HYDROGEN SENSOR WITH PALLADIUM AND METAL-FREE PHTHALOCYANINE BILAYER STRUCTURES 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 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 metal-free pthalocyanine (H_2Pc) 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. In such a bilayer structure detection of hydrogen in a medium concentration range (from 1% to 4 % in nitrogen) is possible, even at room temperature. Preliminary measurements of this two bilayer structures has been performed simultaneously in the same chamber for this same measurements conditions. A good correlation of results between these structures has been observed.

Keywords: *hydrogen sensor, palladium, metal-free phthalocyanine, surface acoustic wave, electric method.*

1. INTRODUCTION

Hydrogen gas is used as a reducing agent and as a carrier gas in the process of manufacturing of semiconductors, and it has been increasingly recognized as a clean source of energy or as a fuel gas. Any leak of hydrogen in large quantities should be avoided because, if mixed with air in a ratio of 4,65 - 93,9 vol. %, hydrogen is explosive. Thus, the fast and precise detection of hydrogen near and especially before the explosive concentration at room or near room temperature is highly needed [1-6].

SAW gas sensors are especially attractive because of their remarkable sensitivity due to changes of the boundary conditions of the propagating wave, introduced by the interaction of an active thin film with specific gas molecules. This unusual sensitivity results from the simple fact that most of the wave energy is concentrated near the crystal surface within one or two wavelengths. Consequently, the surface wave is in its first approximation highly sensitive to any changes of the physical or chemical properties of the thin active layer previously placed on the crystal surface.

A number of semiconductor devices have been developed for the detection of hydrogen. Most of them are based on reversible changes produced by hydrogen in bulk and surface properties of palladium [7,8]. D'Amico first developed a SAW hydrogen gas sensor with a palladium film as the selective layer [1,2]. However this sensor was made in a simple Pd layer configuration – as a consequence the response was caused only by mass effect which is very small for thin Pd layers. Further our work introduced a bilayer structure targeting hydrogen gas, with copper and nickel phthalocyanines and palladium film at room temperatures [11]. The bilayer structure was used in attempt to increase the sensitivity to hydrogen gas. The details of the bilayer structures (MPc +Pd) in SAW gas sensor systems are described in our last papers [17].

In the previous papers [11] 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. metal -free phthalocyanine 30-35nm (H_2Pc), and ~ 15 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 the correlation for this novel bilayer structure are showed and discussed from the point of view of hydrogen detection in a medium concentration range (from 3% to 4% in air).

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 [9,10,12,13]. 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 differential frequency for the investigated bilayer structure (H_2Pc + Pd) was rather low ~90 kHz what was very advantages from the practical point of view.

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 – Fig.1a and b.

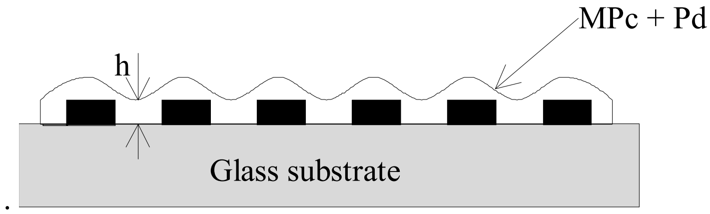

Fig.1a) Bilayer structure made on the surface of interdigital electrode system for electrical measurements

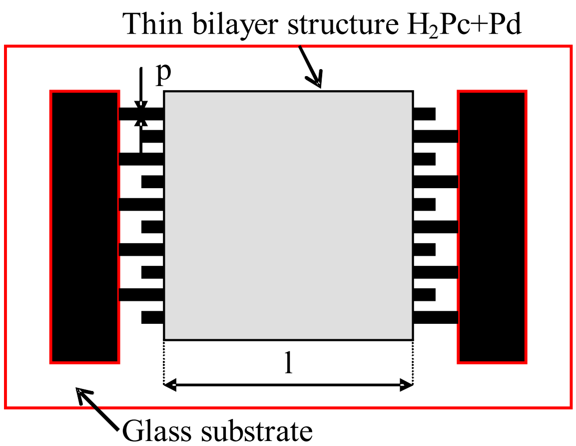

Fig.1b) The idea of electrical measurements. On a glass substrate an interdigital electrode system is made and next a bilayer structure on the top. Interaction of hydrogen with the structure cause a change in electrical conductivity which can be observed by sensitive electrical devices. For practical applied system: p=56μm equal the space between them, l=13,6mm. Number of electrode pairs N=9.

The investigated metal-free phthalocyanine layer with thickness of about 30-35 nm, was made by means of the vacuum-sublimation method, using a special aluminium mask. The source temperature was about 600 ºC and the thickness was measured by the interference method. A copper-constantan thermocouple was used to control the temperature. The thin (~ 15nm) 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 [14-16].

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.

3. RESULTS

An example of preliminary acoustic and electrical measurements is shown in Fig.2. 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 hydrogen 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 the case of the novel bilayer structure (H_2Pc+Pd) 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.2.

A simple graphic analysis of the result from Fig.2 is showed in Fig3.

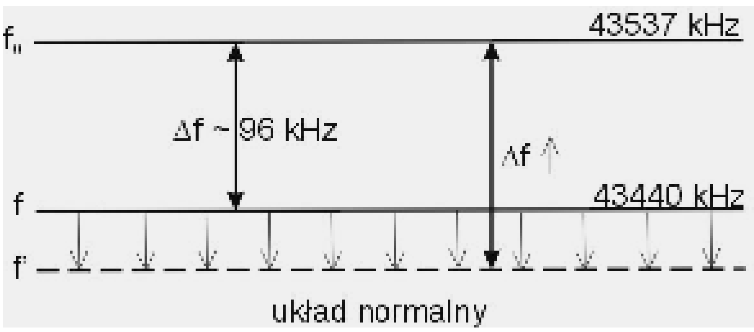

Fig.3. Changes of the frequencies In the SAW sensor system under interaction of bilayer structure (H2Pc +Pd) with hydrogen. Where:
f_0 – frequency in a reference path;
f – frequency in a path with bilayer structure;
f ' – frequency in a path with a structure after interaction with hydrogen;
Δ f - a frequency difference between two acoustic paths.

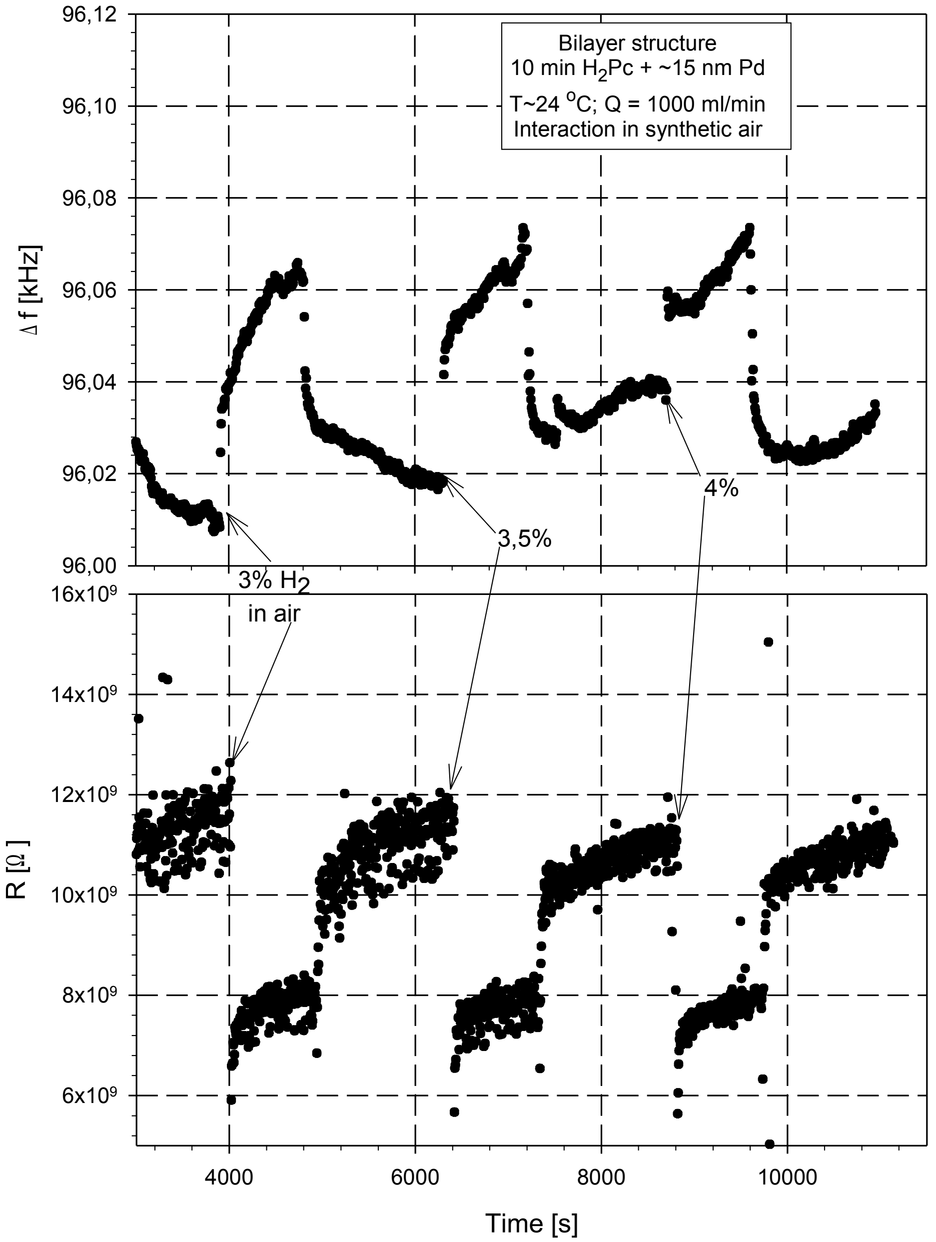

Fig.2 An example of correlation for acoustic(upper graph) and electrical (lower) measurements. For the increase of differential frequency we can observe a decrease in resistance for all hydrogen concentration in air. 10 min H_2Pc – means the time of vacuum evaporation of phthalocyanine film – it is about 30-35nm thickness.

4. CONCLUSIONS

- For measurements in SAW sensor structure the frequency of surface wave slightly decrease what means that the velocity of wave decreases as well.

- An interaction of the structure with hydrogen cause an increase 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. A decrease in resistance of the structure on the level $3 \cdot 10^9 \Omega$ is observed.

The bilayer structure 30-35nm H_2Pc and 15 nm Pd has been investigated from the point of view of hydrogen detection. The best results were achieved after many cycles of interaction and at lower temperatures. The interaction response depends on temperature, and decreases with the increase of the interaction temperature.

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