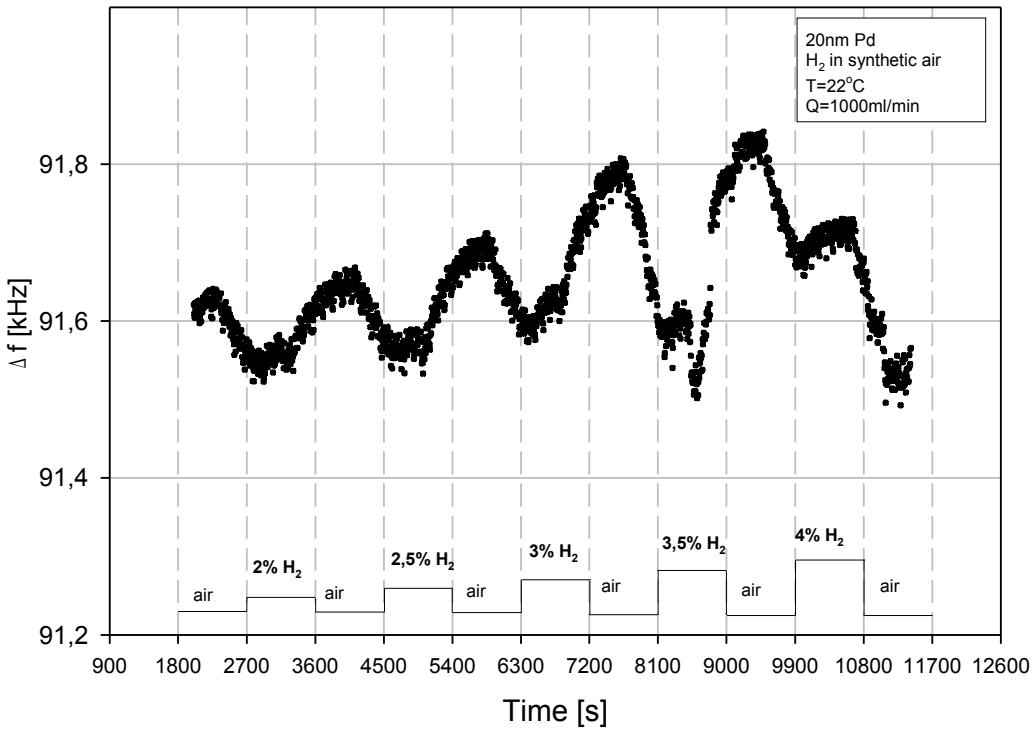

Fig.6. Acoustic interaction of single palladium film 20nm with various hydrogen concentrations in air at room temperature.

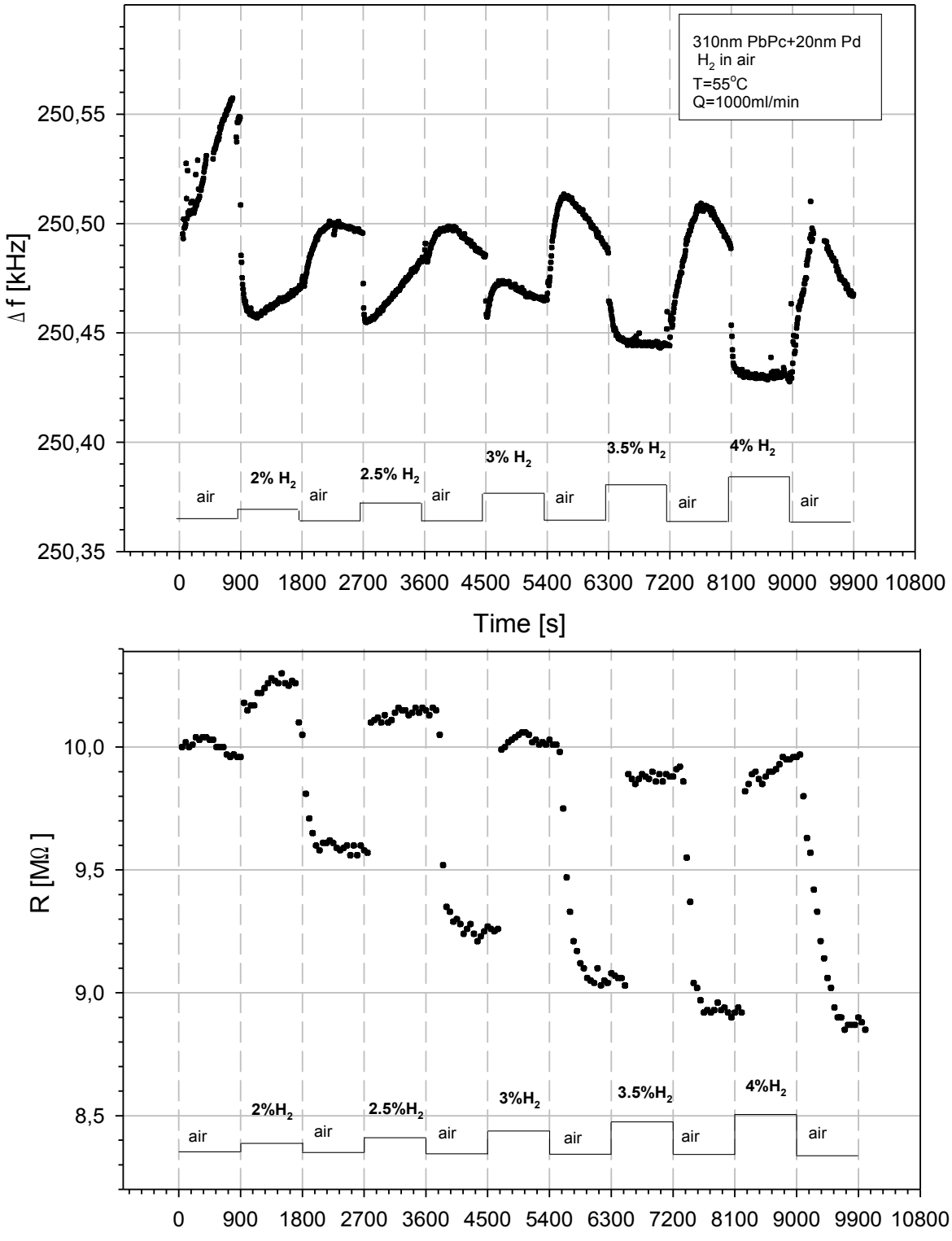

Fig.7. An example of correlation for acoustic(upper graph) and electrical (lower) measurements for bilayer structure PbPc+Pd at elevated temperature. For the decrease of differential frequency we can observe an increase in resistance for all hydrogen concentration in air.

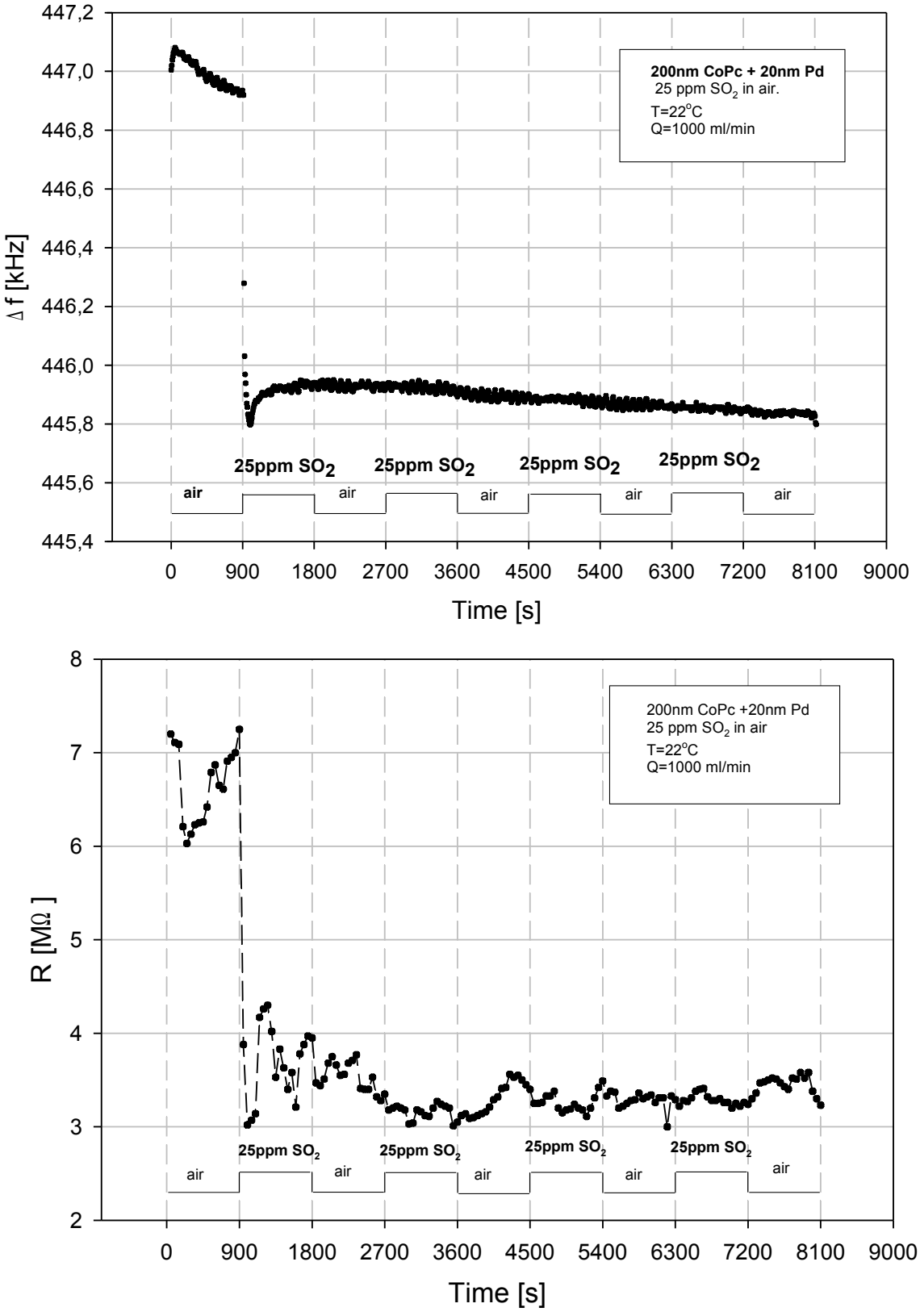

Fig.8. Interaction of structure CoPc+Pd with the same (25ppm) concentration of SO_2 in air at room temperature in acoustic method (upper graph) and electric one (lower graph).

4. CONCLUSIONS

Surface Acoustic Gas Sensors are very attractive because of their remarkable sensitivity which can be adjusted by the film thickness in a bilayer sensor system. The bilayer structure (metal + semiconductor) creates new possibilities of gas sensing in a SAW sensor with the use of an acoustoelectric coupling between the surface wave and the sensor structure. The "work point" of such a structure must be shifted to the high sensitivity region, where even small variations in conductivity (under the influence of gas molecules) cause remarkable changes in the wave velocity. Thus, in order to take full advantage of the high sensitivity offered by the SAW sensor, the entire conductivity of thin films must be contained in some particular range [1]. For example, the bilayer structure (CuPc 720nm + 20nm Pd) on a $LiNbO_3$ Y-Z substrate has its resultant electrical conductivity well fitted to the high sensitivity range of the SAW device and can detect hydrogen molecules even at room temperature [1]. It seems that future researches will be focused on a proper fitting of the entire sensor structure to the high sensitivity region for a given piezoelectric substrate and on a proper construction of the electronic system to excite a surface wave.

- An interaction of the bilayer structure 310nm PbPc + 20nm Pd with hydrogen cause a decrease of differential frequency Δf although these changes are very small - do not exceed 60 Hz.
- The changes in a resistance of the same bilayer structure made for electrical measurements are equivalent to the changes in differential frequencies. An increase in resistance of the structure on the level $3 \cdot 10^9 \Omega$ is observed.

The interaction of the investigated bilayer structures with other toxic gases like SO_2 and NO_2 in medium concentration range (25-500ppm in dry air) was very small – not exceeding the short term apparatus drift level – 10Hz. The best results were achieved after many cycles of interaction and at lower temperatures.

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