Palladium thin films for plasmonic hydrogen gas sensing

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Abstract—In this study, I prepared BK7 glass slides coated by a palladium (Pd) layer by the PVD technique. These samples were employed as plasmon active structures in classic Kretschmann-based SPR set-up. The application of H_2 sensing structures based on palladium plasmonic active thin films were tested and investigated. Hydrogen sensing properties of Pd films were investigated at room temperature. The reflectances of p-polarized light from Pd thin films as a function of angle of incidence and wavelength were measured in synthetic air (or nitrogen) and in gas mixtures including hydrogen. Variations of the reflectance in the presence of hydrogen gas at room temperature revealed that the samples can sense hydrogen in a wide range of concentrations (0–2% vol/vol) without saturation behavior. The dynamic properties with various concentrations of H_2 at low temperature and dry gas mixtures were investigated and the effects of these factors on hydrogen sensing properties were analyzed.

Continuous development and efforts are needed to improve applied sensor techniques for detection and effective measurement of various chemical compounds, including gaseous analites, aimed at safety and control of industrial processes and monitoring of environmental pollution [1].

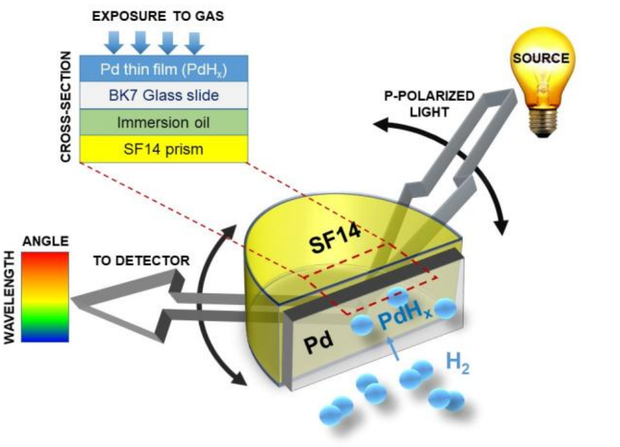

Fig. 1. The schematics of the Kretschmann configuration for testing and observation of the SPR effect on a thin film structure.

Hydrogen detection is a very important problem, especially in the context of applying this fuel as a source of energy in the modern, environmentally friendly energy sector. The technologies of hydrogen energy have already reached the dimension of industrial application thanks to the development of hydrogen fuel cell technologies. H_2 is also an important industrial medium used in modern industry, for example in the procedures of hydrogenating substances, cooling or production of certain compounds in the chemical industry [1–5].

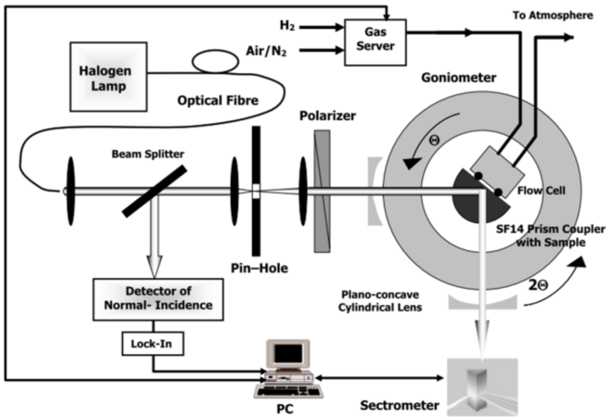

Fig. 2. Experimental set-up for determining a reflected optical signal as a function of wavelength and angle of incident light of thin films of Pd before and after hydrogenization.

Hydrogen also acts as a broadband indicator of early internal damage of electric power transformers with oil insulation [4–5]. The content of gases dissolved in transformer oil indicates a developing process of degraded insulation, which is caused by internal fault. The cause of the fault can be determined, the threat to the transformer can be assessed too, and the response procedure can be determined by examing the composition and concentration of gases. The limitations upon the application of this medium are, among others, safety restrictions, since hydrogen in combination with oxygen at concentrations of 4%–75% (in standard conditions) forms an explosive mixture [1–3].

Some metals such as platinum, nickel, palladium and others, particularly in a thin film or nanostructure form, can be used to observe the adsorption of H_2. As a result of their reaction with hydrogen, they exhibit a change in their electrical, optical and mechanical properties. These changes are used for detection of hydrogen concentration purposes.

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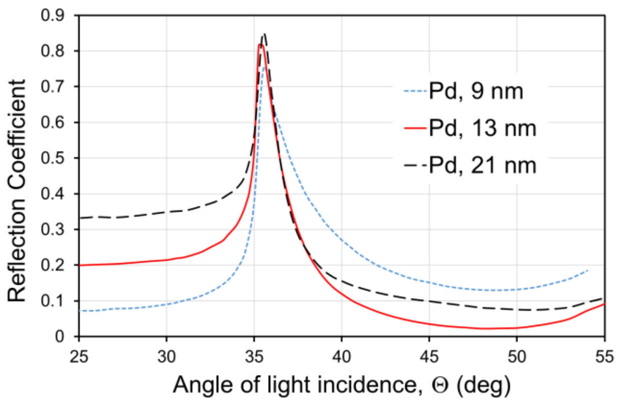


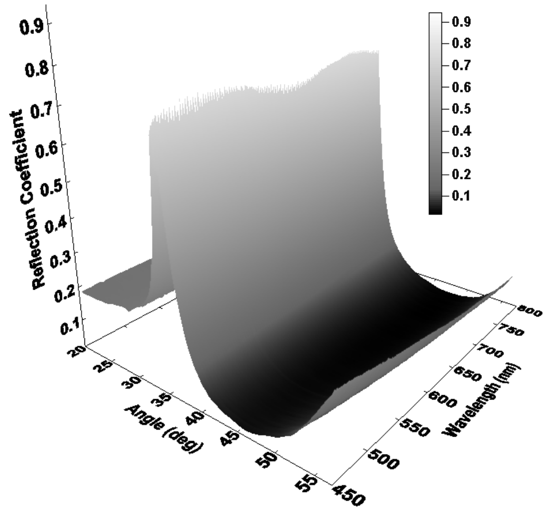
Fig. 3. Comparison of the measured SPR curves for Pd thin films with different thicknesses. The results were obtained at λ = 685 nm, room temperature and synthetic air.

The Pd has an extraordinary ability to absorb in its volume several hundred larger volumes of hydrogen, and besides that, the Pd-H_2 reactions are reversible. Molecular hydrogen is spontaneously absorbed on the surface of a Palladium layer, then it dissociates to atomic hydrogen and diffuses deeper in a Pd film. The H atoms take interstitial positions in the Pd layer's crystal lattice. The population of octaedric holes in a surface centered Pd lattice by atomic hydrogen leads to forming a PdH_x fraction [6].

This paper presents the optical properties of palladium thin films and the H_2 sensing principle investigated in the Kretschmann configuraton. The surface plasmon resonance (SPR) effect is used for detecting reversible changes of optical properties of a Pd thin film exposed to H_2 gas.

Figure 1 shows optoelectronic transducer in the Kretschmann plasmon system with plasmon active Pd thin films. Plasmon configurations are characterized by very good sensitivity to changes in the optical parameters of the structure layer system in which it is possible to excite the collective oscillations of the charge density (of electrons) in the area of metal interphase (plasma active metals – i.e. Au, Ag, etc.)/medium, i.e. the excitation of the so-called Surface Plasmon Resonance – SPR. The excitation of this phenomenon is manifested by the appearance of a plasmonic minimum in spectral-angular distribution of an optical signal reflected from the structure [6–12]. The minimum position in the domain of wavelength and angular distribution of a reflected light beam and the shape of this minimum is closely related to the optical parameters of the layer system of the SPR structure. Thus, the change of optical parameters of the structure, caused by the interaction of the gas analyte with the receptor, which is an integral part of the structure, will be manifested by a shift of this minimum and/or a change in its shape and intensity. The analysis and characteristics of this minimum allows for deducing physiochemical mechanisms of changes in the optical parameters of the layer or structure. In connection with the above, the plasmon configuration, presented in Fig. 1, apart from the role of sensor structure, plays an analytical role, allowing characterisation of optical parameters of low-dimensional receptor materials i.e. metallic plasmon active films.

(a)



(b)

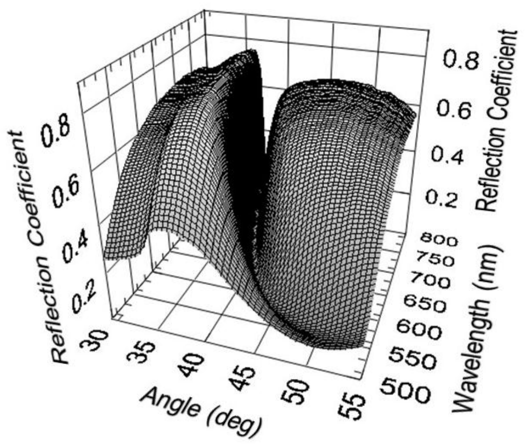
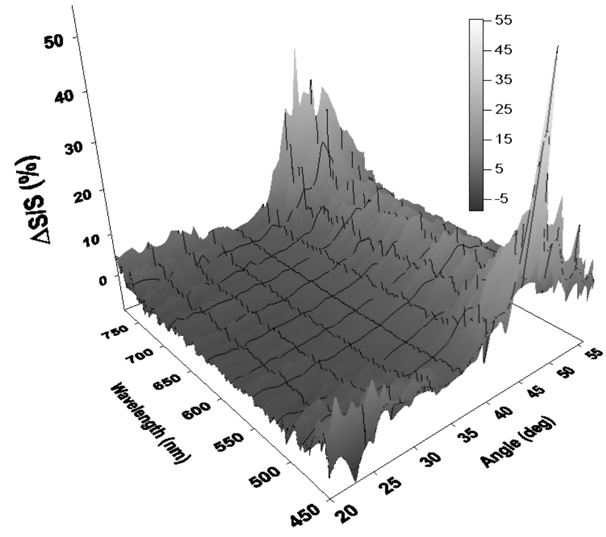
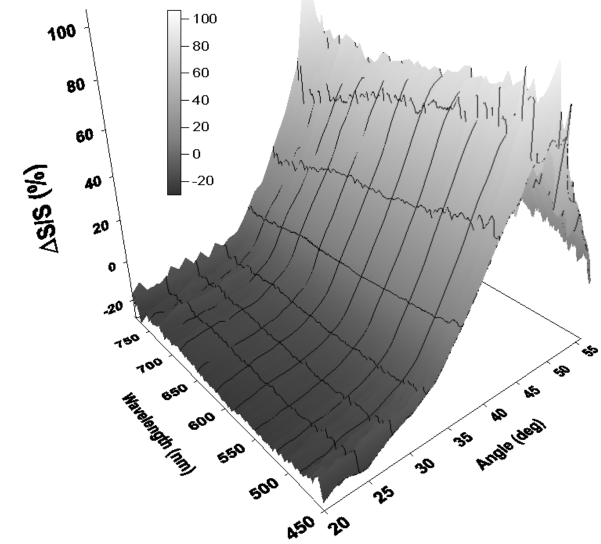


Fig. 4. Measured reflectance of (a) 13 nm thick Pd layer and (b) 48 nm thick Au as a function of wavelength and angle of incident light for p–polarized light.

Pd films were deposited by e-beam vapor deposition on the BK7 glass substrates. A thin layer of chromium (about 1 nm thick) was deposited for adherence first, followed by a Pd layer of optimized thickness. The vacuum chamber pressure was maintained in a 10^{-6} mbar range during both depositions, while the chamber temperature was not changed. The growth of the film was controlled by quartz crystal microbalance (QCM).



(a)



(b)

Fig. 5. Reflected light intensity change (in %) for a 13 nm thick Pd layer upon hydrogenation - PdH_x (a) 1% vol/vol H_2 and (b) 3% vol/vol H_2 as a function of wavelength and angle of incident light for p–polarized light.

Measurement characteristics were obtained using an automated experimental set-up developed in the Sensor Lab Department of Optoelectronics, Silesian University of Technology presented in Fig. 2 and described in the literature [11–12]. The experimental setup is shown in Fig. 2, consisting of a wide band light source (low power consumption halogen lamp), detector (spectrometer HR2000+ES, Ocean Optics), goniometer and flow gas chamber.

The idea of measurements was to obtain the spectral reflection characteristic as a function of wavelength and angle of incident light of thin films of Pd exposed to a mixture of synthetic air or nitrogen with a varying content of H_2 gas. Determined reflectance (reflected optical signal, reflection coefficient) is carrying information about the changes taking place on a sensor structure, as a result of absorption H_2.

The Pd is a highly absorbing metal in the visible spectra region, much more than classic plasmon active metals i.e. gold. However, Fig. 3 has demonstrated that the SPR effect is sufficient in this configuration, but SPR phenomena strongly depend on the thickness of the Pd layer. Additionally, SPR curves have a large width of the Pd SPR peak. The most effective SPR excitation was obtained for a Pd layer thickness of 13 nm. Fig. 3. shows the comparison of the measured SPR curves for Pd thin films with different thicknesses: 9 nm, 13 nm, and 21 nm. The results were obtained at λ = 685 nm, room temperature and synthetic air. To measure the SPR performance of the Pd thin film with an optimal thickness in the entire visible range, the reflectance spectra as a function of angle of incident light for p–polarized light as shown in Fig. 4a, which gives the experimental results and comparison of the results for a classic Au-based SPR system - Fig. 4b. As it can see from Fig. 4a, the Pd presents a much broader SPR peak than Au.

As mentioned above, in the case of Pd, the optical properties of the metallic layer itself changes with the absorption of hydrogen. In order to demonstrate the changes in the optical properties of palladium, measurements showing a change in the optical signal reflected from 13 nm of the Pd layer were made. Measurements were carried out for two levels of H_2 concentration in synthetic air, 1% and 3% vol/vol respectively. Figure 5a, b presents a relative change of the optical signal ΔS/S the interaction in the investigated spectral and angular range due to the interaction of the 13 nm thick Pd and H_2 in synthetic air with a different concentation at room temperature. The investigations concerned the visible range of spectra (450 nm - 780 nm). The relative change of an optical signal has been determined in compliance with the relation (1):

$$\frac{\Delta S}{S} = \frac{R_{H2\_Air/N2} - R_{Air/N2}}{R_{Air/N2}} * 100 \quad (\%) \qquad (1)$$

After the absorption of hydrogen by a Pd film, an optical signal change within the range of the SPR peak due to complex permittivity of this layer has been changed. The variation of the signal is of essential importance, as was expected, in the range of an SPR minimum.

As it can see from Fig. 5, upon hydrogenation – PdH_x form, the width of the SPR peak decreases. As the PdH_x is less absorbing, the propagation length of the plasmon wave is longer. This is due to an efficient transfer of energy to surface plasmon. The decrease of the SPR peak width results in an increase in reflectance for the reflected optical signal upon hydrogenation as shown in Fig. 5. The change in reflectance is more significant near the infrared than the blue wavelength.

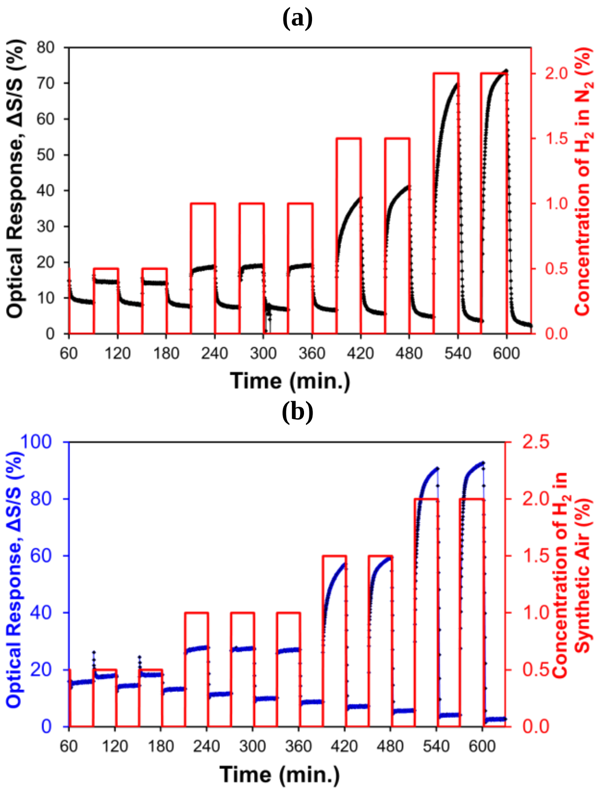


Fig. 6. Optical response signal ΔS/S vs. time of the 13 nm thick Pd SPR film. The signal ΔS/S was recorded for λ = 685 nm and angle of incidence 47.5 deg, carrier gas (a) pure nitrogen, (b) synthetic air.

Finally, investigations of dynamic behavior of the Pd SPR film were carried out. A few cycles of the H_2 switching are measured and shown in Fig. 6. It can be seen that the optical signal ΔS/S increased by ~60% as the H_2 concentration increased from 0% to 2%. The signal ΔS/S was recorded for λ = 685 nm and the angle of light incidence - 47.5 deg. The hydrogen gas concentration level of a gas mixture was balanced by mixing synthetic air or pure N_2 gas and dry Hydrogen 5.0 reference gas (100%, Linde Gaz, Poland) at a prescribed ratio of the flow rate (total flow rate: 1000 sccm). The relative humidity (RH) and temperature of the gas mixture was monitored with a commercial sensor (SHT75; Sensirion AG, Switzerland). The uncertainty of the analyte gas flow rate resulted mainly from limited short-term stability of the MFC at a low dilution flow rate or at short generation time. Consequently, MFCs can provide a highly accurate dilution target gas in air/N_2 flow rates with a relative uncertainty of 0.4%, for flow rates larger than 70% of the MFC's maximum flow rate (full scale) and generation times longer than 5 min. As a result of the use of Bronkhorst MFC with a max flow rate of 100 sccm in an H_2 dosing channel, the multi-gas controller mixed gases with H_2 concentration precision (with relative uncertainty) exceeding from 2.5% for 0.5% H_2 to 1% for 2% H_2 in a carrier gas.

The investigations were carried out for two types of carrier gas: pure nitrogen (Fig. 5a) and synthetic air (Fig. 5b), respectively. In Fig. 5a and Fig. 5b, it can see that the response time can vary during different cycling and depends on the type of carrier gas. The presence of oxygen during the exposure to H_2 leads to an slightly improved response and recovery times, but at the same time increases the drift. Oxygen on the surface of a thin Pd film will promote the formation of OH and H_2O molecules, particularly at low temperature, which increases the desorption rate. Figure 5a, b show preliminary measurement results sensing properties of a Pd SPR active film. In general, the reproducibility in the adsorption and desorption processes of the H_2 gas was satisfactory. Further studies should also investigate the limitations of a Pd film sensing operation in harsh and chemical environments with or without pollutant analytes at different temperatures.

In summary, a simple plasmonic Pd structure used to detect and measure H_2 gas at room temperature is proposed and demonstrated. I find that Pd thin films are sensitive to hydrogen gas concentration due to a change in its optical properties in the spectral range 450-780 nm, while the obtained sensitivities are below 0.5% vol/vol of H_2 in a dry gas mixture and at room temperature.

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