Photomodulated thermoreflectance detection of hydrogen at elevated temperatures: a detection limit

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Laser photomodulated thermoreflectance has been used as a means of detecting, at elevated temperatures, low concentration of hydrogen using an optically thin film of palladium. Data indicate that concentrations as low as a few parts per billion can easily be detected at 100 °C. A semi-quantitative interpretation of the photothermal signal has been achieved using a Langmurian isothermic model. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1543254]

During the last few decades, a considerable effort has been directed toward the development of sensitive hydrogen gas sensors.[1,2]

In this letter, we investigate the detection efficiency of low hydrogen concentrations in optically thin films of Pd on silicon oxide using laser photomodulated thermoreflectance (PMTR) at above 100 °C. A phenomenological, semi-quantitative interpretation was performed using a Langmurian isotherm model. Various PMTR characteristic times, such as the response and recovery time, are also discussed. In this work, PMTR is used to interrogate a 6-nm, optically thin palladium layer evaporated on a silicon oxide substrate, for the purpose of detecting hydrogen gas at temperatures of ~100 °C. PMTR has been demonstrated in the past[3] as a means of detecting hydrogen on similar samples at room temperature. The detection limit in those experiments was estimated at 0.1% hydrogen in N_2. In this work, we demonstrate an increase in sensitivity by several orders of magnitude by simply setting the Pd–silicon sample at a higher temperature of approximately 100 °C.

The experimental arrangement is shown in Fig. 1.[4] In these measurements, periodic sample heating is obtained with laser light from an argon-ion laser operating at 488 nm. The laser beam was amplitude-modulated between zero and maximum at a given frequency by an acousto-optic modulator, and was focused on the sample at nearly normal incidence to a spot size of approximately 50 μm in diameter. Small oscillations in the sample reflectivity were detected with a cu He–Ne laser probe beam (0.5 mW, 632 nm) that was collinear with the pump beam and focused on the area of excitation to a spot size of approximately 35 μm in diameter. The spots sizes and relative positions of the pump and probe beams were determined using a beam analyzer with resolution better than 0.5 μm. The combined pump-probe beams were focused with a lens though the window of the sample chamber. The chamber was designed to hold the Pd sample horizontally, and a temperature-controlled heater system with a feedback control circuit was used to heat the sample and maintain temperature stable within 0.1 °C. The reflected probe beam was collimated and filtered using a grating, and was finally focused within the detection area of a silicon photodiode.

The experimental data were taken for pumping laser powers of up to 100 mW. The thin film palladium–silicon-oxide substrate samples were placed in the closed chamber cell that allowed for the response of the samples to various concentrations of hydrogen in nitrogen to be measured. Gas cylinders controlled by pressure regulators, and subsequently with flow meters, provided the gas mixtures. The gases were mixed to give a homogeneous flow with a flow rate of 150 ml/min. Hydrogen concentrations were varied from 25 to 1000 ppb.

PMTR was first discussed in the literature as a powerful spectroscopic probe with which to study such properties as electron–hole states at critical points in semiconductor energy bands and high-lying electron states in conduction metals. In the case of semiconductors, however, there is an additional effect: the creation of electron–hole pairs. In general, we can write the total induced photomodulated contribution as a sum of the thermal and plasma contributions:[4,5]

$$\frac{\Delta R}{R_0} = \frac{\Delta R_{\mathrm{th}}}{R_0} + \frac{\Delta R_{\mathrm{pl}}}{R_0}, \tag{1}$$

where R_0 is the reflectivity at temperature T_0. ΔR_{th} and ΔR_{pl} are the photothermal signal components due to the thermal and plasma effects, respectively. In the case of low frequencies, the plasma component is negligible, and the photothermal signal will be proportional to the variations in the modulated surface temperature. The resulting signal amplitude attributed only to the thermal contribution, and may be written as:[5]

$$\frac{\Delta R}{R_0} \approx \frac{\Delta R_{\mathrm{th}}(T)}{R_0} \approx \frac{H(n,k,u,w)}{\sqrt{2\pi f D_T(T)}}, \tag{2}$$

where f is the modulation frequency and D_T is the thermal diffusivity, which depends on temperature. $H(n,k,u,w)$ is an essentially temperature-independent factor that is a function of the real and imaginary parts of the refractive index of the medium (n,k) at the reference temperature, and of the local temperature derivatives of the real and imaginary parts of the dielectric constant (u,w). We note that the signal is inversely proportional to the square root of the modulation frequency. It is also inversely proportional to the sample thermal diffusivity that is a function of lattice temperature.

The validity of the above assumption, in which the PMTR signal is only due to the thermal component, has been demonstrated from the variation of the PMTR signal versus modulation frequency. Photothermal measurements have

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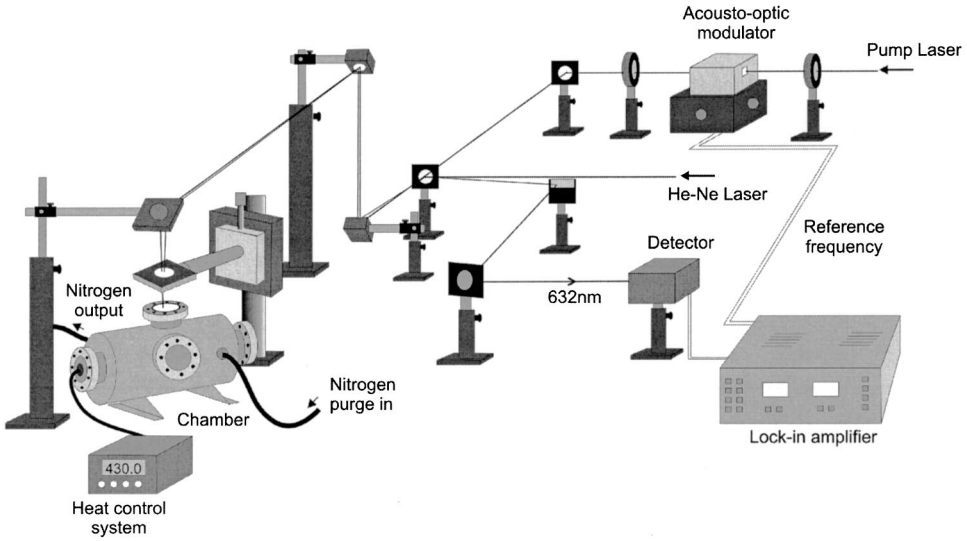

FIG. 1. Experimental setup for detecting hydrogen, using laser PMTR on Pd films.

been performed in the absence and the presence of hydrogen, as seen in Fig. 2. From Eq. (2), the expected frequency dependence of the thermal wave PMTR signal is $\Delta R_{\mathrm{th}} \propto 1/\sqrt{f}$. The log–log plot of the experimental data displayed in Fig. 2 reveals that the power of the exponent with or without hydrogen is indeed close to $-1/2$ (average value). There is a slight departure from the straight line at high frequencies (>2 kHz). This is expected because at these frequencies, the plasma effect starts to play a more significant role. From these results and working at low frequencies (e.g., 1 KHz), it is now clear that the PMTR response is due mainly to the thermal effect. The second important point is the difference between the PMTR curve without the presence of hydrogen and the one with hydrogen. In fact with the hydrogen we have an increase of the signal by almost three times. By looking at Eq. (2), it is obvious that the increase is only due to the H coefficient since the D_T remains constant due to the fact that the measurements were performed under the same experimental conditions. On the other hand, H changes drastically in the presence of the hydrogen due to the changes of the optical index (n,k). These changes have also been confirmed by Butler and Ginley[6] by using a fiberoptic hydrogen sensor.

Figure 3 shows the amplitude response of the PMTR signal at 1 kHz following exposure of the Pd film to various concentrations of hydrogen in nitrogen environment, and its subsequent recovery following purging the sample with nitrogen gas. With the introduction of hydrogen, there is a relatively fast rise in the PMTR signal following a slower rise to a saturation point. The saturation point occurs at longer times with increasing concentrations of hydrogen, as clearly indicated with vertical lines on Fig. 3. For all measurements, the flow rate was constant and equal to 150 ml/min. Once the nitrogen gas was introduced following hydrogen saturation in the chamber, the PMTR signal returned to equilibrium exponentially. It is important to realize that the photothermal signal decreases faster at very low hydrogen concentration. In fact, the recovery time is approximately 33 min in the case of 150 ppb and only 16 min for a hydrogen concentration as low as 25 ppb. This is in good agreement with other findings in the literature.[1] In Fig. 3, we also show the PMTR amplitude signal as a function of frequency before the introduction of H_2 and at the saturation point of 100 ppb hydrogen. In Fig. 4, the changes of the PMTR signal with introduction of H_2 at 100 ppb and recovery due to purge of N_2 are presented. The three curves of this figure correspond to different laser powers. We can point out two important results: (a) the PMTR amplitude changes and (b) the recov-

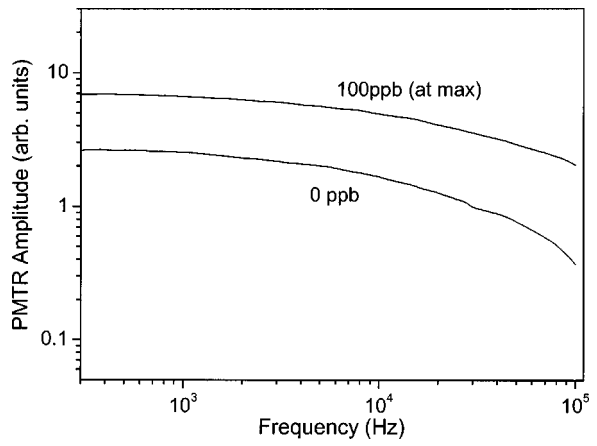

FIG. 2. Logarithmic plot of the PMTR amplitude signal as a function of modulation frequency for the Pd–Silicon film, in the absence and the presence of the H_2 in N_2 gas.

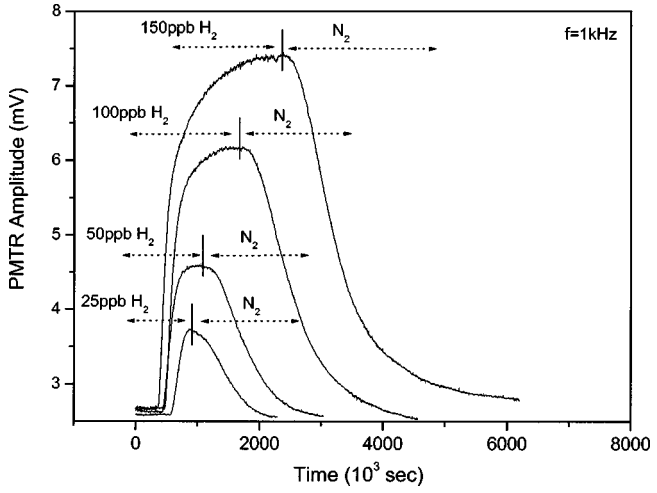

FIG. 3. Change in the PMTR signal amplitude with the introduction of various hydrogen concentrations, followed by the recovery due to purge of the system with nitrogen.

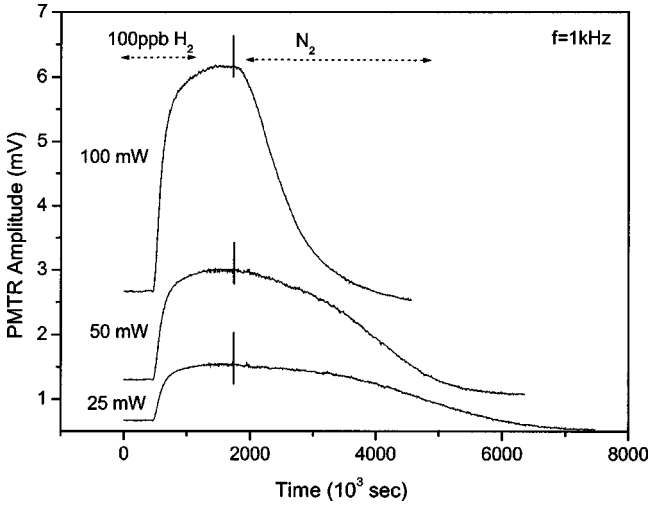

FIG. 4. Change of the PMTR signal with introduction of hydrogen and recovery due to purge with nitrogen. The three curves correspond to different laser powers.

ery times are strongly dependent on the laser power intensity.

To eliminate the possibility of the PMTR signal observed being generated either from the substrate or from the introduction of various concentrations of H_2/N_2 gases in the chamber, we have performed measurements on the substrate where the Pd film was not present. In these measurements, no change in the PMTR signal was noticeable up to concentrations of 4% H_2 in N_2. Furthermore, the average PMTR signal on the silicon substrate was approximately 1.5 mV at 1 kHz. The PMTR signal under the same experimental conditions with the 6-nm Pd film was approximately 2.6 mV, indicating that a large part of the photothermal signal is due to the Pd metal film.

The variation of the PMTR saturated signal $\Delta R_s/R_0$ as a function of hydrogen concentration from 25 to 1000 ppb is shown in Fig. 5. From the results given in Fig. 5, one can advance possible Langmurian behavior. From the general equation of the Langmuir isotherm adapted to our photothermal experiment, we can write the PMTR signal as[1,2]

$$\Delta R_s = \Delta R_{\max}\left[\frac{K\sqrt{P_{H_2}}}{1+K\sqrt{P_{H_2}}}\right]. \tag{3}$$

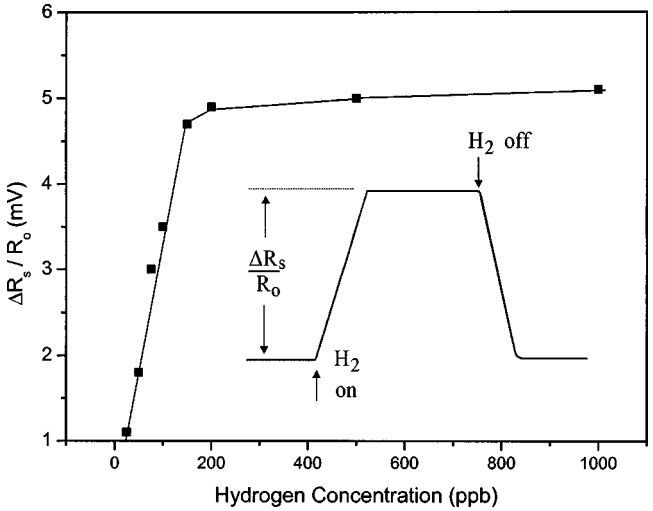

FIG. 5. PMTR saturated signal changes as a function of hydrogen concentration. Inset: definition of the PMTR saturated signal $\Delta R_s/R_0$.

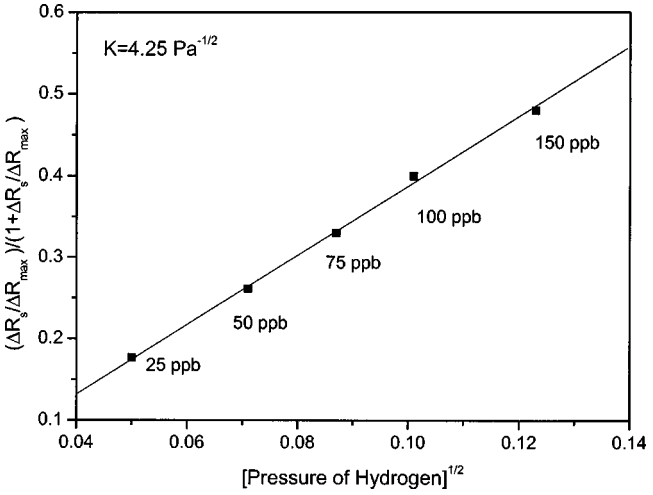

FIG. 6. Data from Fig. 5 plotted as a function of $\sqrt{P_{H_2}}$ after Eq. (4).

This equation can also be written under the following form:

$$\frac{\Delta R_s/\Delta R_{\max}}{1+\Delta R_s/\Delta R_{\max}} = K\sqrt{P_{H_2}}. \tag{4}$$

Upon plotting this equation (see Fig. 6) K is allowed to be estimated from the slope of the curve at 100 °C. We note that the curve is linear and from the slope, K (100 °C) $\approx 4.25\ \mathrm{Pa}^{-1/2}$. This value is of the same order of magnitude as the one found by Lundström *et al.*[7] Lundström estimated K to be equal to $1.3\ \mathrm{Pa}^{-1/2}$ at 210 °C. It is obvious that the combination of the Langmuir isotherm and the photothermal response gives the possibility of quantitative analysis of the signal response $\Delta R_{\max}$. It is important to note that the linearity presented in Fig. 6 is consistent with Lundström's findings using his Pd-MOS device[7] and with the findings of Christofides and Mandelis using their pyroelectric device.[2]

In summary, we have investigated the detection limit of laser PMTR on Pd films. We have demonstrated detection of hydrogen of up to a few parts per billion in nitrogen using thin Pd films on silicon oxide at elevated temperatures. We have also shown that the decay constant following saturation with hydrogen of the Pd films and subsequent recovery due to purge with nitrogen is intensity dependent. From the fundamental point of view, a semi-quantitative phenomenological understanding has been achieved by showing that the PMTR response is consistent with elementary Langmurian adsorption mechanism.

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