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Pd/PVDF thin film hydrogen sensor based on laser-amplitude-modulated optical-transmittance: dependence on H_2 concentration and device physics

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Abstract

A new all-optical laser-intensity-amplitude-modulated hydrogen sensor has been developed as a next-generation device to the earlier photopyroelectric hydrogen sensor. When modulated light is incident on a palladium thin film coated on a polymeric membrane, optical reflectance and transmittance signals are generated in photodiode detectors. When hydrogen gas comes into contact with the thin palladium film the gas is absorbed, altering the optical properties of the palladium and producing a signal output dependent on hydrogen concentration in the ambient. The detection range of this sensor is between 0.2 and 100% $[H_2]$ by volume and is intended for sensitive monitoring of the explosive range, 4% by volume H_2 in air. This sensor is very durable and robust; no palladium delamination or blistering occurs even after repeated exposures to pure hydrogen. The signal dependencies on increasing hydrogen concentration were found to be consistent with increased occupation of empty electronic states by electrons associated with absorbed hydrogen atoms, leading to upward shifts of the Pd Fermi level, E_F, and to decreasing optical transition probabilities. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Optical transmittance; Hydrogen sensor; Device physics

1. Introduction

Concerns about future limitations of the availability of hydrocarbons continue to encourage the widespread use of hydrogen in transportation, residential and other industrial applications as a carrier and storage medium of energy. Furthermore, present technologies often require hydrogen detection, such as the process of lead-acid battery charging. As the hydrogen infrastructure is advanced in all fronts, the development of hydrogen-safety technologies becomes of great importance.

To date work in our laboratory has been directed toward the fabrication of palladium coated polymeric polyvinilydene fluoride (PVDF) thin-film photopyroelectric (PPE) sensors [1,2]. The PPE sensor exhibits a response due to the change in the optical properties of the palladium film as well as a response to the change of the thermophysical properties of the ambient gas. However this latter response is non-selective to hydrogen and is not always desired. Therefore, a compensation channel has to be introduced or an all-optical technique must be considered. Optical monitoring of hydrogen is considered the most appropriate method owing to its inherent safe nature when compared with techniques requiring electrical measurements. For this reason there has been considerable interest in optical detection methods for determining hydrogen concentrations in the atmosphere.

Among the most sensitive optical sensors, Buttler [3], reported one that monitored the amount of light reflected from a thin palladium film at the tip of an optical fiber. It was found that the reflectance of the palladium film decreased when hydrogen was absorbed into the palladium, consistent with earlier reports in the literature [4]. Buttler's fiber-optic reflectivity sensor appears to be capable of detecting down to at least 0.2% (v/v) hydrogen in nitrogen. Oh and coworkers [5] pro-

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posed an optical transmittance (OT) sensor using a thin palladium film on a glass substrate. However blistering or delamination problems can be a problem in this type of arrangement with a solid substrate, owing to the effective lattice constant increase of Pd in the presence of a hydride [6,7]. Chadwick and coworkers [8], reported a hydrogen sensor based on the optical generation of surface plasmons in palladium/nickel alloys. Absorption of hydrogen by the palladium alloy results in large changes in reflected light from a reflection off an alloy/glass interface. This sensor appears to be capable of detecting down to 0.5% hydrogen in air. More recently, following the introduction of a Pd/PVDF PPE hydrogen sensor in this laboratory [1], a combined modulated optical-photopyroelectric hydrogen sensor was developed and reported in a paper by Wagner and Mandelis [2]. It was suggested that the most sensitive method for optically measuring hydrogen absorption into palladium is to monitor the OT change of the thin palladium film. In an effort to implement this observation a novel all-optical-transmittance Pd/PVDF sensor was developed [9] as the next generation device to the Pd/PVDF combined optical-PPE sensor [2]. This sensor has the advantages over the use of a glass substrate [5] of fabrication simplicity and peel-off avoidance due to the accommodation/matching by the PVDF polymer substrate of the Pa-film lattice constant expansion. Furthermore, with the Pd/PVDF sensor the substrate PVDF is completely optically passive and transparent to visible and near-IR radiation, unlike the Pd/WO_3/glass OT sensor of Oh et al [10]. and the Pd/MoO_3/glass OT sensor of Hamagami et al [11]. The relative complexity of these three-layer sensors and the interlayer coloration (absorptance increase) under exposure to hydrogen, make the quantitative analysis of the signals unnecessarily complicated and the sensor fabrication reproducibility and signal response very sensitive to the Pd/WO_3 or Pd/MoO_3 sputtering conditions [10,11]. In the present paper the hydrogen-concentration-dependence of optical properties of the Pd thin film will be reported and the physical origins of the sensor's signal behavior will be investigated.

2. Experimental arrangement and sensor principle

A description of the experimental arrangement has been given previously [9]. A schematic of this experimental set up is shown in Fig. 1. The experiment consisted of four subsystems: gas supply; test cell; signal generation; and data acquisition. The gas supply component mixed hydrogen and nitrogen in a homogeneous flow. The flow rate of each gas could be adjusted and stabilized before the mixture was directed into the test cell. High purity hydrogen (99.999%) and zero grade nitrogen (99.9975%) from Matheson Gas Products were used. The test cell was made out of aluminium and had a volume of 100 ml. The test cell contained an active and a reference sensor. In this way any drift due to the laser and the associated electronics was compensated by measuring the ratio of the active-to-reference signal. The active sensor had a 28 μm thick and 1 cm of diameter PVDF polymer substrate coated on one side with a thin palladium film. These films were obtained from AMP Flexible film sensors, Valley Forge, PA. The reference sensor was unelectroded PVDF with no Pd coating and was surrounded by ambient gas in the test cell. A GaAlAs, 850 nm, diode laser with a fiber optic pigtail EG & G, Vaudrevil, Ouebec) was used to illuminate both sensors. The diameter of the multimode optical fiber was 100 μm. The optical fiber was connected to an integrated beam splitter which divided the laser beam into 90 and 10% components in separate fibers. The 90% component was directed to the active element and the 10% component was directed to the reference element. The two fibers were terminated with metal-shell fiber-optic connectors. The optical fibers were mounted on the lid of the test chamber and lenses focused the beam onto the PVDF-Pd and PVDF-reference elements. When the modulated laser light (10 Hz) was incident on the palladium film an OT signal was produced, as the film allowed some of the light to be transmitted to a photodiode. When hydrogen gas came into contact with the film, it was absorbed in the palladium matrix and altered its optical properties [2,9].Schematic representations of the test cells used for transmittance and reflectance measurements are shown in Figs. 2 and 3, respectively. The test cell for reflectance measurements was a sealed aluminium box with an inlet and outlet for the ambient gas and two windows. The first window was made of a lens to focus the incident light beam to a spherical IR reflectance accessory (fxA-530 from Analect Instruments, Irvine, CA). The second window was also made of a lens to collect the reflected light and focus it to a photodiode detector. The output signals of the photodiodes from the reference and active elements were connected to a standard current follower and preamplifier that converted the short circuit current of the photodiode into a proportional voltage and produced as an output the ratio of the active to reference signals. This output was then connected to a lock-in amplifier. The data acquisition was facilitated by a personal computer through a serial port.

3. Results

3.1. Pd-thickness optimization

PVDF substrates coated with palladium of 50, 80, 130 and 260 Å thicknesses, as specified by the manufac-

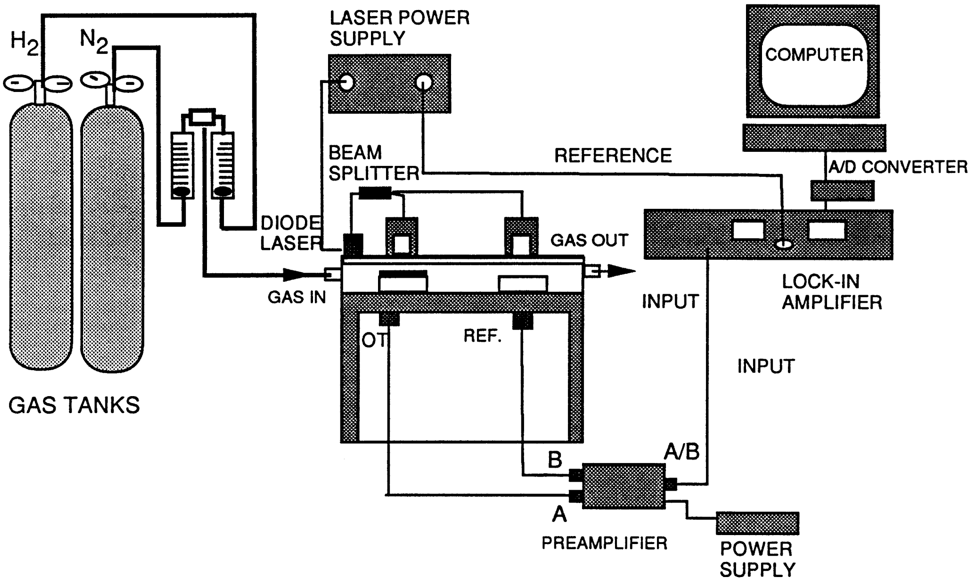

Fig. 1. Schematic representation of the experimental arrangement for the laser-amplitude modulated optical-transmittance (LAMOT) hydrogen sensor [9].

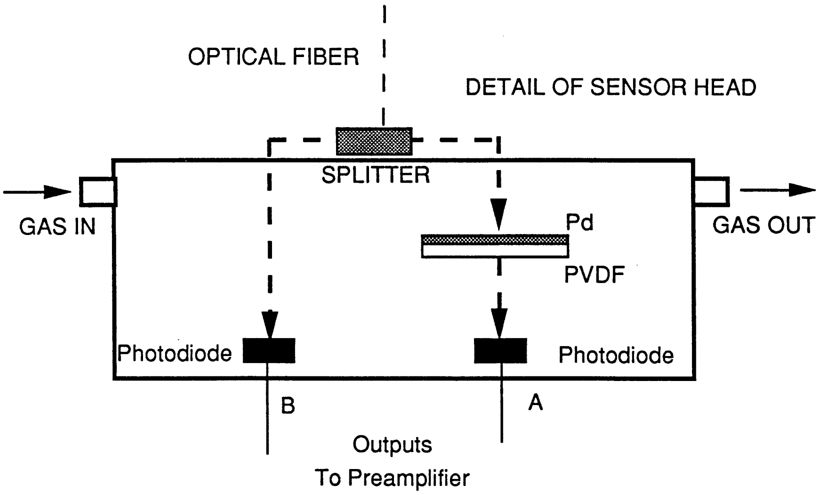

Fig. 2. Schematic representation of the LAMOT sensor principle [9].

turer, were used for the hydrogen sensor. PVDF substrates with palladium films thicker than 260 Å sharply decreased the intensity of the transmitted light, Pd films thinner than 50 Å produced very noisy signals due to low signals levels. All the measurements were carried out at room temperature (20°C). Hydrogen concentrations in nitrogen ranging from 0.2 to 100% by volume were introduced into the test cell with no visible damage (blistering) of the palladium film on PVDF, a distinct advantage over the conventional MOS hydrogen sensors [6,7,13,14]. The absence of measurable structural change of the Pd films was further corroborated by the reliable reproducibility of signals after multiple exposures to hydrogen. This has tentatively been attributed to the elasticity of the PVDF polymer substrate in accommodating the lattice constant changes of Pd upon penetration by hydrogen, hydride formation and α- to β-phase transition of the palladium hydride.

A profile of the transmission signal time dependence upon exposure to 3% by volume of hydrogen in nitrogen and 260 Å thick palladium-on-PVDF is shown in Fig. 4. The baseline corresponds to 100% nitrogen. When the 3% hydrogen mixture was introduced, the signal increased and saturated at a level representative of the steady-state signal in 3% hydrogen by volume in nitrogen, then it decreased back to the baseline when the hydrogen mixture was cut off. The signal was very stable and reversible. The signal for 1% hydrogen by volume in nitrogen showed a similar behavior except

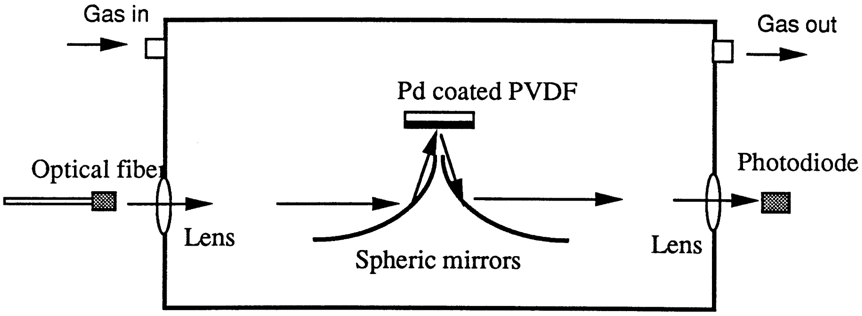

Fig. 3. Schematic representation of the test cell used for reflectance measurements.

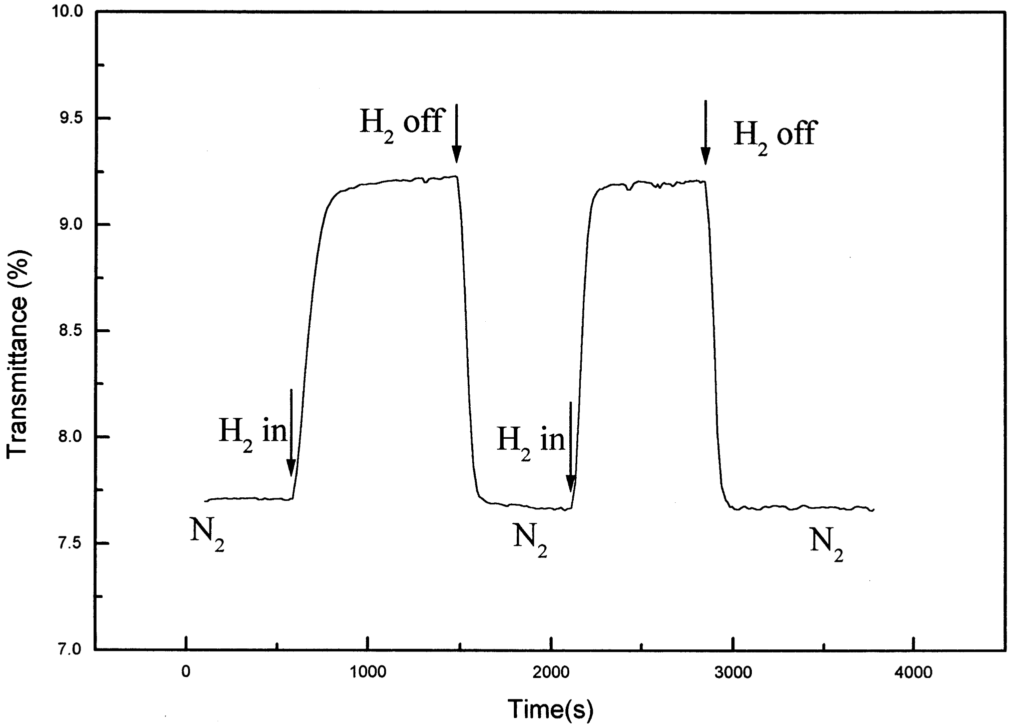

Fig. 4. OT time profile for a hydrogen concentration of 3% by volume in nitrogen. The thickness of the palladium film on PVDF was 260 Å.

that it was noisier and about ten times smaller in magnitude when compared with the previous signal. The fact that the sensor response was not linear with the hydrogen concentration is the result of the transition from α- to β-phase of the palladium hydride [9], see Fig. 5. Cycling between hydrogen and nitrogen showed a relatively fast response of the sensor: Owing to the essentially instantaneous optical response of the sensor, once the hydrogen gas is in contact with the palladium surface, the device response should be, in principle, only limited by the hydrogen dissociation and diffusion into the palladium thin film. However, the overall response in the experiments was limited by the volume of the test chamber and gas lines. The risetime from 0–90% of the saturation value was 50 s for a hydrogen concentration of 3% and a Pd film thickness of 260 Å The width of the α- to β-transition region decreased as the palladium thickness decreased. This has been observed in previous thin-palladium film studies [15,16] and has been attributed to crystallite size effects. The sensor response showed a large increase in magnitude around 2% by volume hydrogen in nitrogen, which is half of the equivalent lower explosive limit of hydrogen in air (4% per volume). This result makes the described device ideal as a hydrogen explosive mixture sensor. Measurable responses to ambient hydrogen in nitrogen were registered down to 0.2% by volume.

The change of transmittance and reflectance as a function of Pd-layer thickness for 100% N_2 and 100% H_2 is shown in Fig. 6. As expected, as the thickness of the palladium layer increases the reflectance also increases and the transmittance decreases due to optical attenuation across the film thickness. Furthermore, the indirectly measured absorptance slightly increases (a linear dependence on film thickness is expected). The change of transmittance and reflectance in the presence

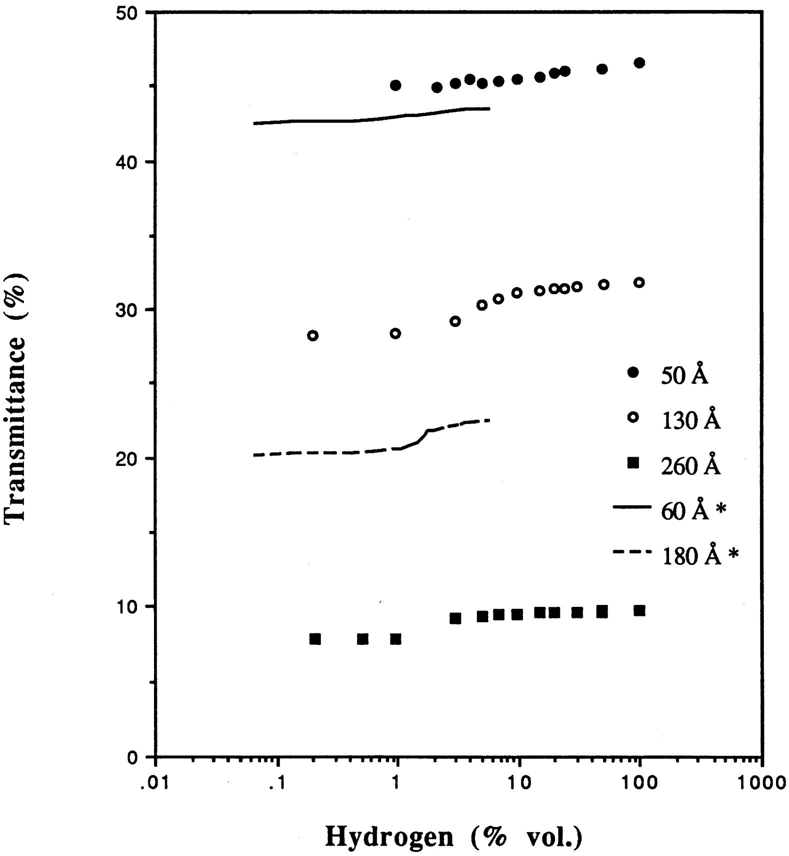

Fig. 5. Isotherms for various palladium thicknesses on PVDF. The solid (60 Å) and dashed (180 Å) lines are isotherms reported by G. Frazier and Glosser [16].

of 100% nitrogen (solid circles) and 100% hydrogen (open circles) indicate that the transmittance of the Pd film increases and the reflectance decreases when exposed to 100% hydrogen. Changes in hydrogen flow rates between 100 and 1900 ml min^{-1} did not result in any signal change in the sensor, Fig. 7. Furthermore, exposure to 100% methane and He did not produce any measurable response, thus indicating the highly selective nature of the sensor to hydrogen gas.

4. Semi-quantitative discussion of device physics

A schematic diagram of a Pd-coated PVDF sensor optical interface irradiated with modulated light is shown in Fig. 8. Assuming that the absorptance of the PVDF film is negligible at 850 nm [12] and that the back and front surface reflectivity's of the Pd layer are equal, one can formulate expressions for the OT, reflectance and absorptance at normal incidence. These optical properties of the Pd film are assumed to depend on hydrogen concentration in the Pd matrix only. Taking into account sums over infinite interreflections between the front and back surfaces of the Pd layer one can write the following expressions [17,18].

$$T_p([H]) = \frac{\{1 - R([H])\}^2 \exp[-\alpha_p([H])d]}{1 - R([H])^2 \exp[-2\alpha_p([H])d]} \tag{1}$$

$$R_p([H]) = \frac{\{1 - R([H])\}^2 R([H]) \exp[-\alpha_p([H])d]}{1 - R([H])^2 \exp[-2\alpha_p([H])d]} \tag{2}$$

$$A_p([H]) + R_p([H]) + T_p([H]) = 1 \tag{3}$$

where T_p, R_p and A_p are the device transmittance, reflectance and absorptance respectively, d is the palladium film thickness, $\alpha_p([H])$ is the absorption coefficient of Pd and $R([H])$ is the reflectivity of the gas-Pd interface. The optical absorption coefficient is related to the extinction coefficient k (imaginary part of the complex refractive index) by

$$\alpha_p([H]) = \frac{4\pi}{\lambda} k([H]) \tag{4}$$

For normal incidence, the reflectivity $R([H])$ is related to both the real and the imaginary parts of the complex refractive index:

$$R([H]) = \frac{(n[H] - 1)^2 + k^2[H]}{(n[H] + 1)^2 + k^2[H]} \tag{5}$$

These expressions for the sensor transmittance, reflectance and absorptance are in terms of the fundamental

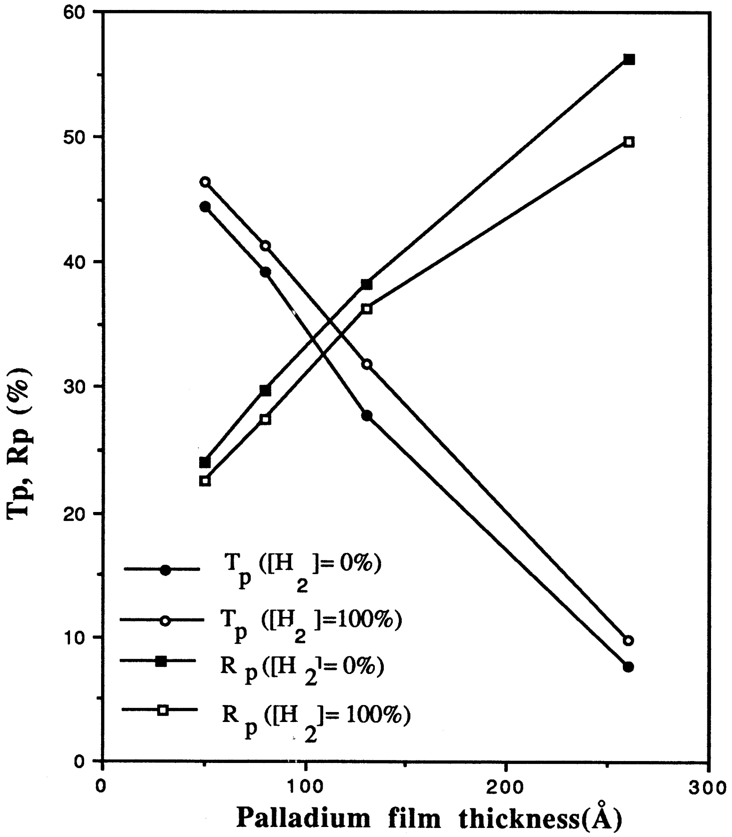

Fig. 6. Transmittance and reflectance measurements vs. thickness of palladium films in the presence of 100% nitrogen (open circles and squares) and 100% hydrogen (solid circles and squares).

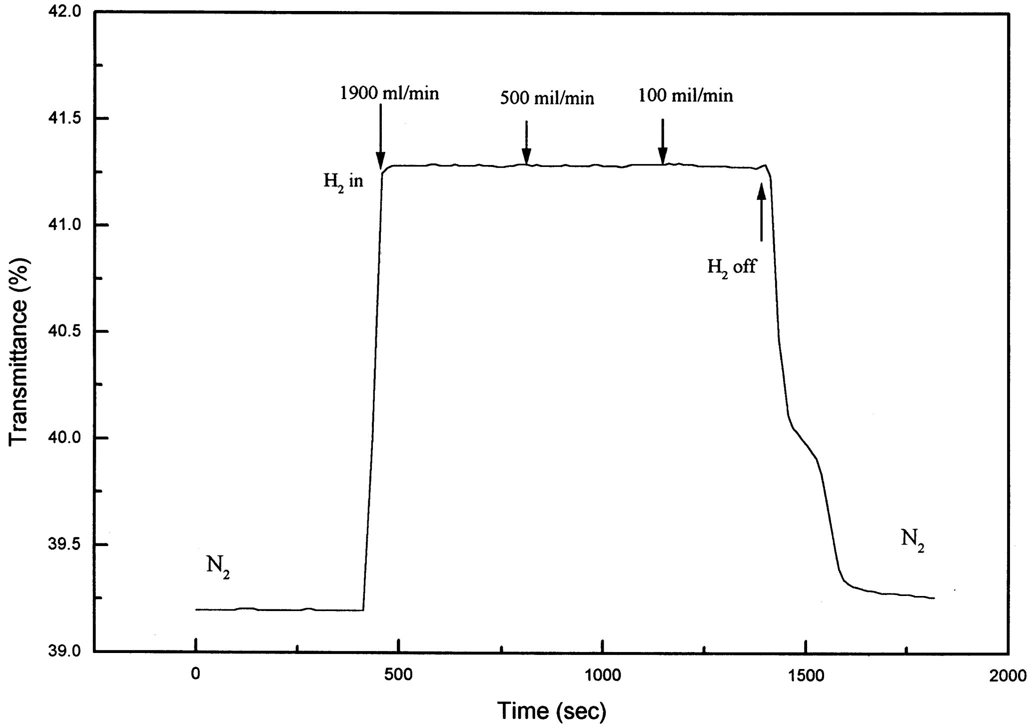

Fig. 7. Sensor response to various flow rates of hydrogen. The thickness of the palladium film on PVDF was 80 Å.

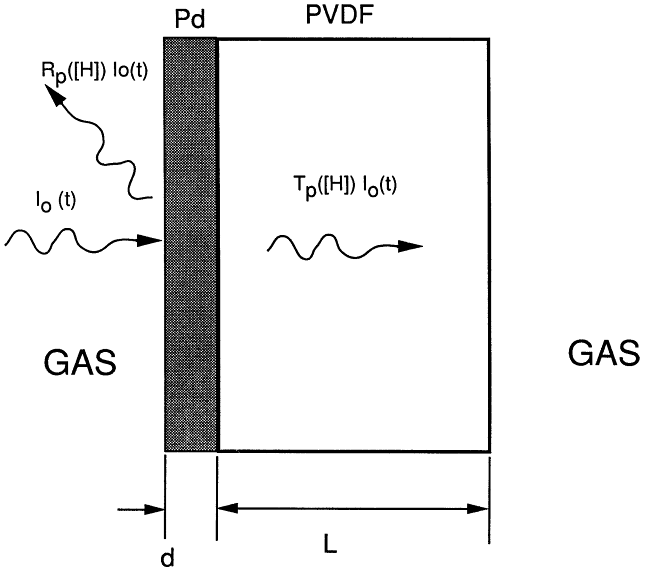

Fig. 8. Schematic geometric and optical representation of a palladium-coated PVDF film.

properties of Pd, i.e. its absorption coefficient and reflectivity. By measuring the reflectance and transmittance as a function of hydrogen concentration and using the above theoretical expressions, one can determine uniquely and quantitatively the reflectivity and the absorption coefficient for a given Pd-film thickness and for a given H_2 concentration in the ambient. The change of transmittance and reflectance as a function of hydrogen concentration for a Pd-layer thickness of 130 Å is shown in Figs. 9 and 10, respectively. The solid lines in both figures are best-fit curves using an exponential function, values of the various coefficients are shown in the figures. These results indicate that the transmittance increases and the reflectance decreases as functions of hydrogen concentration for the given Pd-layer thickness (130 Å). These results are consistent with the results shown in Fig. 6. The sharp increase in the region 0.2–5% by volume of hydrogen in nitrogen concentration indicates the phase change of the palladium hydride [16]. The absorption coefficient and reflectivity of the 130 Å thin film palladium were calculated by solving Eqs. (1) and (2) and using the best-fit curves(exponential function) for the reflectance and transmittance shown in Figs. 9 and 10. The absorption coefficient and reflectivity are shown as functions of hydrogen concentration in the gas phase in Figs. 11 and 12. There exists of course, a one-to-one correspondence between $[H_2]$ in the gas phase and the concentration [H] of adsorbed/absorbed hydrogen atoms in Pd, governed by the dissociation thermodynamics [19].

Even though the details of the electronic structure of the thin Pd film are not known for the particular deposition conditions on the PVDF substrate of the present device, the dependencies of $R([H])$ and $\alpha_p([H])$ on the ambient ($[H_2]$) concentration and hence on the [H] concentration dissolved in the palladium film under

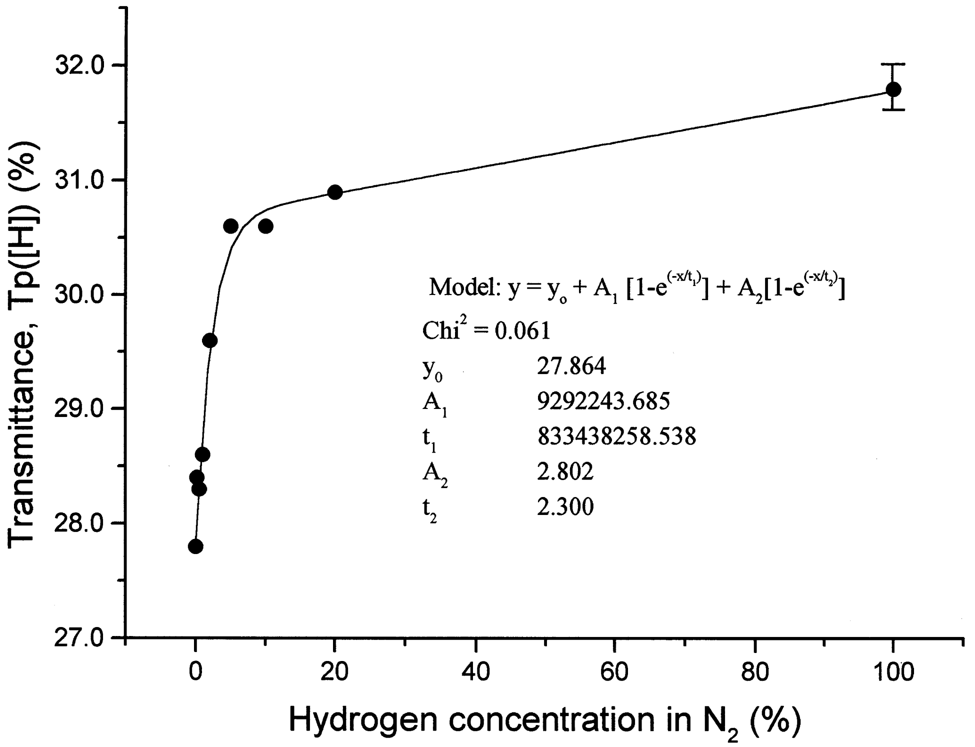

Fig. 9. Experimental transmittance for a palladium thickness of 130 Å on PVDF. The solid line is a best-fit curve of the exponential function with the parameters shown in the figure.

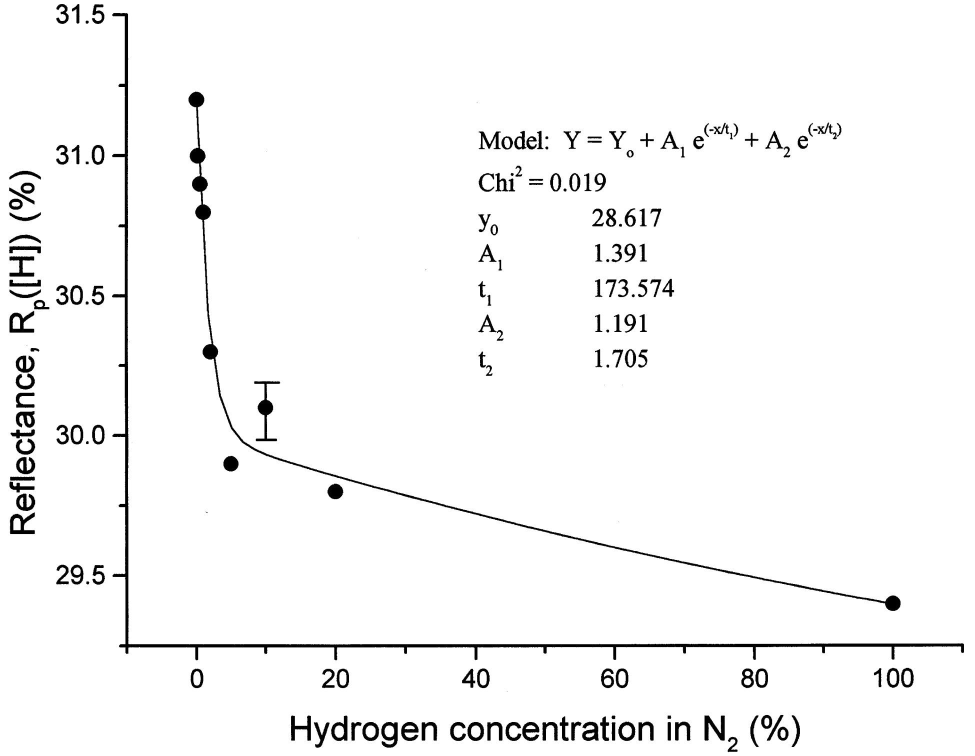

Fig. 10. Experimental reflectance for a palladium thickness of 130 Å on PVDF. The solid line is a best-fit curve of the exponential function with the parameters shown in the figure.

conditions of thermodynamic equilibrium, are consistent with the rise of the Fermi level with increasing [H] concentration [20]. The optical transition rate, $I(E)\,\mathrm{d}E$, in metals, considered in the free-electron gas approximation, is proportional to the number density of electronic states $N(E)\,\mathrm{d}E$ within an energy increment $\mathrm{d}E$ [21]:

$$I(E)\,\mathrm{d}E \propto |F_{\mathrm{if}}|^2 N(E)\,\mathrm{d}E \tag{6}$$

Where $|F_{\mathrm{if}}|^2$ is the oscillator strength denoting the square of the matrix element of the interaction potential between the initial, low-lying core electronic state $|i\rangle$ and some final state $|f\rangle$ which is a Bloch wave function at, or above, the Fermi level. Even without detailed knowledge of the density-of-states spectrum in thin Pd films, the proportionality (6) shows that the optical transition rate (and thus the absorption coefficient) is expected to decrease with a reduction in the number density of optically active states. Earlier electrical [22,23] and optical [4] measurements on Pd thin-film sensors have concluded that there exist adsorption sites at the Pd surface and at the Pd-substrate interface, which become occupied in the presence of dissociated and absorbed hydrogen atoms, acting (in the rigid-band model) as electron donors filling the 4d band and consequently shifting the Fermi level. In so doing, absorbed hydrogen removes those states from those available for an optical transition from low-lying energy states when light of sufficient photon energy impinges on the Pd thin film. It follows from relation (6) that an increase in the concentration of hydrogen atoms dissolved into the Pd thin film will result in decreased $N(E)dE$ in the neighbourhood of $E = E_{\mathrm{F}}$ and thus in a decreased optical transition rate and optical absorption coefficient, α_{p}, consistently with the decreasing trend shown in Fig. 11. Furthermore, the decrease in the upward optical transition rate from $|i\rangle$ to $|f\rangle$ with increasing absorbed hydrogen concentration [H] will also decrease the rate of downward electronic transitions from $|f\rangle$ to $|i\rangle$, which would contribute a photon to the measured reflectance. This effect will result in suppressing the Pd reflectivity R([H]) as shown in Fig. 12. The net measurable results are the decrease in sensor reflectance, R_{p}([H]) and the concomitant increase in its transmittance. Physically, the photons of the incident optical radiation, increasingly unable to interact with the Pd-thin-film electronic manifold, owing to the decreased availability of (occupied) states as [H] increases, can only pass through the (optically thin) film unabsorbed and unreflected and register in the photodiode detector as an increased transmittance. More exact calculations of the α_{p}([H]) and R_{p}([H]) dependencies on the Pd-matrix dissolved [H] concentration will require a detailed knowledge of the density of states spectrum in a given Pd thin film and are left for future consideration.

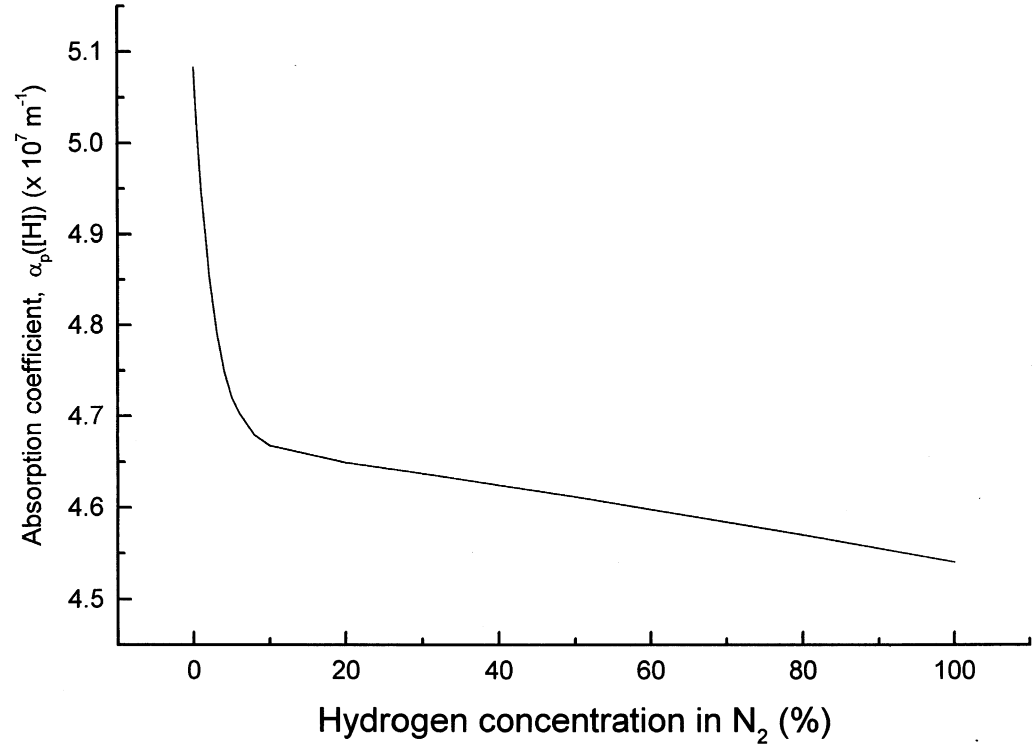

Fig. 11. Absorption coefficient vs. hydrogen concentration for a palladium thickness of 130 Å on PVDF. This curve was obtained by solving for the absorption coefficient from Eqs. (1) and (2) and using the best fit curves for reflectance and transmittance shown in Figs. 9 and 10.

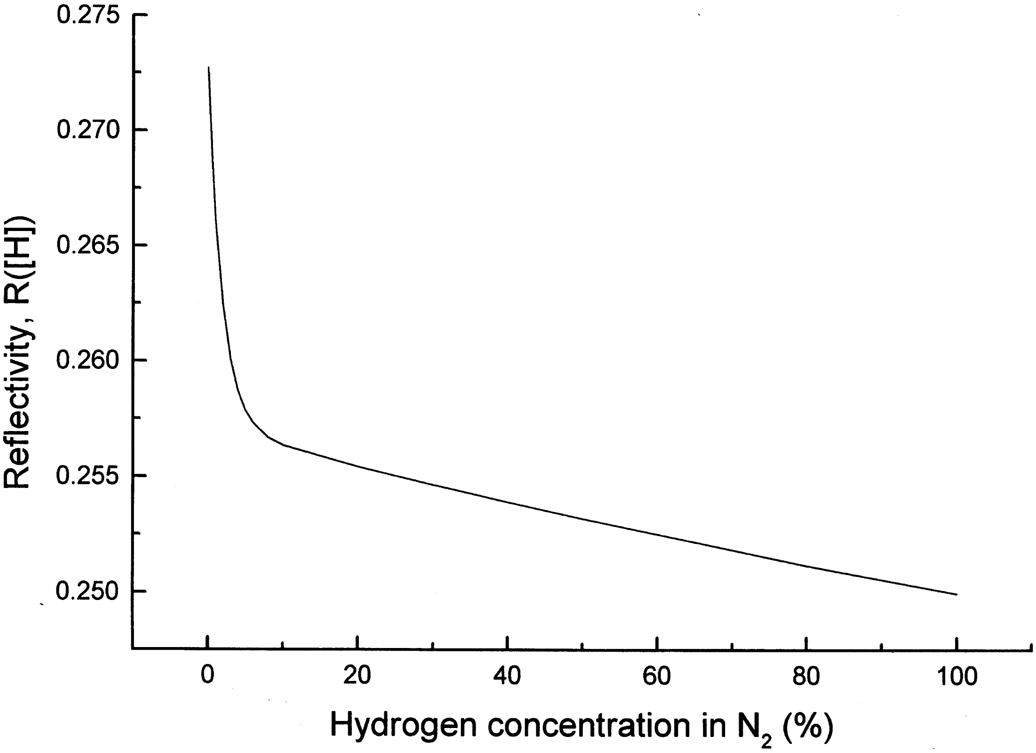

Fig. 12. Reflectivity vs. hydrogen concentration for a palladium thickness of 130 Å on PVDF. This curve was obtained by solving for the reflectivity from Eqs. (1) and (2) and using the best fit curves for reflectance and transmittance shown in Figs. 9 and 10.

5. Conclusions

A new, simple and reliable all-optical, amplitude-modulated hydrogen sensor has been developed and the physics of signal generation has been investigated. The sensor consists of a polymeric film (PVDF) coated with a Pd thin-film and operates on the principle of laser radiation amplitude-modulation, with the concomitant dependence of the Pd optical properties on the concentration of absorbed and dissociated hydrogen atoms or ions. Physically, the signal is consistent with the change in the optical absorption coefficient and reflectivity of the thin-Pd film as a result of changes in the occupation of electronic states and Fermi-level shifting in the palladium, following absorption of hydrogen and accommodation of its electrons.

The sensor is inherently safe, it does not require electrical inputs/leads and can be powered very remotely through a long optical fiber. The rise and decay times of the signal are only limited by the arrival of the hydrogen molecules to the active surface element. The sensor is absolutely selective to hydrogen and its sensitivity lies in the 0.2–100% by volume hydrogen concentration range. This device is durable and laboratory testing has shown it to be very stable, with no Pd blistering or peel-off effects. This sensor is potentially suitable for investigating optical transitions in thin Pd films and unraveling the interaction dynamics of the hydrogen–thin-Pd-film system.

Acknowledgements

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References

[1] A. Mandelis, C. Christofides, Photopyroelctric (P^2E) Sensors for trace hydrogen gas defection, Sens. Actuators B 2 (1990) 79–87.

[2] R Wagner, A. Mandelis, Separation of thermal-wave and optical reflectance effects in palladium-photopyroelctric hydrogen sensors, Ferroelectrics 165 (1995) 193–203.

[3] M.A. Buttler, Fiber optic sensor for hydrogen concentrations near the explosive limit, J. Electrochem. Soc. 138 (1991) 46–47.

[4] G. Fortunato, A. Bearzotti, C. Caliendo, A. D'Amico, Hydrogen sensitivity of $Pd/SiO_2/Si$ structure: A correlation with the hydrogen-induced modifications on optical and transport properties of α-phase Pd films, Sens. Actuators 16 (1989) 43–54.

[5] Y. Oh, J. Hamagami, Y. Watanabe, M. Tanaka, H. Yanagida, A novel palladium thin film hydrogen-detector, J. Ceram. Soc. Jpn. 110 (1993) 618–620.

[6] S.Y. Choi, K. Takahashi, M. Esashi, T. Matsuo, Stabilization of MISFET Hydrogen Sensors, Sens. Actuators 9 (1986) 353–361.

[7] M. Armgarth, C. Nylander, Blister formation in Pd gate MIS hydrogen sensors, IEEE Electron Dev. Lett. EDL/3 (1982) 384–386.

[8] B. Chadwick, J. Tann, M. Brungs, M. Gal, A hydrogen sensor based on the optical generation of surface plasmons in a palladium alloy, Sens. Actuators B 17 (1994) 215–220.

[9] J.A. Garcia, A. Mandelis, Study of the thin-film palladium/hydrogen system by an optical transmittance method, Rev. Sci. Instrum. 67 (1996) 3981–3989.

[10] Y.-S. Oh, J. Hamagami, Y. Watanabe, M. Takata, Preparation and characterization of an optically-detectable hydrogen H_2 sensor consisting of Pd/MoO_3 thin films, Sens. Actuators B 13/14 (1993) 547–548.

[11] J. Hamagami, Y.-S. Oh, Y. Watanabe, M. Takata, Preparation and characterization of an optically detectable H_2 gas sensor consisting of Pd/MoO_3 thin films, Sens. Actuators B 13/14 (1993) 281–283.

[12] Pennwalt Corporation, KYNAR Piezo Film Technical Manual, King of Prussia, PA (1983).

[13] I. Lundström, M. Armgarth, L.-G. Petersson, Physics with catalytic metal gate chemical sensors, CRC Crit. Rev. Solid State Mater. Sci. 15 (1989) 201–278.

[14] S.Y. Choi, K. Takahashi, T. Matsuo, No blister formation Pd/Pt double metal gate MISFET hydrogen sensors, IEEE Electron Dev. Lett. EDL/5 (1984) 14.

[15] M.-W. Lee, R. Glosser, Pressure concentration isotherms of thin films of the palladium-hydrogen system as modified by film thickness, hydrogen cycling and stress, J. Appl. Phys. 57 (1985) 5236–5239.

[16] G.A. Frazier, R. Glosser, Characterization of thin films of the palladium hydrogen system, J. Less-Common Met. 74 (1980) 89–96.

[17] H. Wolter, in: S. Flugge (Ed.), Handbuch der Physik, vol. XXIV, Springer, Berlin, 1956, p. 461.

[18] L. Ley, Photoemission and Optical Properties, in: J.D. Joannopoulos, G. Lukovski (Eds.), Topics in Applied Physics, vol. 56, Springer, Berlin, 1984, pp. 61–168.

[19] I. Lundström, Hydrogen sensitive MOS-structures. Part 1: Principles and applications, Sens. Actuators 1 (1981) 403–426.

[20] E. Wicke, H. Brodowsky, in: G. Alefeld, J. Volkl (Eds.), Hydrogen in Metals II, Topics in Applied Physics, vol. 29, 1978, p. 73.

[21] W. Jones, N.H. March, Theoretical Solid State Physics, vol. 2, Dover, New York, 1973, ch. 77, p. 109.

[22] I. Lundström, C. Svensson, in: J. Janata, R.J. Huber (Eds.), Gas-Sensitive Metal Gate Semiconductor Devices, Solid State Chemical Sensors, Academic Press, Orlando, 1985, pp. 1–163.

[23] R.R. Rye, A.J. Ricco, Ultrahigh vacuum studies of Pd metal/insulator/semiconductor diode H_2 sensors, J. Appl. Phys. 62 (1987) 1084.