SURFACE ACOUSTIC WAVE HYDROGEN SENSOR WITH NICKEL PHTHALOCYANINE AND PALLADIUM THIN LAYERS

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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 system. The sensor material consists of two layers produced in two different vapour deposition processes. The first one is a 230 nm nickel phthalocyanine (NiPc) layer, whereas the second is a 20 nm thin palladium (Pd) film. This structure was formed in one of the dual delay line systems on a $LiNbO_3$ Y-cut Z-propagation substrate, while the other serves as a reference, permitting an easy detection of the arising differential frequency Δf. This frequency, depending on the operating frequency modes, is in the range of 20 to 30 kHz, whereas the oscillator frequencies are in the range of 43,6MHz. The wavelength is 80μm. 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. For the investigated structure the interaction response depends on temperature, and decreases with the increase of the interaction temperature. For the structure an interesting "interaction jump" has been observed, which is connected with the phase transition in the palladium film. At higher temperatures this interaction jump shifts in the direction of higher hydrogen concentrations.

***Keywords**: surface acoustic wave, nickel phthalocyanine, palladium, hydrogen sensor*

1. INTRODUCTION

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 [1-4]. 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. As long as the thickness of the sensor film, h, is substantially less than the wavelength of the surface wave, we can speak of a perturbation of the Rayleigh wave (in our case h ~230 nm and λ ~ 80μm). Otherwise, we have to take into account other types of waves, such as Love waves, which can propagate in layered structures [5].

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 [6-8].

As has been mentioned above, any change of the physical or chemical properties of a thin active layer 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 layer and a change of its electrical conductivity cause a significant change of the velocity and attenuation of SAW. These two effects (often called mass and electric ones) occur simultaneously in the interaction time of an active film 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 layer. For instance, in polymer films only the mass effect exists, whereas in thin phthalocyanine films as organic semiconductors both do exist, but the electric effect is much greater (several times, depending on the gas concentrations) [9]. The electric effect has one very interesting feature, namely it causes significant changes in propagation the velocity of SAW only in some particular range of surface conductivity of the sensor film. 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. When only a metal layer is used (for instance palladium as a well-known material for hydrogen detection) on a piezoelectric substrate (which was $LiNbO_3$ 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). The acoustoelectric effect is not effective in the case of a simple metal film (Pd) because in spite of substantial changes of the conductivity it does not cause any significant changes in the wave velocity – it is the "Pd" region in Fig.1. We have almost the same situation in the case of simple metallophthalocyanine compounds; the „work point" is this time rather at the beginning of the characteristics – the "MPc" region in Fig.1. It seems that the bilayer structure should have its resultant electrical conductivity much better fitted to the high sensitivity range – the "MPc+Pd" region in Fig.1.

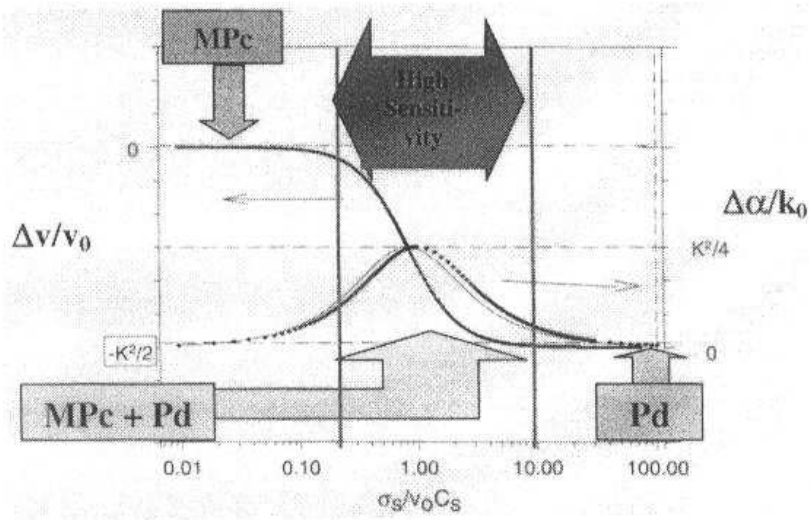


Fig.1. Theoretical dependence of relative changes of the SAW velocity and attenuation versus the normalized surface conductivity σ_s of a thin film on a $LiNbO_3$ Y-Z substrate; v_0 is unperturbed SAW velocity, C_s is the sum of the piezoelectric substrate and environment permittivities

The central metal atom in a phthalocyanine macromolecule has a great influence on the physical and chemical properties of the compound. Besides the electrical properties, i.e. electrical conductivity is also influenced. In Table1 the conductivity of the three various phthalocyanine compounds for single crystals in vacuum at room temperature are showed [10].

Table 1

Conductivity for single crystal in vacuum at room temperature in $[\Omega m]^{-1}$	
Free phthalocyanine H_2Pc:	$3x10^{-9}$ to $3x10^{-14}$
Nickel phthalocyanine NiPc:	$1x10^{-8}$ to $4x10^{-11}$
Copper phthalocyanine CuPc:	$1x10^{-8}$ to $6x10^{-11}$

In one of the previous paper [11] the idea of a new two-layered structure (20nm palladium thin film on cooper phthalocyanine 720 nm as a buffer layer) 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 phtalocyanine as buffer layers, i.e. 230 nm nickel phthalocyanine (NiPc), and the same 20 nm thick palladium film. The thickness of the buffer layer was chosen arbitrarily.

The structure was produced in two different vapour deposition processes. In this paper, the temperature measurements of this novel bilayer structure are showed and discussed from

the point of view of hydrogen detection in a medium concentration range (from 1% to 4% in nitrogen).

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 [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 (NiPc + Pd) was rather low ~20 to 30 kHz what was very advantages from the practical point of view. An interesting feature of the set-up was the fact that for this same frequency mode and amplifier gain coefficient the frequency Δf was decreasing as the interaction temperature increased.

The investigated nickel phthalocyanine layer with thickness of about 230 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 NiPc powder (Aldrich) was initially out-gassed at 200 °C for 15 to 20 min in vacuum (10^{-4} Torr). The NiPc vapour source consisted of a crucible placed in a properly formed tungsten spiral. A copper-constantan thermocouple was used to control the temperature. The thin (~ 20nm) 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

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 (NiPc+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.

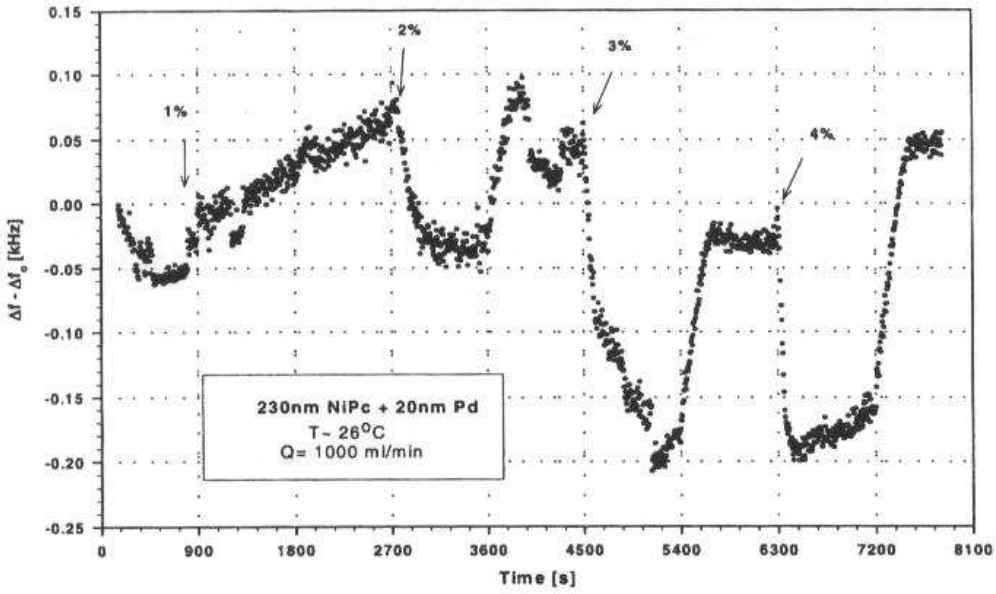
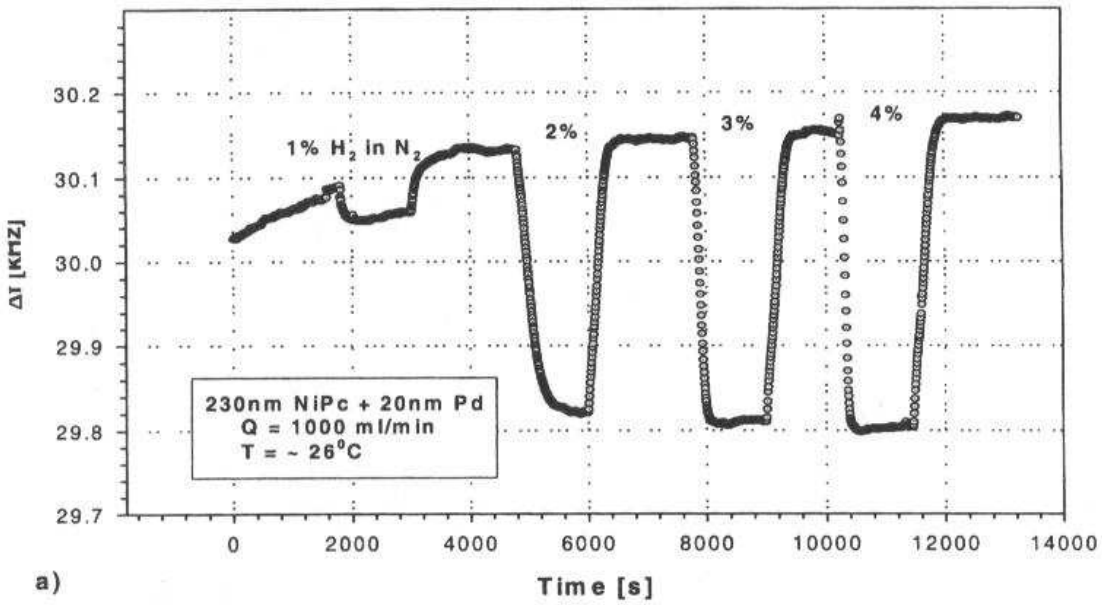


Fig.2. Interaction of the bilayer structure at the beginnig of the measurements at 26^0C – in the first cycle of interaction. Changes of the Δf frequency are ~0.2 kHz in maximum.

After many cycles of interaction the response was however stabilized and the steady – state effect for 2, 3 and 4% of hydrogen in nitrogen is easy observed also at 26^0C and 40^0C, as shown in Fig.3a and b. The saturation level, i.e. the equilibrium between adsorption and desorption, is reached very quickly, especially at lower hydrogen concentrations. It is also interesting to note a great change in the interaction between 1% and 2% of hydrogen in nitrogen. This interesting interaction "jump" is completely reversible and is probably connected with phase transitions in the palladium hydride film (PdH_x), which has two solid phases α and β , depending on the Pd/H composition. The reversible α phase is found at a low hydrogen concentration. As the hydrogen concentration increases, Pd is transformed to the β-phase [7]. The hydrogen concentration at which the phase transition takes place depends on the film thickness and temperature, which can be observed as the interaction "jump" in Fig.3.

At higher temperatures the interaction "jump" shifts in the direction of higher hydrogen concentrations – Fig.4 a and b.



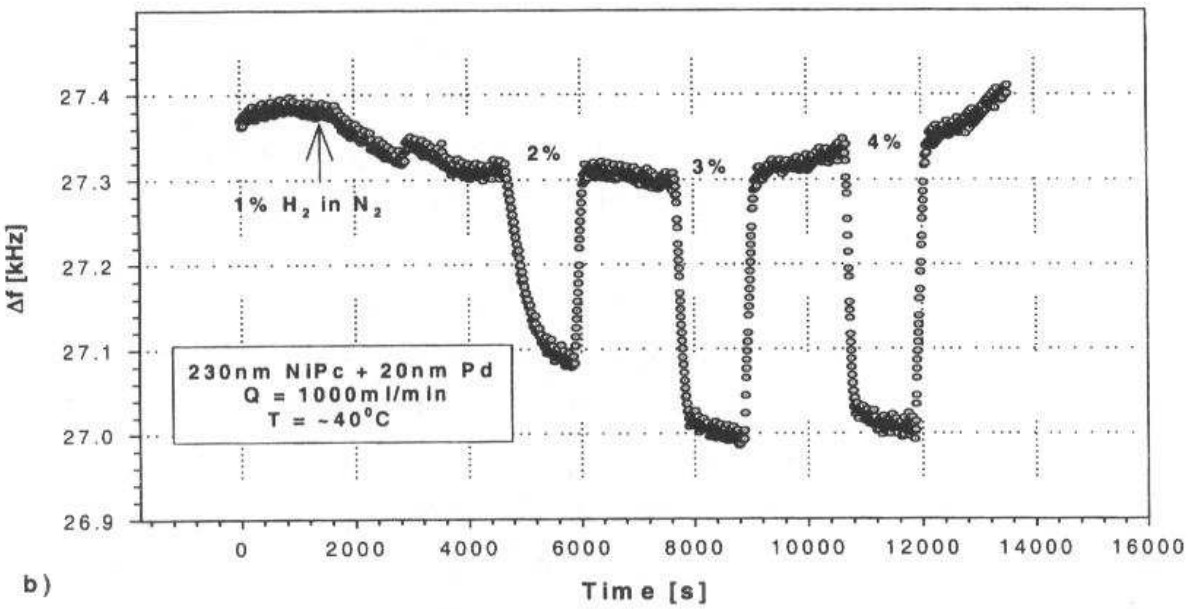


Fig.3a and b. Changes of the frequency Δf versus time in bilayer structure 230 nm NiPc and 20 nm Pd at 26^{0}C (a) and 40^{0}C (b) at four concentrations of hydrogen in nitrogen after many cycles of interaction.

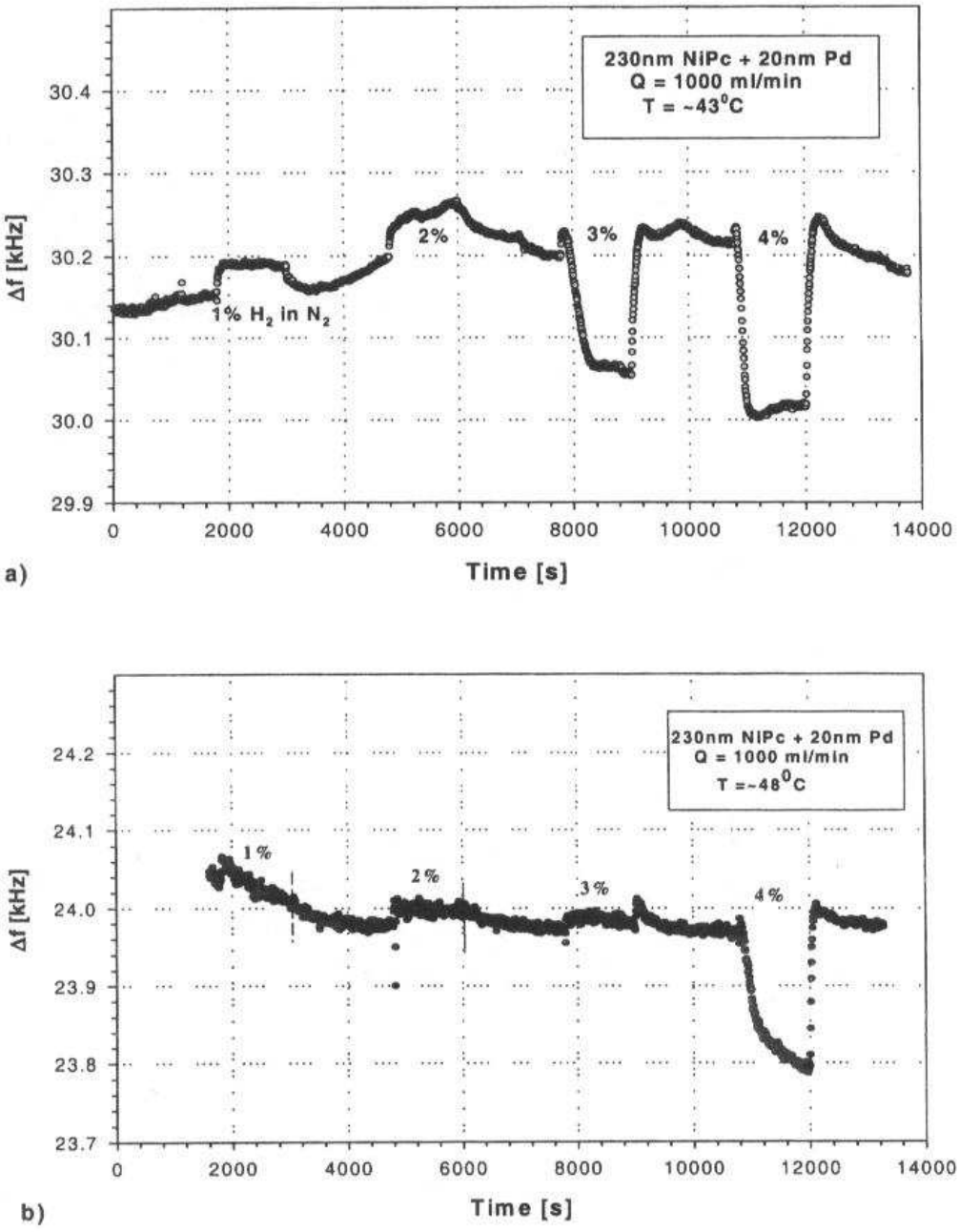


Fig.4a,b. Changes of the differential frequency at two different temperatures 43^0C (a) and 48 ^{0}C (b) and this same hydrogen concentration (from 1% to 4% in nitrogen).

We can approximate the steady-state value for Δf changes and read the absolute changes concerning all hydrogen concentrations. These absolute changes δ(Δf), defined as Δf(nitrogen) minus Δf(hydrogen) in the investigated bilayer structure as a function of a

medium hydrogen concentration, are shown in Fig.5. An increase in the changes of $\delta(\Delta f)$ as a function of hydrogen concentration is to be observed at 26°C after some interaction cycles and at 48°C, whereas at 70°C – a decrease is observable in the negative range. At 26°C after many interaction cycles a steady-state level is to be observed.

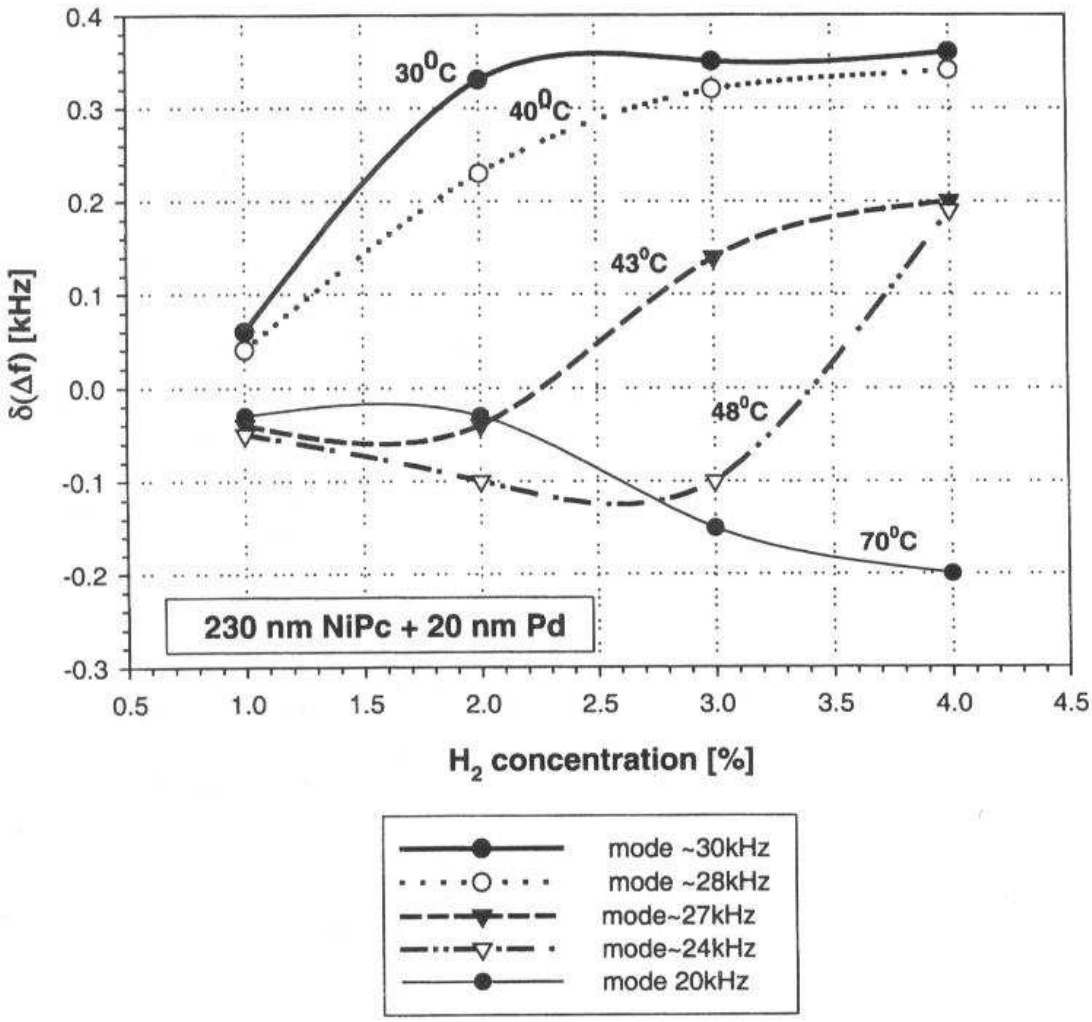


Fig.5. Changes of $\delta(\Delta f)$ –definited in the text- in the 230nm NiPc and 20nm Pd structure as a function of hydrogen concentration at five different interaction temperatures. For the increasing of the interaction temperature one can observe the decreasing of the differential frequency Δf depicted as "mode" on the figure.

4. CONCLUSIONS

The bilayer structure 230 nm NiPc and 20 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 26^0C temperatures although saturation effect is easy visible for 3% and 4% of hydrogen in nitrogen. The bigger response ~0,36kHz has been found for the concentration 4%. The interaction response depends on temperature, and decreases with the increase of the interaction temperature. At higher temperatures (especially for 48^0C and 70^0C) the change of interaction character can be observed – negative values of $\delta(\Delta f)$ on Fig.5. For the structure an interesting "interaction jump" has been observed as for the former structure (CuPc+Pd) [11] which is connected with phase transition in the palladium film. At higher temperatures this interaction jump shifts in the direction of higher hydrogen concentrations. This interesting phenomenon will be investigated in future research.

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