# SURFACE ACOUSTIC WAVE SENSOR FOR HYDROGEN DETECTION WITH A TWO-LAYERED STRUCTURE

Wiesław JAKUBIK, Marian URBAŃCZYK, Stanisław KOCHOWSKI, Marcin NADOLSKI

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

### ABSTRACT

Results concerning a hydrogen sensor based on a two-layered structure in a Surface Acoustic Wave dual-delay line system are presented. The sensor material consists of two layers performed in two different vapor deposition processes. The first one is a 720 nm CuPc (or 110 nm H<sub>2</sub>Pc) layer, the other one – a 20 nm thin palladium film. This structure was formed in a one of the dual – delay line system on a LiNbO<sub>3</sub> Y-cut Z-propagation substrate. In such a multilayer structure can detect hydrogen in a medium concentration range (from 0,25 % to 3 % in nitrogen), even at room temperature. The sensor has a very good sensitivity, stability and is entirely reversible. The response and recovery times are very short (~200 s – 800 s), which is very important from the practical point of view.

Keywords: SAW, hydrogen sensor, palladium, phthalocyanine

# **1. INTRODUCTION**

There are many methods for hydrogen detection and a comprehensive review can be found in literature [1]. Since the early MOS field transistors and Schottky diodes sensors through the first SAW devices made by D'Amico [2] we have now many different fiber optic hydrogen sensors [3]. Hydrogen gas has been used as a reducing agent and as a carrier gas in semiconductor manufacturing process and it is has been increasingly noted as a clean energy resource or a fuel gas [4]. A hydrogen leak in large quantities should be avoided because if mixed with air in a ratio of 4.65 - 93.9 vol. % hydrogen is explosive [1]. Thus the fast and precise detection of hydrogen near the explosive concentration and at room temperature is still a great problem.

Almost all the sensors referred above use thin palladium films as sensor material because of their well-known absorption properties relative to hydrogen [1-3].

According to D'Amico [2] we have tried to use thin (~20 nm) palladium layers in a SAW system to detect hydrogen. Unfortunately, the interaction was very weak, even at a relatively high (3%) hydrogen concentration. When we used only a thin CuPc film (~720 nm), the interaction was much better, but only at higher temperatures of about 70 °C. We decided to form a multilayer structure consisting of a copper phthalocyanine (CuPc) layer 720 nm and a 20 nm thin palladium layer in two different vacuum deposition processes - Fig.1.



Fig.1. The sensor material consists of two layers produced in two different vapor deposition processes. The first one is a 720nm CuPc layer the second one – a 20 nm thin palladium film. The thickness of the sensor material, h, is considerably less than the wavelength λ of the SAW.

The addition of a thin palladium layer to the CuPc film greatly enhanced the sensitivity to gaseous hydrogen in a medium concentration range (from 0,25 % to 3 % in nitrogen), even at room temperature. Besides that, the sensor has a good stability, a short response, short recovery times and is entirely reversible.

# 2. EXPERIMENTAL

The experimental set-up is based on frequency changes in a surface acoustic wave dual delay line system, which is nowadays well known [5-7] - Fig2.



Fig.2 The SAW dual delay line system based on frequency changes

The abbreviations: MPc - multilayer structure,  $\Phi_A$ ,  $\Phi_{tr}$  - phase shift introduced by amplifier and transducer respectively, A - amplifier; v, v<sub>0</sub> - velocity of the SAW in a measuring and reference paths

On a piezoelectric LiNbO<sub>3</sub> substrate two identical acoustic paths were formed using interdigital transducers. Next a multilayer active structure is formed in the measuring line by 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 multilayer is detected as a change in the differential frequency  $\Delta f$ , i.e. the difference between the two oscillator frequencies f and f<sub>0</sub>.

Principally, any change in the physical properties of a thin active multilayer (MPc), upon an interaction with gas molecules, placed on a piezoelectric surface can affect SAW propagation. However, from the practical point of view only the two following effects have a potential meaning. Namely, a change in the mass density of the multilayer, and a change in its electrical conductivity cause significant changes in the velocity and attenuation of the SAW and consequently the changes in the frequency f and  $\Delta f$  [8].

## 3. RESULTS 3.1 Results for Pd and CuPc films

At first, accordingly to D'Amico [2], we used a palladium (Pd) layer as a sensitive material in experimental results. A palladium film absorbs easily hydrogen molecules and is well known material for detection of hydrogen. Hydrogen absorption and desorption cause changes in the density, elastic properties and the conductivity of the Pd film [9]. The process is completely reversible. The obtained result was unfortunately very weak - Fig.3. The changes of the frequency  $\Delta f$  are not more than 50 Hz for 0.5 % and 1 % for hydrogen in nitrogen at 30  $^{\circ}$ C and this is almost the detection limit of the equipment. At higher temperatures there were no better results.



Fig.3. Changes of the differential frequency versus time for two concentrations of hydrogen for 20 nm of palladium at 30  $^{0}C$ 

When a 720nm CuPc layer was used the sensor response was about 600 Hz, but only at higher temperatures  $\sim$ 70  $^{0}$ C. The result is shown in Fig.4. It is also a well- known fact, that phthalocyanine films have to be thermally activated for gas detection.



Fig. 4. Changes of the  $\Delta f$  frequency for 720 nm CuPc film for 3 % of hydrogen in nitrogen at 70 °C

The investigated CuPc layer with a thickness of about 720 nm was made by means of the vacuum sublimation method, using a special aluminium mask. The source temperature was about 600 °C and the thickness was measured by the interference method. Before the specific process of sublimation, the CuPc powder (Aldrich) was initially out-gassed at 200 °C for 15 to 20 min in vacuum ( $10^{-4}$  Torr). The CuPc vapour source consisted of a crucible placed in a properly formed tungsten spiral. A copper-constantan thermocouple was used to control the temperature [10].

### 3.2 Results for a two-layered structure

For the multilayer structure the obtained preliminary results are very promising. We can observe recurrent changes of the differential frequency of the measurements system in the function of the medium hydrogen concentration in nitrogen at 30  $^{0}$ C and 50  $^{0}$ C of interaction – Figs.5 and 6.



Fig.5. Changes of the differential frequency  $\Delta f$  versus time for a two-layer sensor structure at 50  $^{\circ}$ C at 3 % concentrations of hydrogen in nitrogen



Fig.6. Changes of the differential frequency ∆f versus time for a two-layered sensor structure at 30 °C at six different concentrations of hydrogen in nitrogen

The inclination of the diagram in Fig.5 is connected with the thermal drift of the experimental set-up. This is especially possible to see at higher temperatures than 50  $^{0}$ C. Although the thermal drift from the substrate is compensated, the drift from the sensor material is not compensated. The change of the  $\Delta f$  frequency for 3 % of hydrogen in nitrogen at 50  $^{0}$ C is about 1.9 kHz.

At 30  $^{0}$ C we can see the results for six different concentrations (from 0.5 to 3 %) of hydrogen in nitrogen. The saturation level, i.e. the equilibrium between adsorption and desorption, is reached very quickly especially at lower hydrogen concentrations. Besides, it is

interesting to note the great change in the interaction between 1.5 % and 2 % concentrations. This interesting interaction "jump" is completely reversible and is probably connected with surface and volume interactions and the phase transitions for the palladium film [3].

We have been use hydrogen phthalocyanine (H<sub>2</sub>Pc) covered by palladium thin film too. Interaction results with hydrogen gas are shown on Fig 7. In this figure we show changing in differential frequency from start value  $\Delta f_0$  (before interaction with gas).



Fig.7. Changes of the differential frequency ∆f versus time for a two-layered sensor structure at 23 <sup>o</sup>C at four different concentrations of hydrogen in nitrogen

It is very interesting phenomenon observed for low concentration of the hydrogen (1 %) – the change in differential frequency is positive. In higher concentration change in differential frequency is negative. We think that this phenomenon is connected with changing in concentration of the current charge in region of the semiconducting phtalocyanine layer and a palladium layer. Probably we observe depletion and next inversion phenomenon. To explain this we intend to provide simultaneous measuring resistance of the phtalocyanine layer.

#### 3.3 Response and recovery times for a multilayer structure

In Fig. 8 we show the response and recovery times for small concentrations, i.e. between 0.5 % and 1.5 % concentrations and in Fig. 8 - for higher concentrations. The response time, defined almost as a 100 % of the saturation level, increases from  $\sim$ 200 s to 800 s, whereas the recovery time is almost constant, equal to 200 s.



Fig.8. Response and recovery times for lower (0.5% to 1.5%) hydrogen concentrations, where  $T_{RS}$ ,  $T_{RC}$  denotes response and recovery times respectively

For a higher hydrogen concentration the response can be even longer  $\sim 1500s$  - Fig.9. The recovery times are, however, still the same  $\sim 200s$ , which is very important from the practical point of view.



Fig.9. Response and recovery times for higher (1.5% to 3%) hydrogen concentrations

# 4. DISCUSSION

Such a good work of the sensor may be explained as follows. As already mentioned above, it is well known, that the palladium film easily absorbs hydrogen molecules [2,3]. However, when we use only a metal (palladium) layer on a piezoelectric substrate (which was LiNbO<sub>3</sub> Y-Z), 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 [7,10]. 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 [6,8]. So that, to take full advantage of the high sensitivity offered by the SAW sensor, the thin film conductivity must be in some particular range [11]. The two-layer structure (CuPc 720 nm or H<sub>2</sub>Pc 110nm + 20 nm Pd) on a LiNbO<sub>3</sub> Y-Z substrate has probably its resultant electrical conductivity well fitted to the high sensitivity range of the SAW device and can detect hydrogen molecules even at room temperature. This supposition will be more particularly investigated in future researches.

## 5. CONCLUSIONS

1. The preliminary investigations have shown that it is possible to realize a SAW hydrogen sensor for a medium range of concentrations at room temperature.

2. The sensor layer must be prepared in a special way – two-layered structures prepared in two different vacuum deposition processes.

3. The sensor has a very good sensitivity, stability and is entirely reversible

4. The response and recovery times are very short ( $\sim$ 200-1500s for response – depending on the concentration, and  $\sim$ 200s for recovery), which is very important from the practical point of view.

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