

Photomodulated thermorefectance detection of hydrogen gas using optically thin palladium film on silicon oxide

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The sensitivity of various thicknesses of optically thin film palladium layers evaporated onto silicon oxide substrate is investigated in the presence of a hydrogen/air atmosphere at room temperature. The magnitude of the resulting reflectivity change is measured using an excite-probe technique, through laser excited photothermal modulation of a probe beam. This allows for the recovery of information from both the amplitude and phase channels of the hydrogen sensor output. Data indicates that concentrations of 0.1% hydrogen in the presence of a balanced air mixture and at room temperature may be measured with an 8 nm palladium film. The presence of inhomogeneities in the palladium layers leads to anomalous behavior. © 1998 American Institute of Physics. [S0034-6748(98)01003-X]

I. INTRODUCTION

The ability to actively monitor hydrogen gas has become increasingly important in response to its widening industrial use.¹ Hydrogen is used for the extraction and working of metals and their alloys, the synthesis of ammonia and methanol, the hydrogenation of fats and oils, and in hydrodealkylation. It is also absorbed by several metals causing em-

brittlement in steel and the precipitation of hydrides in both titanium and zirconium.² The storage of hydrogen is also problematic as leakage can lead to explosions if air contains anywhere between 4.85 and 94% of the gas, therefore active detection is required for safety reasons. Sensing applications where real time, continuous monitoring of the gas using sensitive, and hydrogen selective, detectors are necessary.

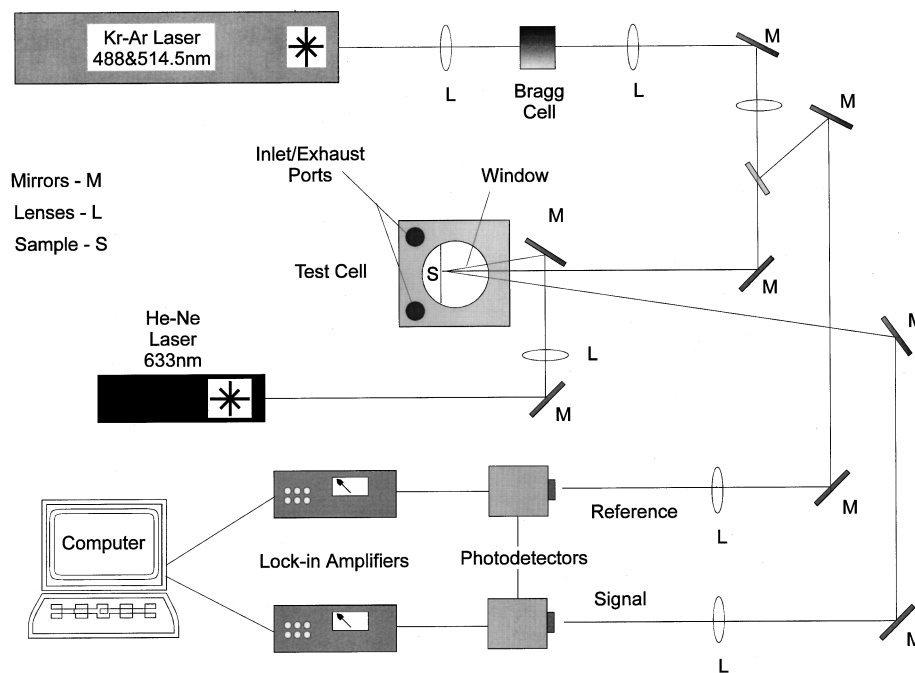


FIG. 1. The experimental configuration depicting the excite-probe technique for characterizing the optically thin palladium metal films.

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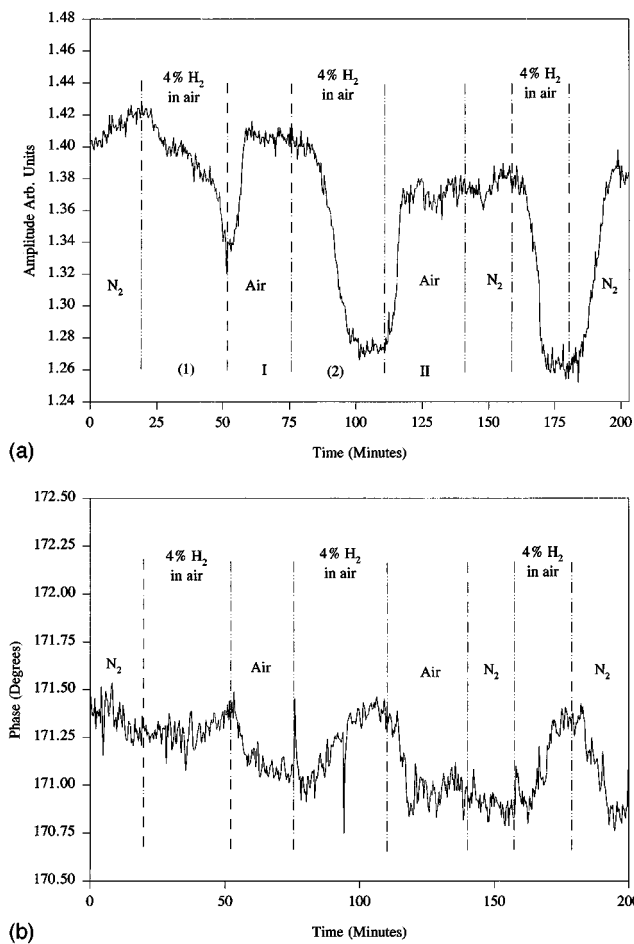


FIG. 2. (a) The initial amplitude response of an 8 nm palladium film on exposure to 4% hydrogen gas. Region (1) indicates an initially sluggish response while the surface is first activated, producing a reflection change of $\approx 5.5\%$. The surface fully recovers (region I). In region (II) the response is more rapid and results in a percentage change in reflection of $\approx 8\%$. The reordering on the metal film on further exposure to hydrogen gas results in a small drop in the absolute reflectivity. (b) The output from the phase channel providing complementary information and indicating that the surface reaction is releasing thermal energy, in addition to any thickness change that may result. Pumb beam chopping frequency=32 Hz.

The transition metal palladium has a high hydrogen solubility and this has resulted in its use as a filter for hydrogen purification and to provide hydrogen selectivity for gas detection, as has been applied here. The level of absorption depends on both the temperature and hydrogen partial pressure. On exposure to hydrogen, palladium forms a hydride complex that depends directly on the concentration of hydrogen gas, through a reversible reaction process. This knowledge has been used to implement various forms of hydrogen sensor systems.²⁻⁴ The behavior of bulk palladium in a hydrogen atmosphere is well understood, where the bulk regime generally refers to film thicknesses that exceed 100 nm.⁵ For optically thick samples there can be a modification of the surface properties resulting from chemisorption and hence a change in the Fresnel coefficients at the surface, this in turn leads to changes in reflectivity. Jansson *et al.*⁶ have shown using ellipsometry that the optical properties of the surface of thick (180 nm) Pd films change upon exposure to hydrogen and oxygen. They detected both reversible changes

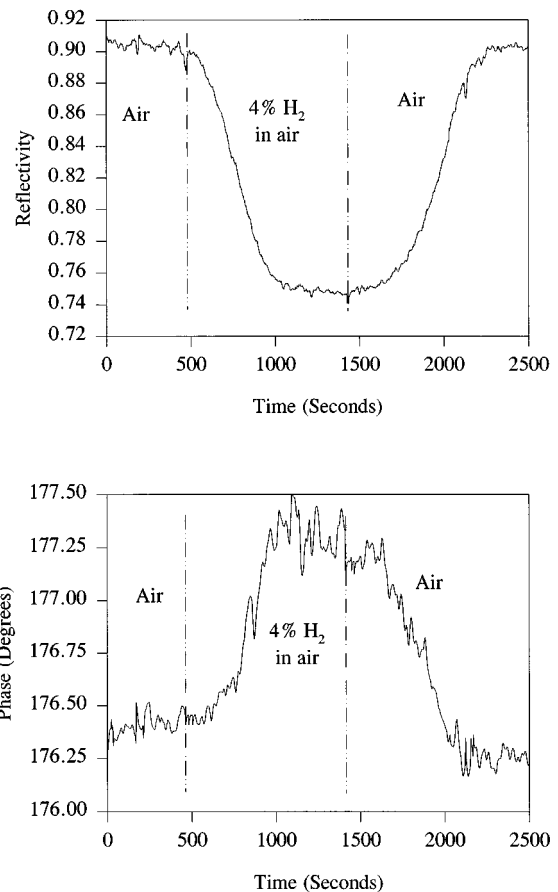


FIG. 3. A typical result for the change in reflectivity of another 8 nm palladium film on exposure to 4% hydrogen in air at room temperature, producing a reflectivity change of 16% after several cycles. The contribution from the phase channel indicates a change in phase as great as 1 degree. Pumb beam chopping frequency=32 Hz.

due to hydrogen exposure and irreversible changes related to the poisoning of the metal surface. The observed changes in the ellipsometric parameters or the pseudo dielectric function suggest, however, that for thick films the change in reflectivity would be very small. According to Butler⁷ palladium films thicker than 50 nm are destroyed by exposure to high hydrogen concentrations resulting from changes associated with the transition to the β -hydride phase. The limiting β -phase concentration increases with increasing film thickness until bulk behavior is approached.

For optically thin metal films there is a systematic deviation from bulk measurements, as reported by Frazier and Glasser.⁸ In these films there is also chemisorption of gases on the surface that occurs rapidly and results in reflectivity changes. In this case there is an altering of both the optical thickness of the film and the Fresnel reflection coefficients, the former being the dominant contributor, and results in reflectivity changes that are significantly larger than those resulting from changes in the reflection coefficients alone. The primary cause of reflectivity changes occurs through the hydride formation reaction, changing the electron density of the metal and thereby producing a considerable decrease in reflectivity.

In this article we use photomodulated thermoreflectance (PMTR) to interrogate an 8 nm optically thin palladium layer

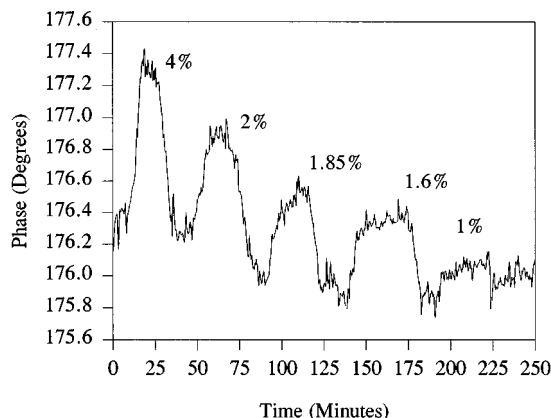
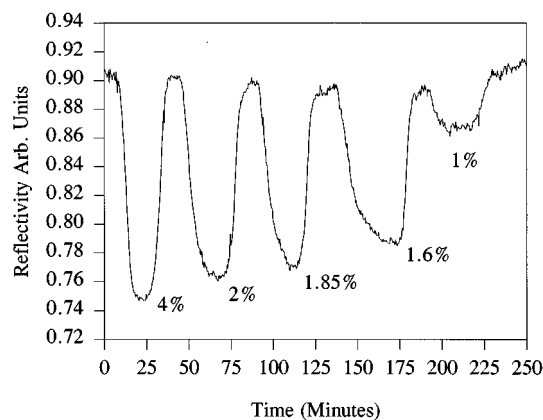


FIG. 4. The palladium surface response when cycled between balanced air and various concentrations of hydrogen in air at room temperature, where the exposure levels are from 1 to 4% of hydrogen in air. Pumb beam chopping frequency=32 Hz.

evaporated on a silicon oxide substrate, sensing hydrogen gas at room temperature. Additional thin films having thicknesses of 100 and 500 nm have also been examined. PMTR relies on using an optical pump to generate a steady-state ac temperature field within a material via amplitude modulated laser irradiation, such that any changes in the temperature distribution and/or surface properties, due to the interaction of the hydrogen gas with the palladium may be interrogated with a second laser beam that probes the Pd surface. Monitoring the reflected probe beam's phase and amplitude, gives the necessary information. Here reflectivity refers to the ac field of the thermally modulated reflectivity (TMR); the pump beam is absorbed by the metal film changing the energy into heat. The resulting increase in temperature of the metal film changes its optical properties and thus the reflectivity. This approach allows for an entirely passive sensor, with the signal demodulation derived from well known and widely implemented lock-in techniques. The hydrogen sensor presented here is therefore entirely passive and, as will be shown, allows for low concentrations of hydrogen gas to be measured in air and at room temperature, close to the lower explosive limit. That there are no electrical conductors required may make it suitable for use in potentially explosive environments.

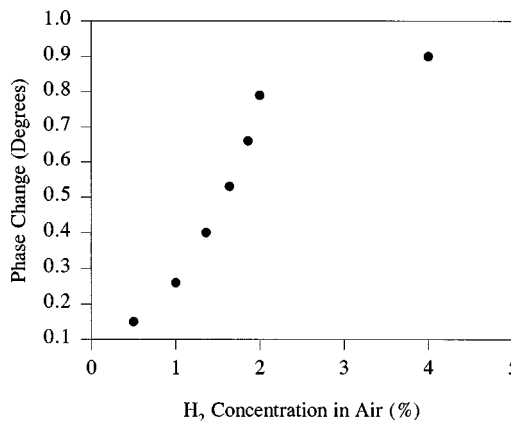
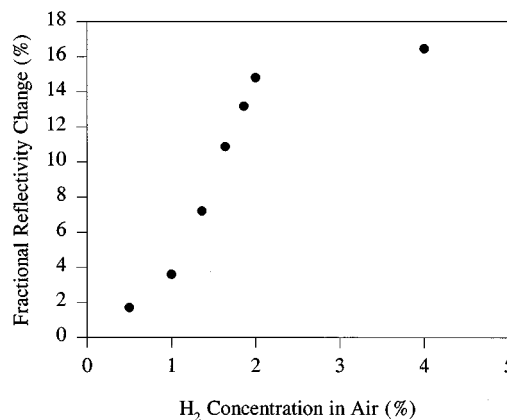


FIG. 5. The cycling of an 8 nm palladium film on exposure from 0.5 to 4% hydrogen gas. There is an abrupt change in the magnitude of the reflectivity response, for the amplitude and phase channels, at ≈2% hydrogen concentration. Pumb beam chopping frequency=32 Hz.

II. EXPERIMENTAL DETAILS

A. Experimental setup

The experimental arrangement is shown in Fig. 1. A mixed krypton-argon ion laser operating on the main lines at 488 and 514.5 nm was used as the optical pump. The beam was coupled, with a focusing lens, into a Bragg cell that amplitude modulated the pump beam. A function generator drove the Bragg cell with a square wave having either constant or variable frequency. This allowed for a periodic heating of the sample, therefore facilitating the use of a lock-in amplifier for enhanced signal demodulation. A lens at the output focused the pump light onto the palladium sensor surface directed by a mirror to be at normal incidence. This beam was intercepted by a microscope cover slide in order to direct a fraction of the pump onto a detector to monitor the stability of the krypton-argon laser. The detector was coupled to a lock-in amplifier to allow for ratiometric measurements. A He-Ne laser was used as the probe laser, focused onto the Pd surface ensuring that the probe beam was contained within the pumb and aligned such that the signal was maximised. The modulation of the pump beam intensity resulted in harmonic changes in the temperature field which subsequently gave rise to a harmonic perturbation of the probe beam. The reflected probe light was directed to an

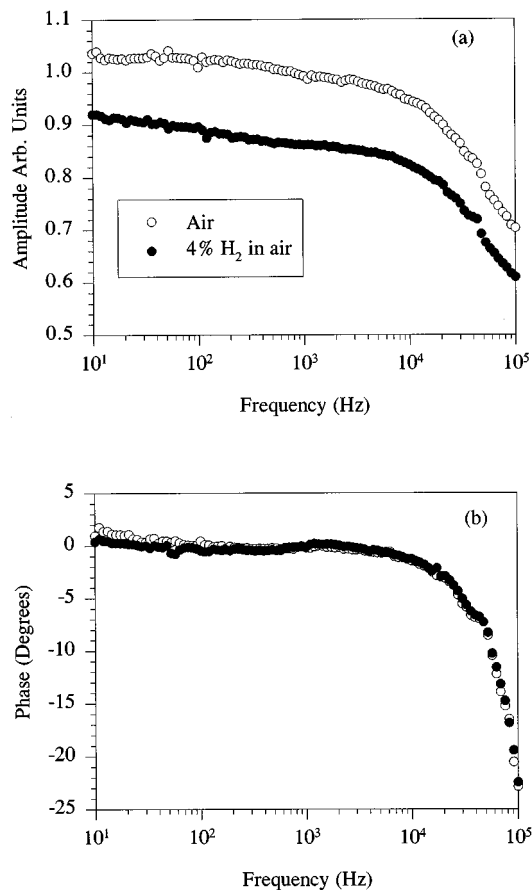


FIG. 6. The change in signal amplitude (a) and phase (b) as a function of frequency for the sample exposed to a balanced air mixture. Similar data are recovered for the sensor response on exposure to 4% hydrogen and after the signal levels have reached saturation.

another detector the output of which was coupled to a lock-in amplifier whereby the ac modulated probe beam was synchronously detected, thus providing a means for demodulating both amplitude and phase information. The lock-in amplifiers were interfaced to a personal computer for subsequent data acquisition via the use of Labview acquisition software.

The thin film palladium-silicon oxide substrate were placed in a closed cell which allowed for the response of the samples to various concentrations of hydrogen in balanced air and pure nitrogen to be measured. This test cell was equipped with suitable inlet and exhaust gas ports and glass apertures for the probe and pump beam to illuminate the sample. The method allows for basic studies of the interaction of the gases with the thin catalytic metal-insulator system. All gas mixtures were provided by gas cylinders controlled by pressure regulators and subsequently with flow meters. The gases were mixed to give a homogeneous flow with a flow rate of up to 65 ml/min. Hydrogen concentrations were varied from 0.5 to 4%.

B. Optically thin films

Three samples consisting of an 8, 100, and 500 nm films of palladium evaporated onto silicon oxide were investigated. Silicon wafers (*p*-type 3–10 Ω cm) were cleaned ac-

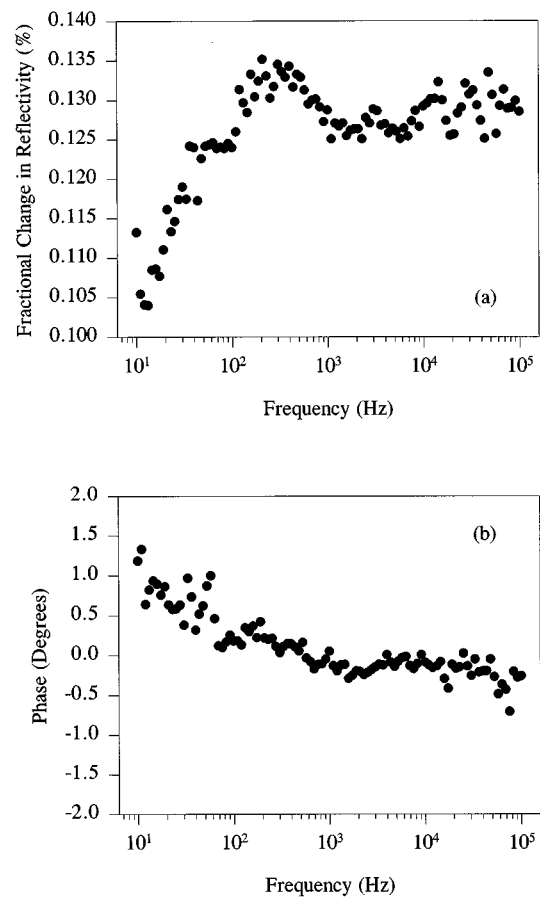


FIG. 7. The fractional change in reflectivity (a) and phase (b) as a function of frequency. This data is derived directly from Figs. 6, and clearly indicates frequency dependent behavior in both information channels. Peaking at a value of 13.5% at 250 Hz in the amplitude channel, after which saturation is reached at 1.1 kHz. The saturation point is also demonstrated in the phase channel.

ording to standard methods. They were oxidized in dry oxygen at 1100 °C to a thickness of the SiO₂ of about 100 nm. The oxides were cleaned prior to the metal deposition by H₂O₂/H₂SO₄ (1/3). The palladium films were deposited by thermal evaporation at a background pressure of about 1×10^{-7} Torr and at a deposition rate of 2–3 Å per second. The samples were kept at room temperature during the evaporation. No annealing of the films had been performed before the measurements were made.

III. EXPERIMENTAL RESULTS

Figure 2(a) shows the initial build up to the amplitude response of the 8 nm thin film palladium sensor, resulting from changes in the TMR, on first exposure of 4% hydrogen in air. The first cycle results in a 5% change in TMR. Figure 2(b) shows that this is accompanied by a small increase in the phase channel. The fractional change in the TMR quickly increases to 8% on the next cycle, as the surface has become activated on continued exposure to hydrogen. After several such cycles the fractional change in TMR reaches a steady-state value of $\approx 13\%$. Although, as we will show, this can reach 16% (for 4% hydrogen), depending on the composition and deposition of the palladium layer.

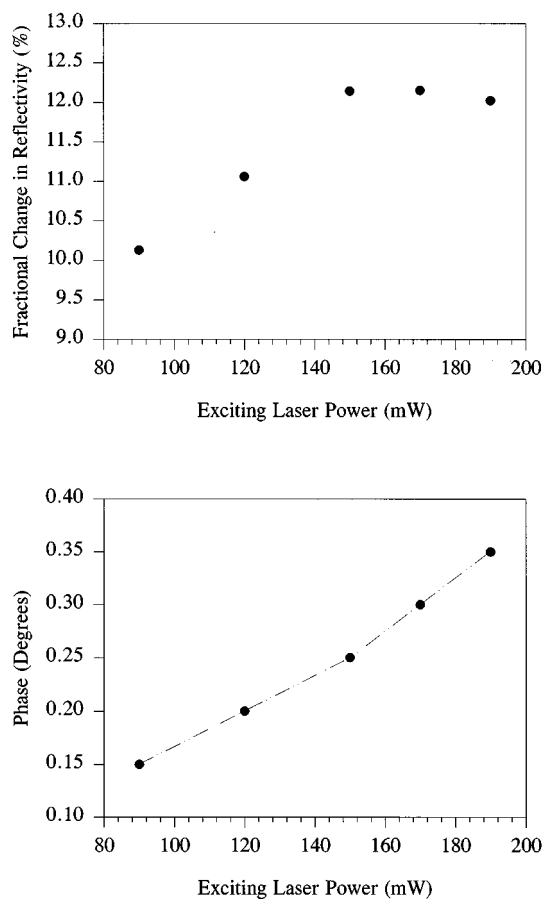


FIG. 8. The response of the 8 nm palladium surface as a function of laser power increases and saturates at 150 mW of argon pumping power. This is complemented by data from the phase channel where there is a linear increase in phase up to and beyond saturation. Pump beam chopping frequency=32 Hz.

A typical result for the change in the TMR of another 8 nm palladium film is shown in Fig. 3 on exposure to 4% hydrogen in air at room temperature. It was again found that the initial change in the TMR in this film increased on continued exposure, from an initial value of 8 to 16% after several cycles. There is also a signal contribution from the phase channel that results from the thermal modulation generated by surface heating via the pump laser, and the subsequent modulation of this thermal field by the energy released during the chemical reaction between the palladium surface and hydrogen gas, this change is approximately 1 degree.

The sample was also cycled between balanced air and various concentrations of hydrogen in air at room temperature to provide the data of Fig. 4, where the exposure levels are from 1 to 4% of hydrogen in air. Data were acquired for both increasing and decreasing gas cycles with good repeatability and reversibility demonstrated between results. In Fig. 5 the cycling of the sensor from 0.5 to 4% was examined, it should be noted that there is an abrupt change in the magnitude of the TMR response, for the amplitude channel, at $\approx 2\%$ hydrogen concentration. The values above this point increase more gradually. This is also indicated in the information from the phase channel. This response is consistent with earlier data⁷ and results from the transitional hydride phase, where both α and β phases exist and result in greater

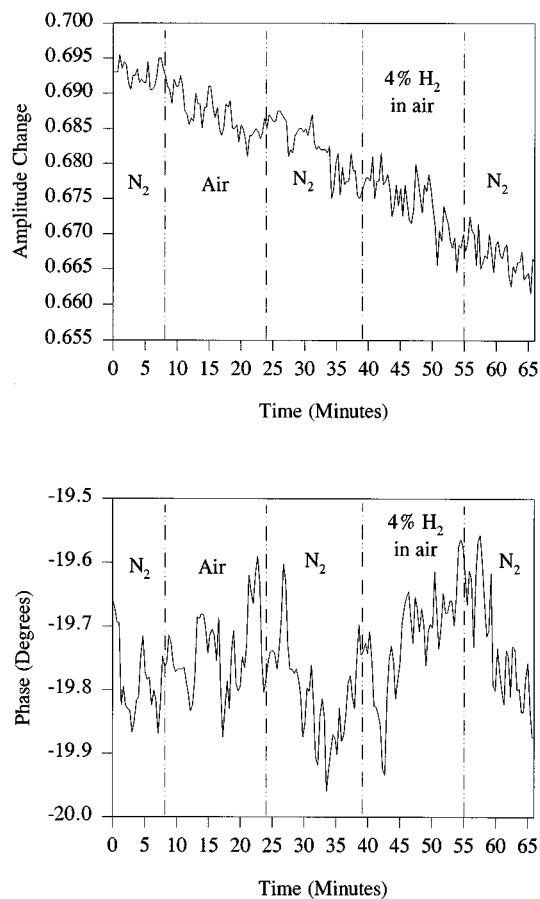


FIG. 9. Several films having thicknesses of 100 and 500 nm were also examined, but were found to be nonreactive to the presence of various concentration levels of hydrogen gas, up to the maximum 4% level used here. Pump beam chopping frequency=32 Hz.

responsivity to smaller changes in the concentration of hydrogen. However, the 16% TMR change at 4% concentration is larger by a factor of 2 than that quoted for other similar palladium based sensors.⁶ In the scheme used by Butler, consisting of a palladium micromirror deposited on the end of an optical fibre, the reflected light is affected through the process of chemisorption having passed through the metal sensing film twice. In the reflectivity measurements reported here the light is incident on the same surface where chemisorption takes place. Additionally, Butler modulated the total laser beam, thereby the resulting demodulated signal of the reflected light gave a measure of the absolute reflectivity of the sample. The decrease in reflectivity results from a change in the electronic structure of the metal, either by modification of the refractive index of the film or a change in its thickness, but more probably through a combination of both effects. Any index change could either occur near the surface or throughout the palladium layer, however one cannot distinguish between these effects and hence the net result of a combination of phenomena is observed.

Figures 6(a) and 6(b) show the change in signal amplitude and phase as a function of frequency for the sensor exposed to a balanced air mixture. Similar data are recovered for the sensor response on exposure to 4% hydrogen and after the signal levels have reached saturation. From these

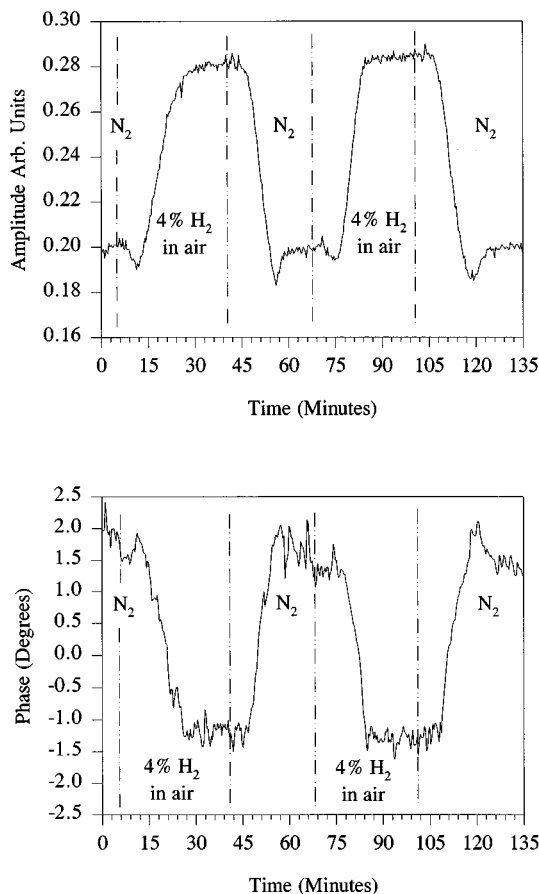


FIG. 10. Anomalous surface behavior for which the 8 nm Pd sensor was cycled between exposure to pure nitrogen gas to 4% hydrogen in air. This shows an increase in reflectivity of almost 30% on exposure to the gas and phase change of 3 degrees. Pump beam chopping frequency = 32 Hz.

curves one can say that there is no particular frequency at which to work, suffice to say that the lower frequencies provide the greatest signal level, which is consistent with the fact that the penetration of the thermal field from the pump source is frequency dependent. It should also be noted that at low frequencies the noise increases due to the environment.

In Figs. 7(a) and 7(b) we observe, respectively, the fractional change in TMR and phase difference as a function of frequency. These data are derived directly from Fig. 6, and clearly indicates frequency dependent behavior in both information channels. As the frequency increases the effective depth of penetration of the pump beam is reduced, resulting from the time window in which the returning signal is accessed — at low frequencies information from the entire sample thickness is recovered, whereas at high frequencies a finer probing of the surface results. The fractional TMR change increases almost linearly to approximately 70 Hz and peaks to a value of 13.5% at 250 Hz after which saturation is reached at 1.1 kHz. The saturation point is also demonstrated in the phase channel. Given the frequency range covered a contribution from the palladium layer is always present.

Note that the fractional change at 32 Hz, at $\approx 12\%$, is less than that recorded in the data presented above and results from inhomogeneities in the surface of the film, several 8 nm palladium samples were tested throughout this work,

showing marginally different reflectivities, although ultimately the same sensitivity to low gas concentrations. The phase response varied to a greater extent from sample to sample, being as great as 1 degree to a minimum of 0.4 degrees for 4% hydrogen gas. Other anomalies result from the inhomogeneities of the surface, as we will be observed later.

The response of the sensor as a function of laser power is seen to increase and saturate in Fig. 8. The amplitude channel shows a clear point of saturation for approximately 150 mW of argon pumping power. This is complemented by data from the phase channel where there is a linear increase in phase up to and beyond saturation, with a corresponding change in the slope of the response at 150 mW, from $1.67 \times 10^{-3} \text{ deg/mW}$ for lower powers to $2.5 \times 10^{-3} \text{ deg/mW}$ for higher powers.

Several films having thicknesses of 100 and 500 nm were also examined, but were found to be non-reactive to the presence of various concentration levels of hydrogen gas. Figure 9 shows the sensor's amplitude and phase output when the 500 nm palladium layer was exposed to 4% of hydrogen. Similarly for the 100 nm film, there is no indication of a measurable signal for this film in either amplitude or phase channel. That no signal is observed for the thick Pd films possibly reflects that these films have a greatly increased heat capacity and thus the temperature change of the film produced by the probe beam is much smaller.

As referred to earlier there are points on the surface of the palladium for which there is interesting but anomalous surface behavior that is currently under investigation. This is best represented by the data of Fig. 10 for which the sensor was cycled between exposure to pure nitrogen gas to 4% hydrogen in air. This shows an increase in reflectivity of almost 30% on exposure to the gas and a phase change of 3 degrees. One possible explanation may result from the fact that films essentially have an island-like structure for which the absorption of hydrogen and oxygen probably influences the electronic properties of a significant part of the metal film. In such a case it is easy to understand why we find much larger reflectivity changes in thin films compared to thick films. This positive change in the signal on exposure to hydrogen gas may result from passive through the β -phase transition and delamination of the film from the surface that would reduce the heat loss to the substrate and result in larger thermal modulation.

IV. DISCUSSION

We have examined the behavior of 8, 100, and 500 nm, optically thin palladium metal film deposited on silicon oxide. The 8 nm film was shown to produce significant changes in its TMR on exposure to hydrogen and was capable of detecting levels of the of gas from 0.5 to 4% in a balanced air mixture at room temperature. Our results indicate that a sensitivity to 0.1% gas at room temperature is possible. The modulation scheme of PMTR has allowed for information to be recovered from both the amplitude and phase channels of the synchronous detection. We have seen TMR changes of 16% in response to the presence of 4% hydrogen, twice that

reported for a similar sensing scheme, the only apparent differences being the coherence properties of the probe light and that the active surface is directly exposed to both pump and probe laser excitations. However, it must also be noted that the homogeneity of the films is crucial for the successful realization of a stable and consistent sensor surface. The difference in behavior between the 8 nm and thicker films may result from the fact the differences introduced by hydrogen is mainly located at the surface of the metal and at the interface between metal and oxide. Therefore, the total influence would then be much higher for the thin film. Additionally, any differences between similar thin palladium films (having the same thickness) might be due to recrystallization of the metal film. This may occur due to hydrogen exposure and possible due to heating by the laser excitation.

ACKNOWLEDGMENTS

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