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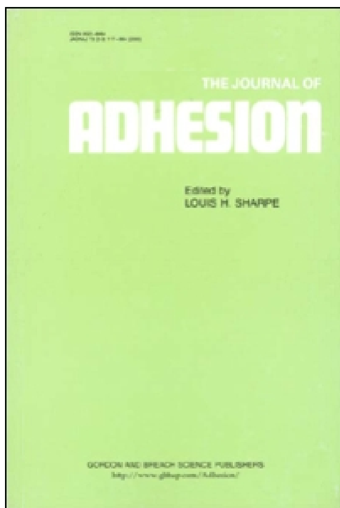

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Water Adsorption in Interfacial Silane Layers by Neutron Reflection: 2. Epoxy Silane Finish on Silicon Wafers

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To cite this Article Kent, M. S. , McNamara, W. F. , Baca, P. M. , Wright, W. , Domeier, L. A. , Wong, Apollo P. Y. and Wu, W. L.(1999) 'Water Adsorption in Interfacial Silane Layers by Neutron Reflection: 2. Epoxy Silane Finish on Silicon Wafers', The Journal of Adhesion, 69: 1, 139 — 163
To link to this Article: DOI: 10.1080/00218469908015923
URL: http://dx.doi.org/10.1080/00218469908015923

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J. Adhesion, 1999, Vol. 69, pp. 139–163
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Water Adsorption in Interfacial Silane Layers by Neutron Reflection: 2. Epoxy +Silane Finish on Silicon Wafers*

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(Received 2 January 1998; In final form 17 July 1998)

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The interaction of water with an interphase composed of a common commercial glass cloth silane finish and an epoxy resin is explored by neutron reflection. The silane finish was applied to the oxide surfaces of polished silicon wafers. The epoxy resin (diglycidyl ether of bisphenol A with dicyandiamide curing agent) was then roll-coated over the silane finish and cured. Profiles of D_2O in the interphase were measured by neutron reflection after varying periods of exposure to air saturated with D_2O at 22°C and at 80°C. A significant uptake of D_2O into the interphase region is observed after exposure at 80°C for 3 days. The D_2O profile in the interphase can be described by a two-layer model composed of a thin (~15 Å) layer with ~50 vol% D_2O next to the silicon oxide surface and a second layer corresponding to the remainder of the silane-epoxy mixed layer with a much lower D_2O level. No excess D_2O is detected (detection limit ~3%) in the interface region under the same conditions if the silane finish is not present. For samples conditioned at 22°C, no D_2O is detected in the silane interphase after exposure for 18 days, but a significant uptake is observed after exposure for 6 months. The profile in the latter case can again be described by a two-layer model with a thin D_2O-rich layer near the silicon oxide surface. The nature of the interaction of D_2O with the interphase is further probed by exposing samples to vacuum following humidity conditioning. After evacuation for ~1 month, near complete removal of interfacial water is observed for samples conditioned at 80°C for 3 days and also at 22°C for 6 months. These observations are interpreted in terms of a reversible chemical interaction (hydrolysis) between water and the silane finish.

*This work was partially supported by the U.S. Department of Energy under contracts DE-AC04-94AL85000 and W-7405-ENG-36.

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

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I. INTRODUCTION

The subject of this and the preceeding article [1] is the interaction of water with a silane/epoxy resin interphase. The work was driven by concerns over delamination and electrical resistance failure in printed circuit boards. In this report we describe detailed interfacial profiles of water following various humidity conditioning treatments in order to elucidate the mechanisms of interaction of water with the silane/resin interphase. The profiles are obtained by neutron reflection, using H/D substitution to provide contrast. With this technique, D_2O concentration profiles are obtained at the buried interface *in-situ* with ~5 Å resolution normal to the surface. Due to the excellent resolution, the distribution of D_2O within the silane layer is obtained, rather than only the integrated total amount. Previous studies of the interaction of water with silane/resin interphases and proposed mechanisms were discussed in the preceding article. The preceding article focused exclusively on experiments involving only the silicon substrate (with native oxide) and the silane finish layer. In the present article, results are presented for similar substrates coated with both the silane finish and an epoxy resin.

Following a description of the experimental details, D_2O profiles will be reported as a function of the time and temperature of humidity conditioning, and after subsequent exposure to vacuum. After presenting the results, the data will be discussed with respect to the mechanism of interaction of D_2O with the interphase and the degree of epoxy/silane interpenetration. The article concludes with a summary of the most important results obtained from this study.

II. EXPERIMENTAL

Materials

The silicon wafers used as substrates in this study were polished 2- or 4-inch (5.1 or 10.2 cm) diameter single crystals (111) obtained from

Semiconductor Processing Co. [2]. 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 amonium 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 slightly acidic aqueous medium. Originally, the complete finish was obtained from the manufacturer and used as received. However, it was subsequently discovered that the thickness of the coating varied with the age of the bath. For subsequent samples, the finish bath was prepared fresh from the individual components just prior to use. This gave a consistent thickness of ~80 Å, which is more representative of that actually deposited on commercial glass cloths.

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A deuterated epoxy resin was specially synthesized for this work as follows. A 100 ml flask was charged with 1.0 g NaOH pellets (99.9% purity), 3.0 g deuterated bisphenol A (D_{16}, Cambridge Isotopes Labs.) and 9.6 ml of epichlorohydrin. The mixture was stirred and heated, with the heating rate moderated to control the exotherm to a maximum of 107°C. After the exotherm subsided, the temperature was maintained at 105°C for 3 hours. The excess epichlorohydrin was then vacuum distilled (< 1 torr) at 70–80°C. The contents of the flask were then dissolved in benzene and filtered to remove NaCl. The benzene was subsequently removed under vacuum to leave a viscous liquid (4.15 g, 95% yield). Proton and carbon NMR were consistent with the expected epoxy product. The epoxy equivalent weight was determined by C_{13} NMR [3] to be 198 (equivalent to 183 for a protonated resin.)

EPON 1124-80-A commercial brominated epoxy resin was obtained from Shell. Both the deuterated resin and the commercial resin were cured with dicyandiamide (3 g/100 g resin) and 2-methyl imidazole (0.06 g/l00 g resin), obtained from Aldrich. The curing agent and accelerator were initially dissolved in 2-methoxy ethanol (47 g/100 g resin) obtained from Aldrich, and the resin was then added to the mixture. The glass transition of the cured material (120–140°C) is much greater than the highest conditioning temperature of 80°C.

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. A ~2 μm layer of the epoxy resin/curing agent mixture was applied by roll coating a 70 wt.% solution onto the silicon wafers. To cure the resin, the samples were heated in an oven at 60°C for 10 minutes followed by 177°C for 2 hours. Following removal from the oven, the samples were desiccated until the reflectivity experiments were performed. D_2O conditioning and evacuation were accomplished in the same manner as described in the preceeding article.

Neutron reflection was performed on the POSYII reflectometer at Argonne National Labs and on the NG7 reflectometer at the National Institute of Standards and Technology. The method of neutron reflection has been reviewed elsewhere [4], 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. The POSYII reflectometer operates in the time-of-flight mode, using a wavelength range of $\sim 4-12$ Å. The reflectivity curves were typically obtained by merging together data from 2 or 3 angles to obtain a sufficient range of q. The NG7 reflectometer was operated at a fixed wavelength of 4.1 Å. For both instruments, the critical edge for total reflection was obtained and used to normalize the data. During the measurements, the samples were maintained at room temperature in a sealed aluminum 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 silicon side, entering and exiting through the sides of the 0.5 cm thick wafer, in contrast to the experimental configuration in the previous article.

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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 composition and density, 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 each interface [4]. 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 $\chi^2 = \sum((R_{exp} - R_{calc})^2/\sigma_{std}^2)/(N_{pts} - N_{param})$ using the Marquardt algorithm. The goal of the fitting process is to include the minimum amount of complexity demanded by the data. Profiles involving at most a few steps proved to be adequate for the present data.

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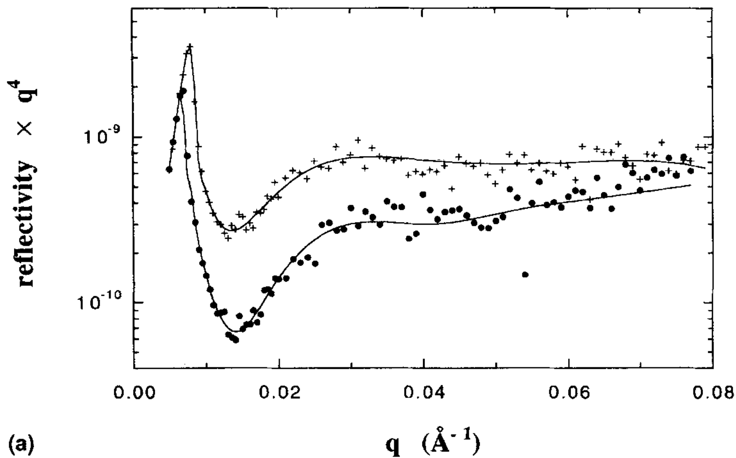
III. RESULTS

1. Samples Conditioned in Saturated D_2O at 80°C

Reflectivity curves from samples conditioned for 3 days in air saturated with D_2O at 80°C are shown in Figures 1a (with silane finish) and 2a (without silane finish). For these samples, a 50/50 mixture (by wt.) of the deuterated resin and Shell EPON 1124-80-A commerical resin was used. This resin composition gives high sensitivity to adsorption of D_2O while still allowing the total reflection critical edge to be obtained for normalization. The data cover nearly five orders of magnitude in reflectivity and are displayed as reflectivity $\times q^4$ for clarity. Since the neutron beam impinges onto the interface from the silicon side, the value of the critical q for total internal reflection ($q_c = \sim 0.007-0.008$ Å^{-1}, peak in Fig. la) is indicative of the atomic composition and density of the bulk epoxy film. The reflectivity at higher q values is sensitive to the SLD profile near the epoxy/silane/silicon oxide interface region.

Figure 1a shows reflectivity curves, both before and after conditioning, for a sample containing the commercial silane finish. The curves through the data are best fits which yield the model SLD profiles shown in Figure lb. Only the region near the interface is shown. The layer on the right side of the figure is the bulk layer which extends out roughly



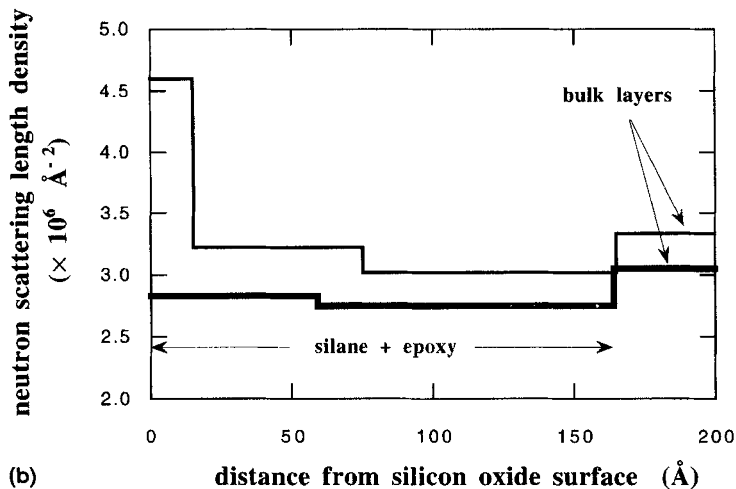


FIGURE 1 (a) Reflectivity from a silicon wafer coated with the commercial silane finish (~165 Å) and a contrast-optimized mixture of deuterated and protonated epoxy resin (~2 μm). Data are shown for the sample in the desiccated state (•) and after exposure for 3 days to air saturated with D_2O at 80°C (+). The curves through the data are best fits corresponding to the SLD profiles in Figure 1b. (b) SLD profiles obtained from the reflectivity data in Figure 1a (thick line-before conditioning, thin line-after conditioning). Only the region near the interface is shown. The layer on the right side of the figure is the bulk layer which extends out roughly 2 μm to the air surface. In the as-prepared state, the SLD within the silane-containing region is much higher than that of a pure silane layer (~$1.0 \times 10^6 cm^{-2}$) [1], indicating significant resin penetration. After conditioning, the SLD is further increased due to adsorption of D_2O. (c) Equivalent concentration profile of D_2O obtained from the SLD profiles in Figure 1b. A high concentration of D_2O is observed at the substrate surface, whereas a much lower level of D_2O is observed in the bulk of the silane/epoxy interphase and in the bulk epoxy film.

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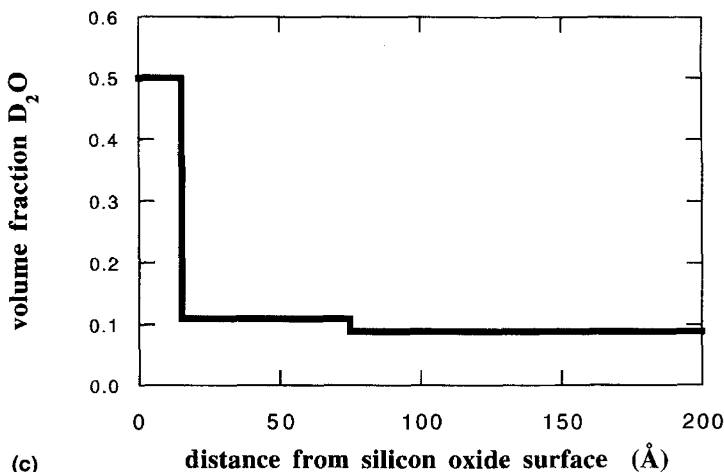

FIGURE 1 (Continued).

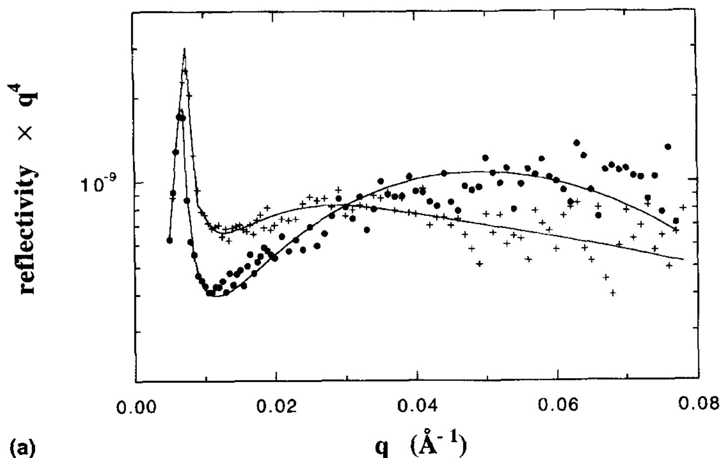

FIGURE 2 (a) Reflectivity from a silicon wafer coated with the contrast-optimized mixture of deuterated and protonated epoxy resin (no silane finish). Data are shown for the sample in the desiccated state (•) and after exposure for 3 days to a saturated D_2O atmosphere at 80°C (+). The curves through the data are best-fits corresponding to the SLD profiles in Figure 2b. (b) SLD profiles obtained from the reflectivity data in Figure 2a (thick line - before conditioning, thin line-after conditioning). The layer of elevated SLD observed at the interface with the substrate may be due to an increased density of the epoxy near the interface or to preferential segregation of the deuterated epoxy components. After conditioning no excess D_2O is observed at the interface, but rather the data are consistent with a uniform level of D_2O throughout the epoxy film. The best-fit profile includes a decrease in SLD near the silicon oxide surface and an increase in the roughness between the layer of elevated SLD and the bulk resin. This may signal the initial stages of delamination.

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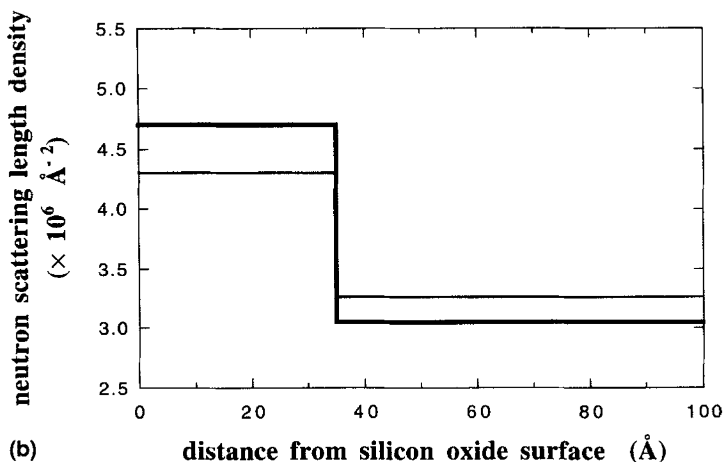

FIGURE 2 (Continued).

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2 μm to the air surface. Before conditioning, the interphase region can be described by a ~165 Å silane-containing layer (thick line in Fig. 1b). In this case the silane bath was obtained complete from the manufacturer, and the time delay between formulation and application led to an increased thickness relative to that obtained for a freshly prepared bath (~ 80–90 Å). Importantly, the magnitude of the SLD (~ 2.7×10^{-6}–2.8×10^{-6} Å^{-2}) for the silane-containing layer is much higher than the value (~1.0×10^{-6} Å^{-2}) for a pure silane film in the absence of epoxy [1]. This indicates that epoxy has penetrated into the silane layer. However, the quantitative degree of intermixing is difficult to determine because it is not possible to distinguish between lateral heterogeneity and gradients in composition or density normal to the interface from the specular reflectivity alone. The value of q at the total internal reflection edge (q_c) indicates an SLD of 3.05×10^{-6} Å^{-2} in the bulk of the epoxy film, which is consitent with the known composition and density of the mixed epoxy resin.

After conditioning, the reflectivity is greatly increased due to incorporation of D_2O into the interphase region. The SLD profile for this case is shown by the thin line in Figure lb. It must be noted that the SLD is determined solely by the atomic composition and the density, and 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. In the following, the results are presented as an equivalent profile of D_2O (assuming all deuterium is present as D_2O). The equivalent profile of D_2O obtained from the SLD profiles of Figure lb is shown in Figure lc [5]. The profile indicates a nonuniform distribution of D_2O within the silane film, with a very thin (~15 Å) D_2O -rich layer near the silicon oxide surface and a much lower level of D_2O throughout the remainder of the silane containing region and the bulk epoxy film.

From the shift in q_c, a D_2O-equivalent of 9 vol.% is obtained for the bulk of the epoxy. This value is much higher than the typical water uptake values obtained gravimetrically for bulk epoxy samples (~1 – 2%), and the difference is beyond the uncertainty in the measurement (± 3%). This anomalously-large increase in SLD in the bulk of the epoxy film appears to be due to D/H exchange between D_2O and the commercial resin during conditioning. Indeed, we have observed a significant level of D/H exchange in bulk samples of the commercial epoxy following exposure to D_2O at 80°C by NMR. This effect has been previously reported in the literature [6].

Reflectivity data for a sample containing only a 2 µm layer of the mixed epoxy resin on a silicon substrate, with no silane coating, is shown in Figure 2a. Data are shown both before and after D_2O conditioning. The curves through the data are best fits which yield the model SLD profiles shown in Figure 2b [7]. Both before and after D_2O conditioning, a thin layer of elevated SLD near the silicon oxide surface is required in the model profile in order to obtain agreement with the data. This has been a consistent finding in our work for samples consisting of only a thin film of epoxy on polished silicon wafers. The increase in SLD is likely due to an increased density of the cured epoxy near the silicon oxide surface, although preferential segregation of the deuterated resin to the interface could also explain these data.

The changes observed upon humidity conditioning in Figure 2a contrast sharply with those observed for the sample with the silane coating in Figure la. Without the silane coating, the reflectivity after conditioning falls off much more rapidly with increasing q, even falling

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below the reflectivity for the unconditioned sample for $q > 0.03\,\text{Å}^{-1}$. This indicates a decrease in SLD near the interface relative to the as-prepared state. This is in contrast to Figure 1a where the increased reflectivity out to high q values indicates an increase in SLD near the interface after conditioning. The simplest model SLD profile consistent with the data in Figure 2a is shown in Figure 2b. This particular profile is only one of many which are consistent with the data. However, there are two essential characteristics which must be present in the SLD profile in order to give agreement with the data after conditioning. First, the SLD of the interfacial layer is decreased relative to the value in the as-prepared state. Second, there must be an increase in the roughness at the interface between the interfacial layer of elevated SLD and the bulk epoxy (not shown in Fig. 2b). The decrease in SLD indicates that not only is there no excess of D_2O in the interfacial region as was observed with the silane film present but, in fact, there must be a decrease in the density at the interface. The decrease in density and the increased roughness may signal the beginning of delamination.

While striking differences exist in the reflectivity for $q > q_c$ (sensitive to the interface region) for samples with and without the silane finish, the q_c values are comparable both before and after conditioning. This is shown in Figure 3, in which only the region near q_c is plotted for the four data sets. This is expected, as the value of q_c reflects the SLD of the bulk of the epoxy film which is identical in the two samples.

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2. Samples Conditioned in Saturated D_2O at 22°C

Reflectivity curves from samples conditioned for 18 days in saturated D_2O at 22°C are shown in Figures 4 (with silane finish) and 5 (without silane finish). The pure deuterated epoxy resin was used for the overcoat layer for these samples, and therefore the q_c values are slightly higher than those for the samples in Figures 1–3. For both samples, the variation in reflectivity observed after conditioning is negligible over the entire q range. The fact that no shift in q_c is observed contrasts sharply with the very significant shift observed in Figure 3. This is consistent with the interpretation of the large shift in Figure 3 as due to H/D exchange between D_2O and the commercial resin. No shift is observed in Figures 4 and 5 since only the deuterated resin was used.

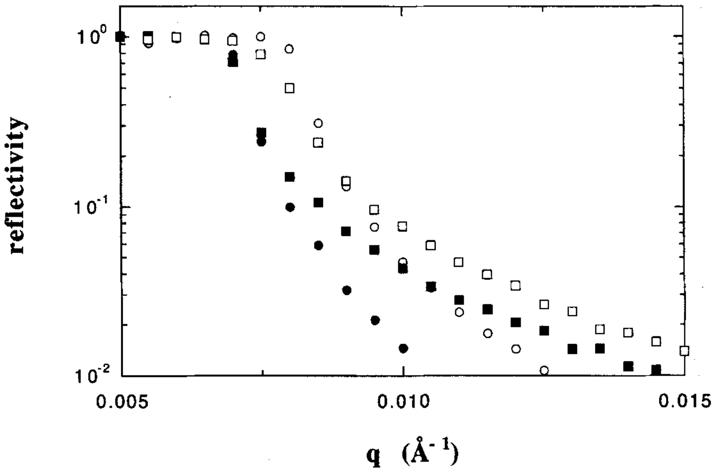

FIGURE 3 (a) Reflectivity in the region of the total reflection critical edge for the data of Figures la (circles) and 2a (squares). Filled symbols indicate data from the as-prepared state, and open symbols represent data obtained after humidity conditioning. The similar increase in q_c following conditioning indicates that the uptake of deuterium into the bulk epoxy film is comparable for the two samples.

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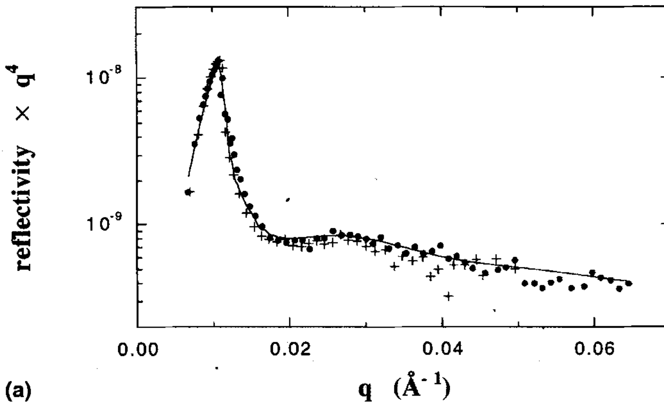
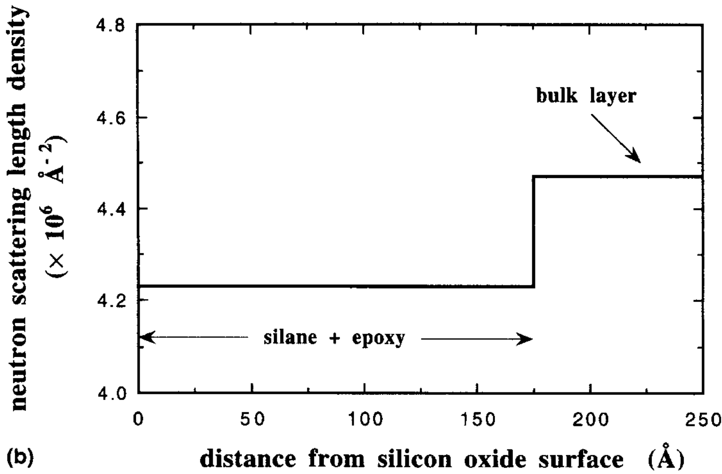


FIGURE 4 (a) Reflectivity from a silicon wafer coated with the commercial silane finish (~175 Å) and the pure deuterated epoxy resin. Data are shown for the sample in the desiccated state (•) and after exposure for 18 days in a saturated D_2O atmosphere at 22°C (+). No variation in reflectivity is observed following this conditioning treatment. The best-fit curve through the data corresponds to the SLD profile in Fignre 4b. (b) SLD profile obtained from the reflectivity data in Figure 4a. The SLD within the silane finish-containing region is again much higher than that of a pure silane layer, indicating significant resin penetration.



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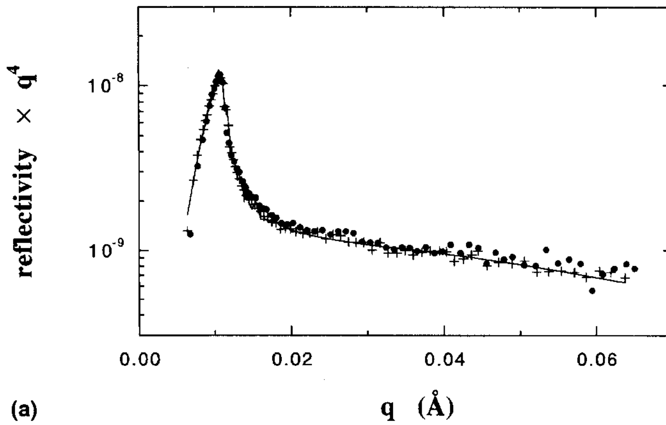

FIGURE 5 (a) Reflectivity from a silicon wafer coated with the pure deuterated epoxy resin (no silane finish). Data are shown for the sample in the as-prepared state (•) and after exposure for 18 days in a saturated D_2O atmosphere at 22°C (+). Negligible variation is observed following this conditioning treatment. The best-fit curve through the data corresponds to the SLD profile in Figure 5b. (b) SLD profile obtained from the reflectivity data in Figure 5a. The layer of elevated SLD at the silicon oxide surface likely indicates an increased density of the epoxy near the interface.

The SLD profiles are shown in Figures 4b and 5b. These profiles are generally consistent with those for the unconditioned samples in Figures lb and 2b, considering the much higher SLD of the purely

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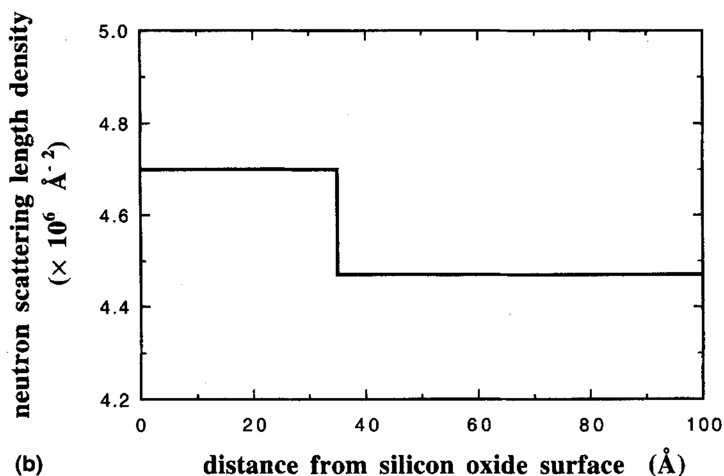

FIGURE 5 (Continued).

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deuterated epoxy resin. Importantly, the SLD within the silane-containing region in Figure 4b is again much higher than that of a pure silane layer, implying that a large amount of deuterated epoxy resin has penetrated into the silane finish layer. Figure 5b shows that once again a thin layer of elevated SLD adjacent to the silicon oxide surface is present for the sample without the silane finish. In this case, there is strong support for interpreting the layer of elevated SLD as an increase in the density of the epoxy near the interface, rather than preferential adsorption of deuterated components, since only the pure deuterated resin was used. However, exclusion of the protonated crosslinker from the interface still remains a possibility.

The fact that no change in reflectivity is observed after conditioning is especially significant since the conditioning time (18 days) is much longer than the time required for diffusion of water through the 2 μm epoxy film. The rate of diffusion of water into a similar epoxy resin system has been measured gravimetrically by Liu *et al.* [8]. Samples were conditioned in 80% relative humidity at various temperatures. From analysis of the weight gain as a function of time, they reported diffusion coefficients of 3.7×10^{-9} cm^2/s and 2.6×10^{-8} cm^2/s at 35°C and 85°C, respectively. From these values, the time required for water to reach the interface in the present samples during conditioning in saturated air at 22°C is estimated to be less than one hour. Therefore,

we conclude that the time required to achieve a quasi steady-state is far less than the conditioning time of 18 days.

An additional experiment was performed to examine the effect of long-term exposure at 22°C. In this case, a sample containing the silane finish was conditioned in air saturated with D_2O at 22°C for 6 months. The reflectivity curves obtained before and after conditioning for this sample are shown in Figure 6a. The SLD profiles before and after conditioning are shown in Figure 6b. Before conditioning, a single mixed layer of silane and epoxy near the interface is again adequate to describe the data. However, the SLD of the silane containing layer is significantly lower than that obtained for the sample of Figure 4b, even though the same pure deuterated resin was used. This indicates a reduced degree of penetration of resin into the

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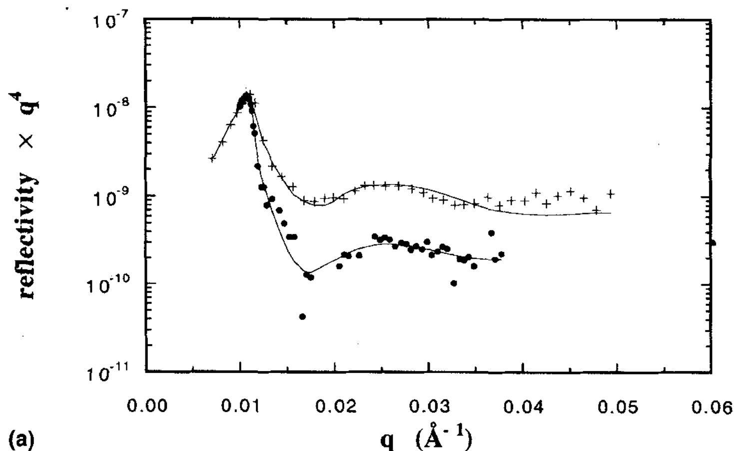

FIGURE 6 (a) Reflectivity from a silicon wafer coated with the commercial silane finish (~200 Å) and the pure deuterated epoxy resin. Data are shown for the sample in the desiccated state (•) and after exposure for 6 months to a saturated D_2O atmosphere at 22°C (+). The curves through the data are best fits corresponding to the SLD profiles in Figure 6b. (b) SLD profiles obtained from the reflectivity data in Figure 6a (thick line – before conditioning, thin line – after conditioning). After conditioning, the SLD is increased due to adsorption of D_2O. (c) Equivalent concentration profile of D_2O obtained from the SLD profiles in Figure 6b. A bilayer profile is observed after adsorption of D_2O. A high concentration of D_2O is observed at the substrate surface, whereas a much lower level of D_2O is observed in the remainder of the silane/epoxy interphase. (d) Reflectivity after evacuation for ~1 month, compared with the best-fit curves for the sample in the as-prepared state and immediately following humidity conditioning. The SLD of the interface region has returned to nearly that of the as-prepared state, indicating nearly complete removal of adsorbed D_2O.

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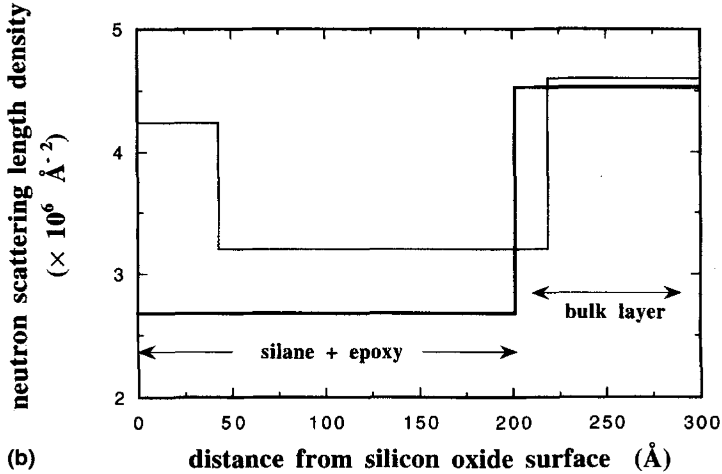

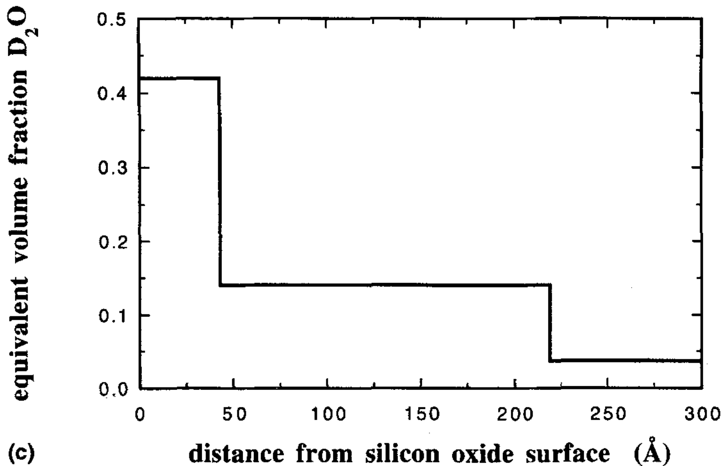

FIGURE 6 (Continued).

silane layer compared with the sample of Figure 4b. The reason for this is not clear. Importantly, after the 6-month conditioning period, a large increase in reflectivity is observed, in contrast to the data in Figure 4. The equivalent D_2O profile obtained from the comparison in Figure 6b is plotted in Figure 6c. The increase in reflectivity can again be described by a two-layer D_2O profile, with a D_2O-rich layer near the silicon oxide surface. In this case, the level of D_2O in the silane

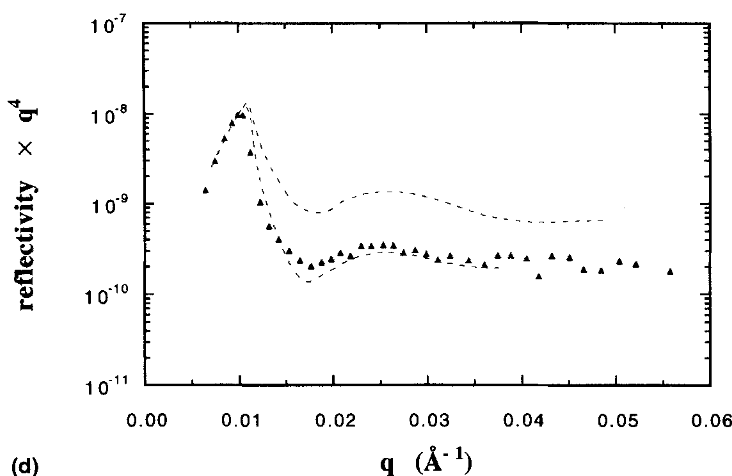

FIGURE 6 (Continued).

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layer is increased relative to that observed in Figure 1. This may be related to the poorer intermixing within the silane/resin interphase. Finally, only a very small shift in the critical edge for total reflection is observed, which is close to the uncertainty in the measurement.

3. REMOVAL OF INTERFACIAL D_2O BY VACUUM

To investigate the nature of the interaction of D_2O with the silane/epoxy interphase, selected samples were exposed to vacuum after D_2O conditioning. It is expected that weakly-bound water or water which is bound by a reversible chemical bond would eventually be removed upon exposure to vacuum, but that water (or individual deuterium atoms) bound by an irreversible (at 22°C) chemical bond would not be removed upon exposure to vacuum. Reflectivity obtained from the sample of Figure 6a after evacuation for one month is shown in Figure 6d, along with the best-fit curves to the data before and immediately after D_2O conditioning. In this case, the reflectivity for $q > q_c$ has returned to nearly that of the virgin state. This indicates that nearly all of the adsorbed D_2O in the interfacial region has been removed. Somewhat surprisingly, the q_c value has decreased slightly from that of

the virgin sample. This seems to suggest the loss of a small amount of volatile, unreacted (deuterated) resin during evacuation.

The experiment was repeated for a sample conditioned at 80°C. Figure 7a shows reflectivity data before and after conditioning in saturated D_2O for 2 days at 80°C. The sample is comprised of an 82 Å silane finish layer coated with the pure deuterated epoxy resin. As in Figure 1, the reflectivity for $q > q_c$ increases upon conditioning. The increase is somewhat weaker than observed in Figure 1a, due to the thinner silane film, the use of pure deuterated epoxy resin rather than the contrast-optimized mixed resin, and humidity conditioning for 2 days rather than 3 days. No change is observed in q_c, which is expected since use of the pure deuterated resin eliminates the possibility of D/H

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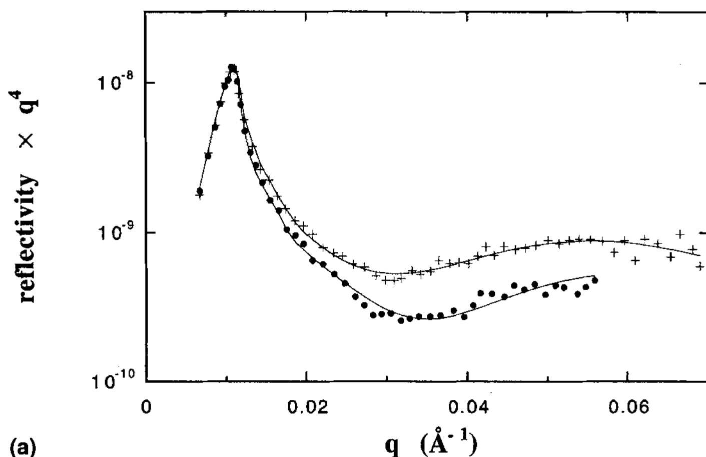

FIGURE 7 (a) Reflectivity from a silicon wafer coated with the commercial silane finish (~80 Å) and the pure deuterated epoxy resin. Data are shown for the sample in the as-prepared state (•) and after exposure for 2 days in a saturated D_2O atmosphere at 80°C (+). The curves through the data are best-fits corresponding to the SLD profiles in Figure 7b. (b) SLD profiles obtained from the reflectivity data in Figure 7a (thick line – before conditioning, thin line–after conditioning). After conditioning, the SLD is increased due to adsorption of D_2O. (c) Equivalent concentration profile of D_2O obtained from the SLD profiles in Figure 7b. A bilayer profile is again observed after adsorption of D_2O. A high concentration of D_2O is observed at the substrate surface, whereas a much lower level of D_2O is observed in the bulk of the silane/epoxy interphase. (d) Reflectivity after evacuation for ~1 month, compared with the best-fit curves for the sample in the as-prepared state and immediately following humidity conditioning. The SLD of the interface region has returned to nearly that of the virgin state, indicating nearly complete removal of adsorbed D_2O.

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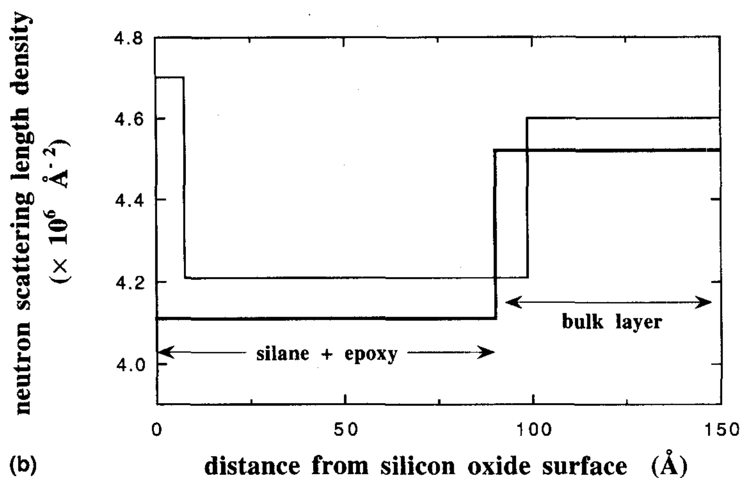

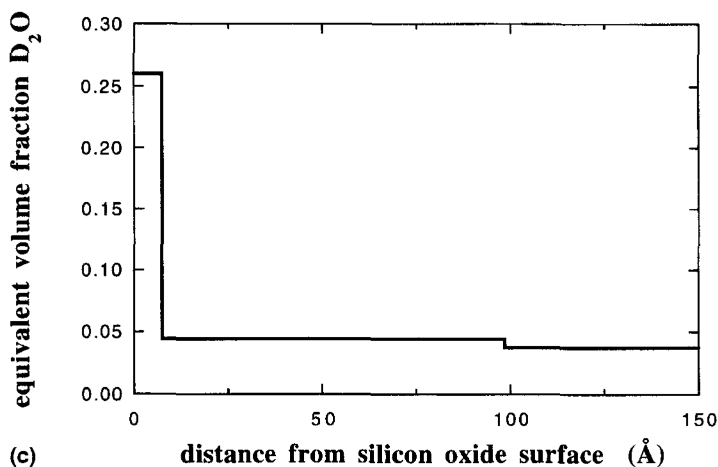

FIGURE 7 (Continued).

exchange with the resin, and the expected 1–2% adsorption is less than the detection limit. The SLD profiles are shown in Figure 7b, which yield the equivalent D_2O profile in Figure 7c. Once again, the increase in reflectivity after conditioning can be described by a bilayer distribution of D_2O within the silane film, with a thin D_2O-rich layer near the silicon oxide surface and a more modest level of D_2O in the bulk of the silane film. The reflectivity curve obtained after evacuation

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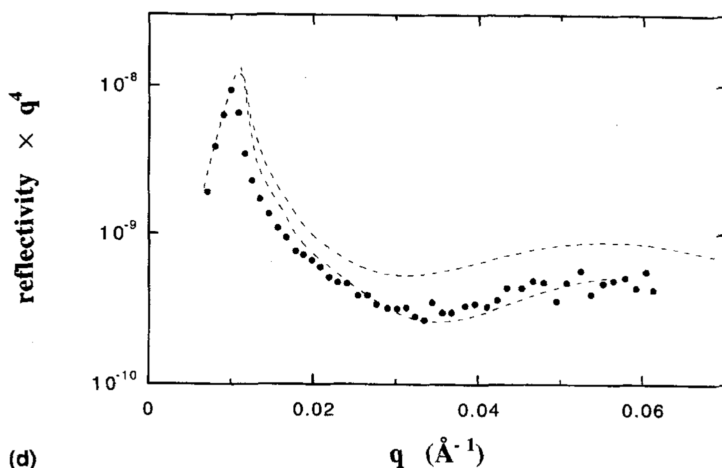

FIGURE 7 (Continued).

for several months is shown in Figure 7d, along with the best-fit curves to the data before and after D_2O conditioning. At $q > q_c$, the reflectivity is again very close to that of the as-prepared sample, indicating nearly complete removal of D_2O from the interface region. The value of q_c has again decreased from that of the unconditioned state.

Thus, for samples conditioned at 22°C (Fig. 6d) and 80°C (Fig. 7d) the reflectivity for $q > q_c$ returns to nearly that of the virgin state after extended exposure to vacuum. This contrasts with the results of Figures 1c and 2c of the preceding article, in which the reflectivity after several months in vacuum deviated strongly from that of the initial state. With an epoxy layer present, no evidence is observed for redistribution and accumulation of D_2O at the interface as was the case in the absence of the epoxy layer. While the sensitivity is somewhat reduced in the present geometry relative to that of the previous article, it is still suflicient to observe such an effect if it were present.

IV. DISCUSSION

Several important results from this study relate to the mechanism of the interaction of water with the silane/resin interphase. First, the

distribution of water within the silane film is nonuniform; in particular, there is a thin D_2O-rich layer adjacent to the silicon oxide surface. A similar result was also observed in the absence of an epoxy overcoat layer, as reported in the preceding article. Second, a reversible chemical interaction between water and the silane finish is suggested from the varying rates of water uptake with exposure time/temperature, and from the nearly complete removal of water from the interface region upon extended evacuation. The differing rates of water uptake cannot be attributed to varying rates of diffusion through the epoxy film, since the time required for diffusion through the film (~ 1 hr at 22°C) is far shorter than all conditioning times employed in this study. A reversible chemical interaction between water and the silane finish was also inferred in the preceding article from differing rates of water uptake and removal upon evacuation for samples without epoxy conditioned at 22°C and 80°C. Third, no interfacial excess of deuterium was observed in the absence of silane. Thus, D_2O uptake is clearly related to the components of the silane finish.

The nature of the chemical interaction is likely hydrolysis of siloxane bonds or hydrolysis of residual alkoxysilyl groups. The fact that a high level of deuterium is observed only near the interface in the silane-containing samples, rather than uniformly throughout the silane-containing layer, is consistent with the observations of the previous article. It may simply reflect a higher density of hydrolyzable bonds near the surface. Alternatively, this result may indicate an accelerated rate of hydrolysis near the interface due to accumulation of water at the substrate surface. We also acknowledge the possibility of composition gradients such that the more hydrophilic silane component or the wetting agent may be in higher concentration at the interface.

Two important differences are observed when the epoxy is present relative to samples containing only the silane finish (previous article) which suggest that the presence of epoxy resin within the silane layer inhibits the interaction of water with the silane molecules or the substrate surface. First, the fact that no interfacial water uptake is observed after 15 days of conditioning at 22°C (sufficient time for diffusion through the epoxy film) contrasts with the data in Figure 2a of the previous article, where a large amount of water adsorption was observed near the interface after 2 days of conditioning at 22°C.

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Second, with the epoxy present no accumulation of D_2O at the substrate surface is observed upon extended evacuation as was the case for the samples with only the silane film. Both of these observations are consistent with epoxy penetration into the silane film. We suggest that epoxy adsorbs to residual sites on the silicon oxide surface and inhibits the build-up of an adsorbed water layer.

The data in Figures 1 and 2 may initially appear to contradict the well-known fact that exposure to water, particularly at elevated temperatures, weaknes adhesion between epoxies and glass or SiO_2 surfaces in the absence of silane coupling agents, but that excellent retention of strength is obtained when appropriate silanes are employed [9, 10]. Indeed, we have obtained similar results with the present silane finish/epoxy resin system using a butt-tensile test with polished E-glass cylinders (Appendix). By comparison with these adhesion test results, we indeed expect that substantial degradation of the interface strength has occurred within the sample of Figure 2, even though no excess interfacial water is detected. There is, however, a hint of degradation in the decreased density and increased roughness of the interfacial layer in the profile in Figure 2b. Therefore, we infer that the strength of this interface has diminished, but that the process is in the early stages, not yet to the point where voids have developed. Large voids would be expected to fill with D_2O upon conditioning and increase the SLD. Likewise, by comparison with the adhesion test results, we expect that the interface of Figure lb has retained most of its original strength, even though substantial D_2O uptake has occurred. The adsorption of water into the interphase region observed in Figure lb apparently occurs in a way that does not catastrophically and irreversibly break the linkage between the substrate and the silane/epoxy interphase. Pluddemann has proposed that the multiplicity of siloxane bonds allows individual bonds to break and reform in reversible hydrolysis reactions without catastrophic failure of the entire network [10]. The notion is consistent with the combined observations of the reflectivity and adhesion data for this system. To our knowledge, this is the first direct observation of water incorporation into the interface region in correlation with the retention of adhesion strength, although we note that the substrates in the adhesion tests were not identical to those of the reflectivity experiments.

The fact that a much larger quantity of water is adsorbed into the interphase region when the silane finish is present than when it is absent,

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is in contrast to the results reported earlier by Wu *et al.* [11] involving polyimide/aminosilane/silicon oxide samples. In those experiments the amount of interfacial water was significantly reduced (from 17% to 12% within a ~30 Å layer adjacent to the silicon oxide) by the presence of a silane coupling agent. In addition, the D_2O profile was consistent with a single layer rather than a bilayer. The difference in the results of the two experiments in the absence of silane finish may have to do with the very weak adhesion of the PI film to the silicon oxide surface. In that case, upon humidity conditioning the water may wet the silicon oxide surface and simply displace the PI film. The epoxy, on the other hand, interacts more strongly with the silicon oxide surface. Therefore, the mechanism by which water detaches the resin from the surface may be very different in the two cases. For the silane-containing samples, the differences in the total amount of water adsorbed and the distribution of water within the silane layer may be due to the very different silane compositions which were employed or to differing degrees of resin penetration.

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V. CONCLUSIONS

The main results from this study are:

(i) Upon humidity conditioning (at elevated temperature for short times or at room temperature for long times), excess water is present within the silane finish layer relative to the bulk epoxy film.
(ii) No excess water is detected in the interface region after humidity conditioning in samples without the silane finish.
(iii) The distribution of water within the silane layer is not uniform. A thin, water-rich layer is present adjacent to the silicon oxide surface, while a much lower level of water is present in the remainder of the silane film.
(iv) A reversible chemical interaction is implied by the time and temperature dependence of water uptake and its eventual removal upon evacuation.
(v) With an epoxy layer present, the uptake of water to the interface region with conditioning is nearly entirely reversible upon extended evacuation. In the absence of an epoxy overcoat layer

(previous article), much adsorbed water is also removed upon extended evacuation; however, a portion redistributes and accumulates at the interface. More work is needed to identify the nature of this process.

(vi) There is a high degree of resin penetration into the silane layer. The presence of the epoxy resin seems to inhibit the interaction of D_2O with the silane or the substrate surface relative to samples containing only the silane finish.

With regard to the properties of printed wiring boards, the present silane finish provides excellent adhesive 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 insulation resistance testing following such conditioning treatments [12]. The observations of this study suggest that reversible hydrolysis reactions could very well be a contributing factor in this behavior. Reversible hydrolysis reactions at the interface can account for the presence of mobile water near the glass fiber surface leading to a degradation of electrical resistance while adhesive strength is still maintained. Many other factors such as microvoids and surface contaminations, which are inevitably present to some degree in commercial circuit board laminates, may also have a strong impact on the performance.

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Acknowledgements

This work was part of a industry/government collaborative program sponsored by the National Center for Manufacturing Sciences. This work benefitted from the use of the POSY II reflectometer at the Intense Pulsed Neutron Source at Argonne National Laboratory and the NG7 reflectometer at the National Institute of Standards and Technology. It was partially supported by the U.S. Department of Energy under contracts DE-AC04-94AL85000 and W-31-109-ENG-38.

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APPENDIX

Butt-tensile tests were performed to assess the relative strength of E-glass/epoxy interfaces with and without the commercial silane finish. Tensile test specimens were machined from E-glass rods. Each end of the rods was polished. For one set of samples, one end of each rod was dipped into a bath of silane finish for 30 seconds, and then the rods were placed into an oven at 90°C for one hour. For the second set of samples, only a cleaning treatment was applied. The samples were then placed into a mold and the epoxy was injected into the 0.5 mm gap. After curing, the specimens were inspected visually for bubbles or other defects by viewing axially through the rods. The samples were discarded if such defects were present. The cured specimens were then exposed to either 100% relative humidity at 80°C or submerged in

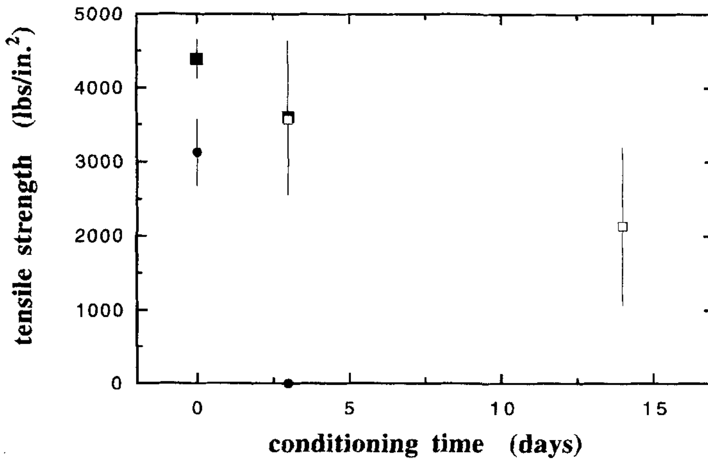

FIGURE 8 Tensile strength of E-glass butt joints using the commercial resin. Data are shown for samples with (squares) and without (circles) the commercial silane finish as a function of conditioning time in either a saturated H_2O atmosphere at 80°C (filled symbols) or in boiling water (open symbols). After H_2O conditioning, all samples were wiped free of residual water and submerged in molten solder at 260°C for 40 seconds. These data document the excellent retention of strength in hygrothermal conditioning provided by the commercial silane finish, and the dramatic loss of strength in hygrothermal conditioning when the silane finish is not applied.

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boiling water. Immediately following the conditioning period, the samples were wiped free of excess water and submerged in molten solder (260°C) for 40 seconds. Figure 8 shows the average tensile loads required to break the joints following this treatment. These data document the excellent retention of strength in hygrothermal conditioning provided by the commercial silane finish, and the dramatic loss strength in hygrothermal conditioning without the silane finish.