Acoustoelectric Effect in Hydrogen Surface Acoustic Wave Sensors (SAW) with Phthalocyanine-Palladium Sensing Bi-layers

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Abstract

Bi-layer structures with various thicknesses of metal-free phthalocyanine (~80, ~120 and ~160 nm) but the same thickness of palladium (~20 nm), have been studied for hydrogen gas-sensing application at ~30 °C and ~50 °C temperatures. The structures were fabricated in two different vacuum deposition processes (first the H_2Pc film and then the Pd) on a $LiNbO_3$ Y- cut Z-propagating substrate for the SAW sensor tests and additionally on a glass substrate with a planar microelectrode array for simultaneously monitoring of the planar resistance. A good correlation has been observed between these two methods (frequency changes for SAW method coincide with decreases of the bi-layer structure resistance) especially for higher hydrogen concentrations. Although simultaneously measurements were not always were possible due to very large resistances of the samples with the most thin phthalocyanine, they gave sufficient information on the acoustoelectric interactions between surface acoustic waves in these structures and charge carriers in the bi-layer.

1. Introduction

Palladium is a very well known material for hydrogen detection and has been studied extensively. However, in SAW gas sensor technology applying single thin films of Pd does not give satisfactory results. The changes in a measured frequency are very small, not exceeding 50 or 100 Hz, even for high hydrogen concentrations, using readily fabricated devices of moderate frequency [1,2]. Our recent work has shown that bi-layers of phthalocyanine-palladium structures can be optimized to construct effective SAW sensors for hydrogen [1, 3-4]. In a bi-layer sensing film structure, we can use the much stronger acoustoelectric effect in the SAW sensor response as the main detection mechanism, for larger magnitude responses. This effect can be many times greater than the mass-loading effect which can be dominant in the typically empolyed nonconductive polymer films and simple metal and dielectric films. The "work point" of such a bi-layer structure must be shifted to the high sensitivity region, where small variations in conductivity (under the influence of gas molecules) cause remarkable changes in the wave velocity (see Figure 1). Thus, to take full

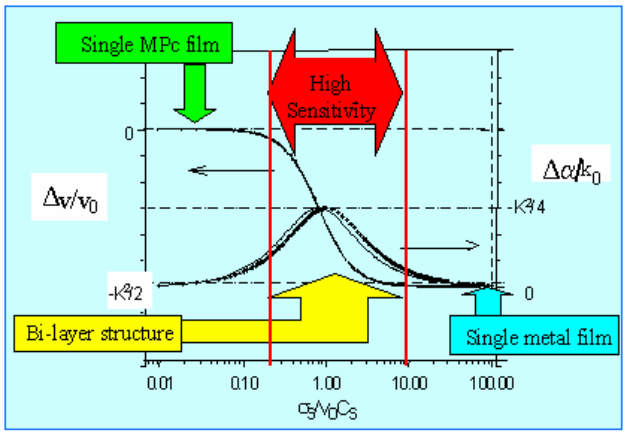

Figure 1. Theoretical dependence of relative changes of SAW velocity and attenuation *vs* the normalized surface conductivity $\sigma_s = v_0C_s = 1.6 \times 10^{-6}$ [Ω^{-1}] for $LiNbO_3$ Y – Z (v_0 is unperturbed SAW velocity, C_s is the sum of the piezoelectric substrate and environment permitivities)

advantage of the high sensitivity offered by the SAW sensor, conductivity of the sensing film must be tailored to a particular range.

The SAW gas sensors can be now divided into two groups: with a single layer and bi-layer (or multilayer) sensor structure – Figure 2. 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. Also, we introduce the concept of measuring interaction speed (a sort of time constant for the sensor response) as a new variable to calibrate the analyte concentration, in addition to the frequency and amplitude changes.

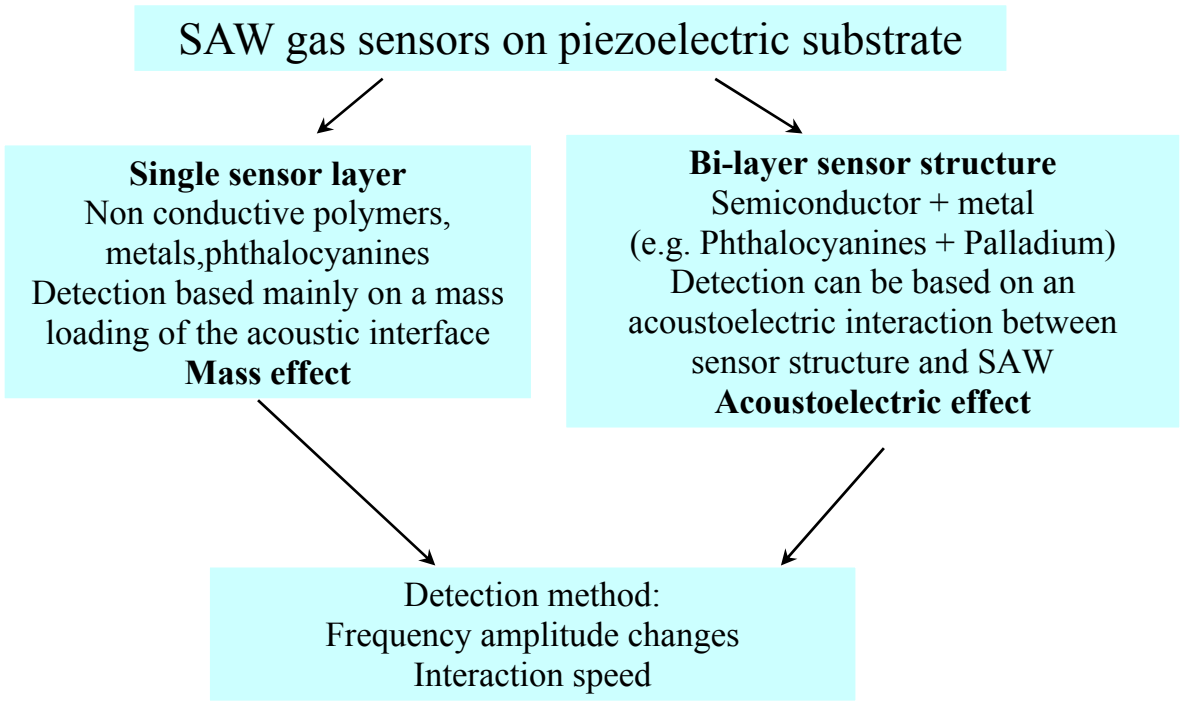

Figure 2. Two groups of SAW gas sensors

In this paper we have also made simultaneous measurements of the electrical resistance using an interdigital transducer structure, as an additional means to investigate the sensor properties of the bi-layer structures. Samples for these measurements were prepared by the same technological processes used for the SAW sensing layers, to achieve nearly identical sensing films. The important feature of this method is that were able to measure resistance for the single layer and later for the bi-layer one. These measurements allow for systematically achieving the desired sheet resistance to optimize the electroacoustic effect. As an example of the range of variation possible, we note that the reduction in resistance for one of the bi-layer structures with CoPc compared to pure Pd is about three orders in magnitude. Simultaneous SAW device and resistance measurements were made in the same measuring chamber at the same hydrogen exposures.

2. Experimental Apparatus

The experimental set-up is based on frequency changes in an acoustic surface wave dual delay-line system, which is currently well known [5-8]. The schematic diagram of the

device and measurements is shown in Figure 3. On a piezoelectric $LiNbO_3$ (Y cut Z propagating) substrate, two identical acoustic paths are formed by interdigital transducers. Next, an active bi-layer structure is formed in the measuring line by two different vacuum deposition processes.

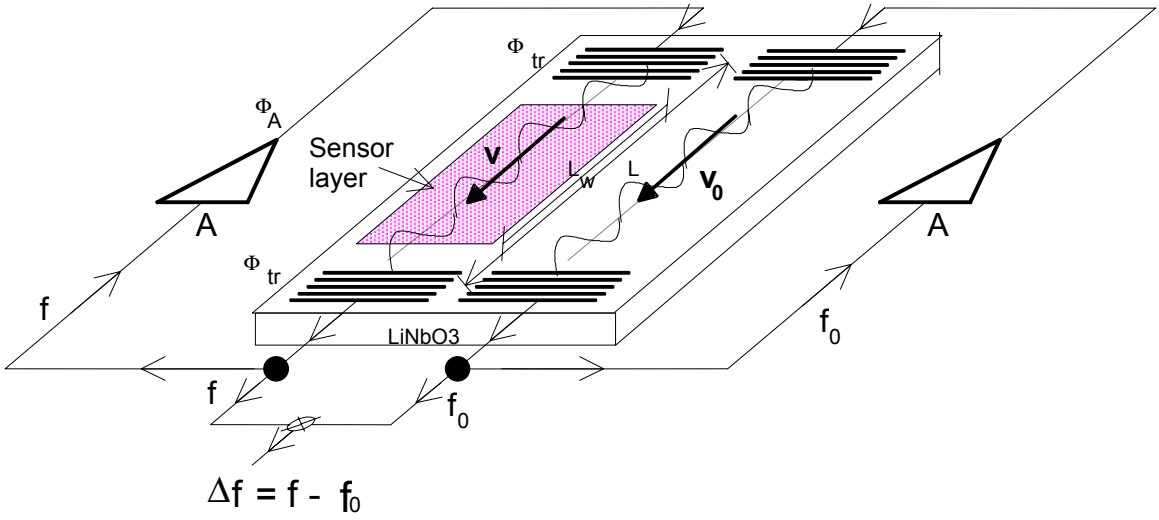

Figure 3. Dual-delay line configuration of the SAW gas sensor

The second path serves as a reference and can compensate for 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 bi-layer is detected as a change of the differential frequency Δf, i.e., the difference between the two oscillator frequencies f and f_0. Principally, any change of physical properties of a thin active bi-layer structure, be it upon interaction with gas molecules or when placed on a piezoelectric surface, can affect the SAW propagation. However, from a practical point of view, only two effects have potential meaning for rigid materials such as used in this work. Both a change of the structure mass density and a change of its electrical conductivity cause significant modifications in the velocity and attenuation of the SAW. These consequently also vary the frequencies f and Δf.

3. Results and Discussion

In our measurements, three bi-layer structures with metal-free phthalocyanine and palladium films were used and very repeatable changes of the differential frequency Δf were observed. Because a practical hydrogen sensor should work in an atmosphere of air, the measurements were carried out in synthetic air with various hydrogen concentrations from 0.5% to 4%.

An example of the first results for the structure ~80 nm H_2Pc+20 nm Pd, obtained in an air atmosphere and a range of hydrogen concentrations (from 0.5% and 4%) is shown in Figure 4. In these measurements, the temperature unfortunately varied in a range from 26 to 33 °C, due to heating from the electronics. A consequent drift in the frequency signal can thus be observed.

In the case of the first few concentrations (0.5%, 1% and 1.5%) a rather small interaction is observed. The differential frequency slightly increases by about 100 Hz for the 1.5% concentration, but the response reaches steady-state very quickly. For this range of hydrogen concentrations Pd film is in an α crystal phase. Whereas, the interaction is much larger at a 2% hydrogen concentration,. A great increase in Δf frequency is obtained, which can be interpreted as a change in crystal phase from α to β. However, steady-state is not reached as quickly as for the α phase.

The interaction for the next bi-layer structure with 120 nm of H_2Pc and 20 nm of Pd with different concentrations of hydrogen in air at about 50 °C is shown in Figure 5.

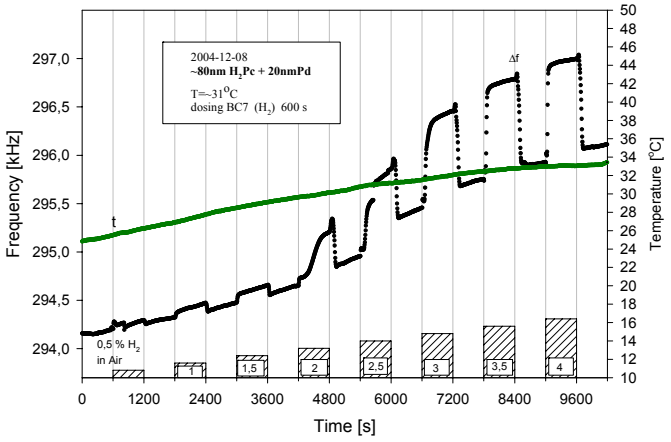

Figure 4. Interaction in synthetic air for bilayer structure ~80 nm H_2Pc + 20 nm Pd, at various hydrogen concentrations and in a range of temperatures 26 – 33 °C.

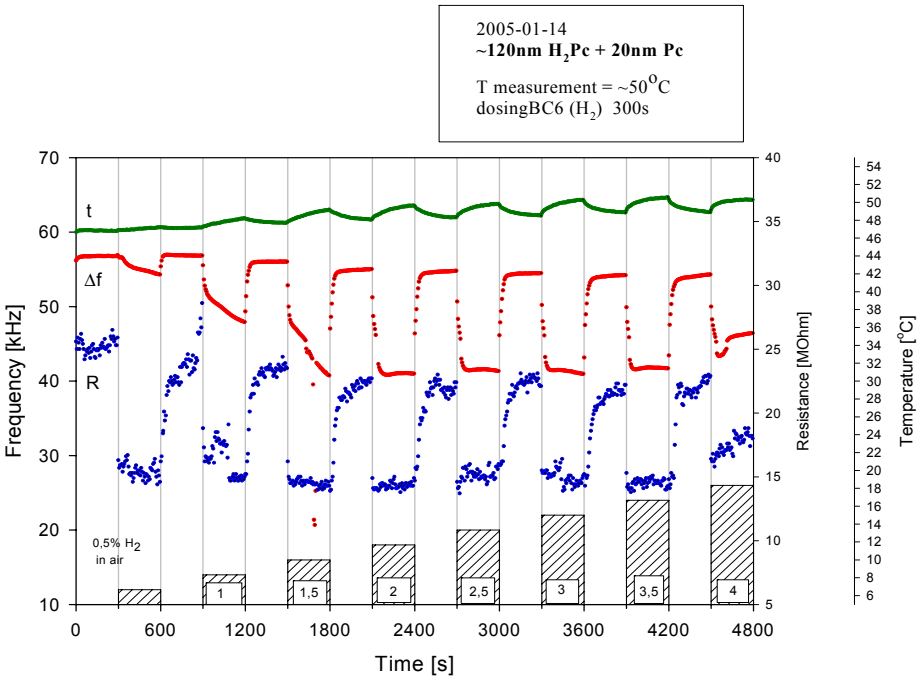

Figure 5. Interaction in synthetic air for bilayer structure ~120 nm H_2Pc + 20 nm Pd, at temperature ~50 °C– maximum changes are the same ~15 kHz but the response times of the signal increase considerably – between 2% and 4% of hydrogen concentrations Resistance of the sample decreases from 25 to 15 MΩ. Temperature fluctuations of about 2 °C can be seen for higher hydrogen concentrations. The temperature slightly increase when structure interacts with hydrogen

For this structure an inverse frequency mode is observed, namely, the differential frequency is decreasing under the hydrogen concentrations. Detailed discussions of these various frequency modes can be found in reference [6]. Additionally, the simultaneous resistance monitoring revealed a corresponding decreasing in the sample resistance. The response based on the change of differential frequency is at an extremely high level for higher concentrations, namely about ~15 kHz! However, the results in a lower temperature ~30 °C are not so good. The maximal changes in differential frequency are on the level 100 – 200 Hz probably due to the presence of α phase.

The interaction for the bi-layer structure with 160 nm of H_2Pc and 20 nm of Pd with different concentrations of hydrogen in air at about 30 °C is shown in Figure 6. In this structure, we can observe corresponding changes in resistance of the sample, which are significant and measurable easily above 2.5% of hydrogen concentration.

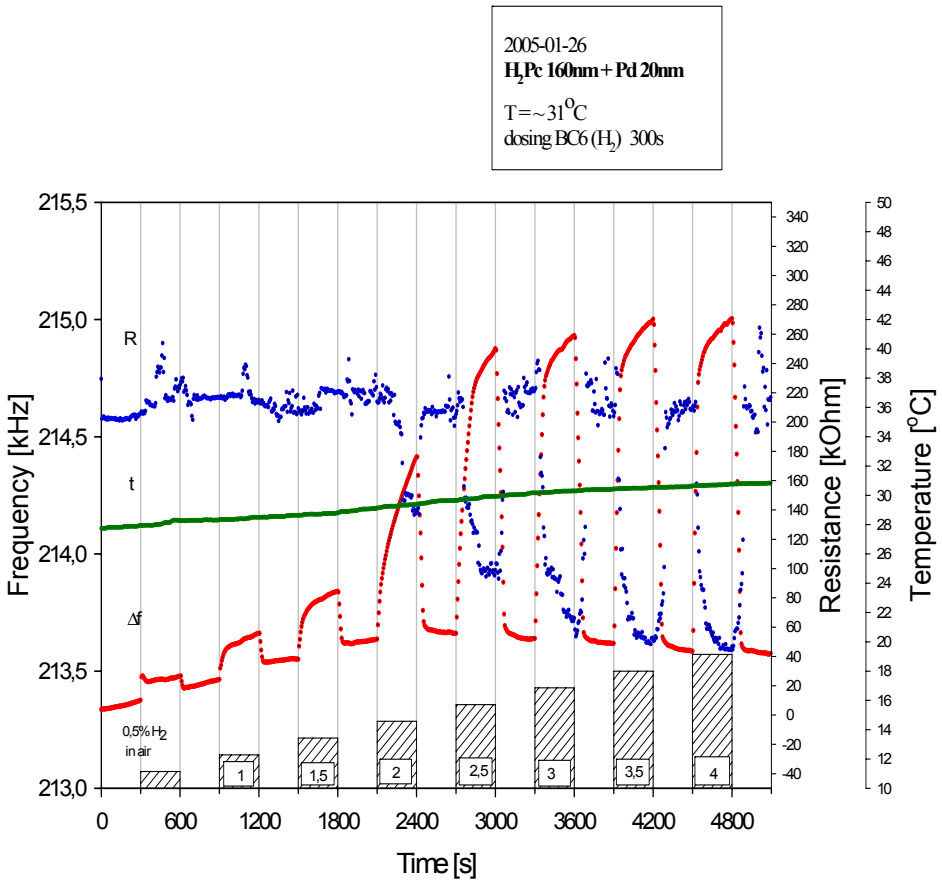

Figure 6. Interaction in synthetic air for a bi-layer structure ~160 nm H_2Pc + 20 nm Pd, at various hydrogen concentrations and at temperature ~31 °C

A simple interaction model of the bi-layer structure (phthalocyanine and palladium) with hydrogen molecules was proposed first by LundstrÖm quite some time ago [9]. 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 fluctuation in the velocity of the acoustic surface wave, which finally leads to a modification in the measured frequency and differential frequency Δf as well. However, as we have discussed in references [1, 3], significant changes in the SAW velocity under surface conductivity variations are possible only when the resulting conductivity of the bi-layer structure is properly fitted to an active range of the acoustoelectric effect. This active range mainly depends on the substrate SAW velocity and the dielectric properties of the substrate and environment.

4. Conclusions

Hydrogen molecules can be detected well in the bi-layer structure phthalocyanine and palladium in a surface acoustic wave system with optimized thicknesses of the layers. Quantitative comparisons with perturbation theory and equivalent circuit based models that predict the mass and acoustoelectric contributions to the SAW sensor response are possible and will provide a rapid way of optimizing the Pd and phthalocyanine film thicknesses. We hypothesize that the thin Pd film serves to collect and provide a constant and high concentration boundary condition for hydrogen diffusion into the phthalocyanine film, which can be verified by response-time measurements with and without this film, on resistance-optimized films. Some of these results will be presented in future.

Acknowledgements

This work was funded by research project numbers 3 T10C 009 26 and O T00A 027 26 at Silesian University. University of South Florida research is funded by NASA-Glenn.

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