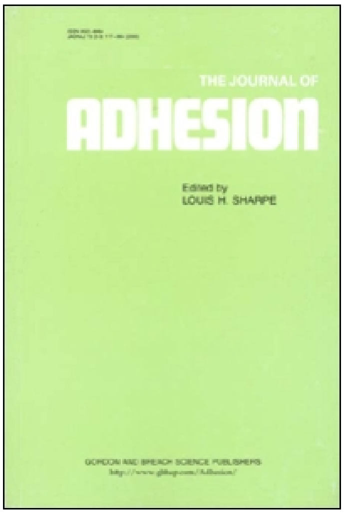

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Water Adsorption in Interfacial Silane Layers by Neutron Reflection: 1. Silane Finish on Silicon Wafers*

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The interaction of water with a common commercial glass cloth silane finish is explored by neutron reflection. The silane coating is applied to the oxide surfaces of polished silicon wafers. Detailed profiles of D_2O within the ~80 Å silane finish layers are measured after exposure for 48 hours to a saturated D_2O atmosphere at either 22°C or 80°C. The nature of the interaction of D_2O with the finish layer is probed by exposing the samples to vacuum following adsorption. In both samples, the profile of adsorbed D_2O is composed of at least two distinct layers: a thin (< 30 Å) D_2O -rich layer adjacent to the interface, and the bulk of the film in which only a low level of D_2O is present. The amount of adsorbed D_2O is greater for the sample conditioned at 80°C than for the sample conditioned at 22°C. In addition, adsorbed D_2O within the interfacial layer is removed more slowly during evacuation for the sample conditioned at 80°C than for the sample conditioned at 22°C. These latter two results are interpreted as indicating increased hydrolysis of siloxane bonds for the samples conditioned at 80°C. Surprisingly, after several months in vacuum the remaining D_2O redistributes within the layer, accumulating within a very thin layer at the interface in both samples. The nature of this redistribution is not understood.

Keywords: Water adsorption; interfacial water; silane coupling agents; hygrothermal conditioning; interpenetration of resin and silane; neutron reflection; durability

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I. INTRODUCTION

It is well known that water plays an important role in the degradation of adhesion strength between organic adhesives and inorganic substrates. It is also well established that silane coupling agents can provide excellent durability in aqueous environments [1]. However, the detrimental effects of interfacial water are not limited to adhesive failure. The present study was motivated by concerns in the printed circuit board industry regarding the degradation of electrical properties, as well as adhesive failure, which may arise from water at epoxy/silane/E-glass interphases. The commercial silane finish used in this study provides excellent adhesion strength between epoxy and E-glass, and remarkable bond durability even after extensive conditioning in boiling water or a pressure cooker. However, circuit boards with this finish do not perform well in electrical resistance testing following such conditioning. The goal of this work is to develop a detailed understanding of the mechanism by which water interacts with a resin/silane interphase, with a focus on the consequences for both electrical resistance and adhesion.

Numerous studies of the interaction of moisture with silane/resin interphases have been reported previously [1–5]. There is strong evidence supporting gradients in crosslink density, hydrolytic stability, and other physical properties within the silane/resin interphase. More highly crosslinked regions of silane near the substrate interface are more resistant to removal by solvents or boiling water. It is also established that chemical bonding and physical interpenetration between the silane coupling agent layer and the resin provide improved resistance to hygrothermal conditioning. However, the detailed mechanism of how water interacts with the resin/silane/substrate interphase, or how strength can be maintained in the presence of water, is not currently understood. Plueddemann proposed that the multiplicity of siloxane bonds allows individual bonds to break and reform reversibly without catastrophic failure of the entire network [1]. Such a mechanism may also explain how adhesion strength can be maintained while electrical resistance diminishes. While plausible, this mechanism has not been directly tested experimentally. Another important aspect is the relative amount of physically-adsorbed water *versus* water which is chemically incorporated into the silane layer, and how the proportions vary with temperature and the degree of resin/silane interpenetration. To our knowledge, the degree of interpenetration between resin and silane, another important aspect of the interphase, has not yet been directly measured for any system.

Many experimental techniques have been employed to study water adsorption at composite interfaces [1 – 5]. Due to the focus of this study, specific mention will be made only of those techniques which provide a direct measure of the amount and distribution of adsorbed water *in-situ.*

Proton NMR imaging and solid state NMR spectroscopy have been used to map the presence of moisture and its influence on relaxations within the interphase region by Hoh *et al.* [6]. The distribution of water was imaged ($\sim 50\,\mu\text{m}$ resolution) inside cylindrical samples consisting of mixtures of epoxy resin and both neat and hydrolyzed silane (aminopropyl triethoxysilane) coupling agent following immersion in water at room temperature for seven days. In both cases, the amount of water detected in the sample increased with the amount of silane coupling agent present, although the distribution of water was quite different for samples containing neat and hydrolyzed silane. For samples containing neat silane, cracks extending from the surface well into the interior were observed. For samples containing hydrolyzed silane, water was concentrated around the outer edges. The increase in water uptake with silane concentration was attributed to the hydrolysis and leaching of silane which creates voids that fill with water.

Another *in-situ* technique which provides complementary information about adsorbed interfacial moisture is dielectric relaxation spectroscopy [7]. With this technique, water within the interphase region can be distinguished from water in the bulk resin, and bound water can be distinguished from mobile water. However, the detailed concentration profile of water cannot be obtained, nor can the specific location and nature of the bound water be determined. In particular, water located on the surface of a glass fiber cannot be distinguished from water in the interphase.

Recently, Nguyen *et al.*, have used FTIR-multiple internal reflection (FTIR-MIR) spectroscopy to study water adsorption at several polymer/inorganic substrate interfaces [8]. This technique has excellent sensitivity to low levels of water within the penetration depth of the evanescent wave (~200–400 nm), and can be performed *in-situ*. Another important advantage of this technique is that the bonding state of water can be determined, allowing one to distinguish betwen physically-adsorbed water and water which has been chemically incorporated into the silane layer. However, the depth resolution is limited due to the fairly large penetration depth of the evanscent wave. Since adhesion-promoting silane films are often several tens of nm thick or less, only the integrated total amount of water at such interfaces, rather than a detailed profile, can be obtained. This technique has been used to study the complete delamination of epoxy/germanium and pigmented alkyd/SiO_2 interfaces upon exposure to liquid water.

In order to understand the mechanisms by which water interacts with resin/silane/substrate systems, information is needed regarding the detailed distribution of water within the silane layer, in addition to the integrated total amount. This requires a length scale resolution in the nanometer range. The measurement must be nonintrusive to ensure that the water profiles are not altered by the measurement itself. In this and the following article, neutron reflection has been used to address this problem. By tailoring the contrast between various components within the interphase by H/D isotopic substitution, it is possible to obtain a concentration profile of adsorbed water and to probe the structure of the silane/resin interphase as well. With respect to the latter, the degree of intermixing and mechanical interlocking likely play important roles in the physical properties of composite materials.

Neutron reflection (NR) has been used previously to investigate the interaction of moisture at silane/polymer resin interfaces. In the first such study, Wu *et al.*, examined water adsorption at the interface between a polyimide and the native oxide surface of a silicon wafer [9]. After exposure to a saturated D_2O atmosphere at room temperature for one week, they reported a D_2O level of ~ 17 vol % within the first 30 Å from the interface compared with ~3% in the bulk of the polyimide film. The D_2O content at the interface was reduced to 12% when a silane coupling agent, aminopropyltriethoxysilane, was first coated onto the surface of the water. The mechanism causing this reduction was not discussed. Kent *et al.*, used NR to study the profile of adsorbed water at a molybdenum/polyurethane interface [10]. A thin D_2O-rich layer adjacent to the interface was observed in the absence of coupling agent. Due to the very high concentration of D_2O within this layer (>80 vol%), this was interpreted as a partial delamination of the polyurethane from the molybdenum surface. The amount of interfacial water was greatly reduced when a silane coupling agent was mixed into the resin. In addition, the penetration of water into the oxide layer of the metal, and the dissolution of the metal oxide and subsequent diffusion into the polymer film were also reported.

In this work we examine the profiles of adsorbed water within a commercial silane finish as a function of the temperature of humidity conditioning. The nature of the interaction of water with the silane layer is investigated by evacuating the samples (at 22°C) following moisture conditioning. It is expected that physically-bound water or water which is bound by a reversible chemical bond would eventually be removed upon evacuation, but that water (or individual deuterium atoms) bound by an irreversible (at 22° C) chemical bond would not be removed upon exposure to vacuum. In the present article, the profile of water within a silane film is examined in the absence of a polymer resin. The following article will describe results for samples which include an epoxy resin overcoat layer.

I. EXPERIMENTAL

Materials

The silicon wafers used as substrates in this study were polished 2-inch (5.1 cm) diameter single crystals (111) obtained from Semiconductor Processing Co. To obtain a reproducible surface, the wafers were subjected to the "RCA" process: a sulfuric acid/hydrogen peroxide clean, followed by etching in an HF solution, and then the regrowth of silicon oxide with ammonium hydroxide/hydrogen peroxide solution. Bare wafers so treated are consistently modelled in neutron reflection experiments using the known density of silicon, a ~15 Å native oxide layer, and ~5 Å roughness.

The silane finish used in this study is a proprietary commercial product commonly employed on glass cloth fabrics for printed circuit boards. It is a mixture of two silanes and a wetting agent dissolved in a mildly acidic, aqueous medium. The finish baths were prepared fresh from the individual components just prior to the application.

D_2O (99.9 atom %) was obtained from Aldrich and used as received.

Procedures

The silane finish was deposited onto the wafers using a glass pipet, left to stand for 30 seconds, and then spun off at 2000 rpm using a Headway photoresist spinner. The samples were then dried in an oven at 90°C for 1 hour. Following removal from the oven, the samples were desiccated until the reflectivity experiments were performed. D_2O conditioning was accomplished by placing the samples into a sealed chamber along with an open beaker of D_2O. The chamber was either maintained at room temperature (22°C) or placed into an oven at 80°C. Evacuation of the samples was accomplished by placing them into a desiccator which was evacuated to $\sim$25 in (635 mm) Hg.

Neutron reflection was performed on the POSYII reflectometer at Argonne National Labs. The method of neutron reflection has been reviewed elsewhere [11], and only a brief description is given here. The intensity of reflected neutrons is measured as a function of momentum transfer ($q = 4\pi \sin\theta/\lambda$, where θ is the angle of incidence and λ is the wavelength). Such reflectivity curves are very sensitive to the profile of the neutron scattering length density (SLD) through the sample. The neutron SLD is determined by the density and atomic composition of the material. The substitution of deuterium for protons has a very strong effect on the SLD, and is used here to enhance sensitivity to water. It must be noted that no information regarding the chemical nature of the species in the interphase region is obtained. In particular, no distinction can be made between the presence of D_2O molecules and the presence of dissociated D^+ and OD^- ions or D and OD species chemically attached to the silane film. The POSYII reflectometer operates in the time-of-flight mode, using a wavelength range of $\sim$4–12 Å. The critical edge for total reflection was obtained and used to normalize the data. The reflectivity curves were typically obtained by merging together data from 2 or 3 angles to obtain a sufficient range of momentum transfer. During the measurements, the samples were maintained at room temperature in a sealed aluminium chamber with quartz windows. The chamber was either evacuated or saturated with D_2O, according to the conditioning treatment. The neutron beam was directed onto the interface from the air side.

SLD profiles cannot be obtained by direct inversion of the reflectivity data, but rather are obtained from a fitting procedure. This involves approximating the model profiles by a series of slabs of constant concentration, and then calculating the reflectivity from the stack of layers using the Fresnel equations with a Debye–Waller factor to describe the effect of roughness at the air interface [11]. The resolution, $\Delta q/q$, where Δq is the standard deviation of a Gaussian function, was fixed at 0.03. Best fit parameters were determined by the minimization of $\chi^2 = \sum((R_{\text{exp}} - R_{\text{calc}})^2/\sigma_{\text{std}}^2))/(N_{\text{pts}} - N_{\text{param}})$ using the Marquardt algorithm.

III. RESULTS

III.1. Reflectivity Data

D_2O Conditioning at 22°C

Figure 1a shows the neutron reflectivity from a thin layer of the commercial silane finish on the native oxide of a silicon wafer in the as-prepared state, and again after exposure for 48 hours to air saturated with D_2O at 22°C. The data cover nearly five orders of magnitude in reflectivity and are displayed as reflectivity $\times q^4$ for clarity. In the dry state, the minimum in the curve is a very sensitive function of the overall thickness of the silane film. The large increase in reflectivity observed after conditioning is due to adsorption of D_2O. Adsorption of D_2O leads to an increase in reflectivity due to its very high SLD ($6.4 \times 10^6 \text{Å}^{-2}$). The shift in the minimum to higher q indicates that a layer of adsorbed D_2O has formed at the silicon oxide surface. The magnitude of the shift is related to the thickness of the D_2O-rich layer. In Figure 1b, the reflectivity from the sample following ~6 hours exposure to vacuum is shown compared with the reflectivity in the asprepared state and also immediately following conditioning. After ~6 hours in vacuum. the reflectivity has shifted substantially from the curve obtained immediately following conditioning towards the curve for the as-prepared state, although it is still clearly distinguishable

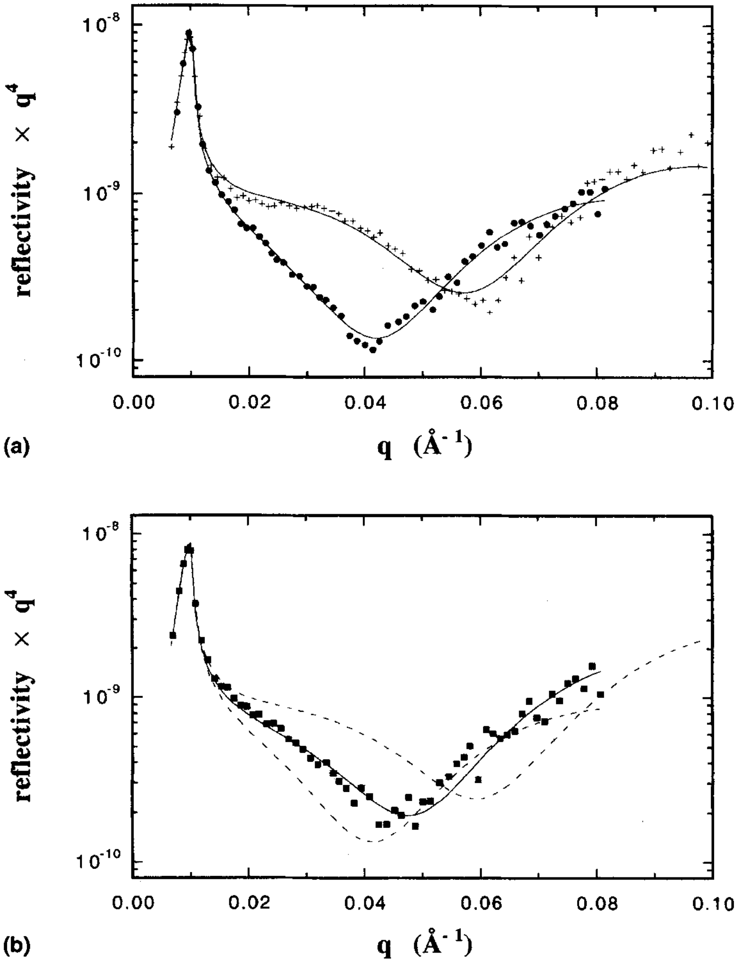

FIGURE 1 Reflectivity from a silane finish-coated silicon wafer (a) in the desiccated state (•) and after exposure for 48 hrs to air saturated with D_2O at 22°C (+); (b) after exposure so vacuum for ~ 6 hrs (■); (c) after exposure to vacuum for several months (▲). The dashed lines in (b) and (c) represent the data for the two states in (a).

from the latter. The minimum has moved a large fraction of the way back toward the value of the as-prepared state. Reflectivity after several months in vacuum is shown in Figure 1c, again compared with the reflectivity in the as-prepared state and immediately following conditioning. Surprisingly, after several months in vacuum, the

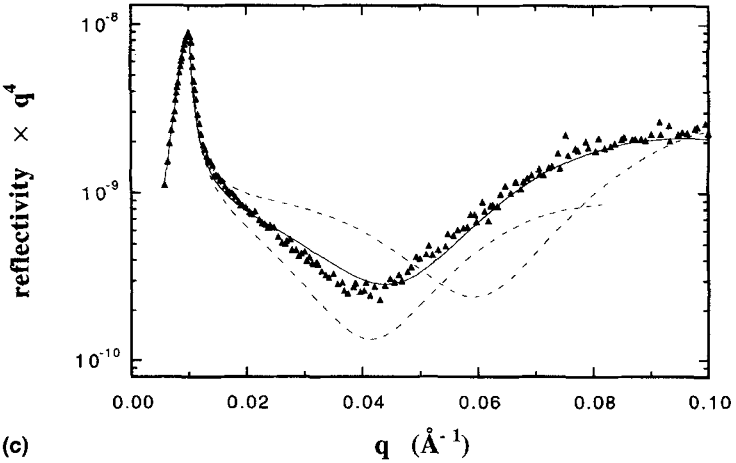

FIGURE 1 (Continued).

reflectivity has increased over most of the q range rather than returning to that of the as-prepared state. The minimum has moved even closer to that of the as-prepared state.

D_2O Conditioning at 80°C

Figure 2a shows the neutron reflectivity from an analogous sample in the as-prepared state, and after exposure for 48 hrs to air saturated with D_2O at 80°C. For the as-prepared sample, the minimum in the curve again occurs at a *q value* of ~ 0.04 Å^{-1}, indicating a thickness which is nearly identical to that for the sample in Figure 1a. After conditioning, a large increase in reflectivity is again observed, which is even more pronounced than that in Figure 1a. The minimum again shifts to higher q, indicating an adsorbed water layer at the silicon oxide surface. In Figure 2b, the reflectivity following ~ 13 hours exposure to vacuum is shown compared with the reflectivity in the asprepared state and immediately following conditioning. After ~ 13 hours in vacuum, he reflectivity has decreased substantially, shifting back towards the curve for the as-prepared state. However, the reflectivity curve remains further from that for the as-prepared state than for the previous sample (conditioned at 22°C) after evacuation

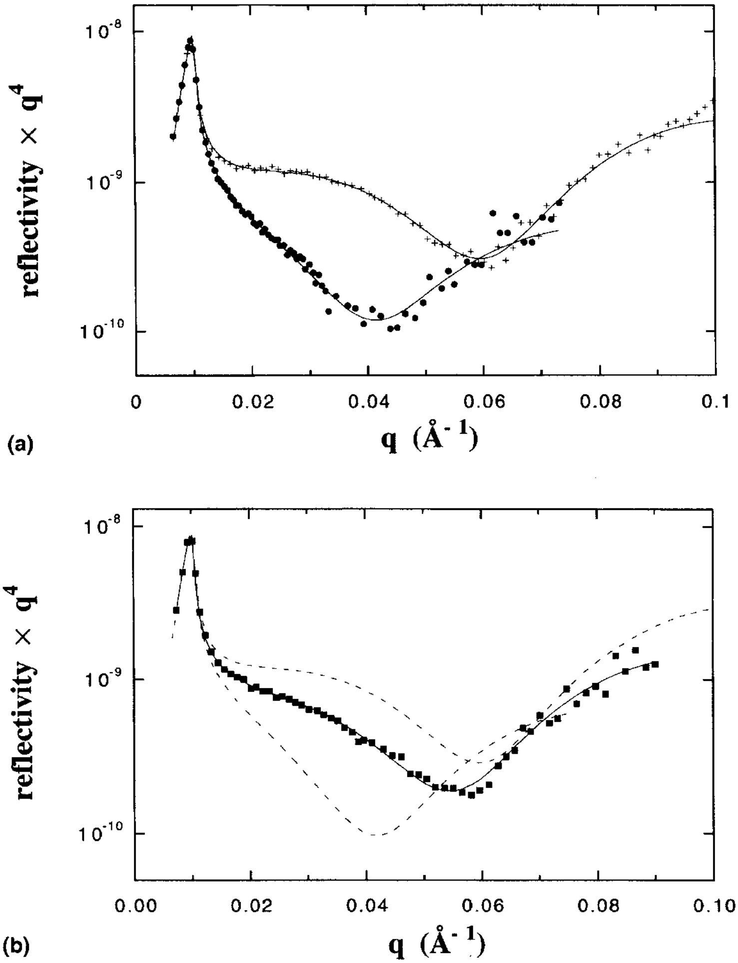

FIGURE 2 Reflectivity from a silane-finish-coated silicon wafer (a) in the desiccated state (●) and after exposure for 48 hrs to air saturated with D_2O at 80°C (+); (b) after exposure to vacuum for ~ 13 hrs (■); (c) after exposure to vacuum for several months (▲). The dashed lines in (b) and (c) represent the data for the two states in (a).

for only 6 hours. Also, the minimum shifts only slightly toward the value in the as-prepared state. Reflectivity after several months in vacuum is shown in Figure 2c, again compared with the reflectivity in the as-prepared state and immediately following conditioning. After

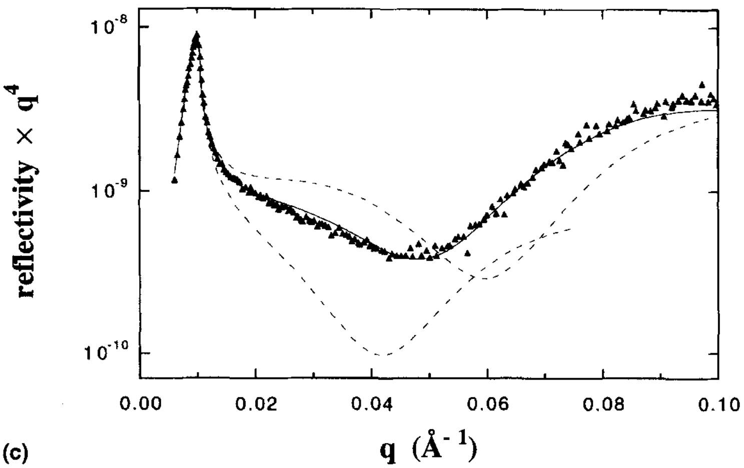

FIGURE 2 (Continued).

several months in vacuum, the reflectivity has again increased over most of the q range rather than returning to that of the as-prepared state. The minimum remains at a q value which is noticably greater than that in the as-prepared state.

III.2. Analysis

D₂O Conditioning at 22°C

We begin with the analysis of the reflectivity data from the first sample in the as-prepared state. The curve through the data in Figure 1a is the best fit which yields the SLD profile shown by the thick line in Figure 3a. The reflectivity can be modelled using a single uniform 81Å thick layer with a SLD of $0.78 \times 10^{-6}\text{Å}^{-1}$ on the substrate. This SLD value corresponds to a density near unity [12]. The thickness of the film is determined with a high degree of accuracy due to the presence of the minimum in the curve near $q = 0.04\ \text{Å}^{-1}$. The model profile includes a roughness of 13Å at the air surface (not shown in Fig. 3a). The values for the roughnesses at the air surface for all the best-fit model profiles in this work are collected in Table I.

Next we discuss the reflectivity for the sample obtained immediately following humidity conditioning, shown by the crosses in Figure 1a.

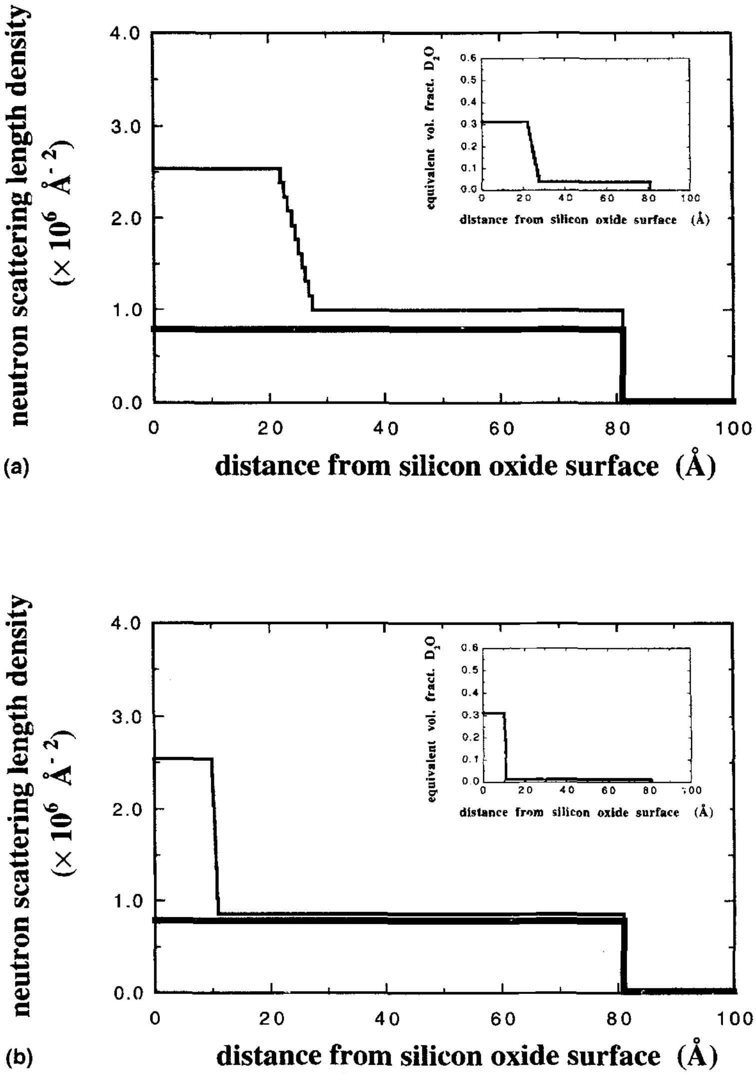

FIGURE 3 (a) Neutron scattering length density profiles giving the best fits to the data for the sample conditioned at 22°C: (a) as-prepared (thick line) and following humidity conditioning (thin line); (b) as-prepared and following ~6 hours evacuation after humidity conditioning (thin line); (c) as-prepared and after evacuation for several months (thin line). Adsorption of D_2O increases the scattering length density. The equivalent concentration profiles of D_2O are given in the insets. The profile of adsorbed D_2O is composed of at least two distinct layers.

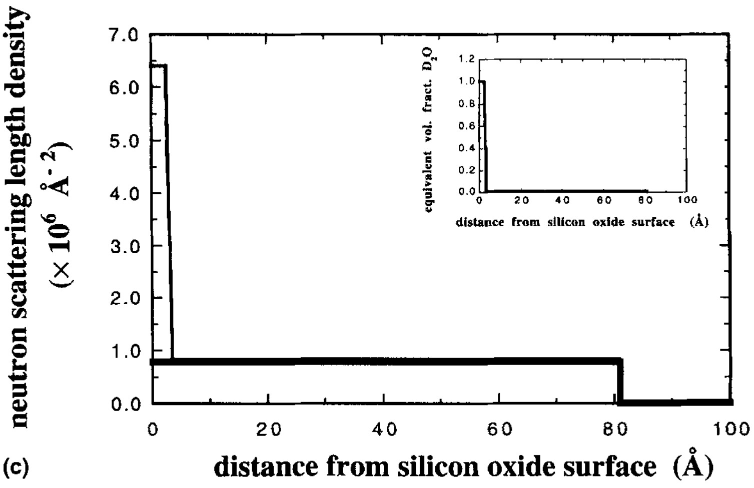

FIGURE 3 (Continued).

TABLE I Debye–Waller factors (Å) describing roughness at the air surface of the silane film

	22°*C*	80°*C*
as-prepared	13	28
immediately following conditioning	3	3
after short period in vaccum	9	9
after several months in vacuum	12	11

These data are not consistent with a single-layer profile, but rather the adsorbed D_2O is distributed in at least two layers. The best-fit SLD profile is shown by the thin solid line in Figure 3a. Elevated SLD relative to that of the dry state indicates the presence of D_2O. The equivalent volume fraction profile of D_2O (assuming all deuterium is present as D_2O) is given in the inset to Figure 3a. A layer of elevated D_2O concentration is observed near the interface, which corresponds to the shift of the minimum to higher *q*. The rest of the adsorbed D_2O is distributed uniformly throughout the bulk of the silane film at roughly 5 vol%. The gradient between the two layers is modelled by a series of thin slabs, and occurs over roughly 5 Å. The roughness at the silane/air interface is substantially reduced relative to the as-prepared state as shown in Table I.

Next, we address the data obtained after exposure to vacuum for ~ 6 hours, shown by the squares in Figure 1b. The best-fit SLD profile is shown in Figure 3b. The thickness of the D_2O-rich layer is substantially reduced relative to that obtained immediately following conditioning. This is indicated by the shift of the minimum in Figure 1b back towards that of the dry state. In addition, most of the D_2O is removed from the bulk of the silane film, and the roughness of the air surface has returned to nearly that of the as-prepared state. Thus, upon short term exposure to vacuum, weakly-bound, physically-adsorbed water is removed from the bulk and interfacial layers causing the film to return to nearly its initial state, except for the presence of the strongly-adsorbed, ~ 10 Å D_2O-rich layer at the substrate surface.

Finally, we turn our attention to the reflectivity in the final state given in Figure 1c. The best-fit model profile, shown by the thin line in Figure 3c, is composed of two layers: a very thin (~ 3 Å) layer at the substrate surface with very high SLD, and a second layer representing the bulk of the film with an SLD nearly the same as that of the as-prepared state [13]. The high value of the SLD of the first layer suggests a nearly pure D_2O layer. Thus, it appears that during long term exposure to vaccum, the D_2O (or deuterium) redistributes within the layer, accumulating within a narrow region immediately adjacent to the substrate surface. The nature of this redistribution is not understood.

D_2O Conditioning at 80°C

Analysis of the reflectivity data from the second sample in the as-prepared state yields a similar SLD profile to that for the sample conditioned at 22°C. The profile in the desiccated state, shown as the thick line in Figure 4a, again is modeled with only a single layer, but with a slightly higher SLD than for the first sample. The thickness (79 Å) is comparable with that obtained for the first sample but the roughness at the air surface is considerably higher (27 Å). The SLD profile after conditioning at 80°C for 48 hours is shown by the thin line in Figure 4a. The corresponding equivalent volume fraction profile of

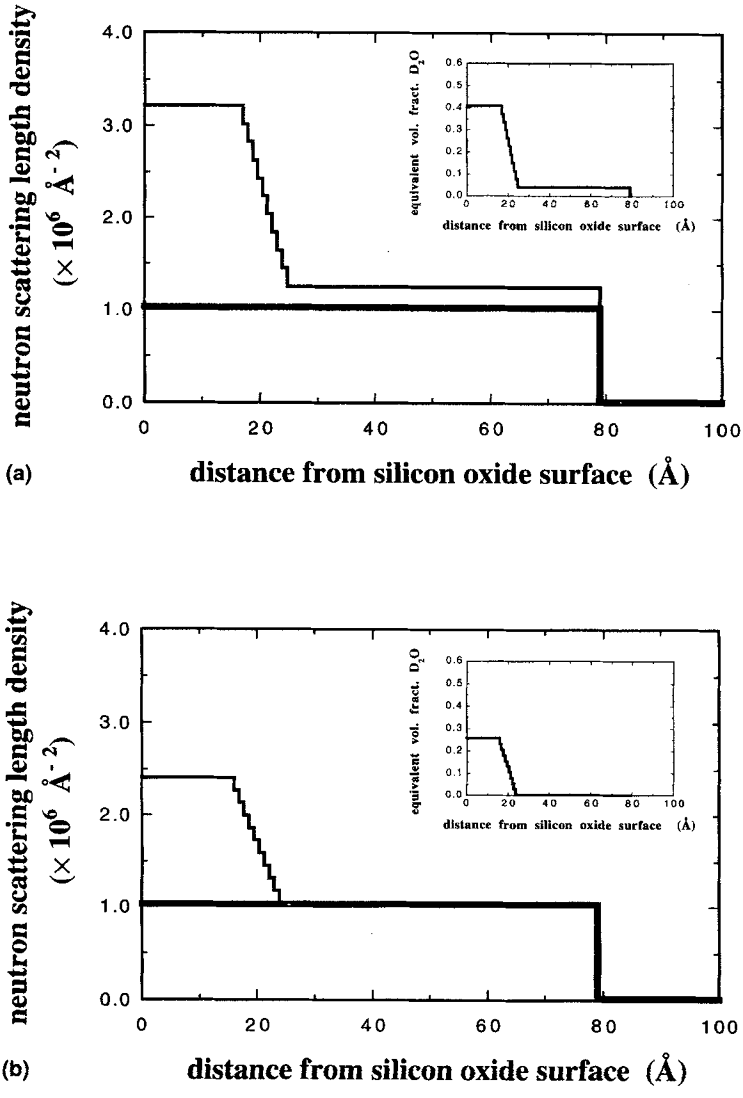

FIGURE 4 (a) Neutron scattering length density profiles giving the best fits to the data for the sample conditioned at 80°C: (a) as-prepared (thick line) and following humidity conditioning (thin line); (b) as-prepared and following ~13 hours evacuation after humidity conditioning (thin line); (c) as-prepared and after evacuation for several months (thin line). The equivalent concentration profiles of D_2O are given in the insets. The profile of adsorbed D_2O is again composed of at least two distinct layers. More D_2O is adsorbed for conditioning at 80°C than at 22°C. Also, more D_2O remains after evacuation for several months for the sample conditioned at 80°C.

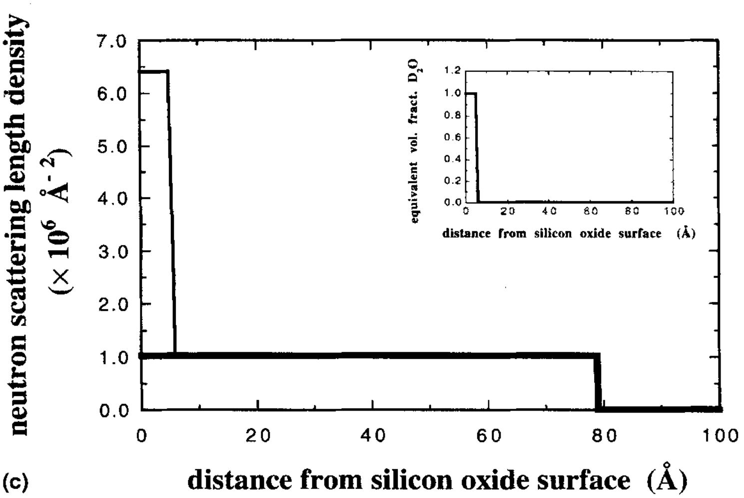

FIGURE 4 (Continued).

D_2O is given in the inset. The D_2O uptake is greater than was observed after conditioning for the same period of time at 22°C. In particular, the concentration of D_2O within the interfacial layer is even higher (~40% for conditioning at 80°C *versus* ~30% for conditioning at 22°C). The roughness of the silane/air interface is again considerably reduce relative to that for the as-prepared state.

The SLD profile after 13 hours in vacuum is shown in Figure 4b. Much of the D_2O from the interfacial layer has been removed, as was the case for the first sample after 6 hours in vacuum. However, there is a higher percentage of adsorbed D_2O remaining in the film after 13 hours than was present after 6 hours in vacuum for the sample conditioned at 22°C (compare Figs. 3b and 4b). The thickness of the layer is comparable with that observed immediately following conditioning, which is indicated by the fact that the minimum in Figure 2b is at nearly the same q value as observed immediately following conditioning. The profile after evacuation for several months, shown by the thin line in Figure 4c, is also very similar to that for the first sample, revealing a thin, nearly pure D_2O layer at the substrate surface. However, the thickness of this layer is twice that of the sample conditioned at 22°C

IV. DISCUSSION

This work demonstrates that detailed profiles of adsorbed water within commercial silane finish films can be measured noninvasively by neutron reflection. Upon humidity conditioning for 48 hours at either 22°C or 80°C, excess water is present within the silane finish layer. The main result obtained from these experiments is that the distribution of water within the silane finish layer is not uniform. In particular, the profile is composed of at least two distinct layers. The first is a thin D_2O-rich layer at the substrate surface. At least a portion of the D_2O in this layer is strongly bound, as much D_2O remains within this layer after several hours in vacuum whereas most of the D_2O in the bulk of the film has been removed. The D_2O-rich interfacial layer is present for both conditioning temperatures, but the quantity of D_2O within this layer is greater for the sample conditioned at the higher temperature. In addition, the removal of D_2O from this layer upon evacuation is slower for the sample conditioned at elevated temperature. These latter observations likely indicate a greater degree of hydrolysis of siloxane bonds for the sample conditioned at 80°C.

The redistribution of D_2O (or deuterium) within the silane film upon long term evacuation to form a thin layer of high D_2O concentration at the interface is an unexpected result of this work. This may indicate the gradual removal of certain adsorbed molecules from the interface during evacuation, which then allows D_2O to adsorb to the vacated sites. It may also indicate that adsorbed D_2O is in dynamic chemical equilibrium with the silane film, and that the most stable state is only achieved when water interacts with adsorption sites on the substrate surface or with molecules directly in contact with the substrate. Also to be considered is the fact that this commercial finish is composed of two silanes and a wetting agent, and hence gradients in chemical composition within the layer may play a role in the redistribution of adsorbed D_2O. It is not yet known whether the same redistribution of D_2O occurs in the absence of vacuum. It is interesting to note that the redistribution of D_2O and formation of a very thin, high D_2O concentration interfacial layer is not observed when an epoxy resin is coated over the finish layer. This is discussed in the following article.

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[12] For a precise determination of the density from the fitted neutron scattering length density, the atomic composition within the finish layer is required, which depends upon the degree of hydrolysis of alkoxy silyl groups, and the extent of crosslinking reactions and reactions with the substrate surface. If all the alkoxy silyl groups were hydrolyzed and reacted with other such groups or with the surface, the density within the finish layer determined from the measure SLD value is 0.78 g/cm^3. This value is a lower bound. The actual density of the film must be higher if only partial hydrolysis of the alkoxysilyl groups or if only partial reaction of silanol groups has occurred.
[13] The value of 3 Å for the layer in Figure 3c is determined from the best fit to the data using a model profile. Model-independent information regarding dimensions can be obtained if fringes are observed such as that occuring at $q = 0.04$ Å^{-1} in Figure 1a. However, the q value at which a fringe would be expected for a 3 Å layer is well beyond the accessible q range.