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CHARACTERIZATION OF INTERPHASE STRUCTURE USING NEUTRON REFLECTION

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Neutron reflection is one of only a few characterization techniques which can be used to study buried interfaces *in situ*. While restricted to model samples, interfacial density and composition profiles can be obtained with a resolution of ~ 5 Å using isotopic substitution (typically H/D for organic materials). We are using neutron reflection to address several problems of fundamental importance to the durability of organic/inorganic interphases. One important focus of this study is water adsorption within interphases with and without coupling agents. From the time and temperature dependence of moisture uptake and removal in vacuum, information regarding the nature of the interaction of water with the interphase species can be obtained. Another concern of this study is the density and composition of an epoxy in the immediate vicinity of a solid surface. In particular, variations in the crosslink density near an interface may have important implications for stress localization and energy dissipation mechanisms. A third focus is the development of damage at a thermoset/solid interface subjected to cyclic stress loading. Irreversible damage within the interphase region can be detected by swelling with a solvent following cyclic loading. From differences in the interfacial profile of the swelling solvent before and after cycling, the evolution of irreversible damage and the length scale of the damage zone can be determined.

Data from the latter experiment are shown in Figures 1-3. A ~ 2 μm film of deuterated bisphenol A-based epoxy resin with T403 curing agent (36 phr) was roll-coated onto a polished 2-in. silicon wafer. The resin was cured at 80 °C for 1 hour followed by 125 °C for two hours. Two identical samples were prepared. The first was desiccated in the as-prepared state while the second was cycled from 40 C to -65 C for 40

cycles (3 hours per cycle, 1/2 hour dwell at 40 C and -65 C.) The large difference in thermal coefficient of expansion for these materials leads to a maximum strain in the epoxy of approximately 0.3% during cycling. Neutron reflection was performed with the neutron beam impinging onto the silicon/epoxy interface from the silicon side (silicon is nearly transparent to neutrons). For each sample, neutron reflectivity data were collected in the dry state, and then again after swelling with toluene. The reflectivity curve for the two samples in the dry state are nearly identical, as shown in Figure 1. However, a significant difference appears in the reflectivity pattern of the swelled samples as shown in Figure 2a and Figure 2b. The data are displayed as $R \times q^4$ to clearly reveal the differences in form. In particular, two peaks appear in the q range from 0.01 to 0.03 Å⁻¹ after 40 cycles. The toluene/epoxy volume fraction profiles obtained from these data are shown in Figure 3. The profiles represent averages over the surface of the wafer. For the sample with 0 cycles, the toluene concentration is uniform throughout the sample, while the sample with 40 cycles shows an excess of toluene within a layer of ~ 400 Å at the interface.

The excess swelling near the interface shown in Figure 3 seems to indicate that the stresses induced by thermal cycling have led to permanent changes in the epoxy network structure, perhaps including bond scission. Currently, our focus is on following the evolution of interfacial damage until failure, and studying this process as a function of strain amplitude, epoxy structure (dimensionality of the crosslinker), and the strength of bonding to the substrate. Work is also ongoing to correlate the observations of structural changes with a measurement of interfacial strength.

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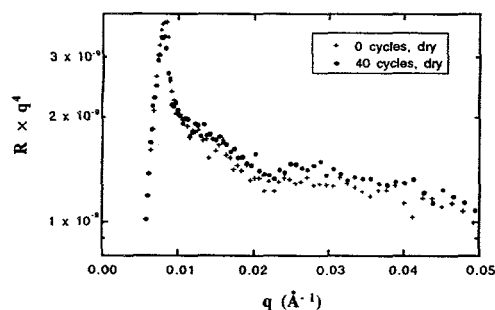


Figure 1. Reflectivity for samples with 0 and 40 cycles, dry.

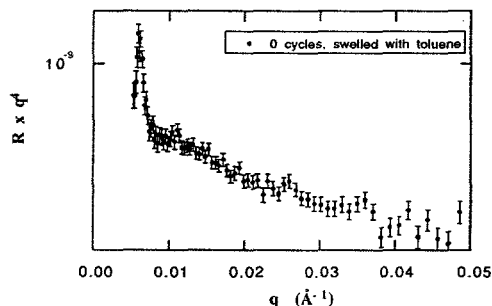


Figure 2a. Reflectivity for sample with 0 cycles, swelled with toluene.

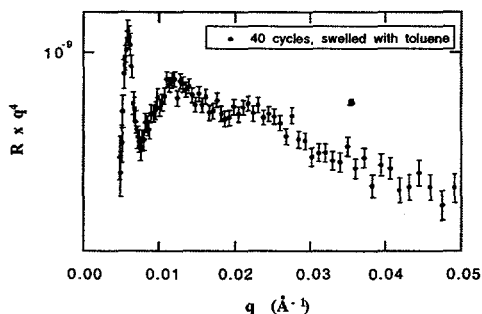


Figure 2b. Reflectivity for sample with 40 cycles, swelled with toluene.

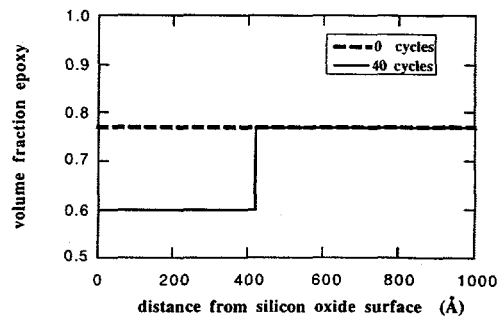


Figure 3. Epoxy/toluene volume fraction profiles obtained from data in Figure 1. The excess concentration of toluene within ~ 400 Å of the interface indicates irreversible damage induced during thermal cycling.

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