AN OPTICAL SENSOR BASED ON LAYERED FABRY-PEROT INTERFEROMETER FOR MEASURE OF GASENOUS H_2 IN VARIOUS MEDIA

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The paper presents a layered sensing structure that permits to detect and to measure the concentration of hydrogen in a gaseous medium. This metal-dielectric-metal structure is a layered Fabry-Perot interferometer. The resonant cavity is made of SiO_2 by sol-gel method. The catalysis of molecular hydrogen to atomic hydrogen occurs in the palladium layer, which is also one of the mirrors of the interferometer. The measurement of the hydrogen concentration consists in the scanning of the angular variation of the interference peak position due to the absorption of hydrogen. The change of the peak position results from the change of the optical parameters of the Pd layer.

Keywords: Optical hydrogen sensor layered interferometer Fabry-Perot.

1. INTRODUCTION

In latest times more and more new industrial applications of hydrogen have been introduced. Among others, it has been planned to employ it as a pure energy carrier. High expectations are connected with its application as a source of energy in fuel cells and also to drive motor-car engines. Moreover, due to its considerable thermal capacity it is used as a cooling agent, e.g. in power stations. Because jointly with oxygen at a concentration of 4% to 74% it is a highly explosive gas, its utilisation requires special safety measures [1-3]. This is connected with the necessity of monitoring its effluents to prevent explosions. Hence the necessity of monitoring its concentration in an air, and also the designing of hydrogen sensors.

Hydrogen sensors, now commercially available, are not applied on a larger scale is due to their large dimensions, complicated structure, considerable costs of production and - which is most important - due to the high hazard of explosion in a medium constituting a mixture of hydrogen and air. Therefore, new solutions must be looked for, which would warrant an exact, cheap and safe detection of hydrogen in a wider range of concentrations. Optical hydrogen sensors display better properties than other sensors; among others they are resistant to

electromagnetic disturbances. Thanks to their construction they warrant safety, which is of much importance in media with a high hazard of explosion. This is their integral feature. Moreover, the sensor layers of optical sensors are characterized by their long-term stability. The degradation of sensor layer structures caused by measurements is slower than in the case of electrical measurements.

In the present paper the authors suggest the ides of a gasochromic hydrogen sensor based on the structure of a layered Fabry-Perot interferometer. The resonance cavity is a layer of SiO_2. The function of the first mirror is performed by a semi-permeable thin Au layer. The second mirror is a thin Pd layer. The sensor part is optionally equipped with an additional Ag layer, 100 nm thick, with the purpose of providing a screening of the field of the electromagnetic wave outside the layer system. Such a system of layers is insensitive to variations of the refractive index of the medium above the system of layers. It is, however, sensitive to changes of the optical properties of the resonance cavity and the mirror made of palladium, due to the penetration of hydrogen through the system of layers. As hydrogen is an element with the shortest ion radius, this penetration is comparatively fast. Such a solution makes it possible to measure the concentration of solved hydrogen not only in gases but also in liquids.

The Fabry-Perot interferometer is a kind of an optical resonator, containing two semi-permeable mirrors spatially separated from each other by the resonance cavity with the thickness d and the refractive index n. Let's assume that both mirrors are characterized by the same coefficient of reflection R and a loss-less resonance cavity. Then the reflectance R_{FP} and transmittance T_{FP} of such a system looks like that:

$$R_{FP} = |r|^2 = \frac{2R(1-\cos\varphi)}{1+R^2-2R\cos\varphi} \tag{1}$$

$$T_{FP} = |t|^2 = \frac{(1-R)^2}{1+R^2-2R\cos\varphi} \tag{2}$$

where $\varphi = (4\pi/\lambda)n\ d\ cos\Theta$, is the shift of the phase of a wave passing the cavity in both directions, λ is the wavelength and Θ is incident angle of light. From equation (1) it results that if the $\varphi = 0$, the intensity of the reflected light reaches its minimum, and if $\varphi = \pi\ rad$ the reflectance of the structure is at its maximum. The phase may be affected by a change of the refractive index and (or) by changing the thickness of the resonance cavity.

Eq. (1) indicates also in which way the phase shift affects the intensity of the light reflected from the structure I_R. The intensity of the light I_R is expressed by Airy's function:

$$I_R = 2RI_0 \frac{(1 - \cos\varphi)}{1 + R^2 - 2R\cos\varphi}, \tag{3}$$

where I_0 is the intensity of the incident light the structure. If the structure is lighted with white light at a given angle, we can observe in the spectrum of the reflected light an interference minimum.

2. CONCEPT OF LAYERED SENSING STRUCTURE

The idea of a layered sensing structure metal-dielectric-metal applied in optical sensors, as proposed by the authors, comprises the application of a catalytic Pd layer and a layer of amorphous SiO_2as the receptor of hydrogen (Fig. 1). In the suggested structure of the sensor the successive layers have the following functions:

a) the thin layer of gold, 30 nm thick, functions as the first mirror of the interferometer,
b) the dielectric SiO_2 layer constitutes the resonance cavity of the interferometer and by adjusting the thickness and affecting the optical properties (refractive index) it makes it possible to tune the interferometer within a wide range,
c) the palladium layer is at the same time a catalyst ensuring the dissociation of molecular hydrogen and the second mirror of the interferometer with modulated sensor properties,
d) the silver layer with a thickness of 100 nm warrants the independence of the measuring system of the parameters of the medium in which measurements are taken and also separates the catalytic Pd layer from the measured, Fig. 1.

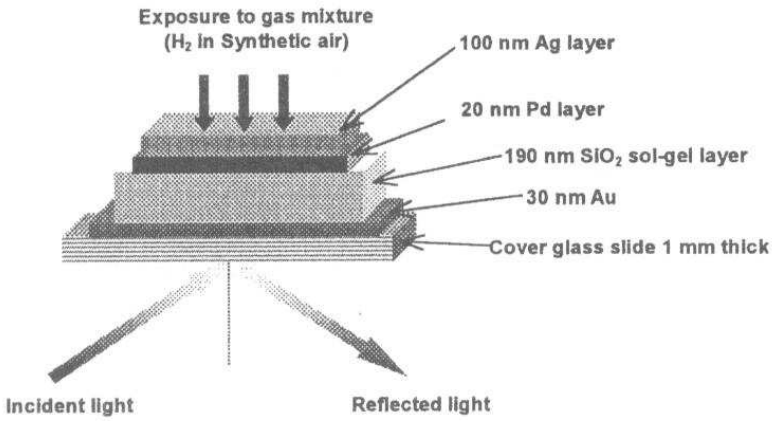

Fig. 1 Configuration of layered Fabry-Perot sensing structure for hydrogen detection.

Structure shows on Fig. 1 is an extremely asymmetric Fabry-Perot interferometer, in which the second mirror has a reflection coefficient about 100 %. The idea of such a sensor element aimed at arresting the whole energy of the light wave inside the structure, so that it would not penetrate the measured medium. Such a construction ensures a shielding of the

electromagnetic field by the Ag layer, and thus a cutting off from the effects of optical variations of the parameters of the measured medium. This sensor is sensitive only to the external agent, i.e. the hydrogen, assuming, of course, that this agent would modify the optical parameters of the structure, or putting it more accurately, would affect the resonance cavity of the etalon.

3. EXPERIMENTAL

The metallic layers were produced by vacuum evaporation at $2^{x}10^{-5}$ Tr of pure Pd, Au and Ag (99.99 % Aldrich) on substrates 1 mm thick made of cover glass slide. The thickness of the vacuum evaporated Pd layers was measured *in situ* by means of a resonance thickness meter with an accuracy of 3 %. The layer of silicon dioxide was produced by sol-gel method.

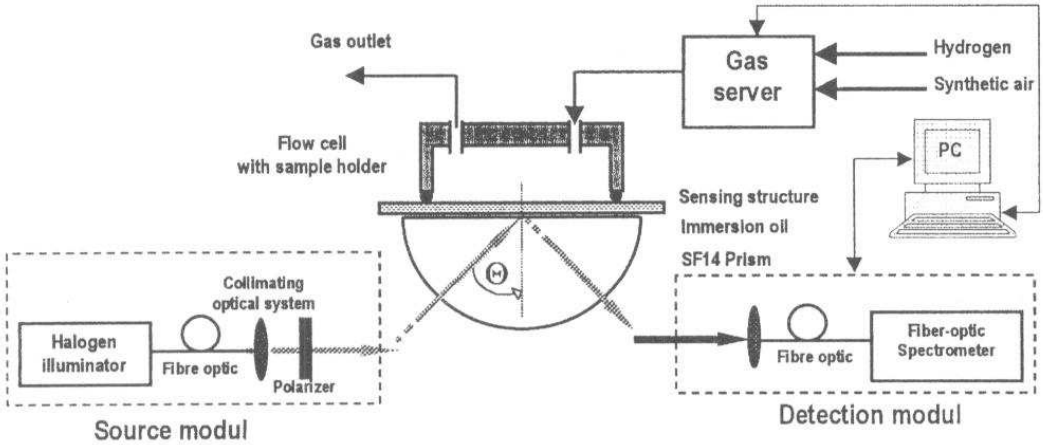

Fig. 2. A experimental set-up for measurements of variations in the optical signal of a white light with p and s polarization reflected from the sensor structures.

The substrates with generated sensor structures were coupled on immersion oil with a cylindrical prism, made of SF14 glass (Schott). This prism ensured a mechanical stability of the optical system and warranted an adequate range of light-wave vectors. The dispersion of the refractive index of the oil was more or less the same as that of cover glass. Fig. 1 illustrates the configuration of the multi-layer sensing structure applied in our investigations of interference phenomena.

The measurement system employed in these investigations has been presented in Fig. 2. The idea of these measurements was to obtain reflection characteristics both as a function of the angle and the wavelength, as well as when exposed to a mixture of synthetic air (80 % N_2, 20 % 0_2) and hydrogen with a varying volumetric content of hydrogen. Gases with a purity of 99.99% were mixed in a stacker provided with *Bronkhorst H-Tech* mass flow-controllers. A gas server permitted the batching of the gas mixture with a precision exceeding 0.1 %. The

gas mixture passed a (teflon) measuring cell with a volume of about 0.8 cm^3 at a speed of 1000ml/min. The tested sensor structures were placed on a goniometer permitting their angular scanning with an accuracy of the angle-setting exceeding 0.01 deg. The system also warranted an automatized determination of the incidence normal of the optical beam.

A halogen illuminator emitted the incident beam of polychromatic light at the structure. By means of the fiber-optic cable it was transmitted to the goniometric measuring system. Light passing through the optical system (Fig. 2) was formed and polarized so that a parallel beam of white light with p or s polarization would incident at the investigated structure. The reflected light was recorded concerning the successive angular positions within the range of wavelengths 450 - 780 nm. For detection a fiber-optic spectrometer produced by *WOCAD* with a resolution of 7 nm was applied. These measurements were carried out with a tenfold average. The exposure time was in each case 1000 ms. All these measurements were carried out at a room temperature of 23°C.

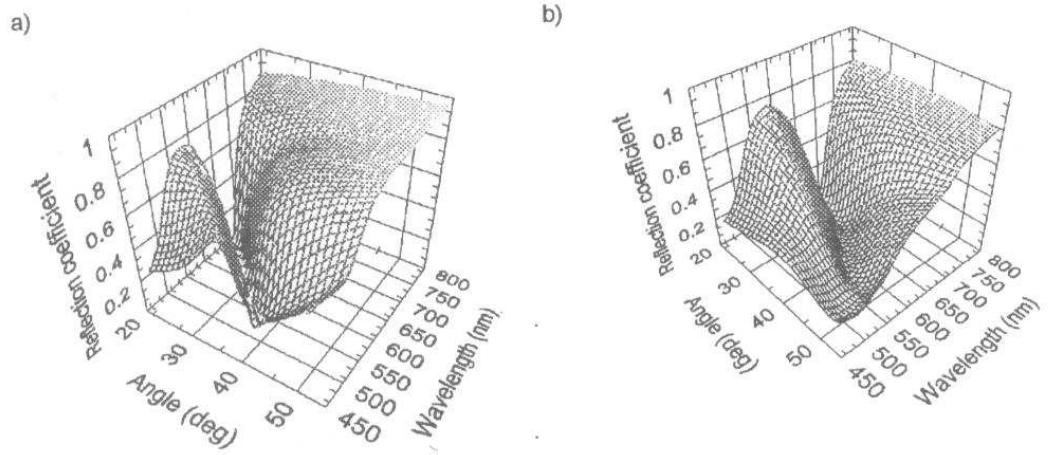

Fig. 3. Calculation reflectance of sensing structure (with an Ag layer) as a function wavelength and angle of incident light for (a) s–polarized and (b) p–polarized light.

4. RESULTS AND DISCUSSION

The spectral reflectance of the investigated structure metal-SiO_2-metal as a function of the angle of incidence on the structure was modeled by means of software developed in the *LabVIEW™*. This model is based on Fresnel's theory and the matrix formalism of the propagation of electromagnetic waves thorough layered structures [4]. The investigations concerned the visual range of spectra (450 nm - 780 nm).

The results of numerical simulation presented in Fig. 3 and concerning orthogonal polarizations illustrate excitation of interference phenomena in the structure metal-SiO_2-metal as a function of the wavelength and angle of incident. During the first stage of investigations a structure with an external silver layer was analyzed. The results of simulations have been

gathered in Fig. 3. These relations present the coefficient of reflection of light from a layered structure with the configuration shown in Fig. 1, as a function of the angle of incidence of light on the surface and the wavelength of the light. These results indicate how the interference minimum of the first order can be adjusted by changing the wavelength and the angle of incidence of the beam of light on the sensor structure.

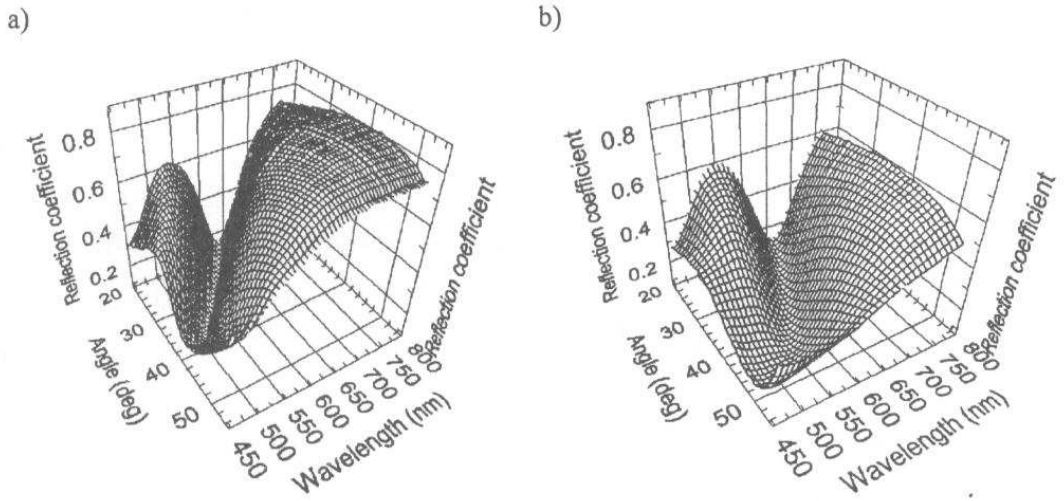

Fig. 4. Measured reflectance of sensing structure (with an Ag on the top) as a function wavelength and angle of incident light for (a) s-polarized light and (b) p-polarized light.

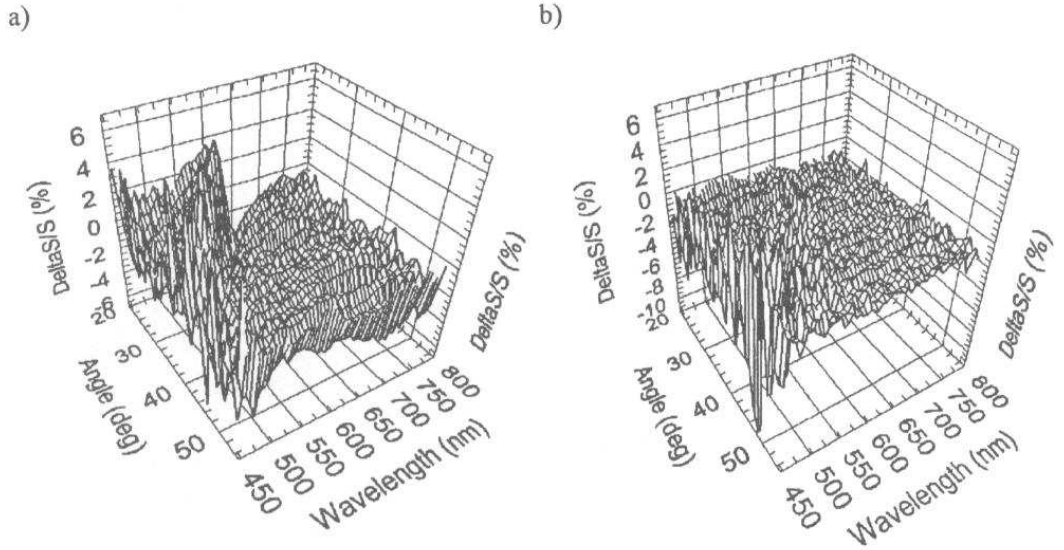

Fig. 5. Reflected light intensity change (in %) for the sensing structure (with an Ag thin film on the top) as a function wavelength and angle of incident light for (a) s-polarized light and (b) p-polarized light. Structure was exposed to gas mixture consisting 2% H_2 in synthetic air.

A layered structure with parameters as presented above has been constructed and its coefficient of reflection was measured for both kinds of polarisation, s and p. The results of

these measurements have been gathered in Fig. 4. A comparison of experimental data with the results of modelling reveal some differences resulting from the somewhat thicker SiO_2 layers than had been measured *in situ*. The reason is that SiO_2 layers obtained by sol-gel method display a porous and less packed structure. This is the main reason of the shift of experimental peaks if compared with the model. The refractive indices of metals characterizing the volumetric material were considered in the calculations, too. As the structure comprises thin metallic layers, the optical constants of which actually differ from metal in its volume [5], there may occur some differences between the compared characteristics.

Fig. 5 presents a relative change of the optical signal $\Delta S/S$ the interaction in the investigated spectral and angular range due to the interaction of the structure and the gas mixture containing 2 % hydrogen in synthetic air. The relative change of the optical signal has been determined in compliance with the relation:

$$\frac{\Delta S}{S} = \frac{S_{air} - S_{2\%H_2\_in\_air}}{S_{air}} * 100(\%). \tag{6}$$

The structure was exposed to the effect of the gas mixture for two hours. After absorption of hydrogen by Pd mirror the optical signal change within the range of the interference peak because reflection coefficient this mirror has been changed.

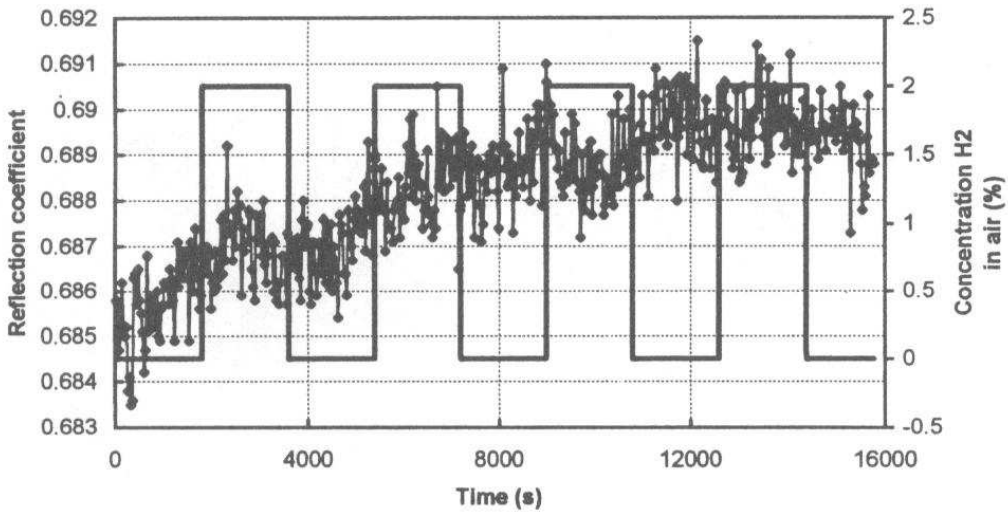

Fig. 6. Optical response vs. time of sensing structure (with an Ag on the top) exposures to 2% of H_2 in synthetic air at room temperature. Experimental conditions: s–polarized monochromatic light λ=550 *nm*, incident angle of light Θ=36 deg.

The variation of the signal is of essential importance, as was to be expected, in the range of interference peaks. The response of the sensor structure to 2 % hydrogen concentration reaches the level of 8 % in the case of s-polarized light. In the case of p polarization the

reaction is a bit smaller, as earlier model investigation have proved. The characteristic of the spectral-angular variations of the optical signal display a considerable diversity of meanings in the case of shorter waves, as results from the low value of signals reflected in the range up to 480 nm. Hence the rather high uncertainty of measurements in this range.

Basing on investigations dealt with above we decided to carry out dynamic measurements only concerning light with a s-polarization. The structure was subjected to the effect of a gas mixture containing hydrogen with a cyclically changing concentration, amounting to 0 % and 2 % solved in synthetic air. Dynamic measurements were carried out in the case of light with a wavelength of 550 nm incident the structure at an angle of 36 deg. Fig. 6 presents the results of dynamic measurements carried out on a structure with an external silver layer. These results prove that a sensor structure with an external metallic layer reacts with a slight delay to the effect of hydrogen. In spite of the only insignificant delay such a structure regenerates, unfortunately, rather weakly. What more, the sensor is slow. Taking, however, into account the essential advantages of such a structure, particularly its simple construction, it might be said that it might be applied for the detection of hydrogen as a single indicator of the hydrogen concentration in various aggressive measured media.

This sensing structure can work without prism coupler. In this case range angle of incident light must be wider. Results of measurements reflection coefficient for both orthogonal polarizations have been shown in Fig. 7.

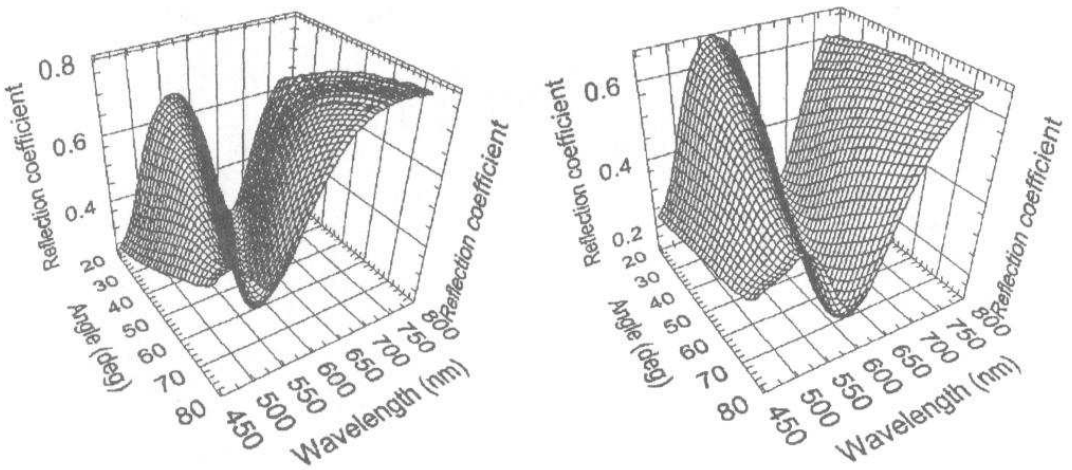

Fig. 7. Measured reflectance of sensing structure (without prism coupler) as a function wavelength and angle of incident light for (a) s-polarized light and (b) p-polarized light.

5. CONCLUSIONS

A new and original idea of the authors is the specific configuration of the layered sensing structure, sensitive to hydrogen, which can be applied in various measured media, in gaseous as wall as in liquid ones.

Basing on preliminary investigations, the authors predict that the structure metal-dielectric-metal can ensure much better results of measurements of hydrogen concentrations in various media than by means of optical methods, applied so far, e.g. by reflection methods. The excitation of these phenomena and monitoring of variations in the intensity of the interference lines arising due to the effect of hydrogen make it possible to achieve a higher sensitivity of the structures than in the case of simple reflection sensors. In this way the sensor properties of the sensors become more universal.

Thus, the suggested structure provides universal sensor properties because the layer constituting a metallic cover permits a shielding of the electromagnetic field penetrating into the measured medium. In this way the influence of variations in this medium can be cut-off and the ageing of the palladium layer can be delayed. The structure displays characteristic angular features (minima), which can be easily recorded and analysed while being exposed to the effect of hydrogen.

ACKNOWLEDGMENTS

The authors acknowledge the Polish State Committee of Scientific Researches (KBN) for financial support under the Grant 4T10C 023 24. Authors would like to thank Dr P. Karasiński and PhD student I. Zielonka for preparation silicon dioxide layers by sol-gel method.

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