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The effect of a silane coupling agent on water adsorption at a metal/polymer interface studied by neutron reflectivity and angle-resolved X-ray photoelectron spectroscopy

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Neutron reflectivity and angle-resolved X-ray photoelectron spectroscopy (XPS) have been used to examine the adsorption of water to a molybdenum/polyurethane interface. The initial quasi-steady state interfacial D_2O profile (obtained after ~1 h exposure to D_2O saturated air at ambient temperature) was determined on a nanometre scale by neutron reflectivity. The profile was obtained as a function of the concentration of a silane coupling agent mixed into the bulk of the polymer. A large concentration of D_2O (> 80 vol%) was observed at the interface when no silane was present. This is interpreted as a partial delamination. Roughly 2 wt% silane led to a sharp reduction in the amount of D_2O at the interface. This is attributed to the silane diffusing to the interface and promoting adhesion. Samples conditioned over longer periods of time and at elevated temperature (~ 16 h, 100% humidity at 80 °C) were examined by angle-resolved XPS. For all the conditioned samples the appearance of an additional molybdenum oxidation state, and significant dissolution of the molybdenum oxide into the polymer layer were observed. These effects were readily apparent even for samples with 2 wt% silane, although the effects were slightly more pronounced with decreasing concentration of silane. Therefore, we conclude that the silane promotes adhesion of the polyurethane to the molybdenum oxide surface, but does not provide an impenetrable barrier to water or restrict its degradative effects.

1. Introduction

For adhesive joints exposed to the environment, long-term reliability is typically much more difficult to achieve than high initial adhesive strength. The effects of water on the structure and chemistry of interfaces are critical in this regard. In this work, we studied the effects of water on a metal (molybdenum)/polymer (polyurethane) interface. We examined the interfacial concentration profile of water, and the physical and chemical changes which water induces at this interface. This information was obtained as a function of the amount of a silane coupling agent present. We were particularly interested in determining the roles that an interfacial layer of silane might play. It is well known that silanes promotes adhesion at a variety of interfaces [1, 2]. However, for the long-term reliability of metal/polymer joints, it is important to determine if a silane layer presents a barrier to water penetration into the metal oxide as well. Evidence is presented which indicates that the present silane acts as an adhesion promotor, preventing rapid delamination in a humid environment, but does not provide an impenetrable barrier to water.

Silane coupling agents are used commonly as adhesion promotors on a variety of inorganic surfaces [1, 2]. Several studies of silane coupling agents on

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metal surfaces have focused on the orientation of the silanes on the surface and on determining which functional groups of the silane bond to the metal oxide surface [3–8]. There has been little work reported on the moisture-barrier properties of silane coupling agent layers [9].

Directly determining the effects of moisture at an interface is a very challenging problem. The structural and chemical changes induced in a buried interface must be examined *in situ* on a nanometre scale. In this work we have employed neutron reflectivity (NR) to determine interfacial profiles of water and angle-resolved X-ray photoelectron spectroscopy (XPS) to determine chemical changes in the surface region after humidity conditioning. Through isotopic substitution, the composition profile of a particular species may be determined by NR with ~0.5 nm resolution. In particular, we have used D_2O to track the location of water in this system. By varying the take-off angle in XPS, chemical changes within a surface region (~5.0 nm) can be distinguished from changes occurring deeper into a sample. We have examined molybdenum substrates coated with very thin (~20 nm) layers of polyurethane in order to monitor the oxidation states and the dissolution of the molybdenum oxide into the polyurethane layer after humidity conditioning at elevated temperature.

In addition to employing different experimental techniques, the two experiments described below also differed in sample history. This gives insight into the changes which occur as a function of exposure time and temperature. In the NR experiment, three samples (varying in silane content) were exposed to D_2O at ambient temperature, and NR data were obtained as soon as a pseudo steady state was established (~1 h). In the second experiment, angle-resolved XPS was performed on samples after they were conditioned in 100% humidity at 80 °C for roughly 16 h.

To our knowledge, this report describes the first use of NR to examine water adsorption at a metal/polymer interface. Wu *et al.* [9] have recently reported the use of NR to examine water adsorption at the interface between a polyimide and the native oxide of a silicon wafer. After exposure to a saturated D_2O environment, they reported an excess of D_2O (~17%) within the first 3 nm from the interface relative to that in the bulk of the polyimide (~3%). The D_2O content at the interface decreased to 12% when a silane coupling agent, aminopropyltriethoxysilane, was first coated on to the surface of the wafer. The mechanism causing this reduction was not discussed.

2. Experimental procedure

2.1. Materials

The resin used in this work, Adiprene L-100, is a polyurethane which was obtained from Uniroyal Chemical Co. The atomic composition, used in the analysis of the reflectivity data, was determined by elemental analysis to be 64.5% C, 10.2% H, 21.6% O, and 3.7% N. The curing agent, 1,4 butanediol, was obtained from Arco Chemical Co., and the accelerator, trimethylolpropane, was obtained from Hoechst Celanese. The silane, 3-glycidoxypropyltrimethoxysilane (A-187), was obtained from Union Carbide. The D_2O used in the neutron reflectivity work was obtained from Aldrich and was used as-received. The molybdenum foils used in the ARXPS work were obtained from Climax Specialty Materials.

2.2. Sample preparation

The samples for the NR work were prepared in the following manner. A layer of molybdenum, approximately 100 nm thick, was sputtered on to the polished surface of a ~5 cm diameter silicon wafer. The surface of the wafer had been previously cleaned by multiple rinsings with methanol and acetone. The Adiprene resin, curing agent, accelerator, and silane were then dissolved in toluene and spin coated on to the surface of the molybdenum. X-ray reflectivity indicates no variation in the roughness of the molybdenum film before and after spin coating (see Appendix). Three samples were prepared containing 0.0, 0.63, and 1.93 wt % silane in the Adiprene. With a solution concentration of $0.02\ \mathrm{g\,ml^{-1}}$ and a spinning speed of 700 r.p.m., a thickness of ~100 nm for the cured Adiprene films was obtained. In the uncured state, immediately following the deposition, the thin Adiprene films were extremely fragile, and were destroyed if placed directly into an oven at the cure temperature. To remove the residual toluene and cure the samples at a sufficiently slow rate, the samples were first left covered at ambient temperature for 24 h, then placed into an oven at 40 °C. The temperature of the oven was ramped from 40 °C up to 120 °C at a rate of $20\ ^\circ\mathrm{C\,h^{-1}}$. The samples were then left at 120 °C for roughly 16 h. Following the cure cycle, the samples were removed from the oven and desiccated until the NR experiments were performed.

The samples for the ARXPS work were prepared in the following manner. A 10% stock solution was first prepared containing 10 g Adiprene and 0.447 g butanediol/trimethylolpropane (1:3.55) dissolved in 90 g acetone. Aliquots of the stock solution were spiked with 3-glycidoxypropyltrimethoxysilane to prepare solutions containing 0%, 0.6%, and 1.9% silane with respect to Adiprene (wt/wt). The three solutions were diluted to 0.1% with acetone. Molybdenum foils were dip-coated in the solutions and allowed to air dry. All operations were carried out in a dry room (relative humidity < 1.2%). After the acetone had evaporated, the samples were placed into a forced air oven and cured overnight at 120° C. Some samples were subjected to a high temperature, high humidity environment (80° C, 100% relative humidity, 16 h); other samples were stored in the dry room until examination by ARXPS.

2.3. Procedure

The NR experiments were performed on the SPEAR reflectometer at Los Alamos National Laboratories. The incident angle and q-resolution were 1.5° and 3%, respectively. The ~5 cm silicon wafers were placed into an aluminium sample holder with windows which allowed the neutron beam to enter and exit. During the experiment, the windows were covered with a thin layer of aluminium foil in order to maintain a controlled atmosphere inside the sample chamber. The reflectivity for each sample was first measured in the desiccated state and then upon exposure to D_2O. These environments were achieved by placing either desiccant or D_2O into a trough underneath the sample. We will refer to the state of each sample as either "dry" or "wet". For samples exposed to D_2O, the reflectivity experiments were initiated as soon as possible (~ 15 min) after placing the samples into the sample holder. Reflectivity data were collected at roughly 30 min intervals until there was no longer any detectable change (~ 1 h). This apparently indicates that D_2O had diffused through the 100 nm Adiprene film, and achieved a quasi-steady state. A new run was then started, and data were collected for a longer period of time (~ 2 h) to obtain adequate statistics. These data are presented in Section 3.

The reflectivity is obtained as a function of momentum transfer, $q(= 4\pi \sin \theta/\lambda)$, which may be thought of as the inverse of the distance scale which is probed. Thus, the reflectivity at higher q values is sensitive to smaller scale details of the structure. With this technique, structures on the scale of 0.5 nm up to several hundreds of nanometres can be probed. A range of q is achieved on the SPEAR reflectometer by variation of the neutron wavelength at a fixed angle of incidence. The data are interpreted in terms of a profile for the neutron scattering length density, Nb, which is proportional to the real part of the neutron refractive index and is determined by atomic composition and the density of the material.

The reflectivity curves were analysed in the following manner. Initially, a model profile was assumed, and the reflectivity was calculated and compared to the experimental curve. The model profile was then adjusted until good agreement was obtained with the experimental curve. In the final step, a non-linear least squares regression was performed to obtain the best-fit parameters. The calculation of the reflectivity was performed by approximating the model profiles with a series of thin slabs of uniform composition. The reflectivity from the stack of layers was calculated using the Fresnel reflectivity coefficients and Snell's law. This method, as well as other experimental details, are described elsewhere in several excellent reviews of this technique [10, 11].

X-ray reflectivity data were obtained using a modified Kratky camera at the Center for Micro-Engineered Ceramics at the University of New Mexico. The setup involves a 12 kW Rigaku rotating anode X-ray generator with an MBraun linear position sensitive detector. The sample holder was modified to support 2 in samples in a vertical position. Sample positioning was accomplished with rotation and translation motors controlled by an Encoder Mike (Oriel). Angles were determined by the positions of the primary and reflected beams on the detector. Reflectivity data were analysed in a fashion directly analagous to that for the neutron reflectivity.

XPS is extremely surface sensitive due to the strong interaction of the photoelectrons with other electrons in the material. Photoelectrons originating near the surface have a high probability of being emitted from the sample without loss of energy, while those originating from below the surface are strongly attenuated. The XPS intensity, I_0, originating from depth, d, is exponentially attenuated as it passes through the sample material. Its value at the surface can be represented by

$$I_d = I_0 (1 - e^{-d/\lambda \sin \theta}) \qquad (1)$$

where I_d is the XPS peak intensity from a film layer at depth d, λ is the inelastic mean free path of electrons in the overlying film, and θ is the angle the detected photoelectrons make with respect to the plane of the sample surface, also referred to as the take-off angle. Thus, by varying the take-off angle, it is possible to obtain information about the distribution of chemical species near the surface. XPS data taken at 45° contain information from a greater depth than spectra obtained at 15°. There is also a decrease in intensity as the detection angle is changed from 45° to 15° because the X-ray surface flux density decreases as the sample is tilted to lower angles.

All XPS spectra were obtained at Martin Marietta with a Physical Electronics Model 5000LS system using monochromatic aluminium K_α X-rays at 4000 W. The spectra were referenced to the carbon peak at 284.8 eV. A low-energy electron flood gun provided specimen neutralization to correct for surface charging. Photoelectrons were collected using a spherical capacitor analyser with its input lens at angles of 15° and 45° relative to the sample surface. The angle between monochromater axis and detector was kept constant.

3. Results

3.1. Neutron reflectivity

Fig. 1a shows the reflectivity for the sample containing no silane in both the dry and wet states. The lines through the data correspond to the best-fit calculated curves. The model profiles corresponding to these curves are shown in Fig. 1b and c, where in Fig. 1c only the region of the molybdenum oxide/Adiprene interface is shown. These profiles are expressed in terms of the neutron scattering length density, Nb. Each layer in the model profile is described by a scattering length density, a thickness, and a surface roughness. The surface roughness values are not shown in Fig. 1b and c, but are given in the Appendix. Owing to the presence of the oxide layers on the silicon and molybdenum, a minimum of 14 parameters are required to describe even the simplest model profile for this system. Because of the large number of variables, independent information is essential in order to arrive at unambiguous conclusions from these reflectivity data. Fortunately, most of the parameters can be determined independently. This is described in detail in the Appendix, along with a complete discussion of the fitting procedure employed for the reflectivity curves for the dry and wet states (leading to the profiles in Fig. 1b and c) and the sensitivity of the calculated reflectivity curves to each of the parameters.

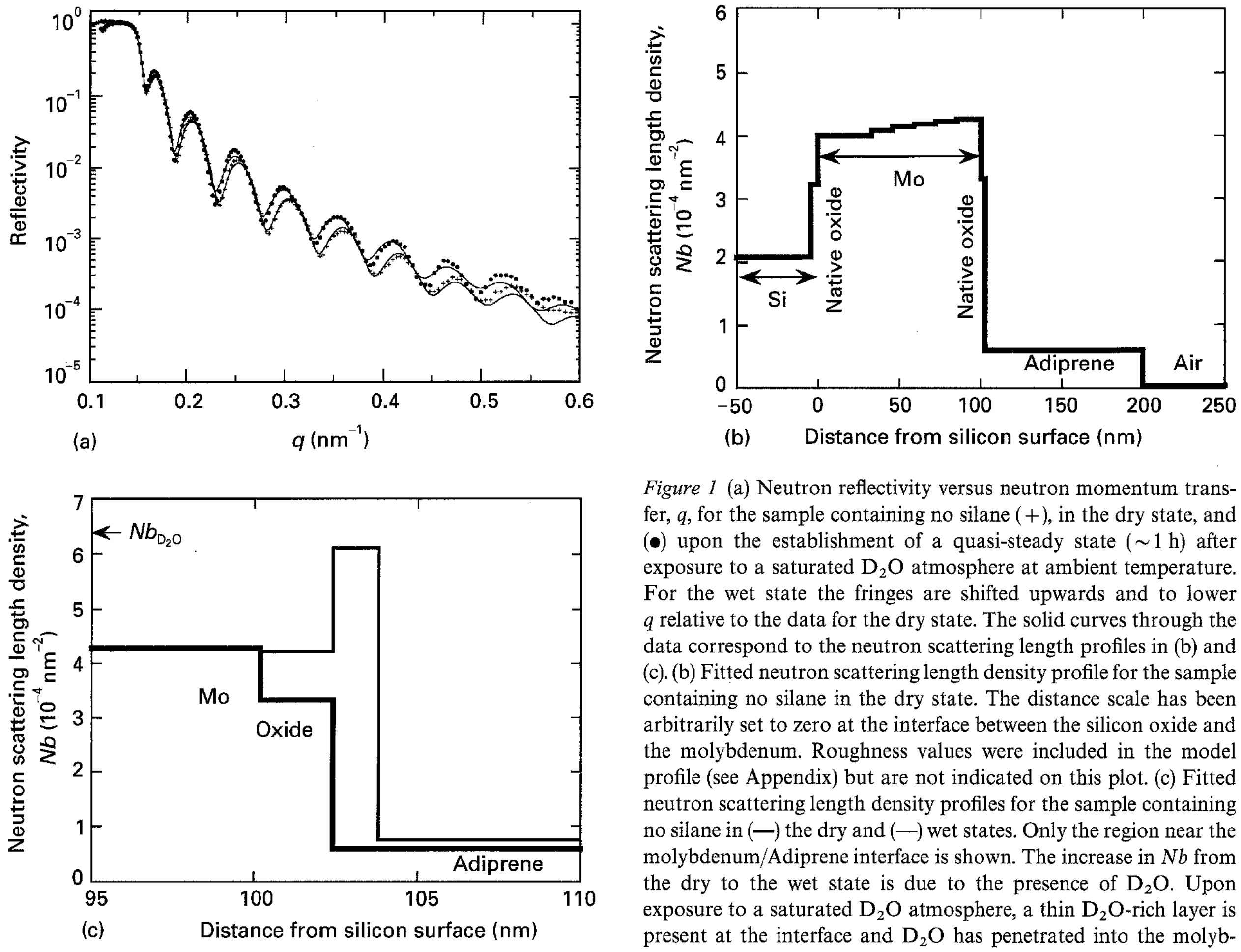

Figure 1 (a) Neutron reflectivity versus neutron momentum transfer, q, for the sample containing no silane (+), in the dry state, and (●) upon the establishment of a quasi-steady state (~1 h) after exposure to a saturated D_2O atmosphere at ambient temperature. For the wet state the fringes are shifted upwards and to lower q relative to the data for the dry state. The solid curves through the data correspond to the neutron scattering length profiles in (b) and (c). (b) Fitted neutron scattering length density profile for the sample containing no silane in the dry state. The distance scale has been arbitrarily set to zero at the interface between the silicon oxide and the molybdenum. Roughness values were included in the model profile (see Appendix) but are not indicated on this plot. (c) Fitted neutron scattering length density profiles for the sample containing no silane in (—) the dry and (—) wet states. Only the region near the molybdenum/Adiprene interface is shown. The increase in Nb from the dry to the wet state is due to the presence of D_2O. Upon exposure to a saturated D_2O atmosphere, a thin D_2O-rich layer is present at the interface and D_2O has penetrated into the molybdenum oxide layer. The D_2O-rich layer (~1.4 nm thick) leads to the shift of the peaks in the reflectivity curve to lower q. The high D_2O content (> 80 vol %) and the roughness of this layer (1.7 nm) seem to suggest a partial delamination.

The best-fit profile for the dry state is in good agreement with most of the parameters obtained through independent measurements or by calculation. The most significant difference is that the roughness values are larger than those measured by X-ray reflectivity (see Appendix). The oscillations in the reflectivity are due to the step of higher scattering length density arising from the native silicon oxide and the molybdenum and its native oxide. The period of the oscillation is inversely related to the total thickness of these three layers. As a final remark on the profile for the dry state, we note that the molybdenum layer is not of uniform density, but rather the density increases slightly away from the silicon oxide surface.

For the wet state, we observe that the fringes are shifted upwards and to lower q values relative to the curve for the dry state. To interpret these data, all the parameters of the profile were fixed to the values obtained for the dry state except those which may be influenced by the presence of D_2O. D_2O has a very high scattering length density, such that the scattering length density of any of the layers into which it diffuses will be increased. The water uptake of a macroscopic Adiprene sample at equilibrium (100% relative humidity, room temperature) was measured in an independent experiment to be 2.5 wt %. Therefore, the Nb value of the bulk Adiprene layer was fixed at 0.75×10^{-4} nm^{-2}, the weight average of the Nb values for Adiprene (0.60×10^{-4} nm^{-2}) and D_2O (6.4×10^{-4} nm^{-2}). Initially, the scattering length density of the molybdenum oxide layer alone was allowed to float as a free parameter, while using the value determined for the dry state as the initial guess. The resulting profile under these conditions leads to poor agreement with the experimental data (χ^2 value more than three times that for the profile shown in Fig. 1c). The profile was then modified by adding an additional layer at the Adiprene/molybdenum oxide interface. When the thickness, scattering length density, and roughness of this layer are allowed to float as free parameters, in addition to the scattering length density of the molybdenum oxide and Adiprene, the best-fit profile gives quite good agreement with the experimental data. This best-fit profile is shown in Fig. 1c.

The additional layer at the interface is relatively thin, ~1.4 nm, with a very high scattering length density. This additional layer leads to the shift in the peak positions to lower q values in Fig. 1a. The high scattering length density indicates a composition which is > 80 vol % D_2O. Such a high D_2O content seems to suggest a partial separation of the Adiprene from the molybdenum oxide surface. A large roughness (1.7 nm) is also indicated for the interfacial layer. Because the roughness value is of similar magnitude as the thickness of the interfacial layer, this D_2O-rich region near the interface is apparently not uniform. This result is

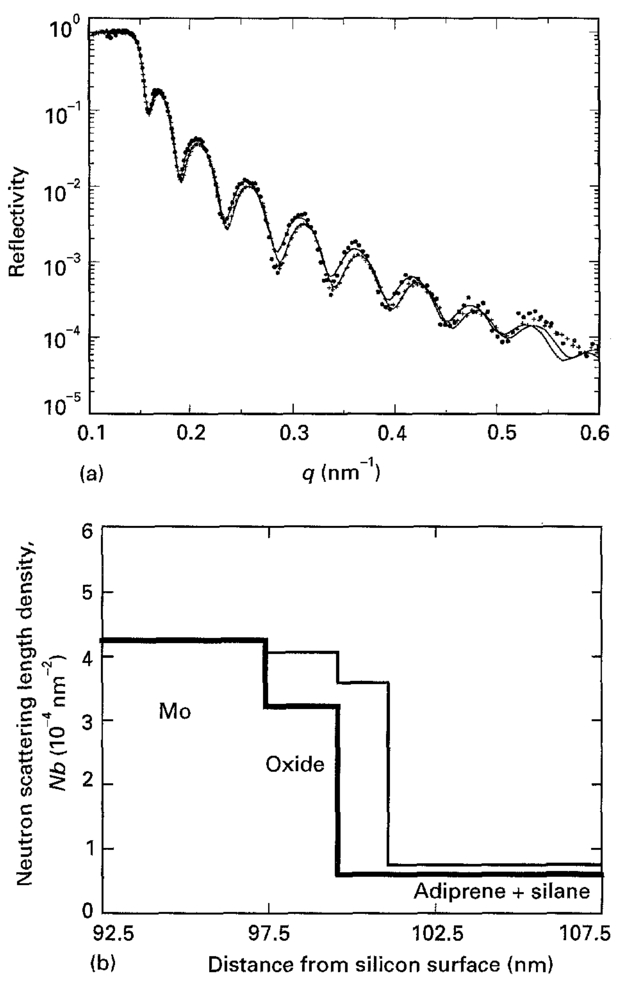

Figure 2 (a) Neutron reflectivity for the sample containing 0.6 wt% silane (+) in the dry state, and (●) upon the establishment of a quasi-steady state (~1 h) after exposure to a saturated D_2O atmosphere at ambient temperature. The curves through the data correspond to the neutron scattering length profiles in (b). (b) Fitted neutron scattering length density profiles for the sample containing 0.6 wt% silane in (—) the dry and (—) wet states. In the sample with no silane, a thin D_2O-rich layer is present at the interface and D_2O has penetrated into the molybdenum oxide layer. However, the quantity of D_2O at the interface is considerably reduced relative to the sample with no silane.

also consistent with an interface which is partially delaminated.

Another important feature of the profile is that D_2O has apparently penetrated into the molybdenum oxide layer. The increase in the scattering length density for the oxide layer corresponds to 29 vol % D_2O, assuming that the thickness of the layer is the same as for the dry state. This is a reasonable assumption because the experiment was performed immediately upon establishment of a quasi-steady state in the system, which occurred within the first hour after the initial exposure to D_2O. The value of 29 vol % D_2O is not unreasonable given that the density of the molybdenum oxide is roughly one-third of that for pure molybdenum. The penetration of D_2O into the oxide layer has important implications for the long-term adhesion of this interface, and this topic will be discussed in more detail below.

Fig. 2a shows the neutron reflectivity curves for the sample with 0.6 wt % silane in the bulk of the Adiprene. The curve for the dry state is very similar to that in Fig. 1a for the sample with no silane. This is because the silane has a scattering length density which is nearly identical to that for Adiprene. The best-fit profile for this sample in the dry state was obtained in the same manner as described in the Appendix for the 0.0 wt % silane sample, and closely resembles that in Fig. 1b.

For the wet state, the fringes are again shifted upwards and to lower q values compared to the curve for the dry state. However, in this case, the shifts are not as large as in Fig. 1a. The best-fit profiles for the dry and wet states are shown in Fig. 2b. The shift in the peak positions to lower q values again indicates a thin moisture-rich region at the interface. However, the scattering length density of this layer is significantly lower, indicating a composition of 49 vol % D_2O. The decrease in the amount of D_2O at the interface clearly demonstrates a significant effect due to the presence of the silane coupling agent. The best-fit profile also indicates that D_2O has again penetrated into the molybdenum oxide layer. In this case the increase in scattering length density corresponds to 27 vol % D_2O.

Fig. 3a shows the neutron reflectivity curves for the sample with 1.9 wt % silane in the bulk of the Adiprene. The curve for the dry state is very similar to those for the other two samples in Figs 1a and 2a. For the wet state we observe that, whereas the fringes are again shifted upwards relative to the curve for the dry state, there is no longer a shift to lower q values as was the case for the other two samples. This indicates that there is no longer an additional D_2O-rich layer at the interface. The best-fit profiles for these curves are shown in Fig. 3b. The results again indicate a significant amount of D_2O in the molybdenum oxide layer (30 vol %).

Thus, there are two main observations from these data. We observe that the D_2O content in the molybdenum oxide is nearly the same for the three samples, whereas the presence of an additional D_2O-rich layer at the interface varies with silane content. This observation suggests that the silane serves as an adhesion promoter, preventing rapid delamination, but does not inhibit the diffusion of water into the molybdenum oxide layer. This conclusion is also supported by the ARXPS data described below.

Before closing this section on the neutron reflectivity study, we report the results of one additional experiment in which the 0 wt % silane sample was examined after a much longer exposure time. After the initial experiments on SPEAR were completed, the sample (which still contained D_2O) was placed into a sealed container and left for a period of roughly 3 months. The sample was then removed from the container and placed into a vacuum chamber at ambient temperature for several days to remove the residual D_2O. The sample was subsequently exposed to a saturated H_2O environment for a period of several hours and the reflectivity obtained on the POSYII reflectometer at Argonne National Laboratory. During that experiment, the sample was held in a sealed chamber with quartz windows which also contained a beaker of distilled H_2O.

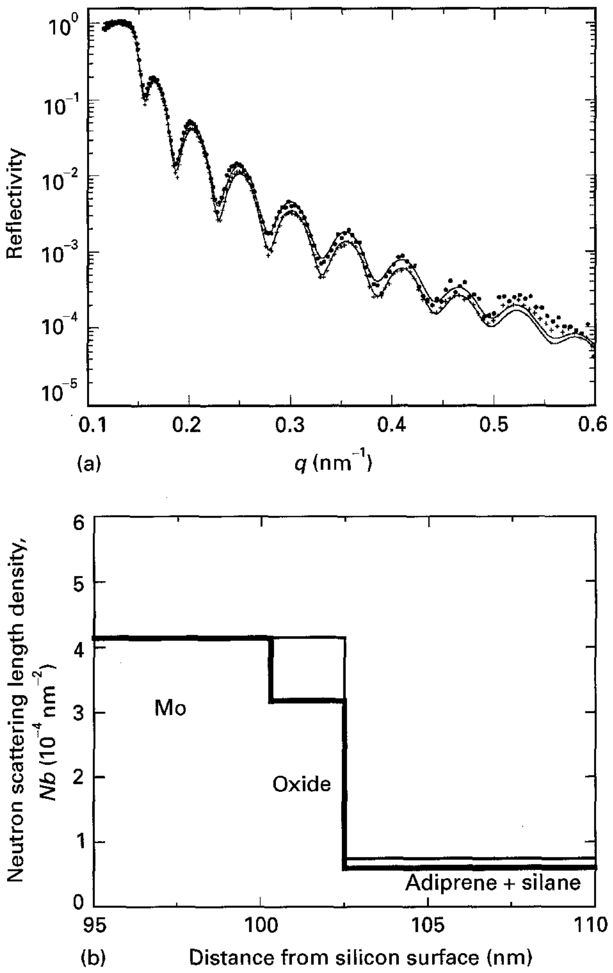

Figure 3 (a) Neutron reflectivity for the sample containing 1.9 wt% silane (+) in the dry state, and (●) upon the establishment of a quasi-steady state (~1 h) after exposure to a saturated D_2O atmosphere at ambient temperature. The curves through the data correspond to the neutron scattering length profiles in (b). For the wet state, the fringes are not shifted to lower q as was the case for the other two samples. This demonstrates a significant effect due to the silane and indicates that the additional D_2O-rich layer at the interface is not present for this sample. (b) Fitted neutron scattering length density profiles for the sample containing 1.9 wt% silane in (—) the dry and (—) wet states. The profile for the wet state suggests that the silane prevents delamination, but does not prevent D_2O from diffusing into the molybdenum oxide.

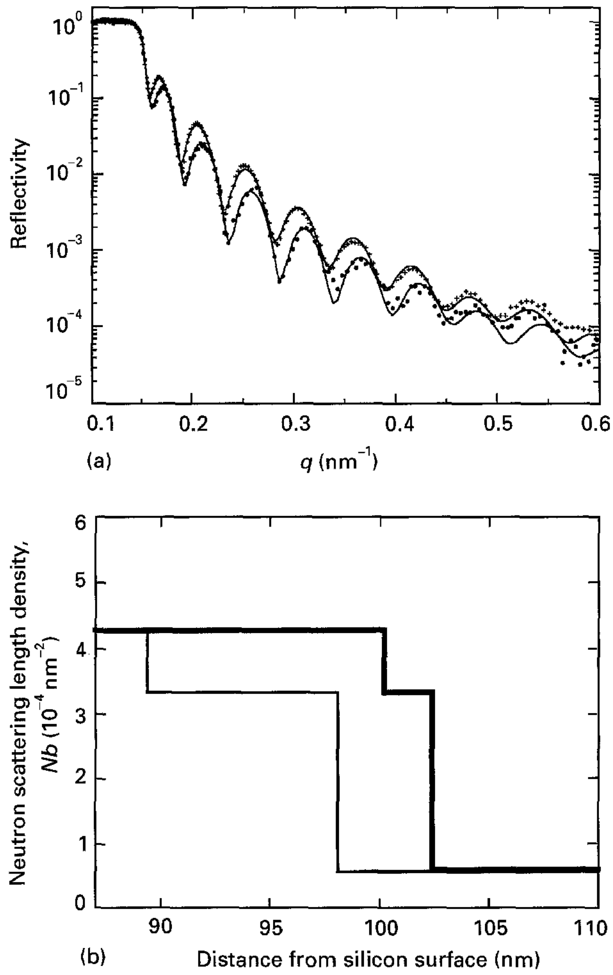

Figure 4 (a) Neutron reflectivity for the sample containing no silane (+) in the dry state, and (●) after several months exposure to residual moisture. (See text for precise sample history.) In this case, the sample was exposed to H_2O rather than D_2O during the reflectivity experiment. The curves through the data correspond to the neutron scattering length profiles in (b). (b) Fitted neutron scattering length density profiles for the sample containing 0.0 wt% silane (—) in the dry state and (—) after prolonged exposure to moisture. In contrast to the results obtained immediately upon the establishment of a quasi-steady state (~1 h) in Fig. 1c, in this case the fringes for the wet state are shifted to higher q. This indicates that the molybdenum/molybdenum oxide layer has become thinner. Apparently dissolution of the molybdenum oxide into the Adiprene has taken place during the longer period of exposure to water.

The result for this experiment is in sharp contrast to the result obtained after only a few hours exposure time, shown previously in Fig. 1a. The reflectivity curve for this sample is shown in Fig. 4. We have also included the reflectivity for the dry state from Fig. 1a for comparison. We observe that the fringes are shifted downwards and to higher q relative to the curve for the dry state. The downward shift is expected as H_2O has a very low scattering length density ($Nb = -0.56 \times 10^{-4}\,\mathrm{nm}^{-2}$) compared to that for D_2O ($Nb = 6.4 \times 10^{-4}\,\mathrm{nm}^{-2}$). However, the shift to higher q is in sharp contrast to that obtained after only several hours exposure time, where the curve was shifted to lower q. The best-fit profile is shown in Fig. 4b along with the profile for the dry state from Fig. 1c. The shift to higher q indicates that there has been a loss of roughly 8 nm molybdenum or molybdenum oxide into the bulk of the Adiprene. In addition, a larger oxide layer is present (about 7 nm as opposed to ~2.3 nm in the dry state). It appears that during the period of 3 months in which this sample was in the sealed container, the D_2O which remained in the sample after the initial exposure apparently reacted with the molybdenum producing additional molybdenum oxide, and that some of that molybdenum oxide dissolved into the bulk of the Adiprene. Thus, the initial state which was found to be independent of time on the scale of a few hours was actually a quasi-steady state which evolved slowly over time due to the interaction of the water with the molybdenum/molybdenum oxide. This phenomenon will be examined in more detail in the following section.

3.2. Angle-resolved XPS

Figs 5 and 6 show the XPS spectra for elemental molybdenum and the molybdenum oxidation states

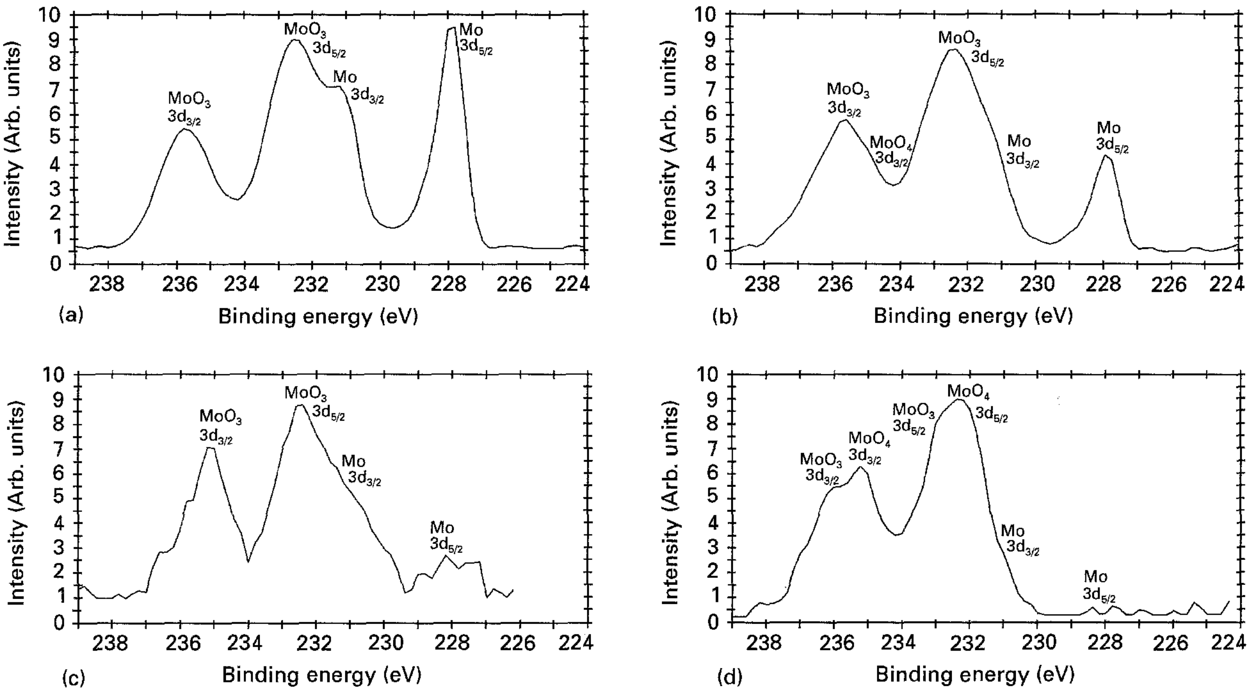

Figure 5 Molybdenum and molybdenum oxide spectra obtained at a take-off angle of (a,b) 45° and (c,d) 15° for molybdenum foil coated with Adiprene film containing 0.6 wt% silane (a,c) dry, and (b,d) after conditioning in 100% humidity at 80 °C for 16 h. The spectra were multiplied by the following scale factors: (a) 30, (b) 11, (c) 333, (d) 83.

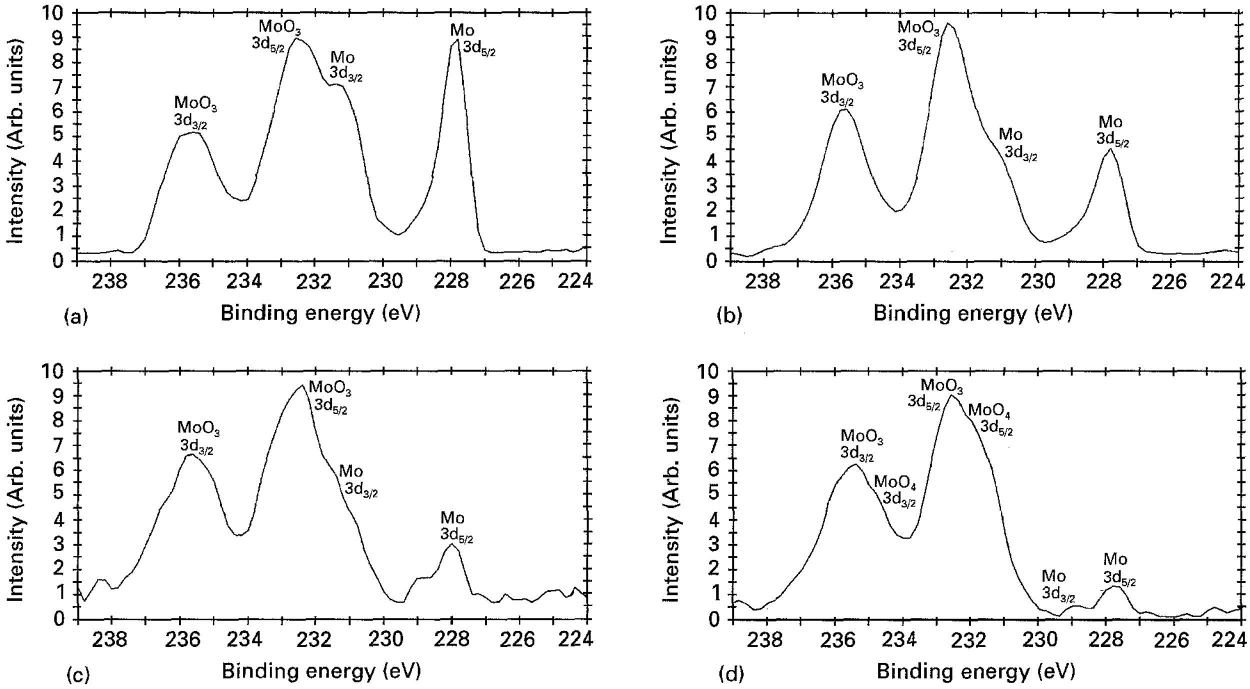

Figure 6 Molybdenum and molybdenum oxide spectra obtained at a takeoff angle of (a,b) 45° and (c,d) 15° for molybdenum foil coated with Adiprene film containing 1.9 wt% silane (a,c) dry, and (b,d) after conditioning in 100% humidity at 80 °C for 16 h. The spectra were multiplied by the following scale factors: (a) 9, (b) 6, (c) 111, (d) 35.

for samples containing 0.6 and 1.9 wt % silane, respectively. These samples were conditioned overnight (~16 h) in 100% relative humidity at 80 °C.

Fig. 5a and b show the spectra for the 0.6 wt % silane sample at a take-off angle of 45° in the dry and wet states, respectively. In the dry state, peaks which correspond to elemental molybdenum and MoO_3 are observed. In the wet state, we observe an enhancement of the oxide peaks relative to the elemental molybdenum peaks. This seems to indicate that humidity conditioning has led either to increased oxidation of the molybdenum in the interface region or to migration of the oxide into the polymer layer and thus closer to the surface of the sample. We also note a hint of two peaks at 235 and 232 eV due to a new oxidation state, MoO_4.

Fig. 5c and d show the spectra for the 0.6 wt % silane sample at a take-off angle of 15° in the dry and wet states, respectively. In the dry state, we observe a very weak signal for the molybdenum and MoO_3 peaks. (Note that the spectrum has been multiplied by a large scale factor to reveal the very small peaks.) The low intensity of these peaks is due to the fact that at this low take-off angle, XPS probes the near surface region of the sample which contains mostly Adiprene. On the other hand, after humidity conditioning at elevated temperature, the molybdenum oxide peaks obtained at 15° are quite strong, as observed in Fig. 5d. This indicates that the molybdenum oxide has dissolved into the Adiprene layer and is present in the surface region. Furthermore, the peaks due to the MoO_4 oxidation state are now much more evident, the intensities of the MoO_4 peaks being greater than those of the MoO_3 peaks. From these data we conclude that the water has diffused into the oxide and reacted with molybdenum or MoO_3 to produce MoO_4, and that the oxides have diffused into the Adiprene.

Fig. 6a–d show the corresponding XPS spectra for the 1.9 wt % silane sample. The spectra are remarkably similar to those for the 0.6 wt % sample. The main observations are again that the spectrum for the humidity-conditioned sample at a take-off angle of 15° shows strong oxide peaks relative to elemental molybdenum, and also that the MoO_4 peaks are again apparent in addition to the MoO_3 peaks. Thus even with 1.9% silane in the Adiprene, water has apparently penetrated into the molybdenum oxide, leading to the formation of a new oxidation state and significant dissolution of the oxides into the Adiprene. However, we note that the MoO_4 peaks are not as large relative to the MoO_3 peaks as was the case for the 0.6 wt % sample. Moreover, the ratios of the intensities of the oxide peaks relative to the elemental molybdenum peak at a 15° take-off angle for the humidity-conditioned samples are larger for the 0.6 wt % silane sample (Fig. 5d) than for the 1.9 wt % silane sample (Fig. 6d). These observations may suggest that the greater concentration of silane reduces somewhat the rate at which water interacts with the oxide. However, the principal result is that there is indeed a great deal of MoO_4 formed and significant dissolution of the oxide even for the 1.9 wt % silane sample.

4. Discussion

Several important conclusions can be drawn from these results. The neutron reflectivity experiments show a significant effect of the silane concentration on the initial ($\sim$several hours) steady-state profile of D_2O at the interface. This is clear, albeit indirect, evidence that the silane has diffused from the bulk of the Adiprene to the molybdenum oxide/Adiprene interface. The results suggest that 1.9 wt% silane is sufficient to prevent a rapid delamination of the Adiprene from the molybdenum oxide. However, after a more lengthy exposure, the ARXPS data clearly show that water has penetrated into and reacted with the oxide, even for the 1.9 wt % sample. This is unambiguously demonstrated by the appearance of the MoO_4 peaks in the spectra. The penetration of moisture into the oxide also causes dissolution of the oxide into the Adiprene bulk. Again, dissolution was observed for the 1.9 wt% silane sample as well as the 0.6 wt% silane sample. Thus we conclude that the silane promotes adhesion of the Adiprene to the molybdenum oxide surface, but does not provide a barrier to moisture penetration, at least for concentrations less than 2 wt%.

The penetration of water into the molybdenum oxide and the subsequent dissolution of the oxide is likely to be detrimental for the long-term reliability of this interface. We would like to add a word of caution, however, in that no information about the thickness of the silane layer was obtained in this study. It is possible that the layer of adsorbed silane is relatively thin. It is entirely possible that a thicker silane layer, such as might be obtained with a much higher initial silane concentration in the bulk Adiprene or by coating the silane directly on to the molybdenum oxide, might provide a more effective barrier to water.

Future work will focus on the rate of water penetration into the oxide and the dissolution of the oxide as a function of the type of adhesion promoter and its concentration. The goal will be to develop interfacial treatments which will slow or even eliminate the penetration of water into the metal oxide layer. It is possible that with higher concentrations of the present silane or with a direct application of this silane to the metal oxide surface, improvements may be made towards this goal. In addition, the characterization information described here will be correlated with adhesive strength.

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Appendix. Detailed analysis of reflectivity data

Below we illustrate the method for interpreting the neutron reflectivity data by describing in detail the analysis for the 0.0 wt% silane sample. We begin with the results for the dry state.

A.1. Dry state

The number of parameters required to describe this sample, a minimum of 14, is too large to allow unambiguous values of all parameters to be determined from the neutron reflectivity data alone. However, it was possible to obtain values for most of these parameters either through calculations or independent measurements. Table I summarizes the values of the parameters which could either be calculated or measured independently.

TABLE I Estimated parameter values for the 0.0 wt % silane sample in the dry state

	Si	*SiO_2*	*Mo*	*MoO_3*	*Adiprene*
Thickness (nm)	–	2[a]	100[b]	2.3[a]	100[b]
$Nb(10^6\ nm^{-2})$	2.07[c]	3.5[c]	4.45[c]	3.2[c]	0.60[c]
σ(nm)	0.2[a]	0.5[a]	1.8[a]	0.1[a]	–

[a] X-ray reflectivity.
[b] Profilometry (Dektak).
[c] Calculated from composition and published value for density.

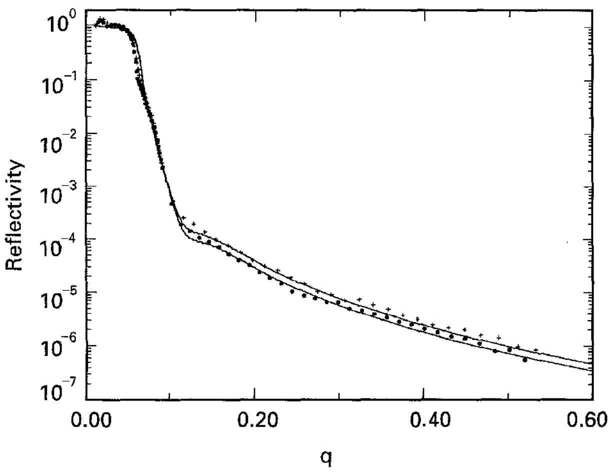

Figure A1 X-ray reflectivity for (+) a 100 nm molybdenum film on a silicon wafer, and (●) the same sample subsequently coated with a 100 nm Adiprene film. The curves through the data are best-fit calculated curves using models of two (molybdenum and molybdenum oxide) and three (molybdenum, molybdenum oxide, and Adiprene) uniform layers on the substrate. The curves correspond to densities of 10.2 g cm^{-3} (molybdenum), 2.6 g cm^{-3} (molybdenum oxide), and 1.3 g cm^{-3} (Adiprene), roughness values of 1.2 nm (silicon/molybdenum), 1.8 nm (molybdenum/molybdenum oxide), 0.1 nm (molybdenum oxide surface/air or Adiprene), and a thickness for the molybdenum oxide layer of 2.3 nm.

In order to calculate the scattering length density, *Nb*, for a particular layer, the atomic composition and the density must be known. The scattering length densities for silicon and molybdenum were calculated using densities of 2.32 and 10.22 g cm^{-3}, respectively [12]. The value of *Nb* for the cured Adiprene film was obtained using the measured composition (64.5 wt% C, 10.2 wt% H, 3.7 wt% N, and 21.6 wt% O, by elemental analysis) and a density of 1.3 g cm^{-3}. The value of *Nb* in Table I for the silicon oxide layer was calculated assuming the composition SiO_2, and a density of 2.32 g cm^{-3}. However, it is known that the oxygen-to-silicon ratio in the native oxide layer is somewhat less than 2:1, and also that the density can be significantly less than that of pure silicon. Thus the value in Table I is an upper bound. The *Nb* value in Table I for the molybdenum oxide layer was calculated assuming the composition MoO_3, consistent with the ARXPS data, with a density of 3.12 g cm^{-3} obtained from the literature [12]. The densities mentioned above are in reasonable agreement with X-ray reflectivity data, shown in Fig. A1.

Values of 100 ± 5 nm for the thicknesses of the molybdenum and Adiprene layers were obtained by profilometry. The thickness of the native oxide on a silicon wafer was measured in our laboratory to be roughly 2 nm (X-ray reflectivity and ellipsometry). A value of 2.3 nm was obtained for the thickness of the native oxide on molybdenum (X-ray reflectivity).

Roughness values for silicon and its native oxide and for molybdenum and its native oxide were also determined independently (X-ray reflectivity). The best-fit to the data in Fig. A1 using a model consisting of two uniform layers (molybdenum and its native oxide layer) on a silicon substrate gives roughness values of 1.8 nm between the molybdenum and the molybdenum oxide layer, and 0.1 nm for the surface of the oxide layer. The fact that the roughness of the molybdenum/molybdenum oxide interface is of the order of the size of the oxide layer suggests that the interface structure may be more complicated than the simple model of two homogeneous layers. This is also indicated by the low value of roughness for the surface. We note that the best-fit for a one-layer model gives a surface roughness of 2.0 nm, which is also in good agreement with the value obtained from analysis of the off-specular scattering (our analysis followed that described by Weber and Lengeler [13]).

While the roughness values obtained by X-ray reflection serve as good initial guesses in the analysis of the neutron reflectivity data, we note that the roughnesses probed by X-ray and neutron reflection need not be the same. That is because X-ray reflection essentially probes density variations within the sample, while neutron reflection is sensitive to the atomic composition as well as the density. It is also important to note that when a Debye–Waller type factor is used to model the roughness, one cannot distinguish between a gradient in scattering length density perpendicular to the surface or roughness in the plane of the surface.

The final remaining variable is the roughness of the cured Adiprene layer. It was not possible to obtain an independent measurement of this parameter, however, we have found that a value of 10 nm is typical for thin, cured thermoset films. Moreover, the neutron reflectivity is fairly insensitive to this latter parameter because the scattering length density of Adiprene is close to that of air.

If the reflectivity is calculated using the above information, compiled in Table I, we obtain the result shown in Fig. A2. While most of the qualitative features in the reflectivity curve are present, quantitative agreement is not obtained. The parameter values obtained from a non-linear least-squares regression, using the estimated values as initial guesses, are given in Table II. The values in parentheses indicate those which were allowed to float in the regression. The other parameters were fixed either because the calculated reflectivity curve is insensitive to those parameters or because the values are known with a high level of confidence. The values in Table II correspond to the calculated curve shown in Fig. 1a and the profile shown in Fig. 1b, and represent the best agreement (lowest χ^2 value) obtained for these data.

We observe *Nb* for the molybdenum layer to be roughly 7% lower than the calculated value. This

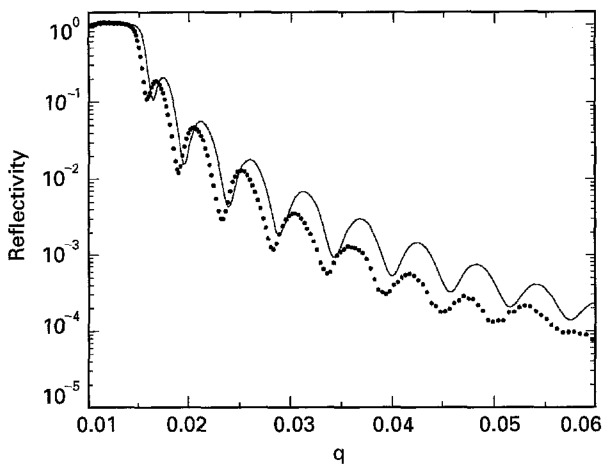

Figure A2 Reflectivity calculated using the estimated parameters in Table I. The calculated curve is compared to the experimental data for the 0.0% silane sample in the dry state from Fig. 1a.

suggests that the density of the 100 nm evaporated film is slightly less than that of a macroscopic sample. This is in agreement with previously reported X-ray reflectivity work on thin metal films [14]. The *Nb* value for the molybdenum oxide is in excellent agreement with the calculated value, but is slightly higher than expected from the density obtained from X-ray reflectivity (a value of $Nb = 2.7 \times 10^{-4}$ nm^{-2} results if the density obtained from X-ray reflectivity is used in the calculation of *Nb*). The value of *Nb* for the silicon oxide is lower than the calculated upper bound, but is consistent with previous measurements of native silicon oxide layers by the authors. We note that the thickness of the silicon oxide layer and the roughness of the silicon/silicon oxide interface are significantly larger than the estimated values. A larger oxide layer may have resulted from heating during the sputtering of molybdenum on to the wafer.

In addition to allowing the parameters to vary from the estimated values, it was also necessary to allow the value of *Nb* to vary within the molybdenum layer. This likely indicates a slight (5%) variation in the density of the molybdenum as it was sputtered on to the silicon. After examining a variety of possible functions for the scattering length density variation in the molybdenum, good agreement with the experimental curve was obtained with the profile shown in Fig. 1b. The results suggest that the density of the molybdenum increases slightly throughout the evaporation process reaching the greatest value at the air surface.

The most significant difference between the estimated parameter values in Table I and those resulting from the regression is that the roughness values for the silicon/silicon oxide, molybdenum/molybdenum oxide and molybdenum oxide/Adiprene interfaces are significantly higher than the values obtained by X-ray reflectivity. The origin of this discrepancy is not obvious to the authors. We note that the X-ray reflectivity curves obtained prior to and following the neutron reflectivity experiments were identical. The results seem to suggest that the interface regions as defined by gradients in composition are broader than the interface regions as defined by gradients in density.

While it is theoretically impossible to obtain a unique set of parameter values from this experiment, it is encouraging to observe excellent agreement between most of the fitted parameters and the parameters which were calculated or measured independently. Moreover, we note that the variation in the scattering length density profile between the dry and wet states is the primary focus of this article, and that obtaining precise values for all 14 parameters in the dry state is not essential to that goal. The conclusions relating to the variation from the dry to the wet states are not dependent on a specific set of parameter values for the dry state.

A.2. Wet state

To interpret the change in reflectivity from the dry state to the wet state, all the parameters were fixed at their dry state values except those which might be affected by the presence of moisture in the system. The moisture uptake of a macroscopic Adiprene sample at equilibrium (100% relative humidity, room temperature) was measured to be 2.5 wt%. The *Nb* value of the Adiprene layer was therefore fixed at 0.75×10^{-4} nm^{-2} for the wet state. In addition, to obtain acceptable agreement with the data it was necessary to allow for an additional layer (rich in moisture) at the interface between the molybdenum oxide and Adiprene. Thus, the only parameters allowed to vary in the regression of the wet state data were *Nb* for the molybdenum oxide and the moisture-rich interfacial layer, the thickness of the moisture-rich layer, and the roughness values of the interface between the molybdenum oxide and the moisture-rich layer and between the moisture-rich layer and the Adiprene layer. As described in the text, the regression indicates that the layer between the molybdenum oxide and Adiprene is a 1.4 nm thick layer with a moisture content greater than 80% D_2O.

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TABLE II Fitted parameter values for the 0.0 wt % silane sample in the dry state

	Si	*SiO₂*	*Mo*	*MoO₃*	*Adiprene*
Thickness (nm)	–	(4.4)	(100.2)	(2.2)	100
Nb (10^8 *nm*$^{-3}$)	2.07	(3.24)	(4.01–4.27)[a]	(3.32)	0.6
σ(nm)	(2.7)	0.5	(5.7)	(1.2)	10

[a] Increases from 4.01 to 4.27 in five steps as: $4.01 + (4.27 - 4.01) \times (i/5)^{0.7}$ where *i* is the number of the step.

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