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Water Adsorption In Interfacial Silane Layers by Neutron Reflection

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INTRODUCTION

It is well known that water plays an important role in the degradation of adhesive strength between a wide variety of materials. It is also well established that silane coupling agents can provide excellent bond durability in aqueous environments. 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 loss of electrical resistance, 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 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. 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. The present report focusses on the measurement of profiles of adsorbed moisture by neutron reflection.

EXPERIMENTAL

The samples were prepared by exposing the polished surfaces of native oxide-coated silicon wafers to a commercial silane finish bath for 30 sec., and then spinning off the excess with a photo resist spinner. This typically resulted in a silane layer which was 80-200 Å thick depending upon conditions. The samples were heated at 90 °C for 1 hr to drive off water and then roll coated with ~2 µm of a 50-50 mixture of deuterated epoxy, specially synthesized for this work, and EPON 1124-80-A brominated epoxy resin. This resin mixture was used to optimize the sensitivity to D₂O. The epoxy was cured at 177 °C for 2 hrs. The samples were then desiccated until the reflectivity experiments were performed (POSYII reflectometer at Argonne National Labs, and the NG7 reflectometer at the National Institute of Standards and Technology). The reflectivity was obtained first from the samples in the desiccated state, then after exposure for several days to a saturated D₂O atmosphere at 80 °C.

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Figure 1a shows reflectivity before and after conditioning in a saturated D₂O atmosphere at 80 °C for 3 days, for a sample with the commercial silane finish. The value of the scattering wave vector q at the total internal reflection edge ($q_c = \sim 0.007 - 0.008 \text{ \AA}^{-1}$)

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is indicative of the atomic composition and density of the bulk epoxy film, while the reflectivity at higher q values is sensitive to the composition and density profiles near the epoxy/silane/silicon oxide interphase region. The curves through the data are best fits which yield the model neutron scattering length density (β) profiles shown in Figure 1b. Before conditioning, the silane-containing region can be described by two layers of slightly differing β , where the layer with higher β is adjacent to the silicon oxide surface. The thickness of the silane-containing layer is roughly 165 Å. Importantly, the magnitude of β

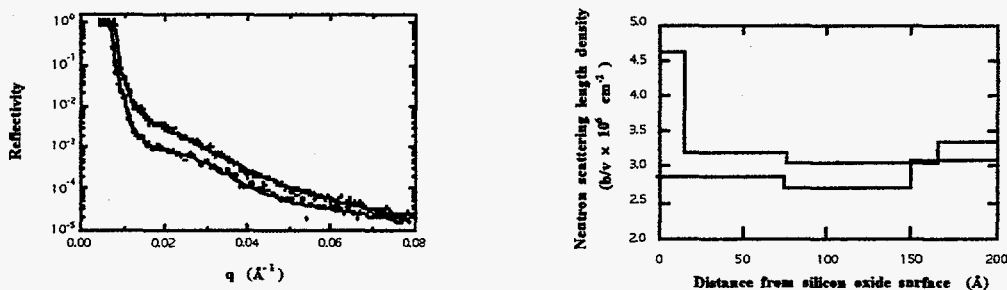


Figure 1. a) Neutron reflectivity and b) scattering length density profiles for samples containing the silane finish.

for the silane-containing film ($\sim 2.7 \times 10^{-6} - 2.8 \times 10^{-6} \text{ cm}^{-2}$) is much higher than the value for a pure silane film in the absence of epoxy ($\sim 1.0 \times 10^{-6} \text{ cm}^{-2}$). This indicates that a large amount of epoxy has penetrated into the silane layer. However, the precise silane/resin interface structure is difficult to determine. The value of the momentum transfer at q_c corresponds to $\beta = 3.05 \times 10^{-6} \text{ cm}^{-2}$ in the bulk of the epoxy film, which is consistent 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. From a comparison of the two β profiles in Figure 1b, an equivalent profile of D_2O can be obtained as presented in Figure 1c. However, it must be noted that β 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. The equivalent D_2O profile indicates a nonuniform distribution of D_2O within the silane film. A very thin ($\sim 15 \text{ Å}$), D_2O -rich layer is obtained near the silicon oxide surface, with a much lower level of D_2O existing throughout the remainder of the silane 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 FR-4 epoxy samples ($\sim 1 - 2\%$), and the difference is beyond the uncertainty in the measurement ($\pm 3\%$). NMR has shown that this large increase in β in the bulk of the epoxy film is due to H/D exchange between D_2O and the nondeuterated commercial resin during conditioning.

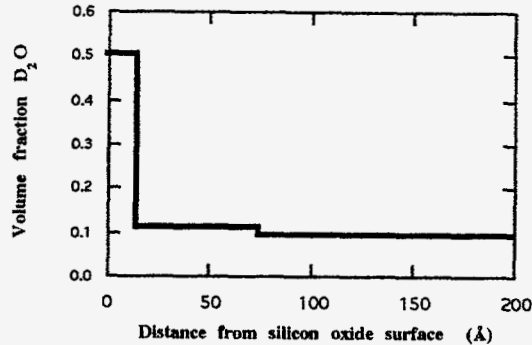
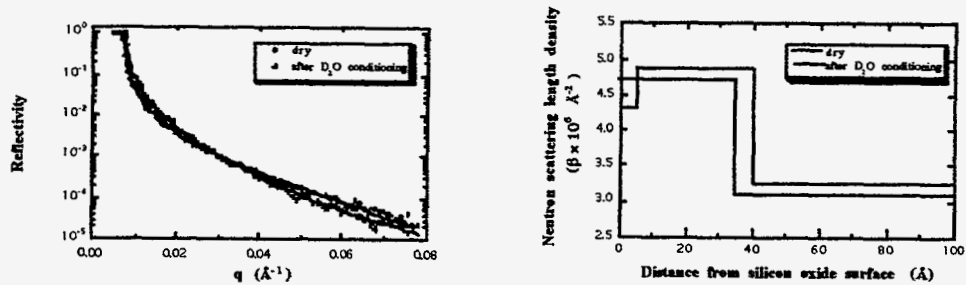


Figure 2a shows reflectivity before and after D_2O conditioning for a sample without the commercial silane finish. The curves through the data are best fits which yield the model β profiles shown in Figure 2b. Both before and after conditioning, a thin layer of elevated β is required near the silicon oxide surface. The increase in β could be due to preferential segregation of the deuterated resin to the interface, or to an increase in the density of the cured epoxy near the silicon oxide surface. While striking differences exist in the reflectivity for $q > q_c$ for samples with and without the silane finish, the q_c values are comparable both before and after conditioning. This result is expected, as the value of q_c reflects β of the bulk of the epoxy film which is identical in the two samples.



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