Deuterium phase behavior in thin-film Pd

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The absorption of deuterium from the gas phase into two Pd thin films 668 Å and 1207 Å thick was measured at room temperature with *in situ* neutron reflectometry. Room-temperature solubility isothermal curves, out-of-plane film expansion, and deuterium depth profiles were determined from fits to the neutron reflectivity data. The measurements demonstrate that the deuterium solubility behavior, both in solid solution and within the two-phase region, is strongly perturbed by the thin-film geometry, consistent with previous solubility measurements in the published literature. The phase behavior investigated here was observed to depend on film thickness and on deuterium cycling through the two-phase region. The 668-Å film exhibited the greatest initial phase perturbation and most significant changes upon cycling. Upon repeated cycling, both films approach nearly identical deuterium isothermal solubility and out-of-plane expansion behaviors. The observed equilibrium out-of-plane expansion behavior was consistent with the films expanding under an in-plane clamping constraint imposed by the substrate. The effect of this substrate constraining force is to amplify the out-of-plane expansion beyond that expected in bulk Pd. Taken together, these measurements implicate the film/substrate interfacial clamping interaction as the origin of the perturbed hydrogen phase behavior in thin-film geometry. [S0163-1829(98)06025-1]

I. INTRODUCTION

The absorption of hydrogen into thin metal films was actively studied in the 1980s. Thin-film geometry significantly alters hydrogen solubility as compared to bulk behavior and this provoked a fundamental interest in these systems.[1–4] The differences between thin-film and bulk behavior have been explained by a reduction of the hydrogen-hydrogen interaction.[4] The hydrogen-hydrogen interaction, which is elastic in nature, is attractive under bulk conditions. It is this attractive interaction potential that eventually induces precipitation of the high-concentration hydrogen phase. A reduction in the hydrogen-hydrogen interaction is thought to be caused by an elastic (compressive) constraint imposed on the film by the substrate. In fact, Alefeld has demonstrated that the hydrogen-hydrogen interaction can be reduced, even made repulsive, under an imposed compressive stress.[5] The constraint imposed by the substrate in the thin-film geometry acts to inhibit in-plane lattice expansion during hydrogen absorption. The observed modification of the hydrogen phase behavior in thin metal films, as presented below and previously in the published literature, is consistent with a reduction in the hydrogen-hydrogen interaction.

Solubility measurements performed to date with Pd indicate that thin-film geometry results in a lower critical temperature and associated contraction of the two-phase miscibility gap,[1–4] consistent with a weaker (but still attractive) hydrogen-hydrogen interaction in thin-film geometry. However, these measurements only give the film-averaged phase diagram and do not provide any information on lattice expansion during absorption. More recently, x-ray-diffraction measurements have been performed to track lattice expansion during hydrogen absorption by Pd/Nb multilayers[6,7] and Pd films.[7] In the work of Yang *et al.*, Nb was observed to preferentially absorb hydrogen in a manner consistent with a

model allowing for expansion in the out-of-plane direction only.

In this work we present the systematic study of deuterium absorption in thin metal films with *in situ* neutron reflectometry. Unlike x-ray or electron diffraction-based techniques that have poor or nonexistent sensitivity to hydrogen in metals (and therefore derive all structural information from changes in the host lattice), neutron-based techniques are *directly* sensitive to the presence of hydrogen and hydrogen isotopes. As our application of the technique demonstrates, the deuterium phase diagram, film out-of-plane expansion, and deuterium concentration-depth profile are simultaneously obtained during *in situ* measurements. The concurrent measurement of these parameters is unique in the study of hydrogen absorption in thin metal films and helps, we believe, explain the perturbed phase behavior.

II. EXPERIMENT

Two Pd films with thicknesses of 668 and 1207 Å were investigated with neutron reflectivity. The films were grown under identical conditions by magnetron sputter deposition with 10-ppm purity argon gas at 10^{-7} Torr onto polished Si(100) substrates. The substrates were dipped in an HF bath and exposed to air for several minutes before loading into the deposition vacuum chamber. No attempt was made to heat or cool the substrates during deposition. The substrate temperature was below 100 °C under these deposition conditions.

Film orientation, lattice expansion/contraction, and lattice mosaic width were characterized in x-ray-diffraction measurements before initial gas exposure and after repeated exposure. A Rigaku DMAX instrument employing Cu K_α (1.54-Å wavelength) was used for the measurements. Both films exhibited Pd_α [111] preferred growth normal to the substrate surface with a mosaic spread of approximately 5°. Repeated absorption/desorption cycling did not induce ob-
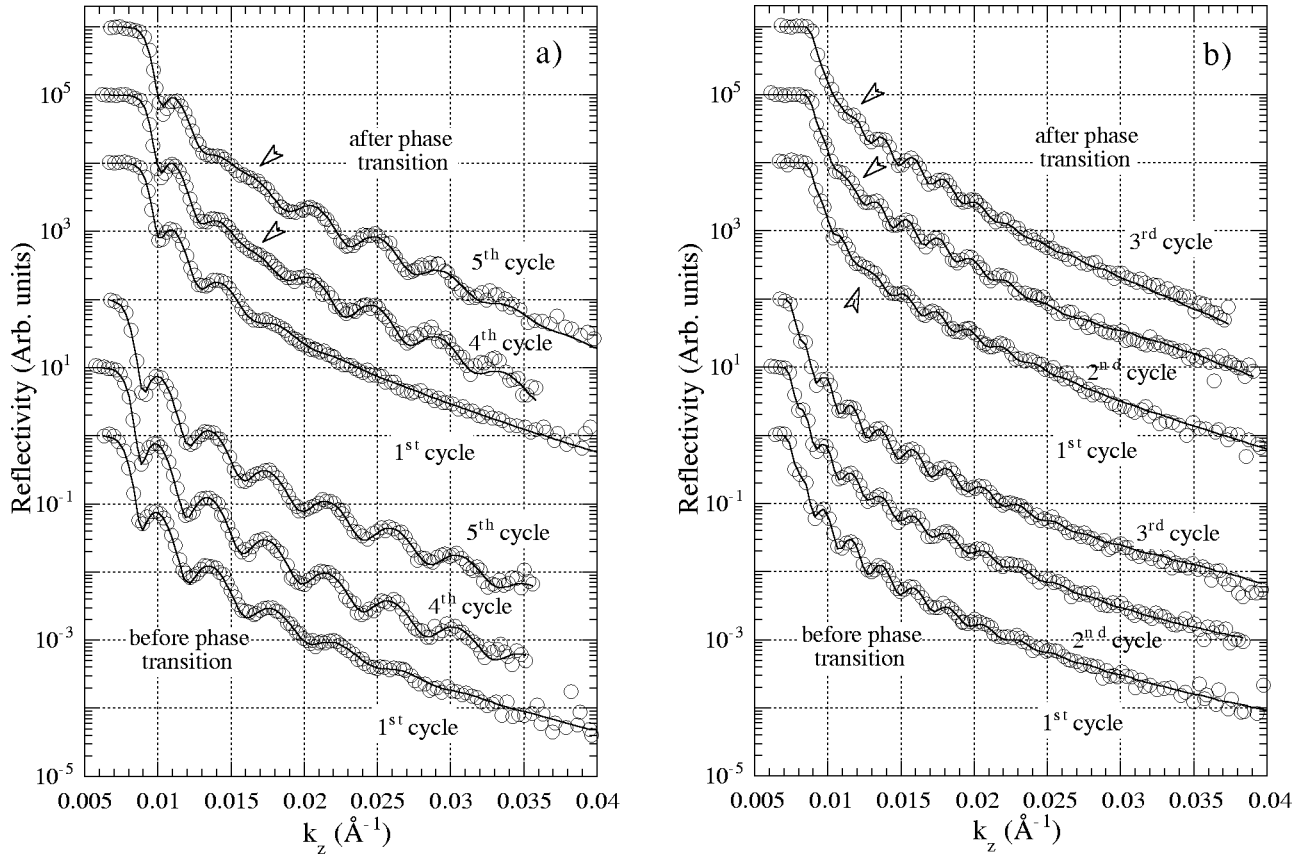
FIG. 1. Reflectivity data sets for the 668-Å and 1207-Å Pd films before and after the phase transition at different cycles. Solid lines are fits to the data. Fits to the first cycle of the 668-Å film use a single SLD layer with a blurred substrate/film interface. Fits to all other reflectivity data sets require two SLD layers, as explained in the text. Location of the cancellation of one short-period oscillation due to the presence of a long-period oscillation is marked.

servable broadening of the $Pd_\alpha(111)$ reflection. However, this is not too surprising given the initial angular width and does not exclude the possibility of cycling-induced deformation of the films.

In situ neutron reflectometry measurements were performed at room temperature for D_2 pressures up to 400 Torr using the POSYII reflectometer at the Intense Pulsed Neutron Source at Argonne National Laboratory.[8] The neutron reflectometry technique is sensitive to variations of the neutron scattering length density (SLD) as a function of depth normal to the film (the z direction). The SLD variation $\rho(z)$ is given by

$$\rho(z) = \sum_i N_i(z) b_i, \qquad (1)$$

where N_i and b_i are the atomic-number density and neutron-scattering length of the ith component. The SLD variation, and therefore $N_i(z)$, was determined from the neutron-reflectometry data using a genetic fitting algorithm.[9]

Adequate differences in SLD (often referred to as the SLD contrast) between the substrate and at least part of the overlayer are typically required to derive useful information from neutron reflectometry. This condition is met for a Pd film ($\rho_{Pd} = 4.01 \times 10^{10}$ cm^{-2}) on a Si ($\rho_{Si} = 2.21 \times 10^{10}$ cm^{-2}) substrate. An additional requirement in the present case is that the absorbed solute further enhances the contrast. It is for this reason that deuterium was used instead

of hydrogen. The deuteron, with a positive scattering length ($b_D = 6.671 \times 10^{-13}$ cm), will increase the SLD and improve the contrast between the deuterium-loaded Pd film and the Si substrate. On the other hand, the scattering length of the proton is negative ($b_H = -3.7406 \times 10^{-13}$ cm); hydrogen absorption in the Pd film will reduce the SLD and result in lower contrast relative to the Si substrate. Further details of the neutron-reflectometry technique and the data-fitting routine applied to hydrogen and deuterium absorption in thin-film metals can be found elsewhere.[10]

III. RESULTS

Figure 1 shows examples of the reflectivity responses from the 668-Å and 1207-Å films at two different D_2 gas pressures corresponding to before and after the phase transformation (see below). In the first cycle of the 668-Å film oscillations are evident that are dampened at high k_z upon initial low-pressure D_2 gas exposure. This dampening progresses to include lower k_z oscillations at higher gas pressures. These oscillations, found in all of our data sets, are due to coherent interference between neutrons reflected from two separated interfaces within the film; in our case, the substrate/film interface and film/air interface. To a first approximation, the period in k_z of the oscillations is inversely proportional to the separation of the interfaces.[10] The dampening of the interference oscillations at high k_z implies that one or both of the interfaces are made diffuse upon deute-
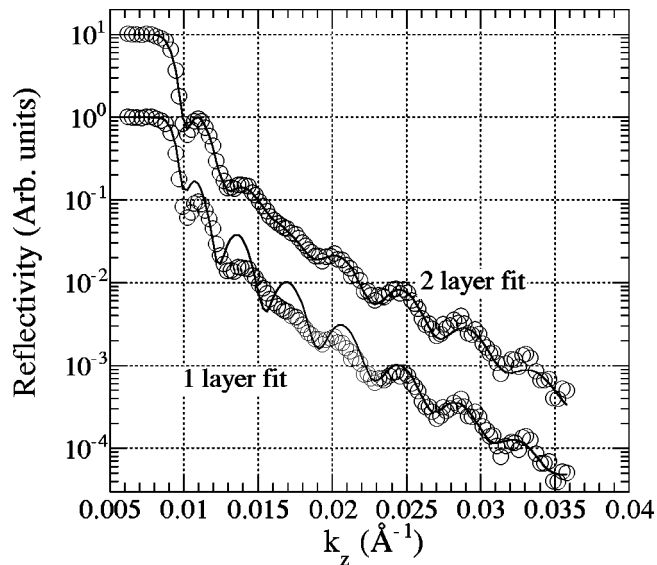
FIG. 2. Reflectivity from the fourth cycle of the 668-Å Pd film at 120-Torr D_2. The lines are examples of fits to the data using one-layer and two-layer SLD profile models shown in Fig. 3.
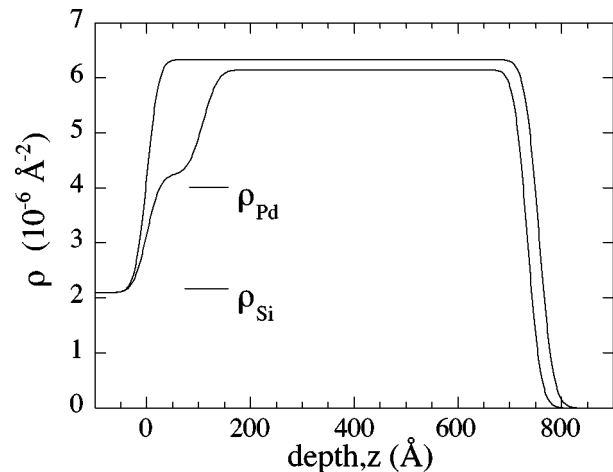

FIG. 3. SLD profiles for the two fits shown in Fig. 2. The SLD is observed to increase everywhere deuterium is absorbed by the film (corresponding to the addition of deuterium with $b_D > 0$). The film-substrate interface is set to a depth of zero.

rium absorption. Fits to our data implicate the film/substrate interface. The progressive dampening of the oscillations in the 668-Å first cycle data is the result of a nonuniform scattering length density near the film-substrate interface. This nonuniformity is, in turn, due to a nonuniform increase in SLD upon deuterium absorption.

The behavior of the 668-Å film is changed during the fourth and fifth cycles in Fig. 1 (the second and third cycles were not characterized with neutron reflectometry). The oscillations are no longer progressively damped, but instead remained well defined in the high k_z range at high pressures. In addition, a second feature develops, as marked in Fig. 1. The feature, in which an interference oscillation near $k_z = 0.01$ is canceled, is due to the presence of a second thickness oscillation (which destructively interferes with the first) with a much larger period. Based on fits to the data discussed below, we attribute the development of this second, large-period oscillation to the formation of a new layer within the deuterium-loaded Pd film.

The 1207-Å film does not exhibit the same effects of cycling. Within the measurement resolution oscillations do not dampen at high k_z for high gas pressures during the first cycle. Furthermore, the above-mentioned cancellation effect (marked in Fig. 1) is present in all cycles, including the first.

We present two fits to the neutron-reflectivity response of the 668-Å film in Fig. 2. The first fit was performed using an SLD profile with a single layer representing the deuterium-loaded Pd film. The profile height (SLD value), thickness (corresponding to the layer thickness), and interfacial widths (or blurriness of the interfaces) are treated as variable parameters during the fitting process. This model successfully fit the response of the 668-Å film during the *first* cycle. However, it clearly does not work for the fourth cycle.

The second fit shown in Fig. 2 is a two-layer SLD profile. As with the single-layer model, the layer heights, thicknesses, and widths are used as fitting parameters. The persistence of the oscillations at high k_z and the cancellation feature discussed above are both reproduced by the two-layer

fitting model. The one-layer and two-layer SLD profiles obtained from the fitting procedure are shown in Fig. 3. From the two-layer model, we can now identify a second layer at the substrate/film interface as a region of the film where deuterium is excluded. We base this conclusion on the fact that the SLD value of the second layer closely corresponds to the SLD for bulk Pd, marked in Fig. 3. Thus the SLD does not increase in this region of the film upon deuterium absorption.

Fits to the measured reflectivity data provide both the overall or average concentration and out-of-plane film expansion. The average deuterium concentration can be calculated at each exposure pressure with the following formula:

$$\frac{[D]}{[Pd]} = \frac{b_{Pd}}{b_D} \left[\frac{\rho}{\rho_0} \frac{t_f - t_e}{t_0 - t_e} - 1 \right], \tag{2}$$

where ρ_0 and ρ are the initial scattering length density of the film before deuterium exposure and the scattering length density of the film above the exclusion region at deuterium gas pressure p, respectively; t_0 is the initial thickness of the film; and t_f and t_e are the thicknesses of the film and exclusion region, respectively, at pressure p. This expression takes into account the reduction of the host Pd SLD during deuterium absorption (due to the induced film expansion) and also the fact that part of the film (the exclusion region) does not absorb deuterium, and therefore should not be included in the concentration calculation.

Once the average concentrations are known, the room-temperature pressure versus concentration isotherms can be constructed. These are shown in Fig. 4 for each cycle of the two films. The phase diagrams we present have several common traits with other Pd-H thin-film phase diagrams in the published literature.[3,4,11] First, the plateau pressure is higher than expected in bulk Pd [approximately 8.5 Torr$^{1/2}$ (Ref. 12)]. In addition, the plateau width is reduced compared to the bulk behavior. Both of these observations are consistent with a general contraction of the immiscible region in the thin-film Pd-D system.

Cycling is seen to have a noticeable effect on the measured phase diagrams in Fig. 4. Notice especially the large
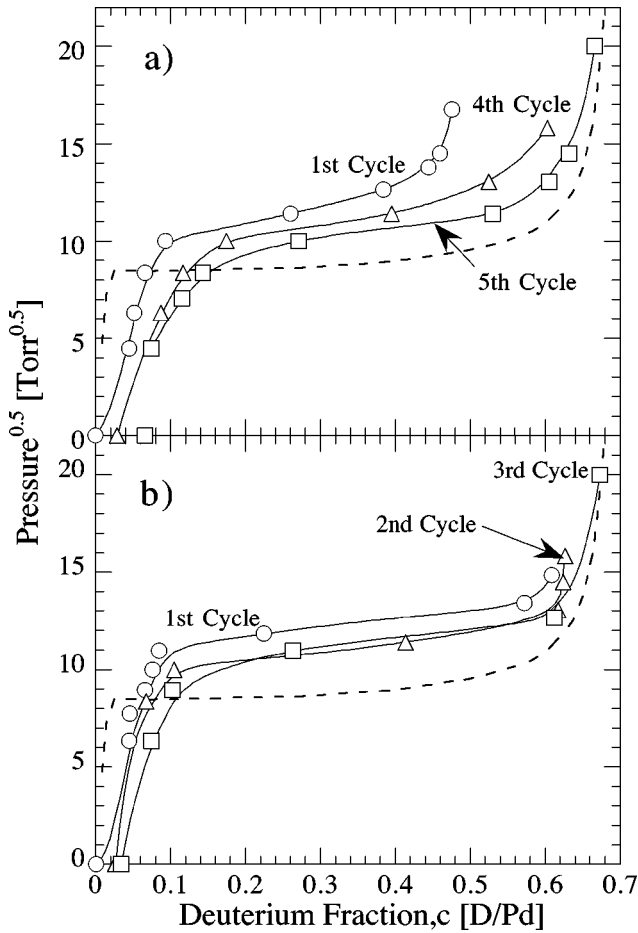
FIG. 4. Pressure vs concentration room-temperature isotherms for the 668-Å (a) and 1207-Å (b) films. Data points at 0 Torr for cycles after the first indicate the presence of residual deuterium. Solid lines are drawn as aides to the eye. The bulk Pd-D isotherm from Ref. 12 is shown for comparison as a dotted line.
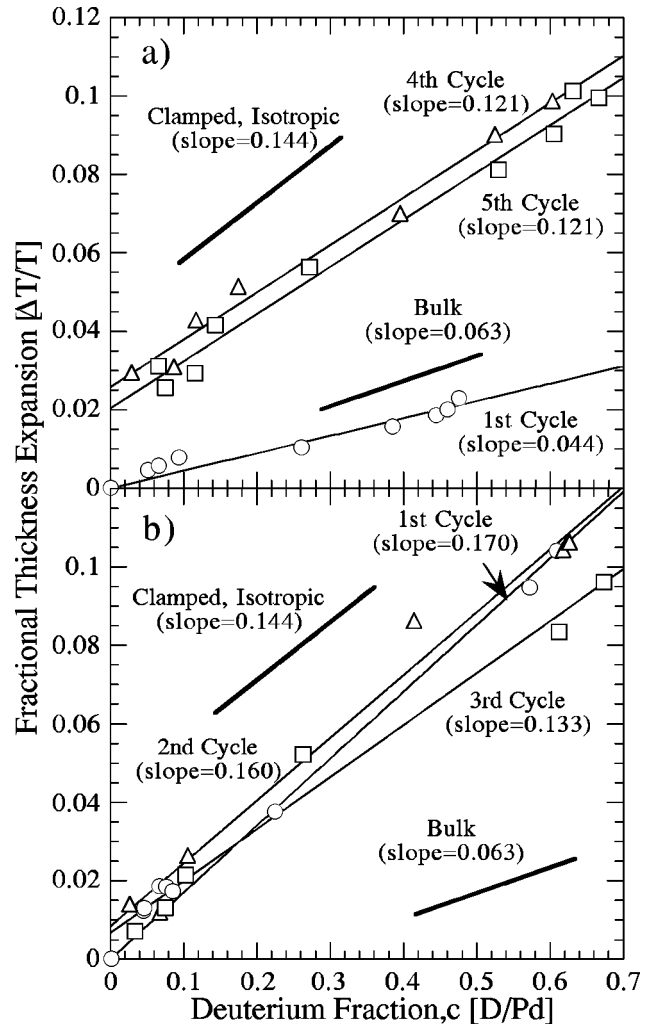

FIG. 5. Pd film expansion vs concentration for the 668-Å (a) and 1207-Å (b) films. The two bold lines represent the slopes for bulk, three-dimensional expansion and for clamped, isotropic, one-dimensional expansion.

change in phase behavior of the 668-Å film during cycling. Both films approach an equilibrium behavior with respect to cycling; the two-phase-region plateau flattens and the maximum solubility within the film increases. In fact, the last isotherms measured for each film are very similar.

The fits to the reflectivity data also give the out-of-plane film expansion at each D_2 gas-exposure pressure. This can be seen clearly in the Fig. 3; the overall film thickness is expanded well beyond the initial 668-Å thickness. (Incidentally, the initial thicknesses of both films were determined from fits to the neutron-reflectometry data before deuterium exposure. In each case, a single SLD layer was used and gave Pd atomic densities within a few percent of bulk.) We can now construct the out-of-plane film expansion behavior as a function of average deuterium concentration within each film. These behaviors, shown in Fig. 5, represent the film expansion above the exclusion region only; the exclusion region does not absorb deuterium to appreciable levels and therefore does not contribute to the overall film expansion.

Two limiting behaviors are identified in Fig. 5. First, the lattice expansion in bulk Pd is known:[13]

$$\alpha = \frac{1}{C}\frac{\Delta T}{T} \approx \frac{1}{3}\frac{\Delta \nu}{\Omega} = 0.063, \qquad (3)$$

where $\Delta T/T$ is the fractional change in the film thickness, $\Delta \nu$ and Ω are partial molar volumes of hydrogen and Pd, respectively, and C is the hydrogen (deuterium) atomic fraction. The other limiting behavior given is characteristic of an isotropic film absorbing hydrogen (deuterium) under conditions where in-plane expansion is prohibited due to the constraint imposed by the substrate,[6]

$$\alpha = \frac{1}{C}\frac{\Delta T}{T} = \left(1 + \frac{2\nu}{1-\nu}\right)\frac{1}{3}\frac{\Delta \nu}{\Omega} = 0.144, \qquad (4)$$

where ν is Poisson's ratio for Pd ($\nu = 0.39$).

The out-of-plane expansion behavior for each film is best summarized in Fig. 6, showing the slope of expansion versus concentration α as a function of cycle number. The different behavior of the two films can be clearly seen in this representation; each approaches the same limit from different extremes upon repeated cycling. The limiting expansion behavior both films approach is just below that expected for a clamped, isotropic film, and is consistent with the preferential alignment of the elastically stiffer (111) direction normal to the substrate.
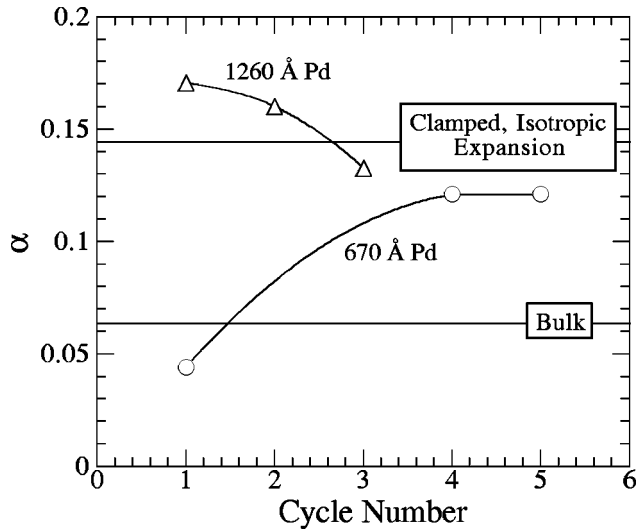
FIG. 6. The derivative of the out-of-plane expansion with respect to deuterium concentration (expansion coefficient α) as a function of cycle number for the 668-Å and 1207-Å Pd films. The lower solid horizontal line represents the bulk expansion limit, while the upper line represents the clamped isotropic expansion limit as discussed in the text.

The results of x-ray-diffraction analysis of the out-of-plane Pd(111) lattice spacing and overall film thicknesses from neutron reflectometry are shown together in Table I. Initially both films are not strained out of plane. After cycling, however, the Pd(111) plane spacing is contracted. This indicates that the films are in a state of compression in the direction perpendicular to the substrate and this is consistent with the observations of Yang et al. The lattice spacing is contracted in spite of the fact that the neutron-reflectivity measurements of the films indicate that the total film thickness remains expanded slightly after deuterium evolution.

We suspect this residual film expansion, which is especially large for the 668-Å film (as seen in Fig. 5), is due to unevolved deuterium and possible dislocation formation. Evidence of this can be seen in Fig. 4(a). The fourth and fifth cycles of the 668-Å film exhibit nonzero deuterium concentration values under vacuum; a reflection of the fact that

residual deuterium was resolved in the neutron-reflectivity vacuum runs prior to the fourth and fifth cycle absorption measurements. This residual deuterium is likely to be trapped at the Pd/silicide interface (see below). We now consider two aspects of our work before final discussion of the results. First, we note that the neutron-reflectometry measurements do not provide any information about the in-plane expansion during deuterium absorption. Accordingly, the reduction of the host Pd SLD due to in-plane expansion cannot be included in Eq. (2). Second, the possibility of Pd silicide (Pd_2Si) formation during film deposition deserves discussion. While postdeposition Pd_2Si growth is unlikely because of extremely slow kinetics, formation during low substrate temperature deposition has been documented.[14] The neutron SLD of Pd_2Si ($\rho_{Pd_2Si} = 3.82 \times 10^{10}$ cm^{-2}) is very close to that of bulk Pd, and the presence of a silicide layer cannot be confirmed with neutron reflectometry. However, adequate *electron* density differences exist between Si, Pd, and Pd_2Si, permitting x-ray reflectivity analysis. The x-ray reflectivity response of the 668-Å film in air after the fifth cycle is shown in Fig. 7. Notice the long-period oscillations present at high k_z. This feature is an indication of a ledge or shoulder in the electron density depth distribution, this time due to a Pd silicide layer at the film-substrate interface. The electron density depth profile, derived from fitting the x-ray reflectivity data and shown in the Fig. 7 inset, confirms the existence of a Pd silicide layer of approximately 100 Å thickness. The x-ray SLD of the silicide in the fitted model is 20% lower than the SLD of Pd_2Si. This is consistent with a Pd_xSi phase with $x < 2$ observed by others to form spontaneously upon deposition.[15]

IV. DISCUSSION

The room-temperature deuterium-absorption isothermal measurements presented here show a strong dependence on film thickness and on deuterium absorption/desorption cycling. The isothermal behavior for the 668-Å film changes significantly upon repeated cycling through the two-phase region and is consistent with the film becoming more compliant with respect to deuterium absorption. Concurrent with

TABLE I. Results of neutron reflectometry measurements of the total film thicknesses and x-ray-diffraction measurements of the out-of-plane Pd(111) lattice spacings for the 668-Å and 1207-Å films.

	668-Å Pd film		1207-Å Pd film	
	Thickness (Å$\pm$5 Å)	Change (%)	Thickness (Å$\pm$5 Å)	Change (%)
Initial	668		1207	
After first cycle	675	1.1$\pm$1.0	1219	1.0$\pm$0.6
After second cycle			1215	0.7$\pm$0.6
After third cycle	688	3.0$\pm$1.1	1215	0.7$\pm$0.6
After fourth cycle	689	3.2$\pm$1.1		
After fifth cycle	691	3.4$\pm$1.1		
	Pd(111) spacing (Å)	Strain (%)	Pd(111) spacing (Å)	Strain (%)
Initial	2.246	0.00	2.246[a]	0.00
After third cycle			2.239	-0.32
After fifth cycle	2.236	-0.44		

[a]This value was measured with a 1500-Å film made under the same conditions as the 1207-Å film.
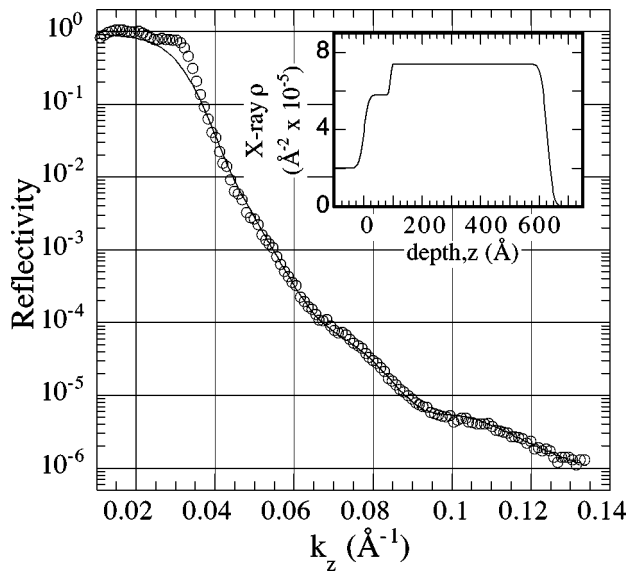
FIG. 7. X-ray reflectivity data from the 668-Å Pd film after repeated cycling through the phase transition. The long-period oscillation from the silicide layer can be clearly seen. The solid line is a fit to the data using the model shown in the inset.

this effect is the development of an exclusion region at the film/substrate interface extending into the film approximately 100 Å. Changes in the room-temperature absorption isothermal curves during cycling of the 1207-Å film are much smaller. Furthermore, a well-defined exclusion region is observed during the very first cycle. The response of this film is therefore consistent with a more equilibriumlike behavior at the onset of deuterium absorption.

The out-of-plane expansion behavior determined for each film during deuterium absorption is strongly dependent on film thickness and cycling as well. In fact, each film approaches the same limiting expansion behavior from different extremes. The initially low out-of-plane expansion of the 668-Å film during the first absorption cycle is consistent with the suppressed deuterium solubility observed in the corresponding absorption isothermal measurement. In other words, initial (first absorption cycle) deuterium absorption in the 668-Å film is inhibited and this is manifested in a suppressed expansion and a more strongly perturbed isothermal behavior. Eventually, after repeated cycling, both films approach an equilibrium expansion and isothermal behavior that are similar.

We believe that the exclusion region corresponds to a Pd silicide layer formed during film deposition. This assumes of course that deuterium solubility is completely suppressed in the Pd silicide layer. However, we know of no hydrogen or deuterium solubility measurements in Pd silicide that can confirm this assumption. Attempts to resolve the silicide layer with Auger electron spectroscopy were not successful, probably because the layer thickness was within the ion-beam mixing limit of the system. However, the x-ray reflectivity measurement of the 668-Å film discussed above confirms the identity of the exclusion region as a form of palladium silicide.

The presence of a silicide layer is strictly a consequence of the Si substrate. It could be argued, then, that the observations presented here are not typical of thin-film Pd. We

view the current measurements in the following way. First, reduced or eliminated in-plane expansion is a necessary condition for film adhesion. If the in-plane expansion is large the film would separate from the substrate during deuterium absorption. The formation of the silicide layer represents a form of diffusional bonding or atomic mixing during deposition that promotes film adhesion and facilitates the clamped expansion behavior of the film. That is not to say films without some type of bonding agent will necessarily debond during absorption. However, the only resistive force available to inhibit the in-plane film expansion must be supplied (or imposed) by the substrate across the film/substrate interface.

The second point of discussion concerns the behavior of the 668-Å film, specifically the resolution of the exclusion region upon deuterium cycling. This development coincides with an overall increase in film compliance, as seen by the increased out-of-plane expansion and higher deuterium isothermal solubility. Similar expansion versus cycling behavior has been observed in the Nb component of a Pd/Nb multilayer on a Si substrate.[6] The observed behavior was attributed to the initial compressive stress state of the Nb component and dislocation generation induced by preferential hydrogen absorption in the Nb. We believe a similar mechanism may be at work here. However, in the present case dislocations are generated at the film/silicide interface. For the 668-Å film, this occurred only upon deuterium cycling, leading to the resolution of the exclusion region after the first cycle. The thickness of the 1207-Å film was such that the interfacial dislocations were generated during the deposition. (An analogous, coherency loss mechanism is know to operate in epitaxial thin films.) Thus, the exclusion region was observed during the first deuterium loading measurement of the 1207-Å film.

V. CONCLUSIONS

Taken together, the Pd film room-temperature solubility isothermal measurements and out-of-plane expansion behaviors reported here represent a consistent set of observations. Two films with thicknesses that differ by a factor of 2 show nearly identical equilibrium deuterium phase behavior after repeated deuterium exposure cycling. This behavior is characteristic of the films absorbing deuterium under a clamping constraint imposed at the film/substrate interface. From this we conclude that the modified deuterium-absorption behavior seen here is due to the clamping constraint placed on the film by the substrate and associated reduction of the hydrogen-hydrogen (or in our case the deuterium-deuterium) interaction energy.

The response of the two films as the equilibrium behavior is approached is significantly different, with the thinner film exhibiting a greater shift from an initially noncompliant to a more compliant behavior. The most unique aspect of the present work is the ability of neutron reflectometry to resolve the deuterium depth profile during the *in situ* measurements. The resolution of the depth profile clearly indicates an exclusion region approximately 100 Å in width. Although this region is attributed to silicide formation during film deposition, we do not consider the film/substrate bonding promoted by this layer to be atypical. Rather, adequate bonding must be maintained if the film remains attached to the substrate

during solute incorporation. It is through this bond that the stress field is imposed on the film by the substrate.

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