Porous Mg formation upon dehydrogenation of MgH₂ thin films

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The hydrogenation and dehydrogenation of a thin film of Mg with a Pd cap layer was measured using neutron reflectometry. Upon hydrogenation, (at 373 K and 0.2 MPa H₂), the Mg film swelled in the surface normal direction by an amount roughly equal to the difference in volume between MgH₂ and Mg. After dehydrogenation (at 343–423 K), the Mg film returned to a composition of Mg but retained the swelled thickness by incorporating voids. The presence of the voids is confirmed by SEM micrographs. The voids may explain some of the changes in absorption kinetics after full cycling of Mg films. © 2011 American Institute of Physics. [doi:10.1063/1.3574664]

I. INTRODUCTION

As a potential hydrogen-storage material, the relatively light element magnesium forms a dihydride (MgH₂) with a favorably high H mass fraction of 7.66%. Yet its usefulness for on-board vehicular applications is precluded by the unfavorable thermodynamics for dehydrogenation (MgH₂ \leftrightarrow Mg + H₂), where a 0.1 MPa equilibrium H₂ pressure requires unreasonably high temperatures close to 600 K. Nonetheless, interest in Mg-based storage systems still persists due to magnesium's relative abundance, low cost, and high storage capacity. For example, recent studies have investigated the utility of magnesium hydride as a component of destabilized, hybrid storage systems.^{1–3}

Although thermodynamic and kinetic studies of the magnesium-hydrogen system have been plentiful,⁴⁻¹⁰ they have, in general, been performed on bulk and often ballmilled polycrystalline powder samples with only limited investigations employing more well-defined thin-film materials, for example, the hydrogenography, positron Doppler broadening depth profiling, and/or x-ray diffraction (XRD) studies of hydrogen interactions with thin films of Mg^{11-13} and Mg-Ti and Mg-V multilayers and alloys.14-17 The recent in situ XRD study by some of us¹¹ to study the limiting kinetic mechanisms of hydride formation in well-ordered, epitaxial Mg thin films capped with thin Pd layers suggested that hydride formation occurs via a growing hydride layer originating at the film surface. While reactions at an interface or diffusion through the Pd layer control the growth rate for hydride layer thicknesses smaller than ~ 600 Å, above this thickness, hydrogen diffusion through the hydride layer becomes rate controlling at the conditions studied. It was also observed that regrowth of Mg from MgH₂ occurs at both the Pd/MgH₂ and MgH₂/Mg interfaces. The former occurs by nucleation and growth with a polycrystalline structure. The latter occurs by solid phase epitaxy given sufficient Mg remaining after the MgH₂

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formation. The rate of this epitaxial regrowth is determined by the diffusion of the hydrogen through the intervening thickness of MgH_2 .¹²

Additionally, altering material microstructure has been shown to significantly affect the kinetics of the Mg-H reaction.^{9,18} Conversely, cycling between the metal and hydride states can induce microstructural changes in metal hydride systems.¹⁹ Even in highly oriented thin-film systems, the hydrogenation/dehydrogenation cycle can alter the microstructure of Mg/MgH₂ films.¹² However, the mechanisms responsible for these connections between microstructure and reaction kinetics remain elusive and poorly understood. Developing an understanding of the mechanisms involved in the hydride formation and decomposition reactions is crucial for engineering new hydrogen storage materials with improved properties.

In the current study, we have further attempted to characterize the detailed mechanisms associated with both magnesium hydride formation and decomposition using a well-ordered, Pd-capped, Mg thin film in conjunction with neutron reflectivity measurements. Unlike XRD, neutron reflectivity (NR) is highly sensitive to hydrogen. As such, the concentration depth profiles of all elements present, including hydrogen, can potentially be mapped out at various stages of hydriding/dehydriding.

II. EXPERIMENTAL

The sample was deposited onto a 25 mm diameter, 1 mm thick, single-crystal Al₂O₃ substrate polished for epitaxial growth to $< 0.01^{\circ}$ mean surface deviation obtained from Meller Optics, Inc.²⁰ Prior to deposition, the substrate was cleaned in a multi-step cleaning process consisting of: (i) a 5 min sonicated soak in acetone, (ii) a 5 min sonicated soak in methanol, and (iii) a 5 min soak in 1:1:98 NH₄OH:H₂O₂:deionized (DI) H₂O followed by a DI H₂O rinse. The substrate was dried with flowing dry nitrogen between steps (i) and (ii), between steps (ii) and (iii), and following the final rinse. After completing the final drying step, the substrate was immediately loaded into a UHV sputter deposition chamber

and pumped down to a base pressure better than 1 μ Pa to prevent surface contamination.

The chamber contains four independently shuttered targets (of which two were used) arranged confocally toward the substrate. Elemental Mg (99.98% pure) and Pd (99.95% pure) targets were used. A set of halogen lamps behind the substrate holder heated the sample when depositing at elevated temperature. A nominally 100 nm Mg film was first deposited at 100 °C at a rate of 0.137 nm/s using 0.20 Pa Ar. Following deposition of Mg, the sample was allowed to cool for 1 h under vacuum before depositing a nominally 50 nm Pd capping layer at room temperature at a rate of 0.086 nm/s using 0.33 Pa Ar. The substrate was rotated at \sim 5 rpm during both Mg and Pd depositions to ensure uniform layer thicknesses across the entire substrate.

After growth, the as-deposited film was analyzed by xray diffraction (XRD) using $Cu_{K\alpha}$ radiation in a PANalytical X'PertPRO diffractometer. Figure 1(a) shows theta – two theta XRD from the sample with the scattering vector aligned along the Mg (0002) Bragg reflection. The presence of only (000L) type reflections from the Mg indicates texture with (0002)-type crystal planes oriented parallel to the sample surface. The Mg(0002) rocking curve shown in an inset to Fig. 1(a) indicates the sharp (0002) texture out of the sample plane with a 0.6° FWHM. The Mg (1011) phi scan of Fig. 1(b) demonstrates the high degree of in-plane texture present in the Mg layer, with ~7° FWHM seen for the six peaks. Further characterization and details of the general film structure can be found elsewhere.¹²

Neutron reflectometry²¹ (NR) data were taken as described previously²² using the NG1 reflectometer (similar to one described in the literature²³) at the NIST Center for



FIG. 1. (a) XRD scan of the as-deposited epitaxial Mg film with Pd capping layer. In addition to the peaks from Mg, Pd, and the Al₂O₃ substrate, small peaks from the Al sample holder (S.H.) appear due to the large beam size. The inset shows a rocking curve of the Mg(0002) peak (FWHM ~0.6°) demonstrating the highly aligned texture of the film. (b) A phi scan of the Mg (10 $\overline{1}$ 1) peaks (FWHM ~7°), which show the biaxial texture of the Mg layer.

Neutron Research. Specular NR is a measure of the reflected intensity divided by incident intensity as a function of $Q_z = 2\pi \sin(\theta)/\lambda$, where θ is the incident and reflected angle and λ is the neutron wavelength. These data can be fit to determine the depth profile of the neutron scattering length density, SLD, which can be interpreted as a composition depth profile when the SLD of the constituents are known. The thickness of films as thin as 1–2 nm can be measured with sub-Ångström accuracy.^{24,25} Modeling is based upon the Parratt formalism,²⁶ and the REFLPAK software was used to fit the data.²⁷

The sample was loaded into a vacuum vessel designed specifically for in situ hydrogen loading and NR. It was pumped with a turbo pump to a base pressure of 0.1 mPa and the "as-grown" data were taken. To load the sample, it was first heated to 100 °C, and then the chamber was filled with high purity H_2 gas to a pressure of 0.2 MPa (2 atm) and sealed. The sample was held at this temperature for 90 min then cooled to 20 °C during which the pressure decreased to 0.178 MPa. At this point, the chamber was pumped down to a pressure of 1.3 Pa and sealed. This residual hydrogen served to prevent desorption from the sample during the NR measurements. It is below the pressure at which measurable amounts of H are absorbed into Pd at the measurement temperature, keeping the SLD of the Pd layer near that of bulk Pd. Temperature was maintained at 20 °C for the NR measurements in the "loaded" condition.

The first desorption occurred by initially pumping the chamber to its base pressure, then heating the sample to 70 °C which took roughly 13 min. This desorption temperature was maintained for 31 min during which time a limited Q-range was scanned to detect changes to the sample, indicating desorption of hydrogen. The sample was cooled to 20 °C (which took 50 min), and then the chamber was isolated from the pump. NR data were then taken at 20 °C. The second desorption was performed in a similar manner, also at 70 °C, but for two intervals, the first lasting 10 min (after which partial NR scans at 20 °C were taken) and the second 75 min.

The third desorption was performed at increasing temperatures until significant changes were seen in NR scans taken at the elevated desorption temperature over a limited Q-range. The temperatures and times (which includes the ramp up to the next higher temperature) were as follows: $80 \degree C$ for 90 min, $82 \degree C$ for 60 min, $84 \degree C$ for 82 min, $88 \degree C$ for 30 min, $90 \degree C$ for 36 min, $96 \degree C$ for 35 min, $100 \degree C$ for 65 min, $150 \degree C$ for 60 min. Note that at $150 \degree C$, no scans were taken due to sample detaching from the holder; the sample was cooled to room temperature and opened to air for reattachment.

Initial analysis of the NR data was performed using adaptive Markov chain Monte Carlo uncertainty estimation.²⁸ In addition to identifying model parameters that show excellent fits to the data, this method showed that the uncertainty in the optimal values can be reasonably represented by the normal distribution. The initial estimates were further refined in REFLPAK using the Levenburg–Marquardt leastsquares fitting technique²⁹ with parameter uncertainties derived from the resulting covariance matrix. Following the neutron reflectometry measurements, the sample was examined using a FEI dual-beam focused ion beam (FIB)/scanning electron microscope (SEM), equipped with an ion beam etching function. To observe a fresh surface prepared in vacuum, the sample is tilted 52° to perform ion milling with a gallium ion beam current of 10 pA operating at 30 kV, in a series of steps across the surface, at increasing depths, until the final layer milled through the metal layers and into the sapphire substrate.

III. RESULTS

The specular reflectivity data are shown in Fig. 2 for the five conditions described in the preceding text. The error bars represent one standard deviation based upon the counting statistics of the specular, background, and slit scans used to obtain the specular reflectivity. The data clearly show changes in the oscillation period as the sample changes thickness and changes in the pattern of peak intensities as the various layers that make up the sample change in thickness and scattering length density relative to each other. The solid lines are best fits, showing excellent agreement to the data.



FIG. 2. (Color online) Neutron reflectivity data (points) plus best fits to the data (lines) for the sample under the five conditions as indicated. For the third desorption, both the best fit (dashed line) and an alternate fit with 2 layers of MgH_x (solid line) are shown. Additional data were taken that showed no features and were not displayed.

The scattering length density profiles corresponding to those fits are shown in Fig. 3 and explained in the following text.

Several models of possible sample structures were fit to the data to determine the structure that best describes the sample in each of the five conditions that were measured within the limitations of the data and technique. These models differ in the number of layers and the ranges of the fit parameters for each layer. Starting at the sapphire substrate these layers are, an interfacial layer, possibly MgO, one or two layers of MgH_x , where x can range from 0 to 2, and the Pd layer. The data sets are fit independently of each other (that is, no parameters were constrained to be the same for multiple data sets so as to enforce agreement among the fit parameters.) This approach allowed us to investigate changes in all the layers of the sample during the experiment to determine if there are systematic trends or if variations represent random variations. While all models that were tested resulted in good fits to the data, some were rejected if either the best fits contained SLD levels that were inconsistent with the known materials in the sample or if they contained more layers than other models with similar χ^2 values. In all models, the substrate SLD values were fixed at the known value for sapphire and the Mg containing layers were constrained to be within the range bounded below by the SLD of MgH₂ (which is negative) and above by the SLD of Mg. See the appendix for a description of the various models that were considered.

Figure 3 shows the SLD profiles corresponding to the best fits. Also indicated are the SLD values of various materials in the sample. The SLD profiles, determined by fitting reflectivity data, have an arbitrary origin of the depth scale. For illustrative purposes, we have chosen the origins to coalign the interface between the MgO and the MgH_x layer above it, for all sample conditions. This highlights the changes in thickness of the MgO and the MgH_x layers. It was found that a thin layer directly above the sapphire substrate was necessary to obtain high quality fits. This layer, with a SLD slightly higher than that of sapphire, can be interpreted as MgO or a similar compound. It may have been formed either by residual oxygen in the chamber during the



FIG. 3. (Color online) Scattering length density as a function of distance from the substrate from the best fits for the five conditions of the sample. Two fits are included for the 3rd desorption, the best fit and a fit to a model with two MgH_x layers.

sputter deposition of Mg or as a result of a reaction between the sapphire and the Mg. The noticeable variations in the SLD of the MgO layer are within the uncertainty of the fits. Fitting models that have initial conditions without the MgO layer but with two MgH_x layers resulted in one of the MgH_x layers replacing the MgO layer for two of the data sets. Removing both the MgO and second MgH_x layer from the model resulted in fits that were considerably worse than for models that allowed an MgO layer. Therefore, the MgO layer is included in the best fit model.

Figure 3 includes a second fit for the third desorption case corresponding to a model with two separate MgH_x layers. While this particular model has a slightly lower χ^2 value, it is not considered as the best fit because it requires three additional fitting parameters and fits the SLD of the upper MgH_x layer higher even than pure Mg (see the appendix for details on alternative models). However, it indicates the possibility that composition or density gradients might exist in this sample beyond the ability of the NR measurements to detect with certainty. This will be further addressed in the discussion section.

The Mg layer of the as-grown sample has an $SLD = 2.2312 \times 10^{-6} \text{ Å}^{-2}$ corresponding approximately to bulk Mg (SLD = $2.3146 \times 10^{-6} \text{ Å}^{-2}$). The small decrease in SLD (96.4% of the bulk) can be attributed to either a decrease in density, 1.675 g/cm³, compared to the bulk density of 1.738 g/cm³ (for example, from pinholes or a slightly porous structure) or to the inclusion of 2.8% by volume MgH₂ or some combination of the two effects. Upon H loading, the SLD lowers to -0.6715×10^{-6} , approximately that of MgH₂ (-0.6849×10^{-6}), and the layer expands in thickness by 28% in rough agreement with the 32% volume expansion expected in MgH₂ relative to Mg. The 4% difference could be attributed to making up for the lower density of the as-grown Mg if we assume that the decrease in SLD of the MgH_x layer in the as-grown condition is entirely due to voids. We make this assumption in subsequent analysis.

Upon desorption, the SLD of the MgH₂ layer rises toward the SLD of Mg, indicating a partial desorption of



FIG. 4. (Color online) Fitted thicknesses (solid lines) and scattering length densities, SLD, (dotted lines) for the five sample conditions. The lines are drawn to guide the eye.

hydrogen. Because the phase diagram shows a two-phase region for Mg/MgH₂ below 566 °C,³⁰ these SLD values between those of Mg and MgH₂ correspond to a mixture of Mg and MgH₂ grains in the layer. This trend continues for all three desorption runs, terminating in an SLD value still below that of Mg for the third desorption. However, as the H is removed from the sample, the thickness remains roughly equal to that of the fully loaded case (within 2.1%) as seen in Fig. 3. Figure 4 summarizes some of the thickness and SLD fit parameters of the best fits. The plus and minus error bar range equals the range of the fitted values for all models considered plus the 68% confidence interval for the best fit model shown in Fig. 3.

IV. DISCUSSION

The increase in SLD of the MgH_x layer as a function of the desorption processes indicates that H (with a negative SLD) is being removed. Furthermore, as seen in Fig. 4, as H_2 is desorbed from the film, the thickness of the MgH_x layers remains roughly constant. Because MgH₂ occupies 132% of the volume of Mg, this extra volume remaining after desorbing the H₂ must consist of voids, that is, porosity of undetermined size, in the remaining Mg film. The MgH_y layer can be characterized with three parameters; the volumes of Mg, of MgH₂, and of voids, given three known parameters. Two of these parameters are determined from the best fits for each condition, the SLD and the thickness of the MgH_x layer. The third parameter is the total amount of Mg in the layer. To determine this, we assume that the amount of Mg in the MgH_x layer remains constant, that is, there is no net diffusion into the Pd or additional MgO formation. As seen in Fig. 4, the SLD and thickness of the Pd layer are roughly constant, consistent with this assumption. In addition, very good fits to the data were obtained with Pd SLD set to the value for pure Pd, indicating that no Mg diffused into the Pd during the course of the experiment. Note that at the temperature/pressure of the measurements, the Pd layer should also contain negligible hydrogen. On the other hand, Fig. 4 shows that the MgO layer thickness increases by roughly 5 nm during the experiment, which would consume an equivalent thickness of 6 nm of Mg. While this increase in MgO thickness is statistically significant, it may not correspond to a loss of the full 6 nm of Mg. The thickness increase may be in part due to Al loss from the substrate or a lowering of the layer density because the SLD of the MgO layer also decreases during the experiment. Compared to the total thickness of Mg in the sample, 110 nm, it can be neglected to first order when calculating the volume fractions in Table I. The amount of Mg in the MgH_x layer, which is conserved, can be expressed in terms of the equivalent thickness of a Mg film, T_{Mg} . Therefore by simultaneously solving the following three equations, the three volume fractions for each condition have been determined and are listed in Table I. The first equation states that the measured SLD of the MgH_x layer equals the sum of the volume fraction of each component times the SLD of the component. In the second, the sum of the volume fractions equals unity. The third equation states that the total amount of Mg in the MgH_x layer (that is, measured as an equivalent layer thickness) is conserved.

TABLE I. Fitted SLD and thickness and calculated component volume fractions for each sample condition.

	Fitted parameters		Calculated volume fractions		
Condition	SLD	T _{meas}	V-Mg	V-MgH2	V-voids
As grown	2.2312	1094.6	0.964	≡0	0.036
Loaded	-0.6715	1401.5	0.003	0.991	0.005
Desorbed #1	0.0011	1371.4	0.217	0.731	0.052
Desorbed #2	1.3018	1368.6	0.621	0.198	0.181
Desorbed #3	1.702	1407.7	0.739	0.014	0.247

$$SLD_{measured} = \sum_{i=1}^{3} SLD_i V_i$$
(1)

$$1 = \sum_{i=1}^{3} V_i$$
 (2)

$$T_{\rm Mg} = T_{\rm meas} \left[V_{\rm Mg} + \left(\frac{W_{\rm Mg} / \rho_{\rm Mg}}{W_{\rm MgH_2} / \rho_{\rm M_gH_2}} \right) V_{\rm MgH_2} \right]. \tag{3}$$

The variables SLD_i , V_i , W_i , and ρ_i are the scattering length density, volume fraction, molecular weight, and density of component *i*, respectively, where *i* refers to each component, Mg, MgH₂, or voids. T_{meas} is the measured thickness of the MgH_x layer for each condition. To determine T_{Mg} , we assume that, in the as-grown case, x = 0 for the MgH_x layer, that is, it consists of 96.4% Mg and 3.6% voids by volume.

As seen in Table I, upon loading, the Mg was fully converted to MgH₂ to within uncertainty. During desorption, the MgH₂ was increasingly converted back to Mg while the volume fraction of voids increased enough to maintain a roughly constant film thickness.

The cross-sectional SEM micrograph of the film after the third desorption and after ion milling is shown in Fig. 5. The Mg and Pd layers are visible in the micrograph above the Al₂O₃ substrate. The pores in the Mg layer are visible in the micrograph, most clearly seen near the Mg/Al₂O₃ interface but also apparent throughout the Mg layer. The presence of large distinct pores near the interface is consistent with the possibility of the two MgH_x layers with a lower SLD level near the substrate as indicated by the alternative model for the third desorption shown in Fig. 3. Because the micrograph was taken at an angle of 52° with respect to the surface normal, the actual dimensions in the vertical direction are



FIG. 5. SEM cross-sectional image of the sample after the final desorption and after stepped ion-milling (as depicted in the inset) to expose the film surface. The image is taken with a 52° tilt from vertical to provide perspective on the vertically etched film surface.

greater than they appear (referenced to the scale bar) by a factor of $1/\sin(52^\circ) = 1.27$. The pores measure 50–75 nm vertically (out of the plane of the film) and 65–115 nm horizontally. Examining Fig. 5 gives an estimated porosity after the final desorption run between 10 and 30%, depending on the criteria chosen for identifying actual porosity in the micrograph. This is in good agreement with the volume fraction determined from the neutron reflectivity data fitting, especially considering the small cross section of the film that the micrograph covers compared to the entire film volume probed by the neutron reflectivity.

V. CONCLUSIONS

Neutron reflectometry has been used to determine the composition depth profile for a Mg thin film with a Pd capping layer for absorption and several stages of desorption of hydrogen. In the fully loaded case, the film expanded by a volume ratio consistent with the ratio of the molar volumes of MgH₂ and Mg. Upon full desorption of the hydrogen, the Mg-containing film retained roughly the same thickness as the hydrogenated film while the composition of the material in the film reverted back to pure Mg with a 25% volume fraction of voids making up the difference in volume and accounting for the lower neutron scattering length density in the film. The presence of pores in the film is confirmed by SEM micrographs. Thus the difference in volume between the two films can only be explained by the formation of voids in the dehydrogenated Mg film under the current experimental conditions.

This retention of the expanded film thickness is different from observations by Rehm *et al.*³¹ in which Nb layers in Nb/Fe and Nb/W multilayer structures were seen to retain a fraction of their expanded layer thicknesses after exposure to hydrogen gas. In that experiment, the Nb host lattice expands by interstitial absorption of H. In the bulk this is isotropic. In thin films, both in-plane and out-of-plane lattice expansion is observed; however, the out-of-plane layer thickness expansion exceeds the lattice expansion, indicating a three dimensional rearrangement of Nb that forms additional atomic planes and many dislocations. Upon H desorption, the film only partially reverts to its original thickness as hydrogen is retained at the dislocation sites. Subsequent cycles of the Nb system are completely reversible.

Hydrogen absorption by Mg is fundamentally different, in that MgH₂ undergoes a more complex two-phase structural transformation, hcp Mg to rutile MgH₂, versus a solid-solution like absorption, accompanied by a much larger volume expansion (32% compared to 12%). The reaction does not occur by expanding the parent phase, rather the parent phase is consumed as the new phase is formed. This most likely occurs in a way that the volume expansion can be accommodated without introducing stress, which is supported by *in situ* stress measurements, which show very little stress associated with the hydrogen reaction in Mg films,³² and by data that show no large changes in lattice parameters for the Mg or MgH₂ away from their bulk values.¹²

Similarly, upon conversion of the MgH_2 to Mg, a large volume reduction must occur. It has been observed¹² that in

the presence of sufficient quantities of residual Mg, this reaction occurs to a smaller extent by solid phase epitaxy at that interface and to a larger extent by nucleation and growth of a polycrystalline Mg. However, in this experiment, the Mg was fully consumed, allowing only the latter process. Because nucleation and growth appear to have occurred for the most part uniformly throughout the film, it is our conjecture that hydrogen transport occurred relatively rapidly via grain boundaries from all depths of the film, during which slower nucleation and growth of Mg from individual grains of MgH₂ occurred in place, which created voids, but retaining some of the original grain structure and the full MgH₂ film thickness. These results help to explain some of the complex microstructural changes that occur in metal hydride materials with cycling and that lead to changes in reaction kinetics.

The porosity observed here may be detrimental to the reversibility of the metal/hydride system if the material is exposed to contaminants (such as H_2O or O_2) that can render the Mg unusable. However, if the system can be kept clean, the formation of pores may enhance the kinetics of the hydride formation reaction by reducing the distance over which hydrogen must diffuse through the growing hydride, as this process has been shown to be the limiting mechanism in the Mg/MgH₂ system under conditions such as the ones used in this experiment.¹¹ This porosity may also provide a new route to the fabrication of useful structures. Furthermore, pore formation in the regrown Mg layer hints at a complex chemical and mechanical process that occurs during the metal/hydride transition. Additional experiments and modeling are needed to shed light on the nature of these processes.

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APPENDIX: DESCRIPTION OF THE SEQUENCE OF MODELS CONSIDERED

To determine the structure that best describes the sample, several models of possible sample structures were fit to the data. These models differ in the number of layers (as described in the text) and the allowed ranges of the fit parameters for each layer. While all models that were tested resulted in good fits to the data, some were rejected if the best fits contained SLD levels that were inconsistent with the known materials in the sample, that is, if they represented a nonphysical symmetry related fit to the data.³³ The best fit model was chosen as the one with the fewest constraints, which did not significantly increase the total of the χ^2 values for the five data sets, while also allowing for the potential variations in the fit parameters.

The initial model had the greatest number of degrees of freedom and consisted of a Pd layer, two distinct layers of the MgH_x material, and the interfacial MgO layer. The sum

of the χ^2 values for the five data sets was 9.33 for models with the Pd SLD constrained to -10%/+0% of the bulk value and 9.30 with the Pd SLD constrained to $\pm 10\%$ of the bulk value. The as-grown, loaded, and first desorption cases resulted in essentially a single MgH_x layer with the SLD of the two MgH_x layers fitted to similar values. However, the fits of this model to the final two desorption data sets contained two distinct MgH_{r} layers. In these fits, the MgH_{r} layer closest to the Pd (that is, the surface) had a greater SLD, indicating less hydrogen. In the case of the second desorption, the uncertainties of the SLD of the two MgH_x layers overlapped, indicating that there is a probability that these are actually the same layer rather than two distinct layers. In the third desorption case (shown, in light blue, in Figs. 1 and 2), the SLD values of the two MgH_x layers were, 1.40 ± 0.25 and 2.3 ± 0.61 , also with nearly overlapping uncertainties. Here the uncertainties are one half of the 68% confidence interval of the fit. The residuals of this fit were compared to those of the best fit model. While there were differences between the residuals of these models with a period corresponding to the thickness of the additional MgH_{x} layer, each model alternatively had the lower residuals as a function of Q, indicating that while the presence of a layer of that thickness did affect the model scattering, it did not necessarily improve it. It was found that the small improvement in χ^2 came primarily from lower residuals for the first two oscillations, indicating that the improvements in χ^2 came from the changes in contrast between the MgO and lower MgH_x layer or between the upper MgH_x and Pd layers, not the layer structure itself. It is noteworthy that the χ^2 of the two layer fit, 1.70, is only slightly improved compared to 2.00 for the one layer model, which was taken as the best fit because it had three fewer fitting parameters. The model with two MgH_x layers also predicts a SLD for the upper MgH_{x} layer that is higher than even Mg (see Fig. 2), further indicating a fit that might be rejected as a nonphysical solution. While this two MgH_y layer model is not taken as the best model, these fits may indicate that a gradient could exist, caused by desorption which started at the sample surface and advanced toward the substrate, or could indicate a higher density of voids at the sapphire interface as also indicated by SEM in Fig. 5. The next more restricted model removes one of the MgH_x layers and its three fitting parameters. The fits are very similar to the previous model, with a combined χ^2 of 11.63, only 25% greater than the models that included the second MgH_x layer. This model was taken as the best fit and is shown in Figs. 1 and 2. A similar model that fixed all the Pd SLD values at the value for Pd had a combined χ^2 of 11.84.

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