ADHESION AND NANOMECHANICAL STUDIES BY INTERFACIAL
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MAY 08 1997

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Scanning probe techniques have shown dramatic growth recently and are presently making significant impact on surface and interfacial problems in material science. The Interfacial Force Microscopy (IFM) differs from other scanning force-probe techniques by its use of a self-balancing, zero compliance force sensor. This allows carefully controlled and mechanically stable force vs. interfacial separation measurements to be obtained which yield unique and valuable information concerning the interfacial adhesive bond and its failure, as well as enabling the study of the mechanical properties of materials, both on the nanometer scale. I will demonstrate the enhanced capabilities of the IFM by presenting two examples involving: 1) the bonding interaction between chemically distinct end groups on self assembling molecules adsorbed on both the sample and probe tip and 2) a study of the effect of morphological defects on the nanomechanical properties of Au(111) single-crystal surfaces.

Interfacial adhesion is of extraordinary technological importance and has long been of intense scientific interest. However, the study of the adhesive bond and its failure is made difficult by the complexity of the interfacial interaction, problems involved with establishing carefully characterized and controlled interfacial surfaces and that of quantitatively evaluating the bonding after its formation. In the following, we outline the results of studies using the IFM to study the adhesive bond formation and failure between differing end-group combinations on self-assembling monolayer (SAM) films covering Au surfaces.

Figure 1 shows the force profiles (interfacial force vs. separation) for end-group combinations consisting of methyl-methyl ($-\text{CH}_3\text{---H}_3\text{C}-$), amine-amine ($-\text{NH}_2\text{---H}_2\text{N}-$), carboxyl-carboxyl ($-\text{CHOH---HOHC}-$) and carboxyl-amine ($-\text{HCOH--H}_2\text{N}-$). These combinations cover the range from pure van der Waals through hydrogen bonding to a full acid-base interaction. We have used the peak bonding force along with a commonly applied adhesion model, and the known molecular coverage, to quantitatively evaluate the end-group bond strengths[1]. These values are shown in Table I compared with values obtained from more traditional methods. Note that beyond the weak van der Waals case, the strength of the bonding interaction increases qualitatively as the product of the acid/base character of the two end groups, i.e., the amine group is a strong base and weak acid while the carboxyl group is a strong acid and reasonable base. This means that the amine-amine bond should be weak, the carboxyl-carboxyl intermediate and the amine-carboxyl strong--as we observe. The remarkable agreement with more classical chemical methods demonstrated in Table I points to the potential of using this technique to evaluate the separate acid/base character of arbitrary surfaces, an important characterization which is not presently possible.

In the course of the SAM adhesion studies, we discovered that methyl-terminated SAM films completely passivate the normally strong adhesive interaction of a W tip with a Au substrate. This finding opened a new area of study using the IFM as a nanoindenter in the classic noninteracting Hertzian approximation. To illustrate this work, we show in Fig. 2 a typical force profile (loading curve) for a 1000 Å W tip indenting a Au(111) surface. Profiles like this allow us to quantitatively obtain values for the elastic modulus and the shear stress at the plastic threshold, both at the nanometer level. In Fig. 3 we show a repulsive-force image of the Au surface with its array of single and double height steps. The surface has been subtly indented (involving the displacement of only a few thousand atoms) in several places at differing distances from these morphological defects. In Table II we show the results tabulating values for the plastic threshold shear stress for the various indentation positions. As can be seen, the yield stress is almost 40% less for the dent straddling a step than for one out on the terrace. Data of this kind can provide important information leading to an understanding of the atomic-level processes involved in the plastic yield of materials and set the stage for being able to tailor such properties for specific applications.

*Work supported by U.S. Department of Energy under Contract No. DE-AC04-94AL85000.

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1. R. C. Thomas, J. E. Houston, R. M. Crooks, T. Kim and T. A. Michalske, J. Amer. Chem. Soc. **117**, 3830 (1995).
2. J. D. Kiely, R. Q. Hwang and J. E. Houston (In Preparation).

Figure 1. Force profiles for two of the various thiol end-group combinations. Top $\text{CH}_3 - \text{CH}_3$, bottom $\text{NH}_2 - \text{COOH}$

Figure 2. Force profile for a W probe indenting a Au(111) surface. The solid line indicates an elastic deformation. Deviation from this relationship signals the plastic threshold. The depth of the hysteresis loop indicates the depth of the resulting dent.

Interaction Couple	Bond Energy kcal/mol	Gas-Phase Dimerization
$-\text{NH}_2$ vs. $-\text{NH}_2$	3.1 ± 0.7	3.4
$-\text{COOH}$ vs. $-\text{COOH}$	7.0 ± 2	14.0
		Enthalpy of Complexation
$-\text{COOH}$ vs. $-\text{NH}_2$	21.0 ± 2	23.0
$-\text{CH}_3$ vs. $-\text{CH}_3$	60 ± 12	W_i 56 SFA HC Films 42-62 Contact Angle HC vs. HC

Table I. Bonding strength values from data compared with those from other methods.

SFA--surface forces apparatus
 HC---typical hydrocarbons

Figure 3. Repulsive-force image of three dents at various distances from steps on a Au(111) surface.

Distance From Step Å	Shear Stress at Plastic Threshold GPa
3400	5.7
1300	5.4
570	4.8
0	3.6

Table II. Shear stress at the yield threshold vs. distance from step edges.