Optimization of the Photopyroelectric Hydrogen Gas Sensor: Geometry and Temperature Measurements

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A new study towards the optimization of a new photopyroelectric hydrogen detector is performed. It has been found that the thickness of the palladium layer evaporated on the active polyvinylidene fluoride (PVDF) film plays an important role in the sensitivity of the device, but it does not influence the time response. In an effort to better understand the thermodynamics of the device during the solid-gas exchange interaction, the influence of ambient temperature has been studied. Further experiments have demonstrated device sensitivity to hydrogen even at cryogenic temperatures.

KEYWORDS: solid state sensors, hydrogen, PVDF, pyroelectric, temperature

§1. Introduction

Very recently, in a review paper published by Christofides and Mandelis[1] on solid-state hydrogen sensors, a general discussion was presented including a critical comparison of the capabilities and parameters of various conventional sensors. Many of these detectors have been found to be problematic due to noise introduced by temperature fluctuations and especially due to the requirement of high ambient temperature (120 to 240°C) for their good operation and performance.[2] In 1988, the development of a new photopyroelectric Pd-PVDF (polyvinylidene fluoride) hydrogen detector was undertaken in our laboratory.[3-7] Initial results have been shown to be very promising toward the development of a new type of gas detection and analysis photothermal solid-state device, partly based on polymer-metal interface phenomena. The new photopyroelectric (PPE) device not only seems to overcome many of the temperature-fluctuation-related noise problems, but it also has an easy, simple, and inexpensive fabrication process. It is thought to be the first non-passive device operating on electronic polymer-metal junction phenomena. This device has attracted attention as a new trace hydrogen sensor[8,9] and has substantial potential for extension to the detection of other gases.

The operation of the PPE detector has already been described in the past and is based on thermal wave generation in the pyroelectric polymer PVDF,[3-7] which results in an alternating voltage due to the photopyroelectric effect.[10]

The device possesses many advantages such as high detectivity through a broad temperature range, as will be concluded from this work, fast response, high selectivity, durability and reversibility at room temperature. Wide temperature response and high room temperature sensitivity are thought to be the main advantages of our device over the well-known metal-oxide-semiconductor field-effect transistor (MOSFET) devices.[2] The work of Lundström *et al.*[11] has definitely established the working detection mechanism of those devices.

This paper deals with the most recent results obtained with the photopyroelectric hydrogen sensor and focuses on two major objectives: (a) the device optimization; and (b) the physical understanding of the detection mechanism. The necessary instrumentation elements are given in §2. Section 3 presents some experimental results and discussion, followed by conclusions in §4.

§2. Instrumentation and Experimental Elements

An overview of the experimental setup of the PPE sensor is shown in Fig. 1(a). The instrumentation is very similar to the one presented previously[3,4] with some extensions (such as the temperature control system and the capacitance meter) and some minor differences. An infrared laser beam served to produce alternating temperature gradients on the Pd-PVDF and on reference Al–Ni–PVDF films, which, in turn, generated ac voltages due to the photopyroelectric effect. Exposure to hydrogen gas was subsequently shown to produce a controlled differential signal between the Pd and reference electrodes; this was attributed to the adsorption, absorption and dissociation of hydrogen molecules on the Pd surface and bulk.

The signal generation and analysis section of the new photopyroelectric detector is also described in Fig. 1(a). The instrumentation consisted of an infrared laser diode powered by an ac current supply. The intensity-modulated output laser beam was directed to a 3-way model fiber-optic coupler where it was split into three unequal parts. One of the three beams was directed to a photodiode (PD), the output of which was then sent to the "monitor" input of the home-made laser current supply for preamplification and feedback control of the laser current, as well as to a miniaturized purpose-built lock-in: in Fig. 1(b) one can see a schematic diagram of the home-made miniaturized differential lock-in analyzer. The lock-in was equipped with a ratio option, allowing a normalized demodulated analog function output. A substantial degree of simplification and miniaturization has thus been achieved, with further incorporation of the laser power supply and the laser diode itself soon to be implemented. Our goal is to eventually
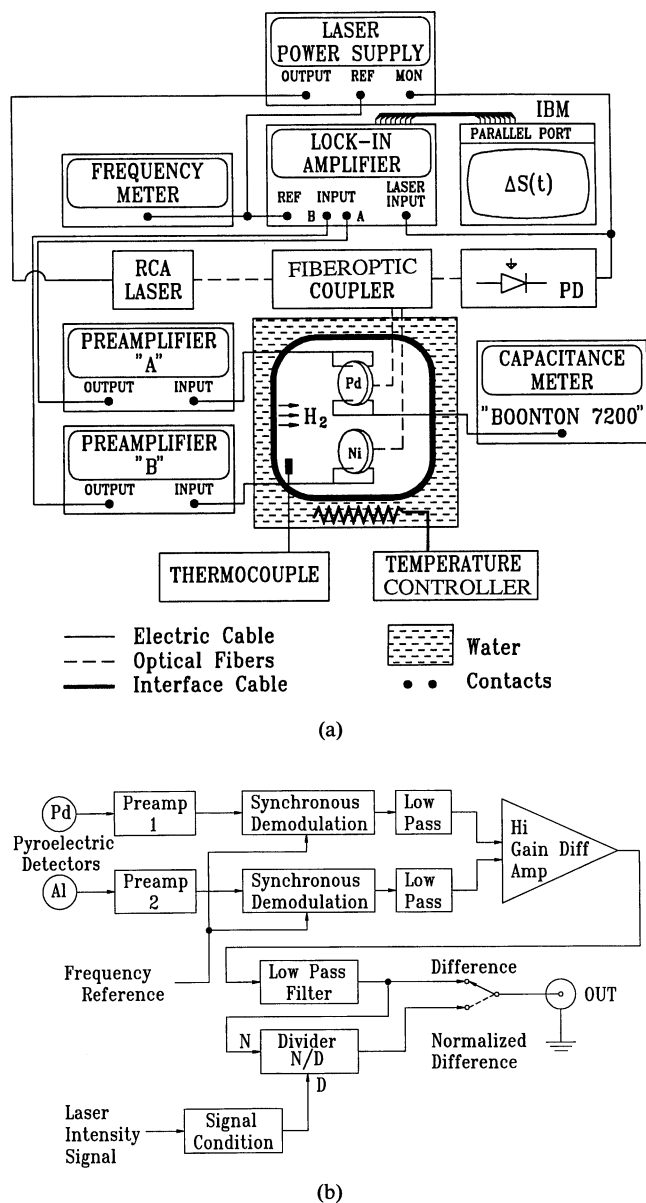
Fig. 1. (a) Schematic diagram of the photopyroelectric detector set-up. (b) Schematic diagram of the home-made miniaturized differential lock-in analyzer.

develop a portable Pd-PVDF PPE sensor head with simple input/output connections to readout voltmeters and alarm circuits via the integrated power supply/detection electronics box. The feedback control consisted of using the optical reference signal to correct for temporal intensity variations in the modulated laser beam. The modulation frequency of the infrared beam was monitored with a frequency meter. The two PPE signals were then connected to the differential lock-in analyzer following two low-noise Ithaco (Model 1201) bandpass-filtered preamplifiers which were referenced by the *ac* laser current supply. The preamplifier gains were adjusted to minimize the lock-in output signals at the beginning of the experiments. The use of the lock-in amplifier technique in signal filtering and normalization enables us to obtain stable differential output signals by adjusting the two gains between 10 to 10000. Providing the input signals

from the preamplifier are set to about the 10 V level, we can achieve $\Delta S \approx 10^{-8}$, where

$$\Delta S = \frac{S_2 - S_1}{S_R} . \tag{1}$$

S_1 and S_2 are the signal outputs from the two channels and S_R is the reference signal. Finally, the home-made lock-in amplifier is interfaced through a parallel port with an IBM PS/2 computer for data analysis and detection. Software capable of data output and data readouts has been developed for this purpose.

It is important to note that some of the experiments presented below have been performed without a reference PVDF signal. Under normal circumstances, a certain amount of dc drift inherent in the signal due to instrumental limitations exists. This is the reason for the use of low-drift preamplifiers in this study. Our pursuit of minimization of this drift with regard to laser modulation has revealed that a modulation frequency of 40 Hz is at least one order of magnitude in signal stability better than 5 Hz.

For temperature control, a long heat exchanger has been used in order to ensure that the temperature of the incoming gas flow would be the same as that of the sensor itself. A thermocouple allowing the monitoring of the cell temperature during the experiments with a precision of $\pm 0.2°C$ has been used. An automatic controller heater (Fenal Model 140) equipped with a second thermocouple has also been used for temperature stabilization in the range of 20 to 60°C. Lower temperatures have been attained using dry ice (measurements down to $-63°C$).

§3. Experimental Results and Discussion

3.1 The influence of the Pd-PVDF device history and of the Pd thickness on the PPE signal

Important "negative learning" concerning the surface of the Pd layer has been achieved in the course of this work. It has been discovered that the history of the Pd-PVDF active element (Pd deposition process, exposure to air) is an important factor affecting performance. For example, a Pd-PVDF film exposed to laboratory air for several months becomes inactive in the presence of H_2, presumably due to oxidation and pollution (impurities) diffused in the Pd layer.[12] Christofides and Mandelis have also shown the influence of oxygen on the Pd surface by using a piezoelectric sensor.[13] However, this phenomenon is reversible and the film can be reactivated after several exposures to pure hydrogen.[13] It was found necessary to keep the Pd film in a low vacuum environment in order to protect it from various types of impurities. Other Pd-based sensors present similar long-term contamination effects and become impaired.[2,14] The definite advantages of Pd-PVDF are that (i) the contaminated active element, Pd-PVDF film, may be changed at essentially no extra cost; and (ii) a sheet of Pd-PVDF capable of yielding over 100 active elements can be easily and effectively stored under low vacuum or a positive N_2 overpressure for long periods of time.

The sensitivity of the Pd-PPE device depends strongly on Pd thickness. This work has unequivocally shown

that thick Pd layers (*ca.* 1,500 Å) exhibit a strong response to H_2 gas, contrary to our earlier experience.[4] It is hypothesized that this is the result of improved Pd deposition methods on PVDF.

Figure 2 shows the variation of the normalized PPE differential signal ΔS as a function of the logarithm of the Pd thickness L in the case of pure hydrogen at 20°C. The logarithmic scale has been used only for convenience. To obtain these measurements, Pd was deposited on pyroelectric PVDF film of 28-μm thickness. In Fig. 2, the datum represented by a large circle well above the straight line (at $L = 130$ Å) corresponds to the only 52 μm thick film, as expected from capacitive response. Furthermore, it was found that Pd-Cu-PVDF films respond in the same quantitative way as the Pd-PVDF films. This is reasonable, because when Cu is used as an interfacial electrical conductor between Pd and the PVDF surface, one expects no electric field in that layer:

$$E = -\text{grad } \phi(r) = 0 \qquad (2)$$

or

$$\phi(r) = \text{constant}; \qquad (3)$$

i.e., there should be no measurable voltage drop across the electrical conductor. This result shows that the hydrogen-sensing action can be achieved upon Pd deposition, even with previously metallized PVDF, and is indicative of the fabrication flexibility built into our sensor.

In terms of signal trends shown in Fig. 2, qualitatively similar results have been reported by D'Amico et al.,[15] who performed measurements using a palladium-coated surface acoustic wave (SAW) device. These authors studied the effect of the palladium thickness on the SAW response in a thicker range of Pd (1900 to 7600 Å). Buccur et al.[16] have also studied the effect of the Pd thickness on the hydrogen/Pd interface by using a piezoelectric quartz crystal microbalance. These authors have further examined the effect of thickness on the rate of hydrogen desorption. The increase of the photopyroelectric signal with the Pd thickness is consistent with an increased pro-

ton charge density in the Pd matrix. A high quality, fast capacitance meter (Boonton 7200) has been used for direct capacitance measurements in the presence and absence of hydrogen. These measurements have shown no measurable (i.e., <1 pF) capacitance change. It is important to note that, as was shown by Lundström et al.,[2] their MOSFET-based device presents a capacitive response in the presence of hydrogen gas of the order of 100 pF in a hydrogen concentration of 1200 ppm. However, the detection mechanism in the MOSFET device is fundamentally different from that of the Pd-PVDF device. The capacitance insensitivity of the latter device to [H] presence shows that no depletion layer participates in the PPE response, which is consistent with the hypothesis that only virtual charge (i.e., displacement or polarization charges) on the PVDF side of the interface may be responsible for coupling to the externally introduced charge density on the Pd side of the interface.[7] In order to test the influence of the Pd thickness on the time response of the device, we plot in Fig. 2 the time response as a function of palladium thickness. There is no significant effect of the Pd thickness on the time response, which remains approximately constant and close to 3 minutes for every thickness and for wide thickness ranges, between 34 and 1588 Å. From the known diffusion coefficient of hydrogen in bulk Pd at room temperature ($\approx 2 \times 10^{-7}$ cm^2 s^{-1}),[17] it follows that H atoms diffuse into the bulk over a mean distance of 1 μm of Pd in 5 seconds.[18,19] This estimate is consistent with Fig. 2, which clearly indicates that H diffusion through the Pd layer is not the rate-limiting factor in the kinetics of the Pd-PVDF sensor. Buccur et al.[16] have also mentioned that for very small thickness (<5000 Å) the diffusion is very rapid and it is not easy to see the difference in time response. An attempt to give a quantitative interpretation to the observed rates of adsorption/absorption/desorption based on signal response, through use of the well-known Wagner model[20] did not succeed because of our working conditions (STP). Very low pressures ($<10^{-5}$ Torr) will be needed for quantitative kinetic analysis. Comparisons with Wagner's model resulted in slower than predicted rates, which is indicative of the presence and influence of surface impurity molecules controlling the kinetics of the adsorption/absorption/desorption process. Specifically, the kinetic process under STP conditions takes 180 seconds, which is 35 times longer than under clean surface conditions. These observations point to the importance of further experimentation under high vacuum and with molecularly clean surfaces.

3.2 The influence of ambient temperature on the PPE sensor

A very important property of the Pd-PVDF sensor proved to be its extraordinary ability to sustain unattenuated sensitivity at low temperatures continuously monitored down to -63°C and also qualitatively observed in the liquid nitrogen temperature range. No other H_2 sensor, to our knowledge, has ever been reported with such ability (or, indeed, with any response at all below 20°C). As such, this property makes the sensor very promising for
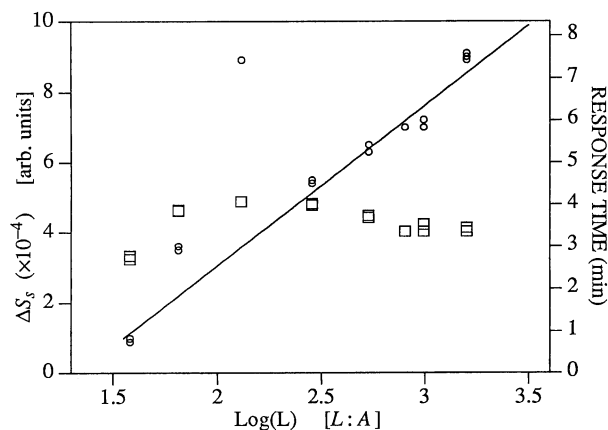
Fig. 2. Photopyroelectric saturated signal ΔS_s (○ ○ ○ ○) and response time (□ □ □ □) as a function of Pd thickness in the presence of pure hydrogen at room temperature. Flow rate: 500 ml/min ($T = 18$°C and $f = 32$ Hz).

outdoor detection in cold climates and for fundamental studies of the hydrogen-palladium system. Temperature measurements from $-63\,°C$ to $+50\,°C$ have been successfully performed, indicating that good detectivity of the sensor is possible across a broad range of low temperatures. In fact, due to the high sensitivity of the pyroelectric effect to temperature fluctuations, special attention has been paid to obtaining high-stability background signals prior to introducing hydrogen gas to the chamber. In the range of -5 to $15\,°C$, achieving stabilization was very different from that in the rest of the reported temperature range due to some supplementary problems introduced on account of signal hysteresis.[21] In the absence of hydrogen gas in that temperature range, the background signal depends on the direction of temperature variation. Another important problem with low-temperature measurements (below $0\,°C$) was presented by the extreme difficulty in evacuating the hydride from the palladium. Due to this problem, low-temperature data acquisition had to be preceded by cycling up to room temperature in order to clean the surface (and bulk) of the palladium. Figure 3 shows the variation of the photopyroelectric signal vs temperature, which was found to satisfy a $T^{-1.4\pm0.2}$ law. This dependence is consistent with a thermostatistical mechanism based on hydrogenic image dipoles performing independent vibrational and librational motions about the polarization field axis of the pyroelectric.[7] Figure 4 shows the variation of the response and recovery time as a function of the working temperature. We note that the response time of Fig. 4(a) depends strongly on temperature: it exhibits a minimum at $ca.$ $20\,°C$ and is seen to increase with decreasing temperature. Although the presence of the minimum is certainly due to several (more than one) mechanisms, the low-temperature portion of the curve is consistent with a gradual "freezing-in" of the PVDF molecular dipole response to the $[H^+]$-induced interface bias. Such a mechanism based on the lowering of the molecular oscillator energy with decreasing temperature would affect (delay) the temporal change of the pyroelectric coefficient in response to the $[H^+]$ field.[7] On the

(a)

(b)

Fig. 4. Photopyroelectric response (a) and recovery (b) times as functions of temperature in the presence of pure hydrogen. Flow rate: 500 ml/min (f = 32 Hz, L = 1588 Å).
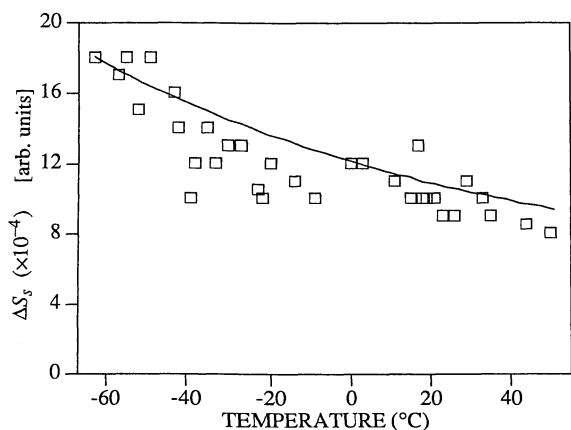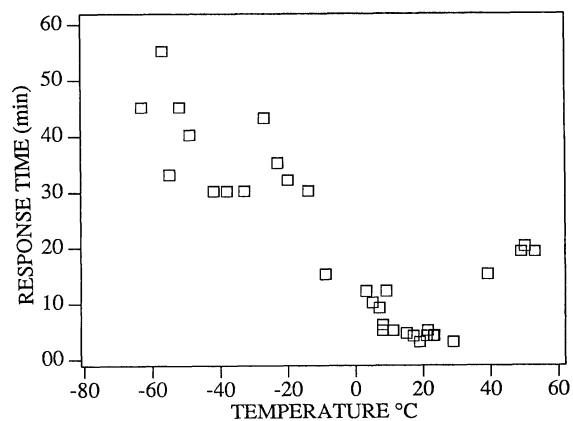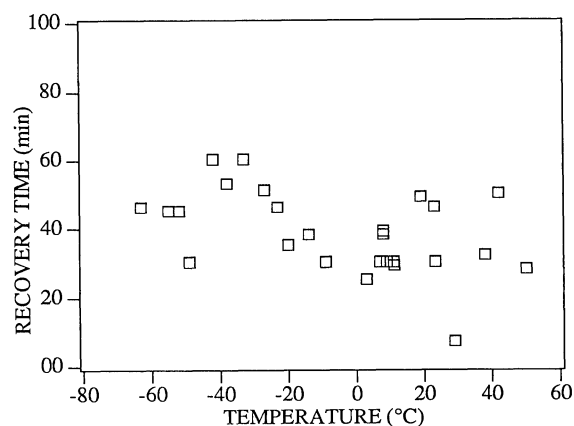

Fig. 3. Photopyroelectric saturated signal ΔS_s as a function of temperature in the presence of pure hydrogen. Flow rate: 500 ml/min (f = 32 Hz, and L = 1588 Å). Solid line represents the best fit to the data ($T^{-1.4}$ law).

other hand, the [H] concentration in the Pd bulk is expected to build itself up to the thermodynamic equilibrium value more slowly at low T, and this effect can also delay the shift of the Pd metal work function with hydrogen, $\Phi_{Pd}([H], T)$, thus increasing the response time of the device.[7,9] No tentative explanation of the increasing response time at the high-T portion of the curve in Fig. 4(a) is possible without further experimentation. No strong dependence on temperature of the recovery time can be seen in Fig. 4(b).

§4. Conclusions

In this paper, we presented some new results toward the optimization and mechanism of the new photopyroelectric hydrogen sensor. Our experimental results suggest that the investigated PPE sensor structure can be implemented as a hydrogen detector, under ambient and low-temperature conditions with flexibility in the substrate geometry on which Pd is deposited. It has been shown that this detector presents high potential towards the study of gas-surface interactions, especially at low temperatures where conventional sensors present problems or are inoperative. It has been found that the thickness of Pd evaporated on the PVDF film plays an im-

portant role in device sensitivity, but not in the value of the response time. The observed response times are likely to be surface impurity-controlled and much longer than would be expected from simple gas clean surface kinetics.

Acknowledgments

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