



Contributions to a reliable hydrogen sensor based on surface plasmon surface resonance spectroscopy [☆]

Martin Morjan ^a, Harald Züchner ^b, Karl Cammann ^{c,*}

^a Sentronic GmbH, Gostritzer Strasse 61-63, 01217 Dresden, Germany

^b Institute for Physical Chemistry, University of Muenster, Corrensstrasse 30, 48149 Muenster, Germany

^c Chair of Analytical Chemistry, University of Muenster, Corrensstrasse 30, 48149 Muenster, Germany

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ABSTRACT

Hydrogen is being seen as a potentially inexhaustible, clean power supply. Direct hydrogen production and storage techniques that would eliminate carbon by-products and compete in cost are accelerated in R&D due to the recent sharp price increase of crude oil. But hydrogen is also linked with certain risks of use, namely the danger of explosions if mixed with air due to the very low energy needed for ignition and the possibility to diminish the ozone layer by undetected leaks. To reduce those risks efficient, sensitive and very early warning systems are needed. This paper will contribute to this challenge in adopting the optical method of Surface-Plasmon-Resonance (SPR) Spectroscopy for a sensitive detection of hydrogen concentrations well below the lower explosion limit. The technique of SPR performed with fiber-optics would in principle allow a remote control without any electrical contacts in the potential explosion zone. A thin palladium metal layer has been studied as sensing element. A simulation programme to find an optimum sensor design lead to the conclusion that an Otto-configuration is more advantageous under intended “real world” measurement conditions than a Kretschmann configuration. This could be experimentally verified. The very small air gap in the Otto-configuration could be successfully replaced by a several hundred nm thick intermediate layer of MgF₂ or SiO₂ to ease the fabrication of hydrogen sensor-chips based on glass slide substrates. It could be demonstrated that by a separate detection of the TM- and TE-polarized light fractions the TE-polarized beam could be used as a reference signal, since the TE-part does not excite surface plasmons and thus is not influenced by the presence of hydrogen. Choosing the measured TM/TE intensity ratio as the analytical signal a sensor-chip made from a BK7 glass slide with a 425 nm thick intermediate layer of SiO₂ and a sensing layer of 50 nm Pd on top allowed a drift-free, reliable and reversible determination of hydrogen concentrations up to about 10 vol.% in dry or humid air with a detection limit of 0.04 vol.% with response times of around 2 min.

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1. Main Text

Hydrogen enjoys a long tradition as an energy carrier as well as a chemical resource. Hydrogen is being seen as a potentially inexhaustible, clean power supply [1]. Research and development in hydrogen production and storage techniques that will avoid negative environmental impacts are boosted by the recent sharp and constant price increases of crude oil. It is now of the utmost importance to evaluate if the development of a new infrastructure based on hydrogen as an energy carrier is possible, maybe even inevitable. Hydrogen is not a source but a storage medium and an energy carrier [2]. Like any other carrier it must be produced from a primary energy source. Currently about 80% of the world energy sup-

ply is based on fossil fuels, resulting in negative ecological and environmental impacts [3]. The exhaustion of oil reserves and other carbon based resources maybe of an even greater importance in the supply area of highly valuable base chemicals on which whole petrochemical industries were built. This seems less discussed when the hidden “fine chemicals” are simply used as an energy source. At the time, air pollution and modification of the atmospheric composition, with their impacts on climate and on human health, are of primary concern.

Among the many advantages to using hydrogen as a fossil fuel replacement is the emission of water, which does not harm the environment at all. Electrochemists are planning fuel cells with at least forty percent efficiency. Compared to the fourteen percent efficiency of gasoline utilized in the current combustion methods, this seems a larger step forward. However, the issue of safety is still considered as a major drawback in using hydrogen. The reason is that the minimum required ignition energy required for a

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* Corresponding author. Tel.: +49 0 25131983; fax: +49 0 251315422.

E-mail address: kcammann@uni-muenster.de (K. Cammann).

stoichiometric fuel/oxygen mixture is only 0.02 mJ for hydrogen compared to 0.26 mJ for propane. Even the smallest energy of a tiny static electric discharge will be sufficient to ignite a hydrogen/air mixture above the minimum explosion limit. This creates an enormous danger potential and potential risk due to the very high energy density of hydrogen and the wide explosion range when mixed with air. What even the smallest leak in a hydrogen powered vehicles can create was dramatically shown on May 6th 1937 when the German airship Hindenburg crash landed in Lakehurst, New Jersey and on January 28th 1986 when the space shuttle Challenger was burst in seconds. Already in 2003, researchers from the California Institute of Technology reported, that leaking hydrogen gas that would inevitably result from a fully developed hydrogen economy, if it accumulates, could indirectly cause as much as a 10% decrease in atmospheric ozone [4]. It seems that especially the last mentioned risk is not always adequately addressed in so-called technological roadmaps. The only way to cope with both risks is by preventing any danger through hydrogen leakages, either through catalyzing a safe oxidation to water at any leak or by installing sensitive leak warning systems along every distribution line and not by keeping silent about identified risks. Many studies reveal that those risks are differently conceived by the public and by experts [5]. Experience with nuclear energy made abundantly clear that public acceptance is mandatory for effective implementation of new technologies in society. It seems plausible that acceptance issues will be very relevant for reactions towards a fully developed hydrogen technology, which is probably not yet very transparent for many people. In the discussions among social scientists concerning the best strategy even the recommendation was made that questions of safety should be a priority in the development of the technologies, not however in the public relations, because intensified treatment of the safety risks would probably induce assessments of danger, even when making the point that the risk is only very limited [6].

The very high danger potential of hydrogen demands a further development of reliable detection and explosion warning possibilities and their adaptation to new hydrogen usage areas. The International Standardisation Organisation (ISO) installed the technical committee TC 197 dealing with production, storage, transport, measurement and usage of hydrogen and has published the instruction ISO/TC 197 hydrogen energy [7]. According to these standards, the prevention, detection, and management of hydrogen leaks is an important safety issue, requiring that areas where hydrogen is stored and dispensed be well ventilated and controlled. The study presented here has to be viewed in the light of this social technical background. Besides demonstrating a general feasibility for selective and sensitive hydrogen detection the special side-conditions, like explosion-proof, robustness, reliability, low-energy and costs, had to be considered.

Many of the commercial hydrogen sensors are based on electrochemical principles, like field-effect-transistors, semiconductor gas-sensors or catalytic pellistors. Palladium is intrinsically selective to hydrogen, and sensors, based on palladium, do not produce false alarms in the presence of other gases, such as CO and hydrocarbons. Hydrogen sensors based on metal oxide and/or electrochemical techniques are cross sensitive to other gases and require modifications for selectivity improvement. Many of those sensors are themselves potential dangerous if they need too much electrical energy to work properly, e.g. to heat sensing surfaces up to several hundred °C. Even the energy of an electrostatic discharge or a tiny spark due to a “bad” electrical contact is sufficient to ignite an explosive hydrogen/air mixture. Thus, elaborate prevention measures, like galvanic isolation, have to be taken in addition to special steps increasing their selectivity. In contrast to this, optical sensors do not need a direct electrical powering at the measuring area which eases remote control and the explosion

safeguard. Therefore the development of optical hydrogen sensors has increased during the last years. Most of those sensors are based on reversible change of the optical density of thin metal or metal oxide film upon contact with hydrogen [8,9]. However, a serious drawback with respect to those sensors is their limited sensitivity and selectivity. A very promising approach to increase the sensitivity of optical hydrogen sensors lies in using the principle of surface plasmon resonance (SPR) spectroscopy of thin metallic layers. This principle has been already successfully used for the detection of other gases than hydrogen [10–12]. For a selective and sensitive detection of the latter the development is still in its infantile and more basic research seems needed especially if robustness and humidity influences are concerned. As sensor elements in hydrogen detectors several metals [13,14] or inter-metallic compounds [15,16], which can react with hydrogen by hydride formation have been studied. Material tested as sensitive receptors were, among others, palladium, tungsten oxides, zinc dioxide, and yttrium. Hydrogen absorption results in the sensor elements in several changes of characteristic properties as there are: change of density, change of mechanical properties, creation of dipoles, creation of heat, and change of optical properties. Those effects are measured with different transducers to deliver a proportional electrical signal. The optical approaches to detect hydrogen can be divided into two groups: principles in which the hydrogen interacts with the electromagnetic wave as there are spectroscopic methods like IR absorption or Raman-spectroscopy [17,18]. For the detection of hydrogen only the latter is suited. In the second group the electromagnetic wave is only the information carrier of those interactions between hydrogen and a receptor as sensing element. Often a thin palladium layer is deposited on optical wave guides [19,20]. Popular methods are based on electro-chromic materials [21,22], interferometry [23], and SPR-spectroscopy [24–26]. This study only deals with the latter method since conflicting results could be found in the literature concerning the excitement of surface plasmon waves in palladium layers and concerning the true analytical performance, like sensitivity and selectivity.

2. Theoretical approaches

For obtaining a sufficient analytical selectivity and high reliability palladium metal was chosen to function as sensing element. Already in 1866 Graham [27] detected a certain solubility of hydrogen in palladium. Later thin palladium membranes were used to separate hydrogen from other gases and some studies were performed with this system [13,28,29]. It became clear that only hydrogen could enter the palladium metal and diffuse through it which indicates even specificity for this gas. Later, neutron diffraction studies have shown that hydrogen atoms randomly occupy the octahedral interstices in the palladium metal lattice. In a face-centred cubic (fcc) lattice there is one octahedral hole per metal atom which can be filled by a hydrogen atom. This is the reason for the exceptional specificity. The palladium–hydrogen system shows two phases, the α - and β -phase which both show an fcc structure. In equilibrium at low hydrogen concentration only the α -phases exists, while at high hydrogen concentrations the β -phase is favoured. At the transition from the α -phase into the β -phase a solubility gap occurs in which both phases exist. At room temperature this two-phase area lies between PdH_{0.008} and PdH_{0.609}. The intake of hydrogen expands the lattice structure in both phases gradually. However, at the transition $\alpha \rightarrow \beta$ a non-steady jump can be observed. At room temperature the lattice expansion by hydrogen in the α -phase is only 0.002 Å, however in the β -phase 0.136 Å. For the use in any reversible sensor any jump in the behaviour is detrimental and should be avoided. However, the addition of about 8% nickel prevents the solubility gap

and guaranties gradual changes being useful for sensing purposes [30].

Besides the lattice expansion also other properties of palladium are changed through the absorption of hydrogen: mechanical, electronic, magnetic, and optical. Those hydrogen specific changes have already being used for different sensor developments. But none of those have been commercially very successful. Surface plasmons, also known as surface plasmon polaritons, are surface electromagnetic waves that propagate parallel along a metal/dielectric (or metal/vacuum) interface. Since the wave is on the boundary of the metal and the external medium (air or water for example), these TM-polarized oscillations of weakly bound free electrons in the vicinity of atomic hull are very sensitive to any change of this boundary, such as the adsorption of matter onto the metal surface, change of the dielectric property, or change of the metal lattice. In order to excite surface plasmons in a resonant manner, an electron [31] or light beam [32,33] can be used. The incoming beam has to match its impulse to that of the plasmon. In the case of p-polarized light (polarization occurs parallel to the surface), this is possible by passing the light through a block of glass to increase the wavenumber (and the impulse), and

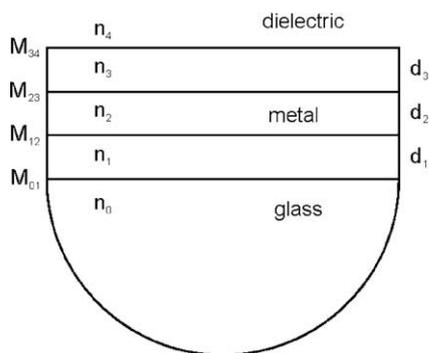


Fig. 1. ATR-coupler consisting of 5 layers; each layer is described by their refraction index n_i , the layers 1, 2 and 3 in addition by their thickness d_i . The interfaces between the individual layers are described by their corresponding matrix M_{nm} .

achieve a resonance with corresponding energy transfer at a given wavelength and incident angle. S-polarized (polarization occurs perpendicular to the surface) light cannot excite electronic surface plasmons. The total reflection of light on a thin metal layer for exciting surface plasmons was firstly described by Turbadar in 1959 [32]. A more accurate description however was simultaneously presented by Otto [34] and Kretschmann/Raether [35] with the method of attenuated total reflection (ATR).

The question arises if those reversible palladium lattice expansions could maybe be detected by the technique of SPR-spectroscopy with the needed sensitivity towards hydrogen. In general, SPR-spectroscopy offers two main possibilities: (a) a thin palladium layer could be deposited onto a layer of gold or silver (as transducer) known to exhibit well studied surface plasmon waves and (b) a thin palladium layer could maybe itself be used as sensing element and transducer together by exciting surface plasmon waves in it. The first approach was not considered further, since an uncontrolled alloy formation at the interface Pd/Au or Pd/Ag during a high temperature fabrication process could lead to difficult interpretations besides irreproducible results depending on the technique for the production of those thin layers prone to surface defects. In order to decide between the two possible basic ATR configurations and to find an optimum sensor design without elaborate experimental tests a theoretical simulation program on the basis of MathCAD [36] was used beforehand. It allows a qualitative description of a multilayer set-up consisting of metal and dielectrical layers. A simple model system was used to test the simulation software. This theoretical simulation program delivers information on the incidence angle for the resonance condition, the width and the depth of the reflectance minimum in dependence of the kind and thickness of the different layers. The program was tested with an experimental set-up as shown in Fig. 1 consisting of a BK7-glass prism with a 50 nm thick gold layer on top in contact with water in a Kretschmann configuration.

Fig. 2 shows the excellent agreement between theory and experiment. The great advantage of the simulation program lies in the possibility to optimise a potential sensor design with respect to all variables: glass, metal, thicknesses, wavelength, and incident angle.

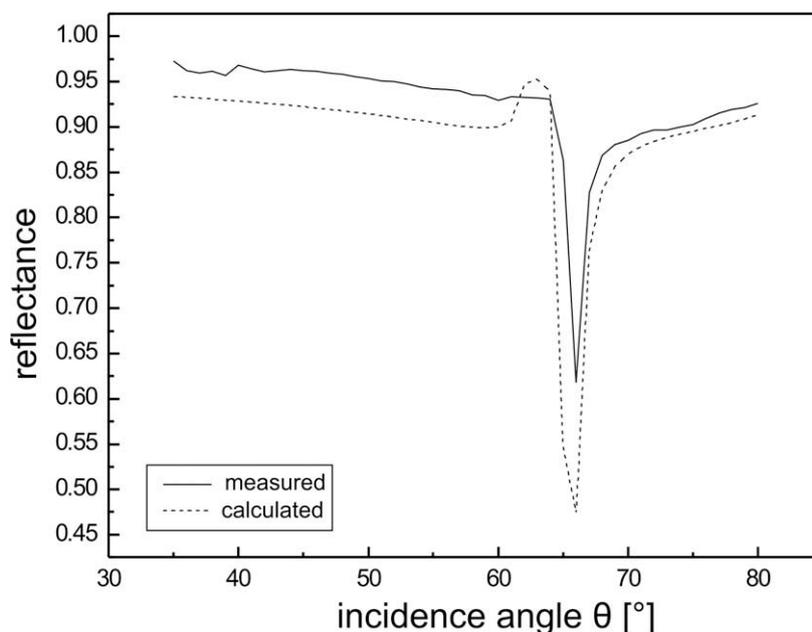


Fig. 2. Calculated and measured resonance angle for the interface: BK7-Glass/50 nm Gold/dielectric with an exciting wavelength of $\lambda = 850$ nm. The refractive index n_4 of the dielectric (water) is 1.333.

After this promising result the simulation program was used for an optimal sensor design for a SPR-spectroscopy using a thin palladium layer as hydrogen sensing layer and transducer. Glass prisms made from optical standard glasses (BK7 ($n_{850} = 1.511$) and SF11 ($n_{850} = 1.762$)) were considered in those simulations. Two hypothetical designs according to Fig. 1 were examined more in depth: the first with a primary gold layer (responsible for surface plasmon waves) and a second palladium layer (responsible for the hydrogen detection), both with variable thicknesses between 20–50 nm for gold and 10–50 nm for palladium. The second design without the gold layer and different palladium layer thicknesses of 20, 50, and 100 nm. This theoretical evaluation revealed that no surface plasmon waves can be generated with those set-ups. Unfortunately, no clear minimum in a reflectivity vs. incidence angle graph caused by surface plasmon resonance will be obtained. This results contradict studies by Chadwick [25,26] who described SPR conditions with a wavelength of 633 nm (He–Ne) above an incident angle of 45°. Also by using SF11 glass as substrate the simulation program indicates no clear reflectivity minimum. This is in agreement with the results of Butler [37,38] and explainable by the fact that no ATR conditions are met under this conditions.

In a SPR set-up according to Otto a very small and controlled air gap in the nm range between the glass substrate and the metal layer has to be present, which is difficult to be experimentally maintained. Therefore, this air gap was replaced in this feasibility study by a corresponding thin layer of a material with a lower refractive index than the glass [39,40]. Magnesium fluoride (MgF_2) and silica (SiO_2) intermediate layers were considered as being appropriate. Fig. 3 shows the general set-up for the simulation program using the Otto-configuration.

The theoretical calculations with the simulation software revealed that under those conditions surface plasmon waves even in palladium could be excited. The lower refractive indices of mag-

nesium fluoride and silica compared to the one of the glasses allows a total reflection and the evanescent wave can reach the outer palladium layer exciting surface plasmon waves there.

3. Experimental

For the measurement of the surface plasmon excitation a set-up as schematically shown in Fig. 4 was used.

The light source consists of different low-cost, low-energy LEDs with the wavelengths 665, 850, 950, and 1300 nm in a receptacle arrangement for a quick wavelength change. The LED light is fed through a flexible optical fiber into the SPR-spectrometer. The half-cylindrical prism is made from borosilicate glass (BK7) by the Hellma Company. It has a radius of 30 mm and a high of 20 mm. The different “sensor-chips” are placed on the base of the prism with the aid of an immersion oil (Leica, $n = 1.518$) with the same refractive index as the glass prism. The different sensor-chips are either 20×20 mm pieces (thickness 0.5 mm) of BK7 glass (Plan Optik Company) or 1 inch in diameter pieces (thickness 0.5 mm) of SF11 glass (Guinchard Company). The different incidence angles of the light beam on the SF11 sensor-chips have been mathematically corrected for their higher refractive index. The light beam reflected from the different sensor-chips passes a Wollaston-prism where it is divided into its TM- and TE-polarized beams. The deflection angle of the used Wollaston-prism is 5°. The separated detection of the intensities of the TM- and TE-polarized light fractions is performed with low-cost Si-photodiodes (type S1227-66BR Hamamatsu Company). The photocurrent of the Si-diodes are converted in a voltage, amplified and digitalized by a self-build electronic device. Noise has been reduced by a low-pass filter of 0.1 Hz. The temperature of the sensor-chip and the gas space above was measured with a thermo-element type K. The measuring cell, which was pressed on the surface of the sensor-chips, was thermostated with a 50×25 mm heating jacket to 25 °C. Calibration gas mixtures of hydrogen and nitrogen/synthetic air were produced from gas cylinders with gas purities above 99.9% using a 2-channel gas mixing device with flow meters using suspension bodies made of glass, sapphire and stainless steel (Aalborg Company). The precision of the resulting calibrating gas mixtures is estimated to lie in the range of $\pm 2\%$. In order to study the influence of humidity the gas mixtures were passed through a gas wash bottle filled with water (establishing a relative humidity of 100%).

All sensor-chips were fabricated in a class 1000 clean room under constant environmental conditions of 20 °C and 30% relative humidity. The different palladium, MgF_2 , and SiO_2 layers were produced using appropriate physical vapour deposition (PVD) methods. The layer thickness was controlled during the deposition process with a quartz microbalance (INFICON, Leybold Company) and verified later with a surface profile meter (P2, Tencor

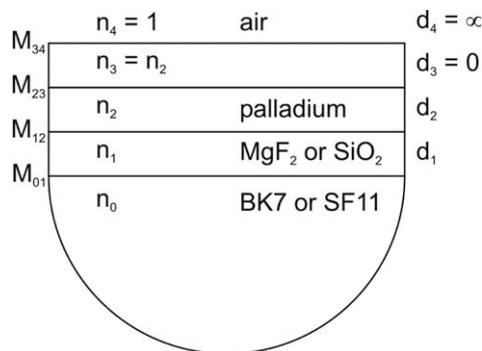


Fig. 3. Schematic sensor design according to the Otto configuration with the layer order: glass prism/intermediate layer/palladium/air as it is used for simulation.

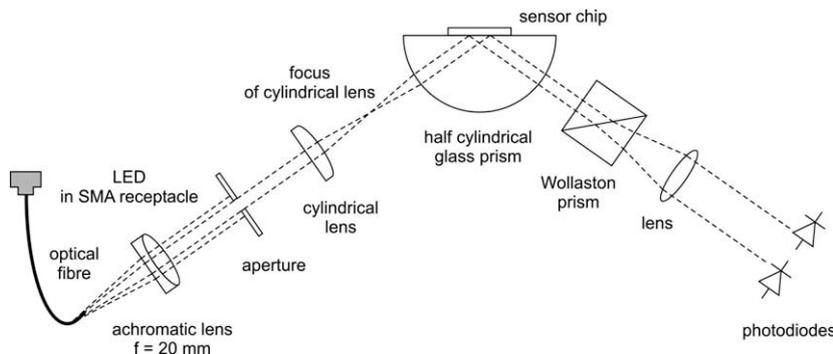


Fig. 4. Schematic arrangement of the measurement instrument (SPR spectrometer; the interrupted lines characterize the light path).

Company). Before the first layer was deposited on the corresponding glass surface, the latter was carefully cleaned in three steps: (1) incubating 20 min in a 10% DeContam solution at 80 °C assisted by ultrasound, (2) rinsing with ultra pure water, blown dry with a nitrogen gas stream, and stored in an oven at 105 °C until completely dry, (3) placed for 10 min in a plasma incinerator (TePla Company) at an oxygen pressure of 0.1 mbar. To improve the adhesion of palladium on the glass surfaces a 5 nm thick chromium layer was produced with an e-gun from a chromium tablet in the vapourisation chamber. The palladium layers were produced by thermal vaporisation of palladium wire in an electrical tungsten oven. In order to increase the stability of the palladium layers 10% nickel powder was added and well mixed by melting.

4. Results

To test the above described theoretical approach sensor-chips made from BK7 and SF11 glasses and covered with an inter-layer of 317 nm MgF_2 and 100 nm Pd–Ni were measured at a wavelength of 950 nm in an Otto-configuration as shown in Fig. 4. Fig. 5 shows again the excellent agreement between the used theoretical treatment and the experiment here for the excitement of surface plasmons in a palladium layer.

After the verification that indeed a plasmon excitation in a palladium layer is possible, the response toward hydrogen was tested. After further optimisations of the different layer thicknesses the sensor-chip of Fig. 4 developed a reversible hydrogen response. Unfortunately the additional adhesion layer of chromium reduced the response towards hydrogen by 75%, but has nevertheless been used due to layer stability reasons. As expected by theory hydrogen affects mainly the TM-polarized light beam due to its influence on the palladium lattice demonstrated by corresponding change of the surface plasmon resonance energy. TE-polarized light cannot excite surface plasmon waves and thus will not show a hydrogen

dependent signal. The TE-part of the light was found to be only affected due to small variations of the reflection properties. Therefore, this light beam is ideal to be used to serve as reference beam for correcting variations of the light source, like it is done in double beam spectrophotometers. The self-built electronic evaluation instrument automatically calculates the ratio TM/TE of the separated reflected light beams and delivers this as analytical signal. Within the hydrogen concentration range 0–8% a calibration curve (exponential with $R = 0.987$) with a detection limit ($3 \times$ standard deviation) of 0.4% (10% of the lower explosion limit) could be constructed with sensor-chips made from SF11 glass containing an inter-layer of 317 nm MgF_2 and a sensing layer of 100 nm Pd–Ni using light of 950 nm at an incidence angle of 52°. The response time was around 200 s to reach 95% of the final signal. According to this incidence angle the quotient TM/TE diminishes with increasing hydrogen concentrations. Increasing H_2 -concentrations lower the refractive index of the Pd–Ni-layer and shift the resonance minimum to lower incidence angles. Depending on the chosen incidence angle relative to the reflectance minimum (decreasing or rising part of the curve), this resulted in a decrease or increase of the measured TM/TE ratio with increasing hydrogen concentrations. Despite a general feasibility of this approach a test for interferences by humidity unfortunately resulted in a marked increase in the TM/TE ratio counterbalancing an increasing hydrogen concentration and preventing reliable results.

In order to overcome the interference by a variable humidity the intermediate layer of MgF_2 was replaced by SiO_2 . Sensor-chips with such an intermediate layer showed different properties depending on the production method. SiO_2 layers made by plasma supported chemical vapour deposition (CVD) with SiH_4 and N_2O gases at 300 °C depend strongly on process details. Depending of the temperature and flow rates of the gases SiO_2 layers of different stoichiometry and refractive indices are formed [41]. Those intermediate layers are not suited for a replacement of the MgF_2 layers.

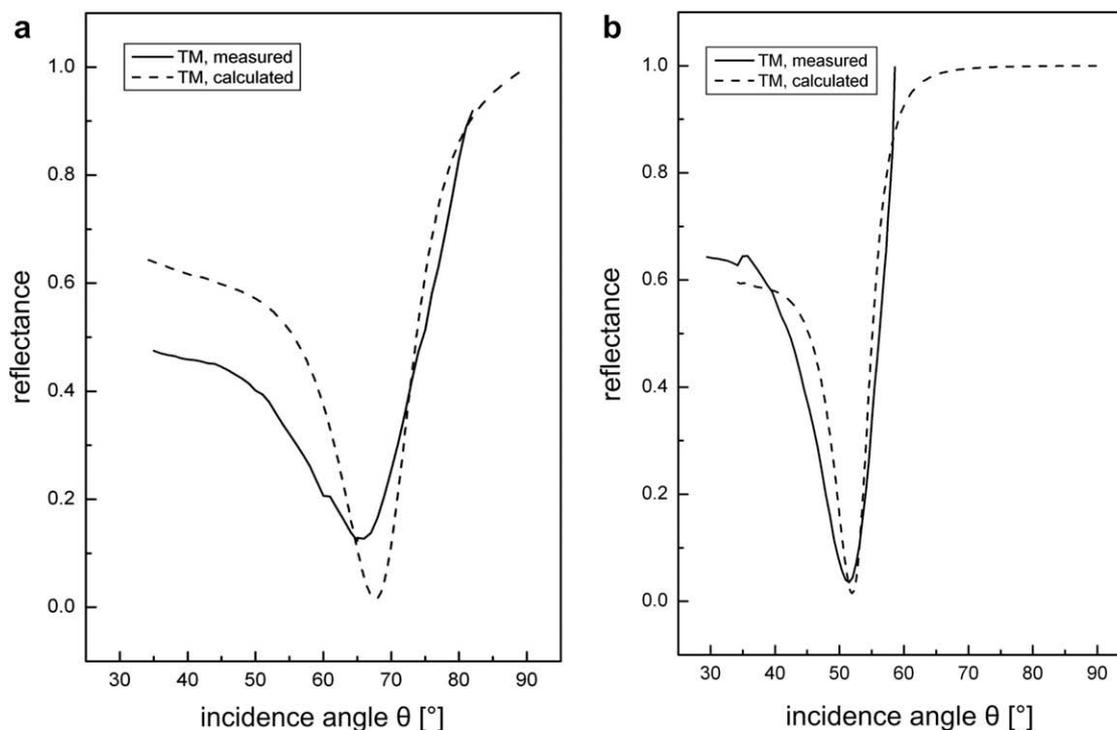


Fig. 5. Comparison of the measured and calculated resonance angles for sensor-chips made from (a) BK7- and (b) SF11-glass, both with an inter-layer of 317 nm magnesium fluorid and surface laser of 100 nm palladium for an incidence angle range between 35° and 90°. The outer dielectric is air with a refractive index $n_4 = 1$. The wavelength used was 950 nm.

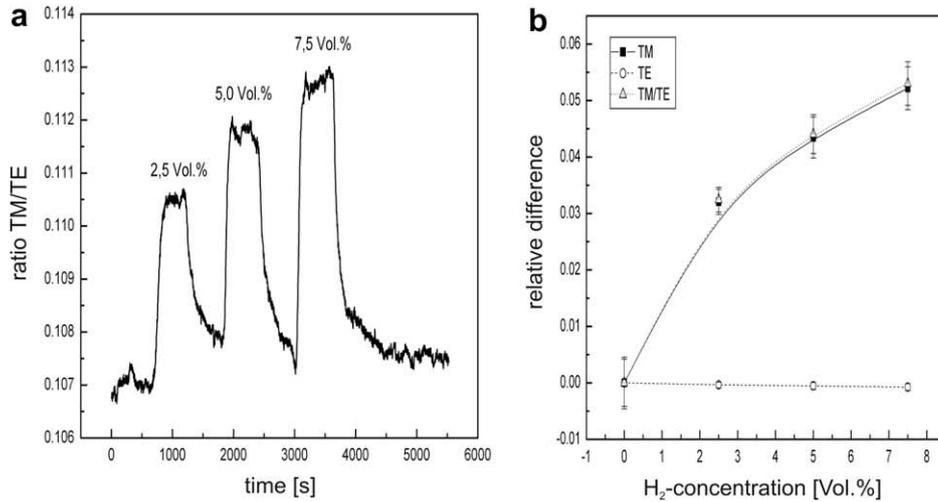


Fig. 6. (a) Original H₂ response (TM/TE ratio) of a sensor-chip made of BK7 glass with an intermediate layer of SiO₂ (317 nm thick) and a top layer of 100 nm Pd–Ni towards different hydrogen concentrations; light with 850 nm was used; fixed incidence angle: 80° (raising part of the SPR-spectrum). (b) For comparison the relative signal differences $(I-I_0)/I_0$ resulting from the response curves are plotted vs. the hydrogen concentrations; the error brackets correspond to the 3 s values of the mean of the measured values.

SiO₂ layers produced by a physical vapour deposition (PVD) method are well suited for the purpose of replacing the air gap in a SPR Otto-configuration. For this study the intermediate layer was produced from SiO₂ granulates with a grain size between 2 and 3 nm in a molybdenum crucible with the aid of an e-gun allowing up to 3500 °C for the evaporation in a high vacuum deposition chamber. The deposition rate was 2.5 nm/s.

To test SiO₂ layers produced by the PVD method BK7 glass substrates were covered with a 317 nm thick intermediate layer and a 100 nm thick layer of Pd–Ni and placed in an environment of different hydrogen concentrations. The light beam with a wavelength of 850 nm was focussed on the Pd-layer at an incidence angle of

80°. The latter lies on the rising curve side of the resonance minimum. Hydrogen which shifts the dip in the reflectance vs. Incidence angle to lower angles would then results in positive signals (higher reflected light intensities). Fig 6 shows a typical result of those sensor-chips, which were not at all influenced by the sample gas' humidity.

Further optimisation studies showed that the best sensitivity towards hydrogen could be obtained with a SiO₂ inter-layer of 425 nm and a sensing layer of 50 nm Pd–Ni, both with BK7 and SF11 glass substrates. Using again a wavelength of 850 nm the optimum incidence angle was under these conditions 75° for BK7 and 56° for SF11. Fig. 7 shows the resulting calibration graphs.

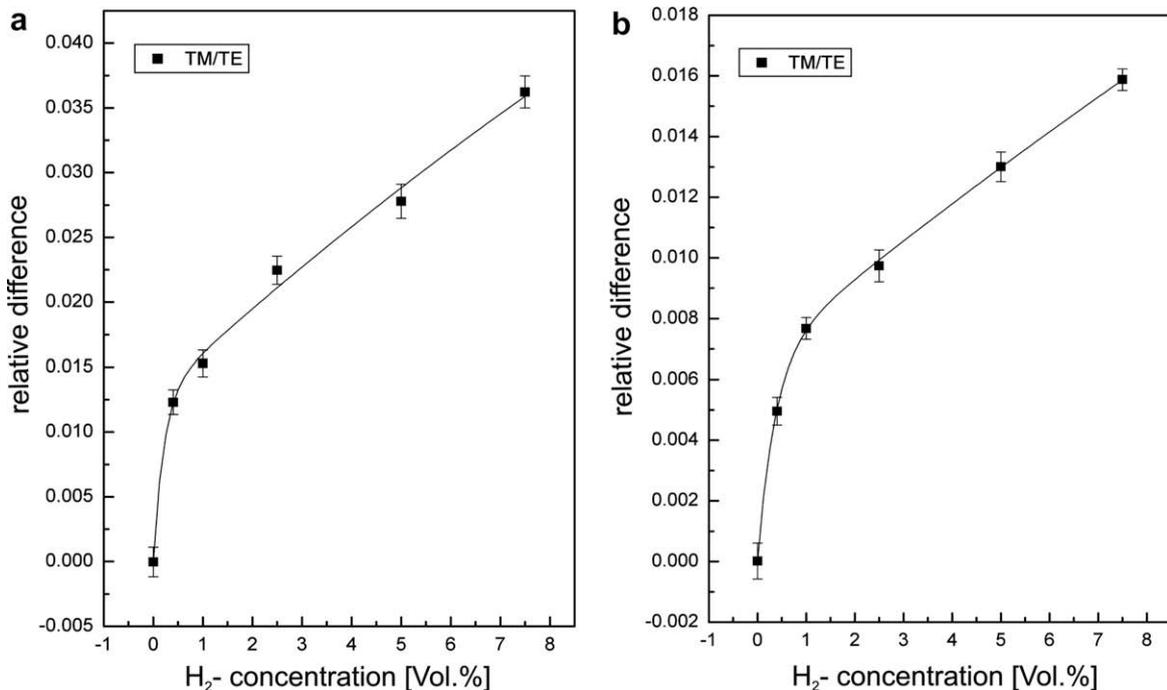


Fig. 7. Calibration graphs of the sensor-chips made from (a) BK7 and (b) SF11 glass with an inter-layer of 425 nm SiO₂ and a sensing layer of 50 nm Pd–Ni at a wavelength of 850 nm. The fixed incidence angle of the light was 75° for BK7 75° and 56° for chips made of SF11 glass. The error brackets are 3 s values of the obtained mean of the measured value.

The difference of the TM/TE intensity ratio is plotted vs. the H₂ concentration in nitrogen.

The analytical function can be described by the following mathematical equation:

$$S = S_0 + A_1(1 - e^{-c(H_2)/t_1}) + A_2(1 - e^{-c(H_2)/t_2})$$

The regression coefficient was $R = 0.9955$ for BK7 and $R = 0.9997$ for SF11. The detection limit based on $3 \times$ standard deviation of the blanks was 0.03 vol.% for BK7 and 0.04 vol.% for SF11. The response times at different hydrogen concentrations varied between 160 sec (for 2.5 vol.% H₂) and 120 s (for 7.5 vol.% H₂). To test the influence of humidity at those SiO₂ inter-layer based hydrogen sensors a calibration plot with dry calibration mixtures (H₂ in nitrogen) and after passing it through a washing flask with water (100% relative humidity) was performed. There was neither a shift of the zero point (base line without hydrogen) nor any change of the sensitivity (slope of the calibration curve) within the concentration range studied (0–10 vol.%) observable. The response of the hydrogen sensor of Fig. 6 towards different other gases (nitrogen, synthetic air, 10% methane in argon) was also studied and no interferences were found within the measurement accuracy. The temperature dependence of the measured signal was also determined between 20 and 30 °C. It resulted in a linear relationship with the mathematical function:

$$S_{25^\circ\text{C}} = S - (B \cdot (T - 298.15))$$

The value for B was found to be $4.5 \cdot 10^{-4} \cdot 2.1 \cdot 10^{-5} \text{ K}^{-1}$ and corresponds to the slope of this signal vs. temperature function. This function was then used to apply automatic temperature compensation.

5. Summary

The presented theoretical and experimental feasibility study could demonstrate that the technique of SPR-spectroscopy with an Otto-configuration using palladium as specific sensor element and transducer (plasmon wave source) is well suited for a sensitive detection of hydrogen in air even at various humidity levels. Main advantages of the developed optical method are:

- High selectivity (nearly specific) → no interference by other compounds.
- High sensitivity → 0.04 vol.% that is 1% of the lower explosion limit is detectable.
- Reversible read-out within about 2 min.
- Explosion proof flexible optical fiber as light source.
- Low cost, low current LED's and photo diodes.
- Rugged construction and miniaturisation in form of a monolithic device possible.
- Further, increase in sensitivity is very likely: the influence of variable daylight on the photo diodes would be better reduced with a signal-to-noise improving lock-in amplifier (chip for around 80 €) than with blocking filters (cut-off 700 nm) and a simple RC filtering.

Acknowledgement

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