

# Temperature-induced reflectivity changes and activation of hydrogen sensitive optically thin palladium films on silicon oxide

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The optical properties of several thin metal film palladium-silicon oxide structures are examined at room temperature before and after annealing to 200 °C and also at 90 °C—in all cases in the presence of hydrogen gas. Multicycling sample activation is shown to occur in the presence of hydrogen at room temperature with an increase in reflectivity on exposure to hydrogen, in contrast to thicker 80 Å films. The reflectivity change increases with increasing film thickness (1–10 Å). The surface activation at room temperature, before and after annealing to 200 °C, is compared with the performance at 90 °C, where it is shown that heat treatment strongly influences the behavior of the metal film. © 1998 American Institute of Physics. [S0034-6748(98)03809-X]

## I. INTRODUCTION

In recent years a great deal of work has been performed towards the study of the hydrogen-palladium system with a primary interest exhibited for thick palladium (Pd) films (in excess of 100 nm). This approach has characterized bulk behavior very well.<sup>1–3</sup> Thinner films, down to 6 nm films of Pd, have also been characterized to a lesser extent.<sup>4,5</sup> However, to our knowledge very thin metal films of thickness less than 1 nm have received little attention.<sup>6</sup> At this thickness the films have abnormal properties since outer surface effects and changes in optical thickness are complicated by the influence of the second boundary layer at the insulator-metal interface and by the essentially island character of the metal (such thin films are nonconducting). Any changes that now occur, on exposure of the palladium system to hydrogen gas, are a combination of the palladium-air interface with the palladium-silicon oxide interface, in addition to any thickness changes in the palladium itself. Additional phenomena relate to hydrogen spillover that is almost certain to occur<sup>7</sup> given the low level of surface coverage.

Optically thick films experience a modification of their 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.*<sup>8</sup> 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 due to hydrogen exposure and irreversible changes related to the poisoning of the metal surface. Thick films have been shown to undergo a significant reordering on heat treatment, affecting both the electrical measurements through resistance changes and removing defects in the palladium films.<sup>5</sup>

For optically thin metal films, measured down to 6 nm,

there is a systematic deviation from bulk measurements, as reported by Frazier *et al.*<sup>5</sup> Again the chemisorption of gases on the surface occurs rapidly and results in reflectivity changes through an altering of both the optical thickness of the film and the Fresnel reflection coefficients. The former is 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.

In this work we have used laser modulated reflectance (LMR) to investigate the behavior of several optically thin palladium metal films evaporated on silicon oxide substrates. LMR relies on using an amplitude modulated laser beam to probe the surface properties of a material having good optical quality. The modulation allows for the generation of an electrical carrier signal, the amplitude of which may be monitored using a lock-in amplifier, thereby enhancing signal demodulation. This approach is entirely passive and is nondestructive in nature given that the optical power density of the probe beam is very small.

The films, having thickness from 1 to 10 Å, are compared before and after annealing to 200 °C in the presence of hydrogen gas at room temperature. Heating the samples to such high temperatures is shown to have a significant impact in the room temperature activity of the palladium to low concentrations of hydrogen gas. Samples are also exposed to hydrogen gas at 90 °C in an oxygen rich atmosphere, again producing intriguing results. Our results are compared with the behavior of an 80 Å sample.

## II. EXPERIMENTAL DETAILS

### A. Experimental setup

The experimental arrangement is shown in Fig. 1. A He-Ne laser operating at 632.8 nm was used as the optical

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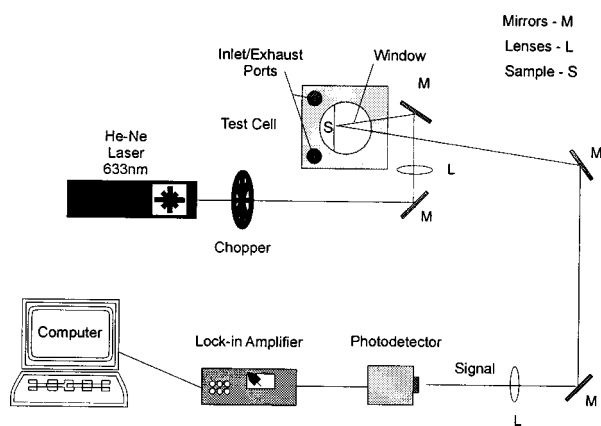


FIG. 1. The experimental configuration depicting the laser modulated reflectance technique for characterizing the optically thin palladium metal-silicon oxide films.

probe. The beam was amplitude modulated using a chopper, thereby generating an electrical carrier signal at approximately 400 Hz, facilitating the use of a lock-in amplifier for enhanced signal demodulation. A lens focused the probe light onto the palladium surface directed by a mirror to be at close to normal incidence. The reflected probe light was directed to a photodetector 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 the amplitude information. The lock-in amplifier was interfaced to a personal computer for subsequent data acquisition via the use of Labview<sup>®</sup> acquisition software. For all the data presented the lock-in time constant was maintained at 5 s.

The thin film palladium-silicon oxide substrates were placed in a closed test cell which allowed for the response of the samples to various concentrations of hydrogen in balanced air to be measured. This test cell was equipped with glass apertures for the probe 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 1% to 4%.

A heating element, placed in close contact to the sample, allowed for controlled heating of the cell to 100 °C, having a long term drift of  $\pm 2$  °C. This level of temperature drift corresponds to a change in the amplitude signal channel of less than 0.15%.

## B. Optically thin films

Three very thin samples consisting of a 1, 5, and 10 Å film of palladium evaporated onto a silicon oxide substrate were investigated and compared with an 80 Å palladium metal film. The samples are processed according to standard methods used to obtain gas sensitive catalytic metal-oxide-silicon devices.<sup>9</sup> Silicon wafers (*p*-type 3–10 Ω cm) were cleaned according to standard methods. They were oxidized in dry oxygen at 1100 °C to a thickness of the SiO<sub>2</sub> of about

100 nm. The oxides were cleaned prior to the metal deposition by H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub> (1/3). The palladium films were deposited by thermal evaporation at a background pressure of about 10<sup>-7</sup> Torr. 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

Issues that are of particular importance on heating are the redistribution of metal coverage and changes in the grain size. Changes will occur in the crack density as stress relaxation in the metal results from the temperature cycling. Additionally, one needs to consider the effect of any oxide layer forming on the surface and the role of the interface between the Pd and silicon oxide layer. The introduction of hydrogen gas, combined with the above alterations in the physico-chemical state of the metal, is anticipated to lead to changes in room temperature behavior of the film and in the formation of the PdH<sub>x</sub> complex. It is known that palladium films as thick as 250 Å can be electrically discontinuous,<sup>5</sup> implying a high crack density, while complementary visual evidence has been given regarding the coverage of metal films in the range 100–300 Å.<sup>9</sup> Very thin films have an islandlike structure and are nonconducting. It has also been shown that films have a discontinuous structure, with increasing metal coverage with film thickness, and this is also valid for very thin films.

Sections III A and III B describe the results obtained for the samples under two different temperature conditions. First, as a result of exposure to hydrogen gas at room temperature and subsequently at a higher temperature of 90 °C. This allowed for a comparison of the system activation under hydrogen exposure. Second, the samples were annealed at 200 °C, prior to exposure of hydrogen gas at room temperature, in order to clean the structures of any residual gas and reactivate the sensor.

### A. Exposure to hydrogen at room temperature and at 90 °C

#### 1. 1 Å Pd on SiO<sub>2</sub>

The behavior of the first of these films, having thickness of 1 Å, to 4% hydrogen in balanced air at room temperature resulted in a flat response with no observable change in the amplitude channel. The noise distribution from the amplitude channel corresponded to a percentage reflectivity change of 0.06%. The same film was heated to 90 °C and exposed to the same quantity of hydrogen gas, Fig. 2(a), with a resulting change in the reflectivity of  $\sim 1.2\%$ . This behavior is essentially reproduced once the film has been thermally activated on heating to 90 °C prior to exposure to 4% hydrogen, as indicated in Fig. 2(b), for a fresh 1 Å sample. The percentage change in reflectivity is marginally greater, at  $\sim 1.7\%$  and is preceded by a rapid response to the presence of hydrogen, after which the film is inactive to further exposure and having a response time of  $\sim 3.5$  min (defined as the time required to reach 10% of minimum value to 90% of the maximum saturated value). Fresh samples were used to further measure the response of the 1 Å palladium films. On the same figure further data indicates that similar behavior oc-

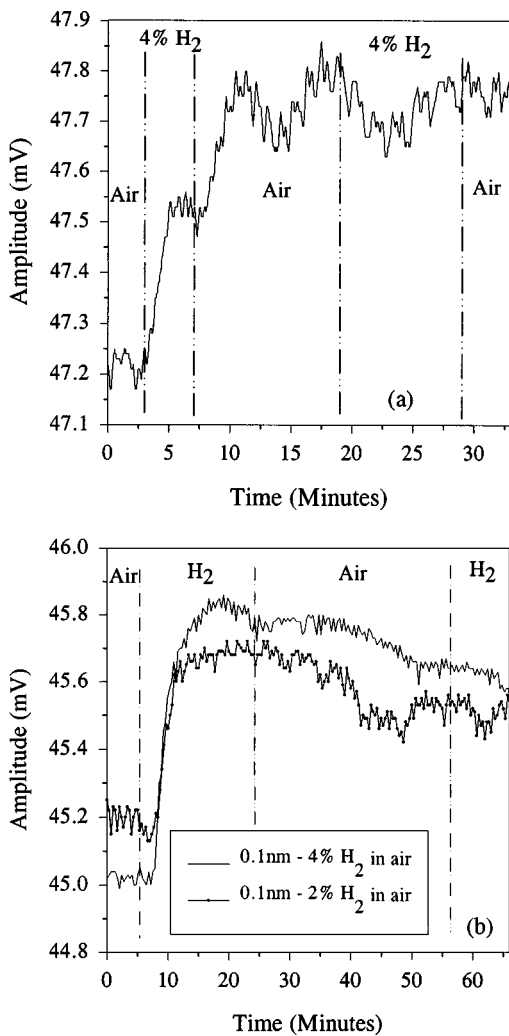


FIG. 2. (a) The amplitude response of a 1 Å palladium film on exposure to 4% hydrogen gas at 90 °C, indicating a 1% change in reflectivity. The sample was first exposed to hydrogen gas at room temperature. (b) The amplitude response of two separate 1 Å palladium films on silicon oxide on exposure to 4% and 2% hydrogen gas, respectively. Both data are taken at 90 °C, without prior exposure of the films to hydrogen gas, showing increments in reflectivity of 1.7% and 1.2%, respectively.

curs on exposure to 2% hydrogen in balanced air, again at 90 °C, however resulting in a smaller amplitude change of 1%. Given the thinness of the palladium layer on the silicon oxide, one cannot isolate the cause of this behavior, either an outer surface effect is responsible, or a phenomenon at the palladium-silicon oxide boundary, or indeed a combination of both effects. It is likely that this behavior may be accounted for by the Pd-SiO<sub>2</sub> interface and/or material activation. For such thin films there is little difference between the surface and bulk changes.

### 2. 5 Å Pd on SiO<sub>2</sub>

There was a marked difference in room temperature response for the 5 Å films. Exposure to 4% hydrogen, again in balanced air, produced a drop in reflectivity of 2.5%, after which the sample was inactive, Fig. 3(a), producing no measurable response on cycling between air and hydrogen in air. Heating the same sample to 90 °C resulted in a large 10% increase in reflectivity, and the sample was cycled between

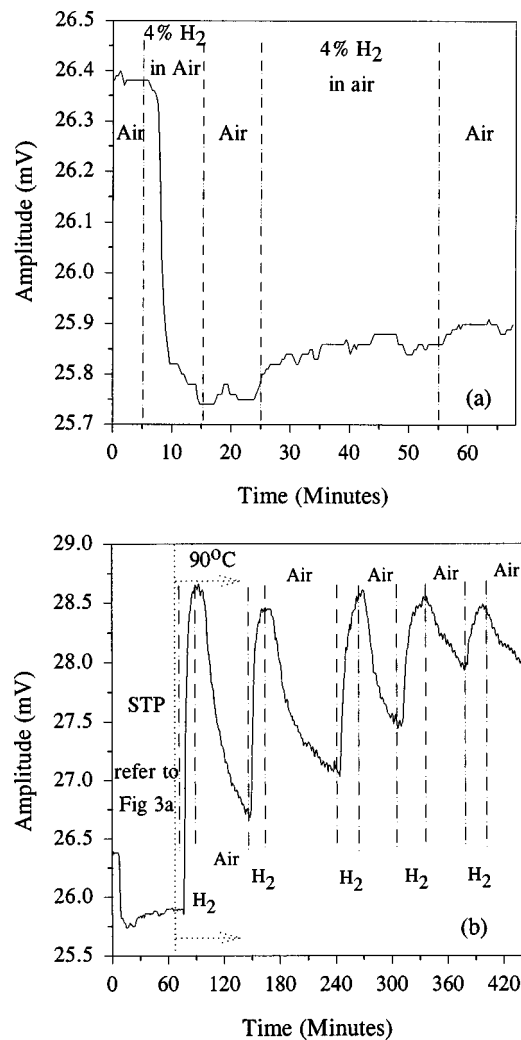


FIG. 3. (a) Room temperature behavior of a 5 Å palladium on silicon oxide film. Exposure to 4% hydrogen in balanced air produces a drop in reflectivity of 2.5%, followed by sample inactivity. (b) The same sample heated to 90 °C results in a large 10% increase in reflectivity, progressively decreasing on cycling between air and 4% hydrogen in balanced air, finally reaching a saturated signal level and inactivation.

air and 4% hydrogen in balanced air, Fig. 3(b). Note there is a dip prior to the rapid increase in reflectivity. When the hydrogen was removed a slow return to the initial value was observed but the sample was not fully recovered, this is also indicated in subsequent cycles.

A fresh sample was used to examine the behavior at an elevated temperature of 90 °C, Fig. 4(a), prior to exposure to 2% hydrogen gas. There is a change in reflectivity of 2.5% between air at room temperature and 90 °C, this is associated with the change in reflectivity resulting from the material dependence on temperature. The release of hydrogen results in a dramatic change in the amplitude channel corresponding to a 65% increase in reflectivity. There is again a very long recovery cycle in the presence of balanced air, which falls short of the original amplitude value, corresponding to a 25% recovery. Again subsequent cycles are characterized by slower response times for both hydrogen and air, as the system reaches a natural damping level. On closer inspection there are two different time scales on both the hydrogen and

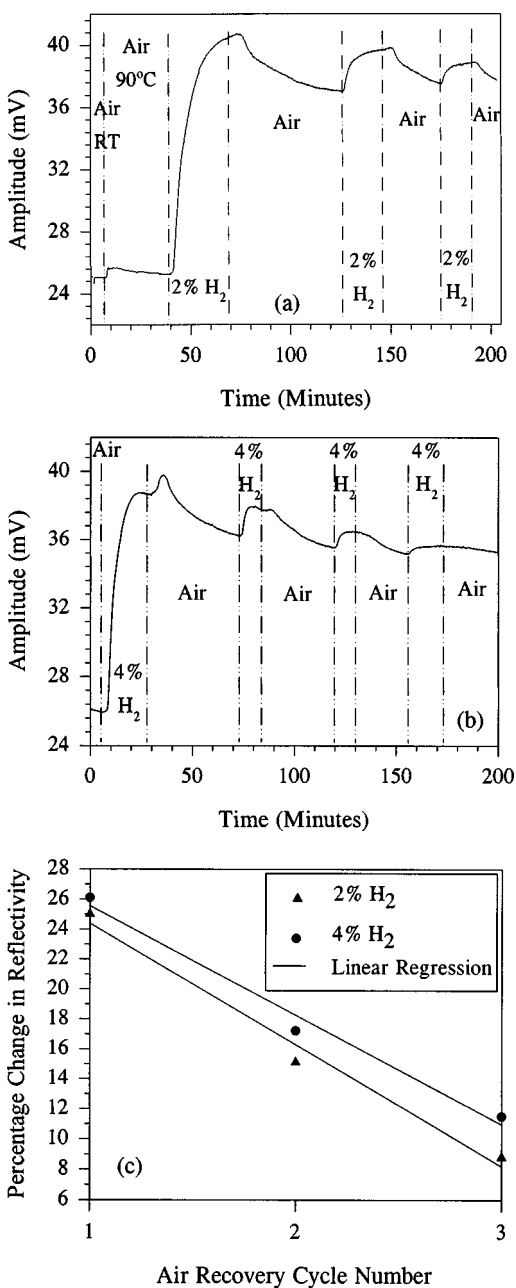


FIG. 4. (a) A fresh 5 Å palladium sample at 90 °C, prior to exposure to 2% hydrogen gas. Hydrogen gas results in a 65% increase in reflectivity. A long recovery cycle reaches a new saturated signal level accompanied by sample inactivity. (b) Unusual behavior is apparent for a new 5 Å sample exposed to 4% hydrogen under identical system parameters. The very pronounced peak on the first cycle is responsible for an initial reflectivity increase of 3%, whereas the percentage change associated with hydrogen gas has dropped marginally to 50%. (c) The change in reflectivity on the air recovery cycle is linear as a function of the gas cycle number, for both 2% and 4% hydrogen gas exposure.

the air recovery cycles, an indication of the two different processes taking place.

One can note that on the first two cycles there is a small peak present that is evident when air is introduced into the system. This phenomena becomes especially apparent for a new 5 Å sample exposed to 4% hydrogen under identical system parameters, Fig. 4(b). The very pronounced peak on the first cycle is responsible for an initial reflectivity increase of 3%, whereas the percentage change associated with hy-

drogen gas has dropped marginally to 50%. The recovery on the air cycle remains at ~25%. Figure 4(c) indicates that the change in reflectivity on the air recovery cycle is linear as a function of the gas cycle number, for both 2% and 4% hydrogen gas exposure. One may also note that the time required for the 5 Å film to reach signal saturation, on the first exposure to 4% hydrogen at 90 °C, is half that required for exposure to 2% hydrogen.

### 3. 10 Å Pd on SiO<sub>2</sub>

The first significant changes in room temperature behavior occur for the 10 Å thin palladium film, Fig. 5(a). The first exposure to 4% hydrogen gas in balanced air results in a similar response as to the 5 Å film, producing a drop in reflectivity of 6%. However, on continued exposure to hydrogen the sample begins to recover, reaching a steady-state level (in strong contrast with the inactivated thinner metal films) after which the response is consistent to several cycles of hydrogen and air exposure, giving a mean change in reflectivity of ~5%. A similarity with the thinner films is retained in that now the reflectivity increases on the hydrogen cycle while decreasing on the air cycle. Figure 5(b) indicates that for a fresh sample, having 90% of the previous samples absolute reflectivity, the initial drop in reflectivity on 4% hydrogen exposure is larger ~7.5%, while the change between several hydrogen/air cycles is marginally less, at ~4%. One can say that even with these small differences the total change in reflectivity is nevertheless very similar. This indicates that there are two phenomena occurring, the first of which is the initial drop in reflectivity and recovery corresponding to large morphological changes in the structure and finally the familiar hydrogen cycling behavior.

After several cyclic exposures to 4% hydrogen, for which the behavior is consistent, the hydrogen content is systematically reduced to a minimum of 1%. Figure 5(c) reveals that the percentage change in reflectivity is a linear function of hydrogen concentration (to 4% at room temperature). Such thin samples are too thin to undergo an  $\alpha$  to  $\beta$  phase shift, that is usually a room temperature characteristic of thicker samples, such as the 80 Å sample. We estimate that the mean noise level corresponds to a reflectivity change of 0.1% for which we can extrapolate from the graph that the minimum measurable level of hydrogen gas is approximately 0.05% (500 ppm).

On continued exposure to hydrogen over a period of several days at room temperature the sample eventually becomes less active, where the initial change in reflectivity of ~3.6% is followed by a drop of 1.4%. Moving the probe beam to a different point on the surface gave the same result, indicating that this deactivation was a universal effect and not limited to a few discrete points on the surface.

In Fig. 6(a) we observe the behavior of a fresh 10 Å film, when heated to 90 °C prior to hydrogen exposure of 2% in balanced air. The general trend is very similar to what has been observed to date, but there are small differences which shall be highlighted as follows. First, the immediate response of the metal film on exposure to hydrogen gas is a drop in the absolute reflectivity of ~3.9%, followed by an

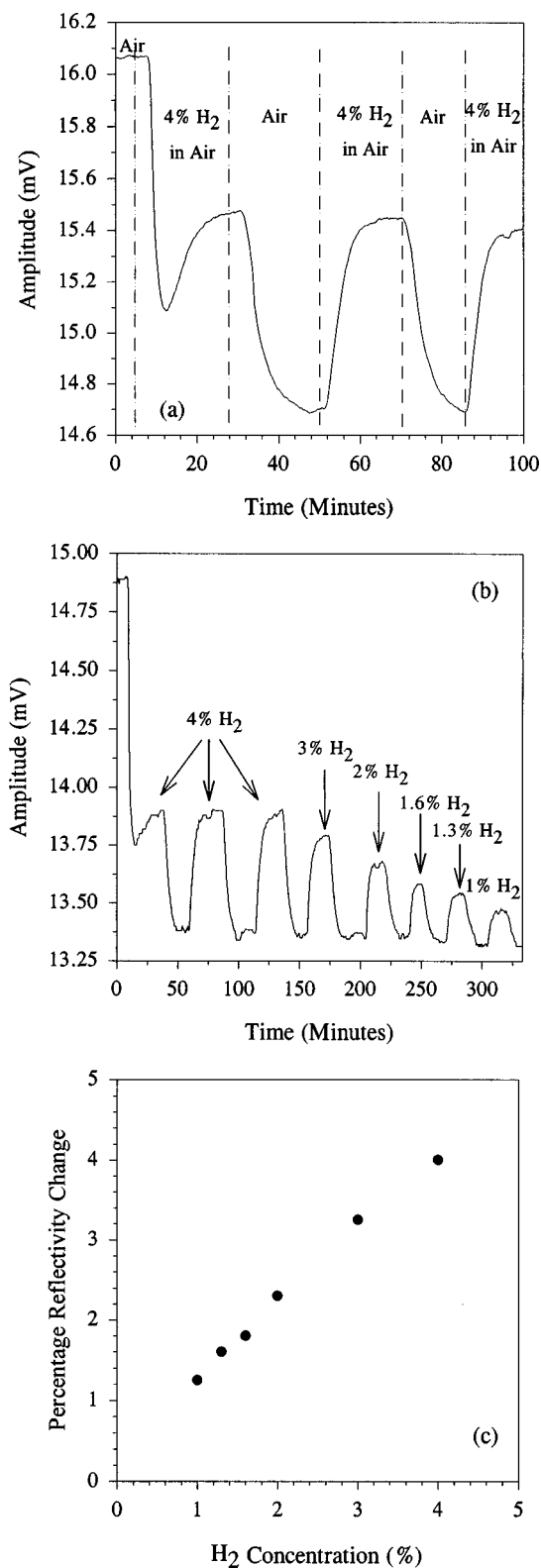


FIG. 5. (a) Exposure to 4% hydrogen gas in balanced air for a 10 Å palladium on silicon oxide film results in a drop in reflectivity of 6%, eventually reaching a steady-state level, after which the response is consistent to several cycles of hydrogen and air exposure, giving a mean change in reflectivity of ~5%. The reflectivity increases on the hydrogen cycle while decreasing on the air cycle. (b) A fresh 10 Å sample, gives an initial drop in reflectivity of ~7.5%, while the change between several hydrogen/air cycles is 3.8%. The total change in reflectivity is approximately the same as before. (c) The percentage change in reflectivity is a linear function of hydrogen concentration (from 1% to 4% hydrogen gas at room temperature).

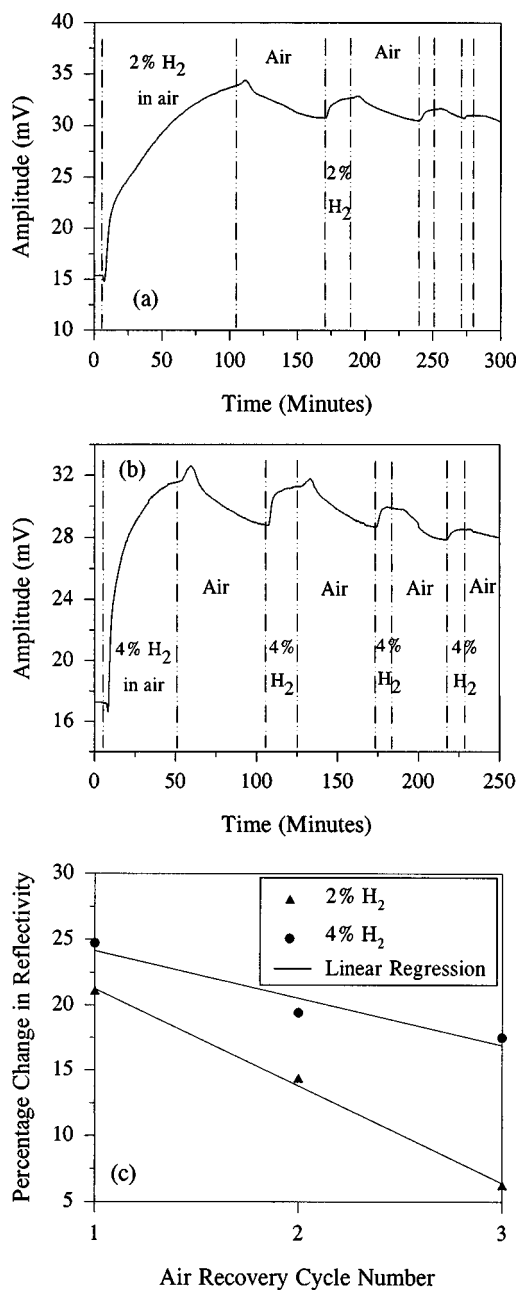


FIG. 6. (a) A fresh 10 Å film, heated to 90 °C prior to hydrogen exposure of 2% in balanced air. The general behavioral trend is similar to the earlier samples, with an increase in reflectivity of 120% and the appearance of small peaks in reflectivity on the introduction of air. (b) The behavior of a fresh 10 Å sample exposed to 4% hydrogen gas in air, again at 90 °C, with a smaller increase in reflectivity of ~90%, but a greater peak on the air cycle of marginally over 3.2%. (c) As characterized for all earlier data, where exposure to hydrogen occurs after heating of the sample, the percentage change in reflectivity on the air recovery cycle is linear.

increase in reflectivity that more than doubles in value, at 120%. Also apparent is the small peak in reflectivity appearing, as before, on the introduction of air.

Figure 6(b) reveals that similar behavior is recorded for a fresh 10 Å sample exposed to 4% hydrogen gas in air, again at 90 °C. The characteristic drop in absolute reflectivity is 3.8%, which is followed by an increase of ~90%. The introduction of air again results in a reflectivity increase marginally over 3.2%. The second peak, on the second cycle, is

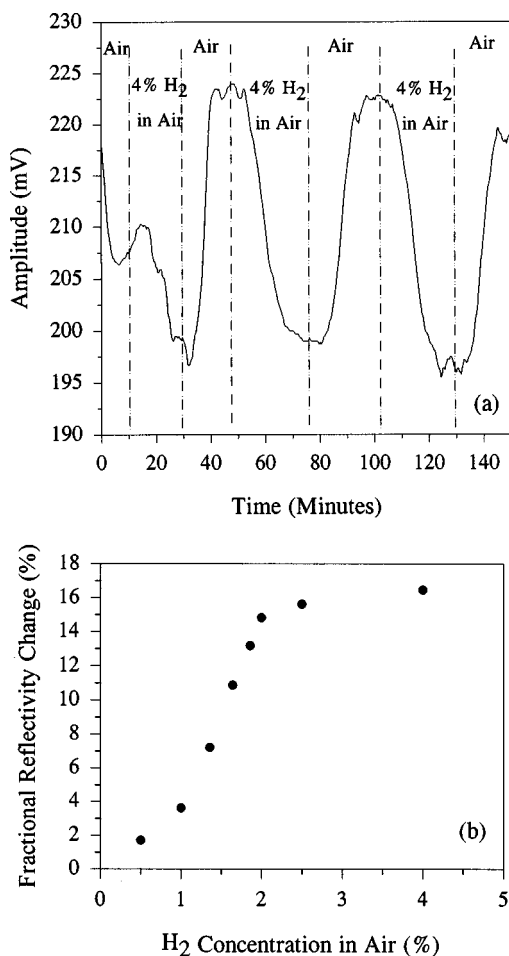


FIG. 7. (a) An initially sluggish response occurs while the surface is first activated, producing a reflection change of  $\sim 6\%$ . The surface fully recovers. Subsequently the response is more rapid and results in a percentage change in reflection of  $\sim 12\%$ . The reordering on the metal film on further exposure to hydrogen gas results in a small drop in the absolute reflectivity. (b) The cycling of an  $80 \text{ \AA}$  palladium film on exposure from 0.5% to 4% hydrogen gas. There is an abrupt change in the magnitude of the reflectivity response at  $\sim 2\%$  hydrogen concentration.

also quite pronounced at 1.5%. As in the earlier data recorded, the recovery cycle is slow and does not return to the original value, giving a maximum recovery of 20%, which is very similar to that obtained for the previous sample exposed to 2% hydrogen in air. As characterized for all earlier data, where exposure to hydrogen occurs after heating of the sample, the percentage change in reflectivity on the air recovery cycle appears linear, Fig. 6(c). The time taken to reach saturation for the  $10 \text{ \AA}$  sample exposed to 2% hydrogen in air is 100 min whereas on 4% exposure this time is halved, as expected.

For the sake of comparison an  $80 \text{ \AA}$  palladium thin metal film on silicon oxide (8–80 times as thick as the thickest and thinnest films) was also examined. The same film has been investigated by the authors using the technique of photo-modulated thermoreflectance<sup>10</sup> and also LMR. We shall highlight the most obvious similarities and differences between this film and the thinner samples, Fig. 7(a).

The first observation pertains to the progressive activation of the surface which follows after several exposures to hydrogen-air cycling, as reported earlier.<sup>10</sup> The change in

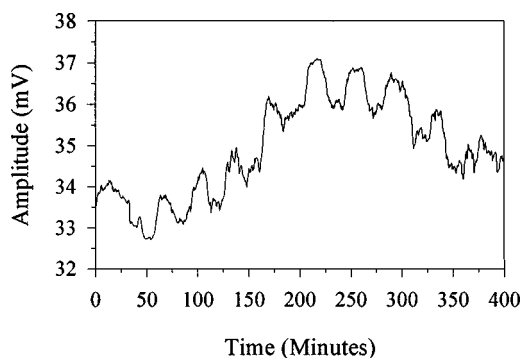


FIG. 8. Annealing a  $5 \text{ \AA}$  sample at  $200^\circ \text{C}$  for 1 h and exposing to 4% hydrogen gas at room temperature resulted in reactivation. Note the oscillating background signal, a result of the high temperature excursion and an indication that the system tends towards a natural damping level on gas cycling.

reflectivity, at 12%, is greater than measured with the thinner samples, whereas the introduction of hydrogen is always accompanied by a decrease in reflectivity. The response to cycling between air and decreasing concentrations of hydrogen shows a saturation point at  $\sim 2\%$  of hydrogen concentration, which we believe to be a  $\beta$  phase transition point, Fig. 7(b).<sup>4,10</sup> For this  $80 \text{ \AA}$  sample, the mixed phase region of the  $\text{PdH}_x$  complex shows that the  $\alpha$  phase, which continues to  $x=0.03$ , is initially dominant.<sup>1</sup> The  $\beta$  phase becomes completely dominant above  $x=0.58$ , at which point the hydride exhibits a slower response due to the compositional change of the  $\beta$  phase hydride. This contrasts with the linear room temperature response demonstrated by the  $10 \text{ \AA}$  sample examined in this work. Such samples are too thin to undergo an  $\alpha$  to  $\beta$  phase transition.

## B. Exposure to hydrogen at room temperature after annealing to $200^\circ \text{C}$

### 1. $1 \text{ \AA}$ Pd on $\text{SiO}_2$

The behavior of the first of these films, having thickness of  $1 \text{ \AA}$ , to 4% hydrogen in balanced air at room temperature resulted in a flat response with no observable change in the amplitude channel. The same film was annealed at  $200^\circ \text{C}$  for 1 h in air at STP and then exposed to the same quantity of hydrogen gas, again without a response to the presence of hydrogen gas. This behavior contrasts with small reflectivity changes that can be induced through a combination of large concentrations of hydrogen gas and high temperatures (Sec. III A).

### 2. $5 \text{ \AA}$ Pd on $\text{SiO}_2$

The room temperature behavior for the  $5 \text{ \AA}$  films is characterized by Fig. 3(a), with the initial response followed by sample inactivity. Annealing the same sample to  $200^\circ \text{C}$  (1 h) and exposing to 4% hydrogen gas at room temperature resulted in reactivation, this made it possible to successively introduce hydrogen and air over many cycles, Fig. 8. The time scales on both the hydrogen and the air recovery cycles appear to be comparable, even though this data is somewhat complicated by its superposition on an oscillating background signal. Reordering of the metal layer occurs as a

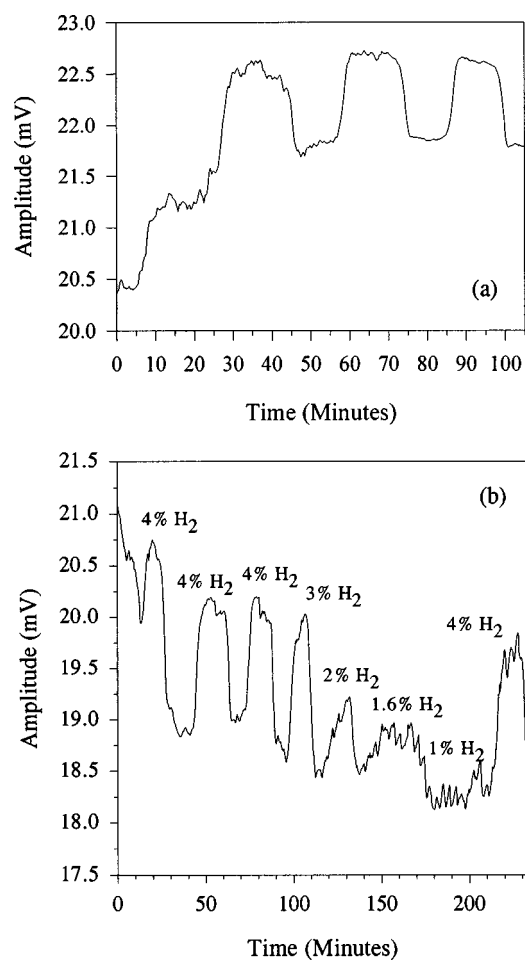


FIG. 9. (a) Grain reordering occurs during annealing to 200 °C, with an indication that cyclic hydrogen impregnation of the palladium film produces a level of reordering similar to the effect of thermal annealing. (b) Departure in the quasistable room temperature behavior of a 10 Å film annealed at 200 °C for 1 h, and subsequently cycled from 4% to 1.5% hydrogen in air.

result of the high temperature excursion, as the system tends towards a natural damping level on gas cycling.

### 3. 10 Å Pd on SiO<sub>2</sub>

The room temperature behavior for the 10 Å Pd film is indicated by Figs. 5(a) and 5(b). A phenomenon particular to the thinner film is that the reflectivity increases on the hydrogen cycle while decreasing on the air cycle, in contrast to the thicker 80 Å films.<sup>4,10</sup>

Figure 9(a) highlights that grain reordering occurs after annealing to 200 °C, as is indicated by the 5% increase in reflectivity of the background signal on the introduction of synthetic air, upon which further data is superimposed. It is clear that subsequent cycling from air to hydrogen results in a progressively improved signal-to-noise ratio. This may be an indication of palladium metal reordering as the reversible hydride complex is formed, with hydrogen impregnation of the palladium film producing a level of reordering similar to the effect of thermal annealing.

Figure 9(b) reveals a departure in this quasistable room temperature behavior using a fresh 10 Å film again initially exposed to hydrogen at room temperature and again annealed at 200 °C (1 h), and subsequently cycled from 4% to

1.5% hydrogen in air. Absolute reflectivity changes between this film and others used earlier differ and are dependent on the homogeneity of the films. Paradoxically, reducing the hydrogen concentration, by mixing down the gas with air, resulted in an increase in the system noise that could not be improved by increasing the gas content back to the original 4% value and we observe an apparent slow down in the response at 3%. This result is completely unexpected.

## IV. DISCUSSION

Our goal was to characterize thin Pd films (on the order of 10 Å and less), first by exposure to a reactive hydrogen/oxygen atmosphere at room temperature and at 90 °C, followed by annealing to 200 °C. The interrogating scheme of LMR allowed for information to be recovered from the amplitude channel, through synchronous detection. There are broadly two important results from this work. First, the promising room temperature hydrogen response of the 1 nm Pd film which may prove useful in the application of a practical hydrogen thin film sensor. Second, the difference between the 80 Å and 1–10 Å films in the sign of the reflectivity change.

There are a number of important issues which require discussion as to the possible causes for the reflectivity changes that were measured. The Pd deposition occurs at room temperature and the film will not be in thermal equilibrium. Increased temperature and gas cycling change the morphology, with the Pd withdrawing from the silicon oxide surface. Generally consisting of isolated islands of metal, thin films exhibit no electrical conductivity. The islands can grow together forming larger structures, even growing in height by as much as ten times the original grain size, significantly changing the surface coverage. However, this change is very small compared with the wavelength of probing laser light, given the very small grain size. The probe beam will average over these regions on the order of the wavelength of light in all spatial directions. It is therefore unlikely that reflectivity changes are associated with changes in the morphology of the films.

A combination of capacitance and ellipsometry measurements by Jansson *et al.*<sup>8</sup> on thick samples has highlighted the importance of the metal-insulator interface which reaches equilibrium faster than the surface; changes in the optical parameters are influenced by the bulk of the metal. For thick films, we have surface, bulk, and substrate effects. However, as the samples become thinner one will expect that the influence of the different interfaces will play an increasingly important role, as the bulk is itself reduced in volume and therefore in importance. For very thin films, consisting of small clusters, we have surface and interface effects. Any probing of an ultrathin metal film with a laser beam will undoubtedly be at a wavelength for which the evanescent field far exceeds the thickness of any of the samples used here. Therefore, any observed changes are likely to be influenced by a combination of phenomena from the different interfaces. On initial exposure to hydrogen, the palladium-silicon oxide interface may provide the immediate response

after which equilibrium is established and the surface properties become important.

An additional effect which needs to be considered is that of hydrogen spillover, in which hydrogen atoms diffuse out from the metal onto the silicon oxide surface and even through to the silicon substrate. The positive charges cause an inversion of the silicon oxide surface. However, the contribution from this phenomena is best studied in a totally inert and dry environment.<sup>7</sup>

The growth of PdO needs to be considered for the experiments of annealing in air. This compound would have different properties from Pd alone and the interaction with hydrogen would be different. This would require a direct comparison with experiments carried out in a completely inert environment. We are currently looking at ways of relating the angular distribution of nonspecularly reflected light and statistical parameters of the surface roughness to the film thickness.<sup>11</sup> Finally, it must be noted that the homogeneity of the films proved crucial for the successful realization of a stable and consistent sample response.

To summarize, the 1 Å film was shown to produce the least significant changes in its reflectivity on exposure to hydrogen and heating, given the low metal coverage for such a thickness this is expected. The 5 Å film gave a small initial response at room temperature, after which the film was inactive. Heating the same film to 90 °C and exposure to high concentrations of hydrogen gas produced large changes in reflectivity that slowly damped out on continued cycles. Large increases in reflectivity were observed for samples that were heated prior to hydrogen exposure. Anomalous features, appearing as peaks in the amplitude channel were also observed during air exposure. Annealing the same film at 200 °C produced further changes in reflectivity, which slowly damped out on continued cycles and were superimposed on a broad background oscillating reflectivity.

The 10 Å palladium film was shown to be capable of linearly detecting levels of hydrogen gas in a balanced air mixture at room temperature over many exposures, indicating a noise equivalent reflectivity change of 500 ppm hydrogen gas. However, continued exposure to hydrogen at room temperature revealed that these thicker films also became

inactive. Heating to 90 °C and exposing to hydrogen gas resulted in a doubling of the reflectivity. As before, anomalous features, appearing as peaks in the amplitude channel were also observed. A comparison of the response time of the 10 Å films exposed to 4% and 2% hydrogen in air, shows that the higher concentration reaches steady-state in half the time of the lower concentration.

Annealing to 200 °C resulted in a deterioration in the general response of the film, however, data also indicated that repeated cycling between hydrogen and air was similar in nature to annealing with an improvement in the observed signal-to-noise ratio. Finally, we observed a departure in the quasistable room temperature behavior for this 10 Å film, with a slowing of the film's response. These data were compared with that for an 80 Å palladium-silicon oxide thin film, which in contrast showed a decrease in reflectivity on exposure to hydrogen gas and was also characterized by having a significant  $\beta$  phase state at room temperature.

## ACKNOWLEDGMENTS

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