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Detectivity comparison between thin-film Pd/PVDF photopyroelectric interferometric and optical reflectance hydrogen sensors

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A novel dual photopyroelectric interference (PPEI)/optical reflectance (OR) solid-state hydrogen sensor system has been developed and demonstrated. Based on the recently developed PPE-interference technique and the variations of optical and electronic properties of Pd metal in the presence of hydrogen, simultaneous signal responses were obtained from a polyvinylidene fluoride (PVDF) thin-film detector and an optical photodiode. The dual measurement of PPEI and OR channels provides not only a more reliable sensor system, but also a powerful tool to identify the operating mechanism(s) in the process of Pd/PVDF/hydrogen interaction. The experimental results show that the detectivity and the signal dynamic range of the PPEI method are much higher than those of the OR method due to the suppression of the large base-line signal and the signal noise. The comparison of PPEI and OR results reveals that both signals are mainly due to the same electronic mechanism. © *1999 American Institute of Physics.* [S0034-6748(99)02311-4]

I. INTRODUCTION

It is widely known that palladium is capable of absorbing/desorbing large amounts of hydrogen reversibly, and this has been making it a promising material for the creation of sensitive hydrogen detectors.[1] Mandelis and Christofides have reviewed a wide variety of Pd-based hydrogen detectors in their book on solid-state gas sensors.[2] Lundstrom, Shivaraman, and Svensson have introduced Pd-gate metal–oxide–semiconductor transistors and Pd-gate metal–insulator–semiconductor sensors.[3,4] Steele and MacIver,[5] and D'Amico, Fortunato, and Petrocco[6] have shown that a Pd–CdS and a Pd–insulator Schottcky barrier diode, respectively, exhibited a response to hydrogen. Furthermore, a surface acoustic wave (SAW) sensor,[2,7] an optical fiber sensor,[2,8] and an optical interferometric sensor[9] have also been developed. All the above sensors employed glass or silicon as the substrate material on which palladium was coated as the active membrane. To date, work in our laboratory has been directed toward the fabrication of a different kind of pyroelectric material-based [e.g., polyvinylidene (di)floride (PVDF)] and Pd-coated thin-film photopyroelectric (PPE) sensors.[10–14] This kind of sensor has advantages over the use of a glass or silicon substrate[3–9] in terms of fabrication simplicity and peel-off or blister avoidance, presumably due to the accommodation/matching by the PVDF polymer substrate of the Pd-film lattice-constant expansion. Mandelis and Christofides detected down to 0.075% hydrogen concentration in a flowing H_2+N_2 mixture by employing two detectors (one active and one reference) and two-signal processing electronics.[10] Since then, efforts have been made to simplify the detection system by employing either a purely optical method[11,12] or by use of a single-detector method.[14] The detectivity, signal quality, and signal dynamic range, however, are compromised due to the large base-line signal and the relatively small signal change coming from the interaction of Pd with hydrogen. In addition, optical noise is also introduced through the intensity fluctuation of the incident light in the single-beam scheme, which further compromises the detectivity. As regards the mechanism of the signal generation, several hypotheses have been made to interpret the experimental results, including the changes in optical properties (surface absorptance and reflectivity) and electronic properties (pyroelectric coefficient of the PVDF and work function of Pd).[10,11,13,15] The relative contribution from each of these possible mechanisms, however, is not clear. In this article, a novel dual and sensitive Pd–PVDF hydrogen sensor is described, in which one channel is based on the photopyroelectric effect[16] and the recently developed PPE-interference (PPEI) technique,[17] while the other channel is based on purely optical detection by measuring the variation in surface optical reflectance of Pd before and after the exposure to hydrogen. The former channel is a fully destructive purely thermal-wave interferometric differential operation mode of high-detectivity, high-signal dynamic range, and a zero-base-line measurement. The latter channel is a more conventional detection mode with proven detectivity of 1000 ppm H_2 in N_2.[18] The design of the new sensor, which utilizes both active surfaces of a PVDF thin film, makes it possible to implement the dual PPEI and optical reflectance (OR) measurements with a single PVDF thin film. The availability of signals from two independent channels yields not only a more reliable detection, but also a powerful tool to study the optical contribution in the PPE response, and therefore, to identify the dominant mechanism in this kind of sensor. The main goal of this study is the fabrication and testing of a Pd–PVDF hydrogen sensor of improved detectivity over the thin-film Pd optical reflectance sensor.

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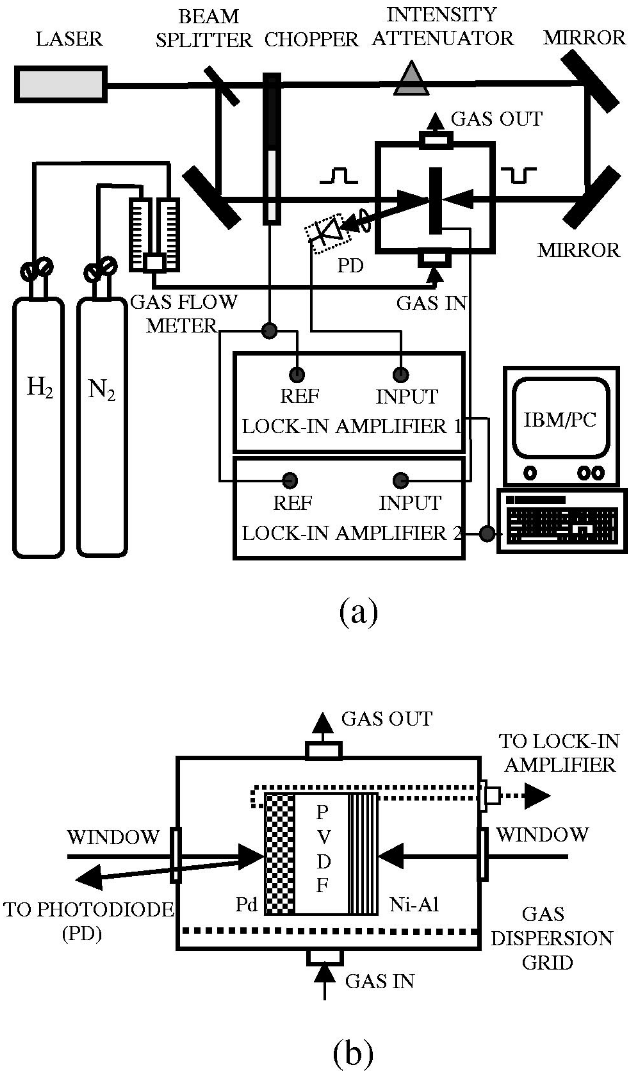

FIG. 1. (a) Schematic representation of a dual OR and PPEI sensor setup; (b) Cross-sectional detail of the test cell.

II. INSTRUMENTATION AND SENSOR PRINCIPLE

A schematic representation of the experimental arrangement is shown in Fig. 1(a). The experimental setup consists of four subsystems: gas supply; test cell; signal generation; and data acquisition. The gas-supply component mixes hydrogen and nitrogen in a homogeneous flow. The flow rate of each gas can be adjusted and stabilized before the mixture is directed into the test cell. High-purity hydrogen (99.999%), zero-grade nitrogen (99.9975%), and 1.07% hydrogen in nitrogen by volume from Matheson Gas Products were used to obtain the desired hydrogen concentrations. The test cell was made of aluminum with an inlet and outlet for the ambient gas, two optical windows for the incident light to enter from opposite sides of the active PVDF element, and had a volume of ~150 ml. The test cell contained a Pd–PVDF–NiAl thin film, which was mounted on an aluminum base. Three different Pd–PVDSF–NiAl thin films were used; they had the same thickness PVDF layer (52 μm), and the same thickness NiAl coating (layers of 15 nm Ni +35 nm Al) on one surface. The opposite surface was coated with three different Pd thicknesses (6.5, 25.6, and 53.4 nm) to optimize the sensor response. A cellular plastic plate was placed in front of the gas inlet to further disperse the gas into a homogeneous stream before it reached the thin film. Special care was also taken to introduce the gas flow parallel to the surfaces of the Pd–PVDF–NiAl film so that both surfaces could be exposed to the gas mixture under the same conditions, which reduces gas-flow anisotropy bias on either surface of the sensor. A detailed schematic representation of the test cell is shown in Fig. 1(b). Two laser beams (intensities I_1 and I_2) were obtained from a single He–Ne laser beam (15 mW) by use of a beam splitter. They were modulated with a mechanical chopper at the same angular frequency (ω) and with a fixed, adjustable phase shift ($\Delta\varphi$). One beam was incident onto the front (Pd coating) and the other beam was directed to the rear (NiAl-coated) surface of the PVDF detector from opposite directions. The signal-generation part includes two output channels: the OR signal, which is received through a photodiode intercepting the reflected laser beam from the Pd-coated surface; and the PPEI signal, which is generated inside the PVDF due to thermal-wave interference. Different ratios of the two incident intensities and the phase shift between the two beams yield different thermal-wave interference patterns inside the PVDF detector.[17] A fully destructive interferometric pattern is produced when the intensities of the two beams are identical and the phase shift between them is 180°. This destructive operating mode of the PVDF detector yields a sensitive coherent differential method to detect minute changes in the PPE output signal using a single transducer.

It is well known that Pd metal interacts reversibly with hydrogen gas to form a hydride. Associated with these compositional changes are changes in the optical and electronic properties, such as optical reflectance, absorptance, and electrostatic charge distribution in the palladium.[1,8,11–13,19,20] In contrast, all the properties of the NiAl coating remain unchanged before and after the exposure to H_2 gas. Therefore, the PPEI signal is differentially produced by the changes in optical and electronic properties between the Pd coating and the NiAl coating on both sides of the PVDF detector. The OR signal is produced only due to the change in optical reflectivity of the Pd surface before and after the exposure to H_2 gas. The OR and PPEI output signals are then fed to two lock-in amplifiers, respectively. The data acquisition was facilitated by a personal computer through a serial port.

III. DETECTION OF HYDROGEN/NITROGEN MIXTURE AND DISCUSSION

A. Identification of system noise

Before the OR and PPEI responses to H_2/N_2 mixtures were studied, the operation of the sensor under fully destructive interferometric (FDI) conditions was tested and the system noise levels from the OR and PPEI channels were identified. In this experiment, two laser beams were directed to the two surfaces of the PVDF detector very close to normal incidence. The reflected light from the Pd surface was directed to a photodiode through a lens. The relative intensities and the phase shift between the two incident beams were then adjusted, so that fully destructive thermal-wave interfer-

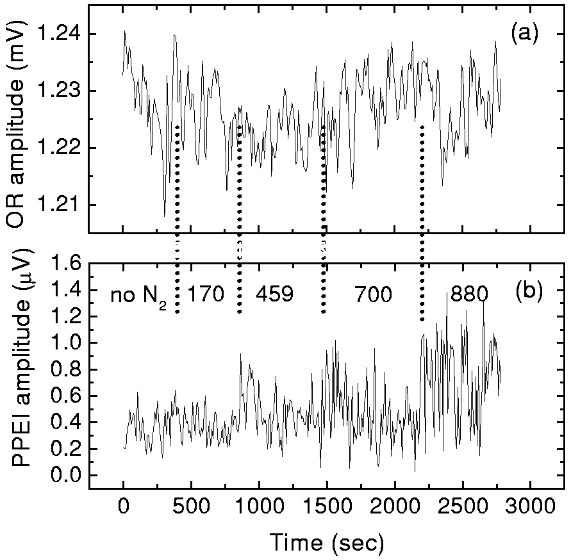

FIG. 2. System noise evaluation of OR and PPEI channels at different N_2 flow rates. The numbers shown in the graph represent the N_2 flow rate, in (ml/min).

ence was obtained, i.e., the PPE output signal was adjusted to zero before introducing any gases into the test cell. Figure 2 shows the system noise levels which were obtained simultaneously from the PPEI channel in FDI and from the OR channel for various N_2 flow rates using a PVDF detector with 53.4 nm Pd coating. The modulation frequency was 10 Hz. It can be seen from Fig. 2(a) that the system noise level from the OR channel is about 20 μV and it seems that the different N_2 flow rates have no effect on the noise level. This phenomenon is understandable due to the fact that the OR signal is purely optical, and as such it should be independent of any nonoptical perturbation, such as small temperature fluctuation or gas-flow turbulence in the test cell. The source of this noise is believed to be mostly from the purely optical fluctuation of the incident beam, the system electronic noise, and the employment of low instrumental sensitivity due to the large base-line signal ($\sim$1.22 mV). In comparison, the PPEI signal output in Fig. 2(b) shows a much smaller noise level than that in the OR channel. The noise level is only about 0.4 μV if there is no N_2 flow into the test cell. With the increase of the N_2 flow rate, the noise level increases only to the level of about 1.2 μV maximum at the N_2 flow rate of 880 ml/min (maximum flow rate available in the experiment). This low noise level can be attributed to the differential FDI mode, in which the optical and electronic noise is greatly reduced due to its real-time coherent cancellation within the single PVDF detector, thus allowing the employment of high instrumental sensitivity. In conclusion, the PPEI channel exhibits an improved noise level by approximately a factor of 20 over the OR channel, despite the fact that the OR channel is immune to flow turbulence inside the test cell.

B. OR and PPEI responses using various Pd-coating thicknesses

Three PVDF thin-film sensor elements with the same PVDF substrate of 52 μm thickness, sputter coated with the same NiAl electrode on one surface but different Pd coatings (53.4, 25.6, and 6.5 nm, respectively) on the other surface, were investigated. Figures 3 and 4 show typical OR and PPEI signal responses using the PVDF detector using 53.4-nm-thick Pd. In the experiment, the instrumental PPE operating mode was adjusted to FDI so that the PPEI output signal was equal to zero before any gases were introduced into the test cell. The signals from the OR and PPEI channels were then recorded simultaneously as a function of time under various H_2 concentrations in N_2 by volume. The modulation frequency was 10 Hz and the experiments were conducted at room temperature. Both Figs. 3(a) and 4(a) show that the response time δt (time required for the OR and PPEI signals to rise to the saturated amplitude following the introduction of H_2 in the cell) varies with H_2 concentration. The response time decreases dramatically with increasing H_2 concentration, while the signal level at saturation slightly increases with increased $[H_2]$ concentration. These features can be understood qualitatively, because the speed of hydrogen adsorption on Pd and subsequent dissociation and absorption,[1] and/or the speed with which the absorbed [H] reaches its thermodynamic equilibrium concentration in the Pd layer, increases with increasing ambient partial pressure (concentration) of H_2.[1,19] Figures 3(b) and 4(b) show the OR and PPEI responses in the region of low- H_2 concentration. Compared with those obtained for high-H_2 concentrations, the response time at 0.2% $[H_2]$ is much shorter, and the saturated signal is much lower, than that at 2.07% $[H_2]$ concentration. This phenomenon is the result of the transition

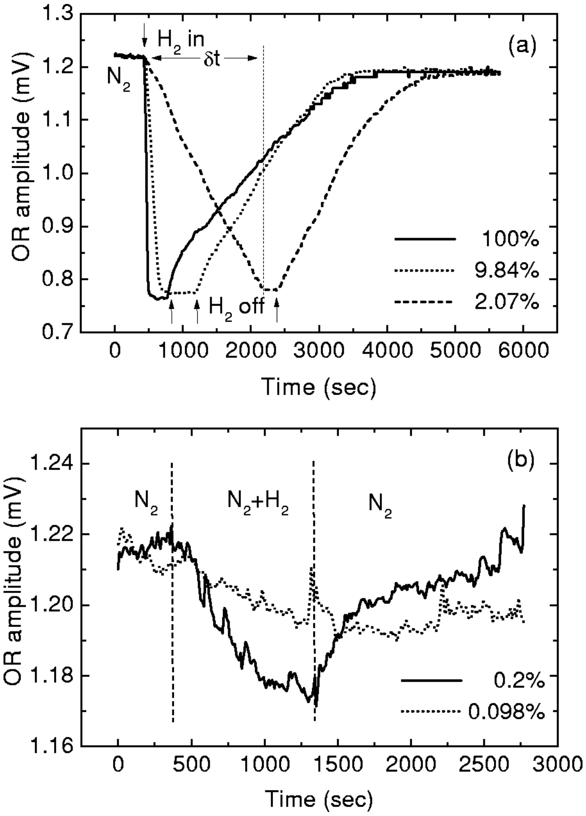

FIG. 3. OR signal as a function of time for various concentrations of hydrogen in nitrogen using a Pd-coated (53.4 nm) PVDF film. The gas-flow rate was 870 ml/min for all the experiments.

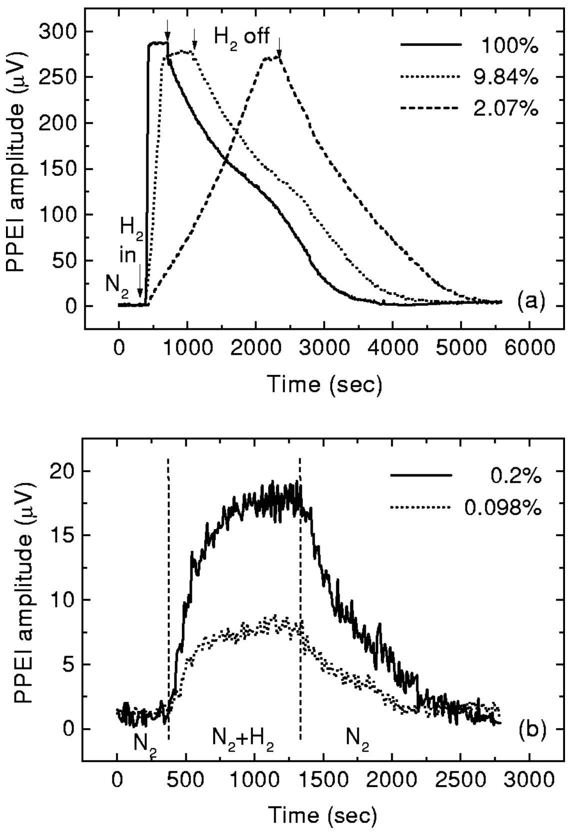

FIG. 4. PPEI signal as a function of time for various concentrations of hydrogen in nitrogen using a Pd-coated (53.4 nm) PVDF film, simultaneously measured with the OR signal in Fig.3.

from *α*- to *β*-phase of the palladium hydride.[1,19]

When the signals from the OR channel [Figs. 3(a) and 3(b)] and the PPEI channel [Figs. 4(a) and 4(b)] are compared, it is found that the amplitudes are anticorrelated. The OR amplitude (i.e., surface reflectivity of Pd) decreases after the introduction of H_2, while the PPEI signal amplitude simultaneously increases. In this region of high-H_2 concentration the quality of both signals, Figs. 3(a) and 4(a) was similar due to the large H_2/Pd-induced signal level. In the low-H_2 concentration level, however, the PPEI signal, Fig. 4(b), exhibits a much better signal quality than the OR signal, Fig. 3(b). This is due to the fact that the H_2/Pd-induced signal level decreases dramatically in the lower-H_2 concentration range while the system noise level remains the same, which results in a large drop of the signal-to-noise ratio. In the OR measurement scheme, the small signal change due to the exposure of Pd coating to H_2 is measured in a background of large base-line signal, large noise due to the laser power fluctuations, and low instrumental sensitivity. In contrast, the PPE signal is detected as a differential, near-zero base-line signal, with high instrumental sensitivity and lower overall system noise due to the coherent cancellation of laser-noise-induced thermal fluctuations within the PVDF detector through destructive thermal-wave interference. As a result, the detection limit using the single-beam OR reflection method was found to be ~0.1% for the 53.4-nm-thickness Pd. The detection limit of the PPEI channel using the same sensor element, as shown in Fig. 5, was found to be ~100 ppm. The sensitivity of the PPEI channel is about 20 times that of the OR channel, which is the same as the noise improvement of the former technique. The present OR channel detection limit is similar to that established earlier with other single-beam optical and photopyroelectric methods, with either glass, silicon, or PVDF as the substrate of the detector.[8,11,12]

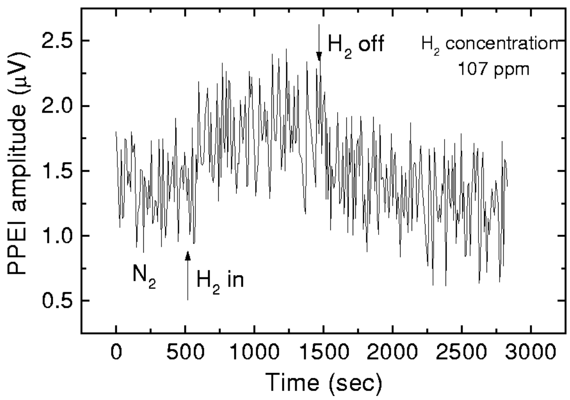

FIG. 5. Detection limit of the PPEI channel using a Pd-coated (53.4 nm) PVDF film.

Figures 6 and 7 show simultaneous OR and PPEI experimental results using a 25.6-nm Pd-coated PVDF thin film with various H_2 concentrations in N_2 by volume. The experiments were performed under the same conditions as those with the 53.4 nm Pd coating. Similar phenomena to Figs. 3 and 4 were observed in Figs. 6 and 7, respectively. Figures 6(a) and 7(a) show similar anticorrelation behavior to that between Figs. 3(a) and 4(a), with the introduction of hydro-

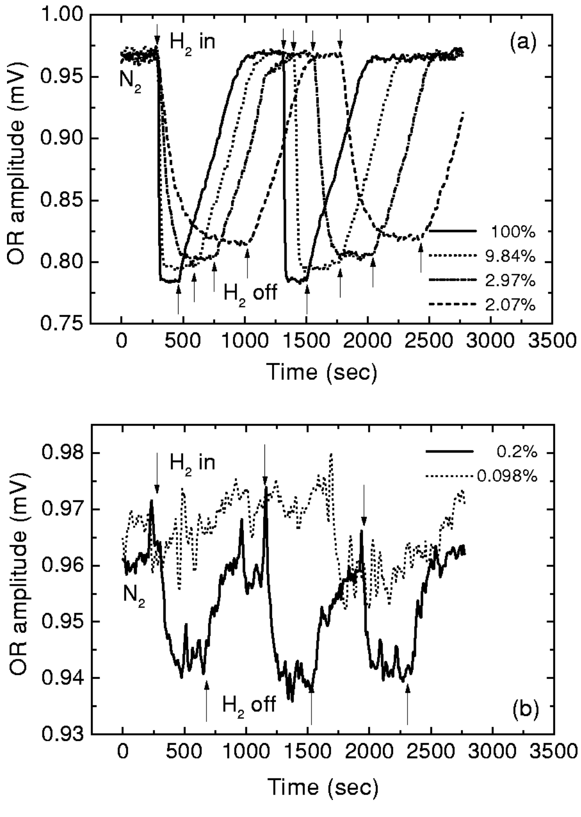

FIG. 6. OR signal as a function of time for various concentrations of hydrogen in nitrogen using a Pd-coated (25.6 nm) PVDF film. The experimental conditions are as in Fig. 3.

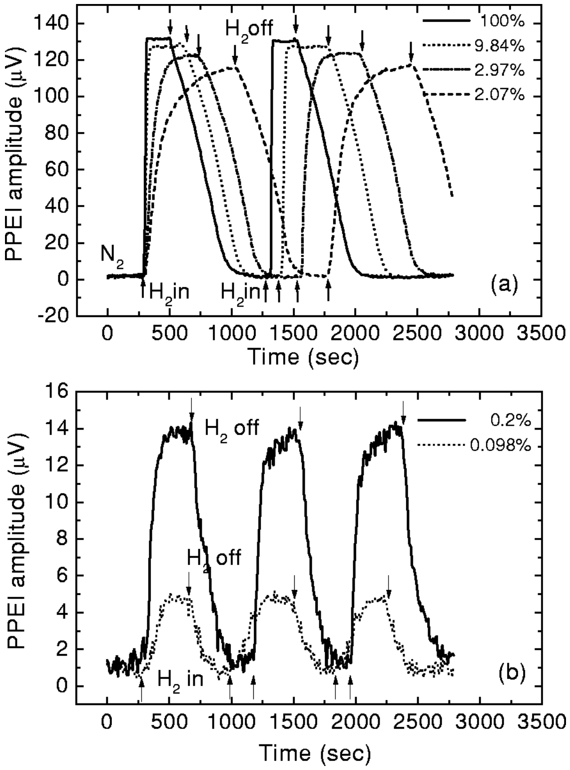

FIG. 7. PPEI signal as a function of time for various concentrations of hydrogen in nitrogen using a Pd-coated (25.6 nm) PVDF film, simultaneously measured with the OR signal in Fig. 6.

gen being accompanied by a decrease in reflectivity. The overall sensor responses (both OR and PPEI signals), however, are much faster than those in Figs. 3(a) and 4(a). Figures 6(b) and 7(b) also show significant drop in signal saturation level compared to the thicker Pd film in Figs. 3(b) and 4(b), when the sensor operates in the low- $[H_2]$-concentration region. In terms of signal-to-noise ratio, Figs. 6(b) and 7(b) show, again, that the PPEI signal quality is much better than the OR signal in the low region of H_2 concentration where the signal induced by the α-phase PdH_x is small. In the OR channel, the signal was completely embedded in the system noise at about 0.1% $[H_2]$, while in the PPE channel the detection limit is somewhat below 175 ppm, as indicated in Fig. 8. This is a sixfold detectivity enhancement of the PPEI mode over OR detection in the case of the 25.6 nm Pd coating.

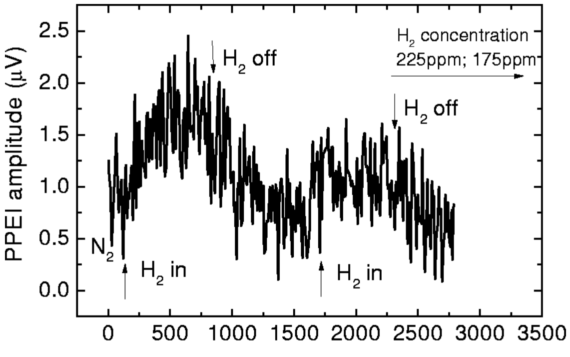

FIG. 8. Detection limit of the PPEI signal using a Pd-coated (25.6 nm) PVDF film.

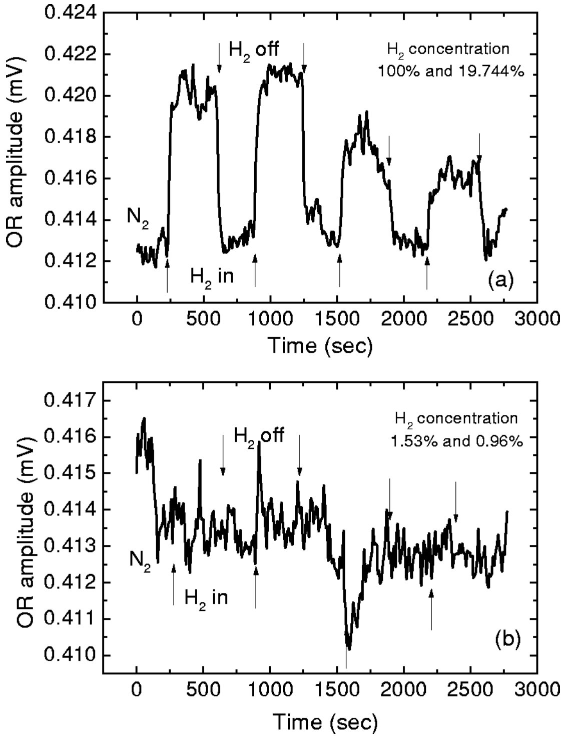

FIG. 9. OR signal as a function of time for various H_2 concentrations in nitrogen using a Pd-coated (6.5 nm) PVDF film. The experimental conditions are as in Figs. 3 and 6.

Finally, a 6.5 nm Pd-coated PVDF film was tested. Figures 9 and 10 show the OR and PPEI experimental results, respectively, at various H_2 concentrations. The experimental conditions and procedures were the same as those used in the previous experiments. Compared with Figs. 3, 4, 6, and 7, Figs. 9 and 10 exhibit much lower signal levels and much lower sensitivity and signal-to-noise ratio, for a given H_2 concentration. The detection limit in the OR and PPEI channels was found to be greater than 2% and 0.5% H_2 in N_2, respectively, which are much lower than those of the thicker Pd coatings. No clear concentration region for the α- to β-phase transition of PdH_x was found. It is interesting to note (Figs. 9 and 10) that the OR and PPEI signals are positive correlated in the case of the 6.5 nm Pd. This is the result of the reflectivity signal inversion exhibited by this sensor upon introduction of hydrogen in the chamber. The surface reflectivity of the 6.5 nm Pd *increases* on exposure to H_2 gas, which is opposite from what occurs when a 53.4-nm-thick or a 25.6-nm-thick Pd are employed. This observation is in agreement with some earlier findings with glass or silicon-based H_2 sensors. In the case of thick Pd coatings (>8 nm), the surface reflectivity of Pd coating is always found to decrease upon exposure to H_2.[8,18,20,21] The reflectance *decrease* in thick films has been attributed to the rise of the Fermi level with hydrogen concentration in the metal. The hydrogen atoms in Pd act as electron donors filling empty electronic states and subsequently shifting the Fermi level upwards, thus reducing the probability for optical transitions. This tends to render the Pd film more transparent to the

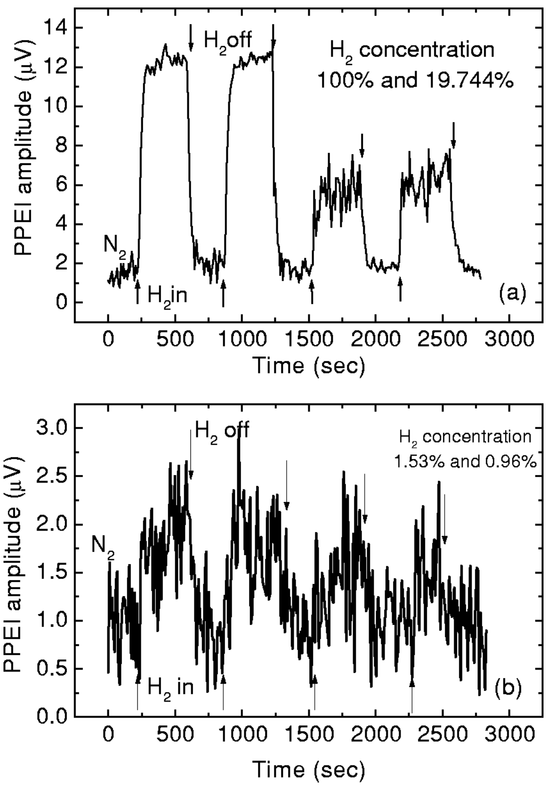

FIG. 10. PPEI signal as a function of time for various H_2 concentrations in nitrogen using a Pd-coated (6.5 nm) PVDF film, simultaneously measured with the OR signal in Fig. 9.

incident optical radiation and enhance the transmittance, while depressing the reflectance. On the other hand, the phenomenon of reflectance *increase* has already been observed in the case of extremely thin Pd coatings (0.1, 0.5, and 1 nm) on silicon oxide substrates.[21] In our case, the reflectance increase has been observed with Pd coatings as thick as 6.5 nm. No definitive mechanism has been proposed for this inversion effect. Further investigations are currently under way.

C. Correlation of OR and PPEI signals

Simultaneous detection of hydrogen via the OR and PPEI channels allows us to obtain a better understanding of the possible mechanisms operating during the interaction of H_2 with the Pd/PVDF system. Comparing the OR and PPEI signals for each thickness of Pd coating, Fig. 3/Fig. 4, Fig. 6/Fig. 7, and Fig. 9/Fig. 10, it is found that the OR and PPEI signals show a very similar temporal profile. More detailed examination shows that the response time at various H_2 concentrations for each Pd/PVDF sensor element for both signals are approximately the same. In Fig. 11, we show the normalized saturation amplitude versus H_2 concentration (an isotherm[22]) for all three sensors with different Pd thicknesses (data in Figs. 3–10 are used). It is seen that the normalized OR and PPEI signals for all three Pd–PVDF sensors are in good agreement, especially for thicker Pd. The consistency of the temporal profile, response time, and the normalized saturation amplitude of OR and PPEI signals indicates that both signals are due to the same mechanism. Considering the nature of the PPEI signal generation,[16,17] this result provides further evidence that phenomenologically the thermal-wave interferometric PPEI response of a Pd–PVDF sensor originates in the change of the optical properties of the Pd thin film upon its interaction with hydrogen. The other possible mechanism of changes in the thermal boundary conditions due to the high thermal conductivity of hydrogen gas,[13,23] appears to be unimportant here, presumably due to thermal-component cancellation by the destructive interference of thermal waves.

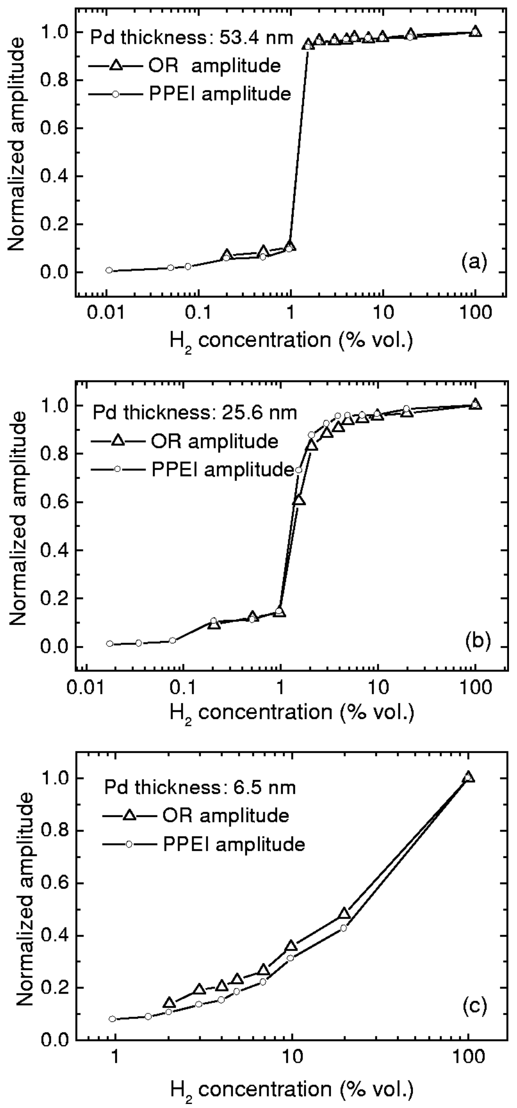

FIG. 11. Correlation of the measured saturation–amplitude isotherms of both OR and PPEI channels for three palladium coating thicknesses, (a) 53.4 nm; (b) 25.6 nm; and (c) 6.5 nm.

IV. DISCUSSION

In this work, a novel two-channel solid-state sensor for trace H_2 detection has been presented. Two signals are simultaneously measured from the OR and PPEI channels using a single PVDF-based device. The photopyroelectric signal was shown to be of superior detectivity in the low-$[H_2]$-concentration range below 1% vol. in N_2. The PPEI channel operates in the thermal-wave interferometric differential-signal mode. In contrast, the OR channel operates in a purely optical single-beam mode. The small variations of the OR signal, due to the interaction of H_2 with Pd, were measured in a large background signal, subject to laser-thermal fluctuation noise. The result was a relatively low instrumental sensitivity and limited signal dynamic range. The thermal-wave interferometric PPEI signal was measured with zero base line and low optical noise on account of the coherent noise cancellation from both laser beams. The result was a much higher instrumental sensitivity and signal dynamic range. The detection limit of the PPEI channel was found to be ~100 ppm while the OR channel was only 0.1% in the case of a PVDF element with a 53.4 nm Pd coating. Furthermore, the thermal boundary-condition component of the PPEI signal was shown to be absent from this sensor through cancellation by the destructive thermal-wave interference.

ACKNOWLEDGMENTS

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