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# USE OF SELF-ASSEMBLING MONOLAYERS TO CONTROL INTERFACE BONDING IN A MODEL STUDY OF INTERFACIAL FRACTURE

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## INTRODUCTION

The relationships between the extent of interfacial bonding, energy dissipation mechanisms, and fracture toughness in a glassy adhesive/inorganic solid joint are not well understood.[1,2] We address this subject with a model system involving an epoxy adhesive on a polished silicon wafer containing its native oxide. The extent of interfacial bonding, and the wetting behavior of the epoxy, is varied continuously using self-assembling monolayers (SAMs) of octadecyltrichlorosilane (ODTS).[3-7] The epoxy interacts strongly with the bare silicon oxide surface, but forms only a very weak interface with the methylated tails of the ODTS monolayer. We examine the fracture behavior of such joints as a function of the coverage of ODTS in the napkin-ring geometry. Various characterization methods are applied to the ODTS-coated surface before application of the epoxy, and to both surfaces after fracture. The fracture data are discussed with respect to the wetting of the liquid epoxy on the ODTS-coated substrates, the locus of failure, and the energy dissipation mechanisms. Our goal is to understand how energy is dissipated during fracture as a function of interface strength.

## EXPERIMENTAL

**Materials.** The substrates used in this study were polished single crystal silicon wafers (type P, orientation 100) from SilicaTek. ODTS was obtained from Akros and used as received. EPON 828 resin (Shell) was obtained from Shell and crosslinked with Jeffamine T-403 (Huntsman Chemical Co.) at 46 phr.

**Procedures.** The wafers were cleaned in a UV-ozone chamber and then submerged in a hexadecane/chloroform solution containing ODTS. The coverage of ODTS was varied by controlling the time of exposure to the solution. The SAM-coated wafers were sonicated in toluene to remove nonbonded material, and then dried. Contact angles were measured using a video system from Advanced Surface Technologies. Mass coverage of ODTS was determined by X-ray reflectivity.[7] Sandblasted steel rings were bonded to the ODTS-coated silicon substrates and the epoxy was cured for 48 hrs at 50 °C. Samples were fractured in a napkin-ring torsion test using a Mitutoyo digital torque wrench mounted in a home-made goniometer.

## RESULTS

Figure 1 shows the maximum shear stress ($\sigma_{max}$) in the napkin-ring torsion test as a function of ODTS coverage, where the latter is reflected in the

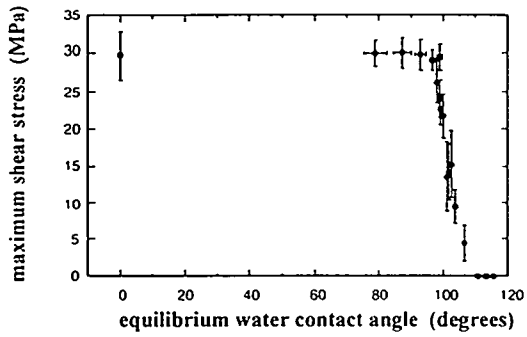


Figure 1. Maximum shear stress versus equilibrium water contact angle on ODTS-coated substrate

equilibrium water contact angle. Each data point represents the average of ten samples. High ODTS coverage corresponds to a high water contact angle due to the methylated tails, whereas the water contact angle is zero on the bare silicon oxide surface. At high ODTS coverage, $\sigma_{max}$ is below the detection capability of our measurement method. With decreasing coverage of ODTS, $\sigma_{max}$ increases over a very narrow range of the ordinate. A plateau value is reached at a coverage corresponding to a water contact angle of 98°. The plateau value of 30 MPa is somewhat lower than the yield stress in shear of the bulk epoxy (~ 40-45 MPa).

We note that the equilibrium water contact angle is a highly nonlinear function of ODTS mass coverage. This is shown in Figure 2. There is a strong decrease in mass coverage (roughly 35 %) as the contact angle decreases from 115° to 95°. Figure 3 shows $\sigma_{max}$ as a function of the relative mass coverage. Full coverage corresponds to a surface density of 1.9 mg/m$^2$. The maximum shear stress is a highly nonlinear function

## DISCLAIMER

of the fractional mass coverage This seems to suggest that $\sigma_{max}$ is a nonlinear function of the interface strength. However, we note that the relation between the mass coverage of ODTS and the areal density of epoxy/substrate bonds is not known. If that relation were known, an a priori estimate could be made of the local stress required to separate the interface using the

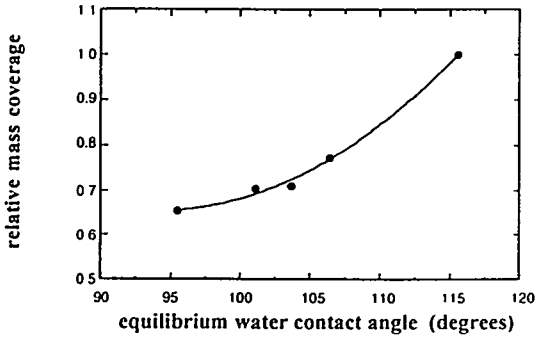


Figure 2. Relative ODTS mass coverage from X-ray reflectivity versus equilibrium water contact angle

bond potential function. A direct comparison of $\sigma_{max}$ and interface strength could then be made. This is one future direction of our work.

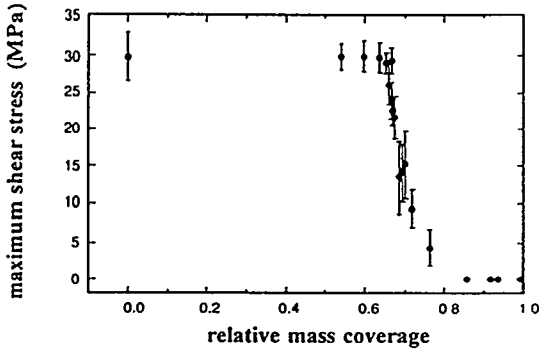


Figure 3. Maximum shear stress as a function of relative ODTS mass coverage

From an energy standpoint, the minimum energy required to separate the epoxy from the silicon substrate is the reversible work of adhesion (WOA). For this system, the work of adhesion can be estimated using the Young-Dupre equation:

$$W = \gamma_{lv}(1 + \cos\theta) \qquad (1)$$

where $\gamma_{lv}$ is the surface tension of the epoxy and $\theta$ is the contact angle of the uncured epoxy on the substrate. The surface tension of the uncured epoxy was determined to be 34.3 mJ/m$^2$ by the Wilhelmy plate technique. Figure 4 shows the advancing and receding contact angles of the uncured epoxy on ODTS-coated surfaces as a function of ODTS coverage, where the latter is again reflected in the

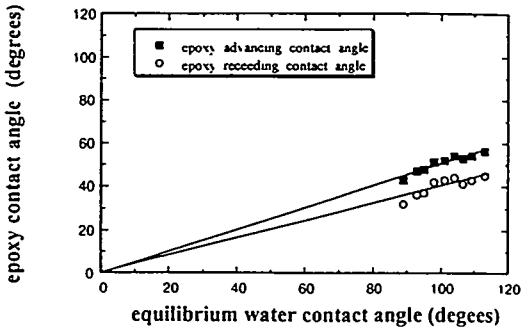


Figure 4. Advancing and receding contact angles of epoxy on the ODTS-coated substrate vs. equilibrium water contact angle

equilibrium water contact angle. Data were obtained over the range where $\sigma_{max}$ increases sharply and the then levels off. We note that the adhesive-to-cohesive transition clearly does not coincide with a wetting transition of the epoxy on the substrate, but rather

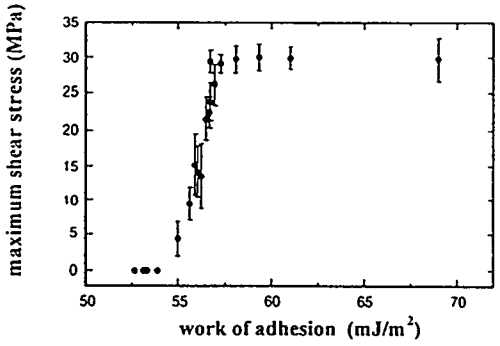


Figure 5. Maximum shear stress versus work of adhesion

occurs entirely in the regime where the epoxy is nonwetting (contact angle > 0).

The $\sigma_{max}$ data are plotted as a function of the work of adhesion in Figure 5, where the latter was determined from the advancing contact angle data in Figure 4. We discuss these data in terms of three regimes.

**Regime I. WOA < 54 mJ/m$^2$** At low WOA, corresponding to high ODTS coverage, the interface strength is very low. The interface separates at such low loads that we are unable to examine the relationship between $\sigma_{max}$ and WOA. The failure is apparently adhesive, as determined by optical

microscopy, AFM, and SEM of the ODTS-coated silicon surface. No deformation of the epoxy surface on the rings is observed after fracture.

**Regime II. 54 mJ/m < WOA < 57 mJ/m²** Over this range of WOA, there is a very strong dependence of $\sigma_{max}$ on WOA. However, the failure mode remains apparently adhesive over the entire WOA range as determined by optical microscopy, AFM, and SEM investigation of the ODTS-coated silicon surface. Examination of the surfaces of the rings at the higher WOA values reveals deformation of the surface of the epoxy which is absent at the lower WOA values. This is best revealed by optical microscopy. This energy dissipation mechanism apparently accounts for a large proportion of the increase in $\sigma_{max}$ over this range of WOA.

**Regime III. 57 mJ/m² < WOA < 69 mJ/m²** For WOA > 57 mJ/m² $\sigma_{max}$ is independent of WOA. However, important changes are observed in the fracture surfaces. At 57 mJ/m² no epoxy can be detected by optical microscopy, AFM, or SEM on the substrate surfaces. However at 69 mJ/m², corresponding to bare silicon oxide (no ODTS), epoxy is observed on the substrate over nearly the entire area which was in contact with the ring. The appearance of epoxy on the substrate surface occurs gradually with increase in WOA. From inspection of the surfaces we are unable to determine whether the crack initiation event remains adhesive with the crack moving into the epoxy during propagation, or whether the initiation event itself moves from the interface into the epoxy. However, the fact that $\sigma_{max}$ is independent of WOA in this regime strongly suggests that the initiation event occurs within the epoxy. The increased amount of epoxy left on the silicon substrate with increasing WOA would then be a result of an increasing resistance to crack propagation along the interface.

## References


1. A. J. Kinlock, R. J. Young, "Fracture Behavior of Polymers", Elsevier Science, NY, 1990.

2. R. P. Wool, "Polymer Interfaces", Hanser, Cincinnati, OH, 1995.

3. C. Carraro, O. Yauw, M. M. Sung, R. Maboudian, J. of Phys. Chem. B, *102*, 4441, (1998).

4. J. Y. Huang, K. J. Song, A. Lgoutchev, P. K. Yang, and T. J. Chuang Langmuir, *13*, 58, (1997).

5. K. Bierbaum, M. Grunze, A. A. Baski, L. F. Chi,. W. Schrepp, and H. Fuchs Langmuir, *11*, 2143, (1995).

6. R. Banga, J. Yarwood, A. M. Morgan, B. Evans, and J. Kells, Langmuir, 11, 4393, (1995).

7. S. R. Wasserman, G. M. Whitesides, I. M. Tidswell, B. M. Ocko, P. S. Pershan, J. D. Axe, J. Am. Chem. Soc. *111*, 5852, (1989).



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