

## Mechanical Relaxation of Organic Monolayer Films Measured by Force Microscopy

Stephen A. Joyce,<sup>(1)</sup> R. C. Thomas,<sup>(2)</sup> J. E. Houston,<sup>(1)</sup> T. A. Michalske,<sup>(1)</sup> and R. M. Crooks<sup>(2)</sup>

<sup>(1)</sup>Sandia National Laboratories, Albuquerque, New Mexico 87185

<sup>(2)</sup>Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131

(Received 12 November 1991)

Using the newly developed interfacial-force microscope, we present results from the first measurements of the mechanical relaxation of a Au supported, self-assembled monolayer film interacting with a microscopic tungsten tip. For a methyl-terminated *n*-alkanethiol film, we observe negligible adhesive film-tip interaction and complete passivation of tip-substrate bonding. The mechanical behavior of the film itself shows a time-dependent, elastic response.

PACS numbers: 61.16.Di, 61.41.+e, 62.20.-x

It has long been recognized that the mechanical response of microscopically thin boundary layer films can have a dramatic effect on macroscopically measured phenomena such as adhesion and friction [1]. As a result, there has been considerable recent effort devoted to investigating the mechanical properties of thin overlayer films; including studies of both fluid and solid layers using the surface-force apparatus (SFA) [2], the nanoindenter [3], and the atomic-force microscope (AFM) [4,5]. However, the conventional SFA can only be used to study materials that can be cleaved atomically smooth over macroscopic dimensions (e.g., mica) and, thus, cannot be used to study metal surfaces which are modified by the application of self-assembled monolayers. A recent study by Chen, Helmond, and Israelachvili describes SFA measurements of adhesive forces between two surfactant-coated mica surfaces [6]. Hysteresis is observed over much longer time scales (several minutes) and is attributed to interpenetration of the molecules across the interface. Clearly, the nature of the hysteresis effects observed in the conventional SFA experiments has origins that differ strongly from those discussed in our study.

In the present study, we have investigated the mechanical properties of a self-assembled monolayer (SAM) of *n*-hexadecanethiol (C<sub>16</sub>H<sub>33</sub>SH) [7] on a gold substrate using the newly developed interfacial-force microscope (IFM) [8]. This technique is applicable to virtually all surfaces and utilizes a self-balancing force-feedback scheme to eliminate the mechanical instability encountered in deflection-based force sensors (of the type presently used in the AFM and SFA techniques). We observe no adhesive interaction between this film and a microscopic W tip and a complete passivation of the adhesive tip-substrate interaction. The repulsive interaction, however, shows a load-rate-dependent hysteresis in the compressive strain recovery indicating that the mechanical properties of the SAM are best described by an anelastic model. These observations suggest that the anelastic recovery rate results from the time-dependent self-assembly process.

Self-assembled monolayer films show considerable promise as models for studying molecular boundary-layer behavior in phenomena such as adhesion and friction, be-

cause of their well-characterized structure and easily tailored chemical properties [7]. One class of SAM consists of sulphur-terminated *n*-alkanes adsorbed on a Au substrate. In recent years, considerable attention has been focused on studying the structural characteristics for these types of films by optical ellipsometry, infrared spectroscopy, electrochemistry, transmission electron microscopy, LEED, neutron diffraction, and x-ray photoelectron spectroscopy [7]. These studies reveal that films consisting of *n*-alkanethiol molecules longer than about 15 Å form well-ordered monolayers with the molecular axis oriented about 30° off the surface normal. A strong thiolate interaction binds the molecule to the Au surface, and intermolecular van der Waal's forces lead to well-ordered and densely packed films [7].

In the present experiments, substrates were prepared by *e*-beam vapor deposition of 200 Å of Ti and 2000 Å of Au onto a silicon (100) surface. Prior to adsorption of the organic monolayer, the Au substrates were electrochemically cleaned in 0.1 M H<sub>2</sub>SO<sub>4</sub>. Self-assembled monolayer films were prepared by immersing Au substrates in 0.5 mM *n*-alkanethiol solutions of ethanol for approximately 2 h. After thiol adsorption, the Au substrates were thoroughly rinsed with ethanol and dried with nitrogen.

The IFM has been described in detail elsewhere [8]. Briefly, the interfacial-force sensor is a force-feedback controlled (balancing) differential capacitor. The sensor uses an rf bridge arrangement to monitor the displacement resulting from the interfacial forces acting on an electrochemically etched W tip attached to one end of the common plate of the differential capacitor and balances this displacement with an externally applied electrostatic force. This scheme prevents the inherent mechanical instability that occurs in any spring-based force sensor when the attractive interfacial-force gradient,  $\partial F_i/\partial z$ , exceeds the sensor's force constant [4]. The common capacitor plate is supported by torsion arms and the feedback effectively stiffens the torsional spring constant. For repulsive forces, other modes in the sensor, most notably the bending mode of the common plate, limit the compliance of the sensor. The measured repulsive force-versus-displacement profiles therefore reflect the series sum of

the sample stiffness and the bending mode force constant ( $1/k_{\text{meas}} = 1/k_{\text{sample}} + 1/k_{\text{bend}}$ ). For the sensor used in these studies,  $k_{\text{bend}} = 1500 \text{ N/m}$ . Note that while  $k_{\text{bend}}$  is a constant,  $k_{\text{sample}}$  will show highly nonlinear behavior [3].

The samples were imaged in constant repulsive-force mode ( $2 \times 10^{-7} \text{ N}$ ) to ascertain their topographical structure. The images generally show polycrystalline, rolling-hill surface structures with average heights of 10–30 nm and diameters of 10–50 nm in agreement with literature reports [9]. Although the results indicate that this structure is representative of the surface used in this study, larger-scale defects are also occasionally observed [10]. The W tip was characterized by scanning electron microscopy and found to have a radius of  $\sim 500 \text{ nm}$ . A simple Hertzian elastic analysis [11] indicates that such a tip structure will produce a contact-area diameter of  $\sim 10 \text{ nm}$  at the applied imaging force. The predicted contact area is in good agreement with the observed limit of spatial resolution supporting our microscopic analysis of the tip geometry. The experiments were performed in a system which had been evacuated to  $10^{-8}$  Torr and then backfilled with dry  $\text{N}_2$  to atmospheric pressure. Prior to each experiment, the W tip was cleaned *in situ* by applying +1000 V to the tip in series with a 10-M $\Omega$  resistor. This procedure “field desorbs” adsorbed species and permits reproducible results to be obtained [12].

A typical force profile (i.e., interfacial force versus relative tip-surface separation) for the SAM is shown in Fig. 1 (corrected for the compliance of the sensor). Three distinct regions are clearly evident. First, prior to tip contact, there is no evidence of appreciable attractive (negative) forces, consistent with the low-energy,

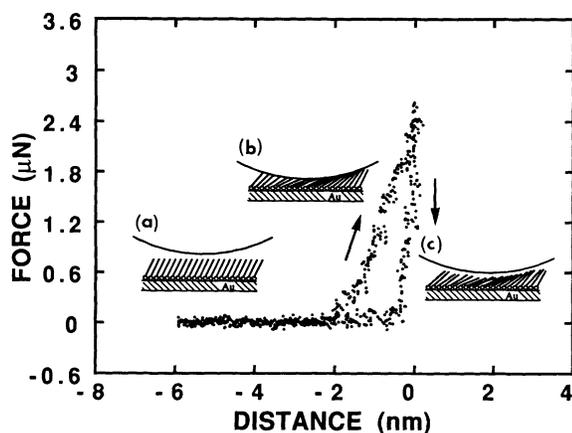


FIG. 1. Interfacial force as a function of relative tip-sample separation with the force sensor under force-feedback control. The rate of sample displacement is 5 nm/s and the data have been corrected for the compliance of the sensor. Zero separation is arbitrarily assigned to the point at which the sample changes direction. Schematic illustrations indicate the proposed film response during various stages of the loading cycle.

methyl-terminated SAM surface. (Although van der Waal's forces between the tip and sample are expected to produce a small attractive force, its magnitude is below our detection limit.) Second, after contact with the SAM surface, the force profile initially shows a rather soft repulsive interaction up to a force of about  $0.8 \mu\text{N}$  which becomes considerably stiffer as the compression proceeds. Third, upon withdrawal, the interfacial force drops to zero at distances smaller than the initial contact separation with no evidence of an attractive interaction. These compressive loading-cycle data are reducible, to within the noise level of Fig. 1, for cycle periods of several seconds.

From the results of Fig. 1, we can establish several general conclusions. First, the methyl-terminated SAM gives rise to a negligible adhesive interaction with the W tip prior to film contact [see Fig. 1, schematic (a)]. Second, there is a distinct hysteresis in the force profile which corresponds to compression and decompression of the SAM between the tip and the substrate. Third, no evidence is seen for an adhesive interaction between the tip and the Au substrate for the level of repulsive forces probed in these experiments (about  $3 \mu\text{N}$ ). This latter result is in contrast to previous AFM studies on “bare” Au substrates which showed the development of considerable adhesive interactions after contact [13]. In addition, the hysteresis “loop” nearly closes for compressive forces above about  $2.0 \mu\text{N}$ . In this region, the slope of the force profile reflects the elastic constant of the Au substrate.

The relative displacement involved in going from initial contact, at just over  $-2 \text{ nm}$  in Fig. 1, to the  $2.0\text{-}\mu\text{N}$  force level corresponds to a displacement of about  $2 \text{ nm}$ . Since the *n*-hexadecylthiol molecule is about  $2.5 \text{ nm}$  in length, it is apparent that the initial force behavior evident in Fig. 1 represents a compression of the SAM to near 20% of its initial thickness [see Fig. 1, schematic (b)]. During the decompression half cycle, the film does not recover from the deformation rapidly enough and hysteresis is observed [see Fig. 1, schematic (c)]. Mechanical hysteresis of this type is best described by an anelastic model rather than one involving plastic or permanent deformation [14].

Anelastic behavior can be modeled by linear combinations of elastic (springs) and viscous (dashpots) elements [14]. The dashpot gives rise to the characteristic relaxation time for the system. For an anelastic film the width of the hysteresis loop is dependent on the ratio of the rate of relaxation to the loading rate. For rapid compression and decompression cycles, the loop will close since the viscous components will not have time to respond. However, the loop will also close for very slow compression and decompression cycles since the system recovers completely during unloading. In our instrument, long loading cycles are impractical due to drift, but we have observed a reduction in the width of the hysteresis loop by cycling the load an order of magnitude faster.

We can make a more direct measure of the relaxation

behavior by instantaneously changing the state of the system and monitoring the subsequent relaxation. An example of such a measurement is shown in Fig. 2. Here, after initial contact with the film, a square-wave  $z$  displacement of 6 nm is applied to the sample while monitoring the displacement of the sensor. (Sensor feedback was not used in order to increase the overall bandwidth of the measurements.) The scale on the right represents the force exerted on the film itself by the sensor displacement. From these data we see that for rapidly applied compressive loads the film is able to support more than twice the force level compared to its steady-state value.

While no single time constant provided a good fit to the entire range of data, a value of 0.08 s yielded the best fit over the broadest range using a simple exponential relaxation model (see the solid curve in Fig. 2). Fitting the data to multiple relaxations is not warranted for a number of reasons. When we apply a square-wave displacement to the sample, the deflection-based sensor produces simultaneous stress and strain relaxation. Therefore, no simple stress-strain relationship for the film alone can be determined [14]. On a more fundamental level, there most likely exists a wide spectrum of relaxation times, making fitting arbitrary. In addition, because the strains in the film are large compared to the molecular dimensions, the stress-strain relationship will certainly be nonlinear, which makes a relaxation time-constant analysis ambiguous. In contrast to the data of Fig. 2, if the film is placed under an initial load of  $1.4 \mu\text{N}$ , then only the 6-nm square-wave displacement of the sensor is observed with no evidence of relaxation. At this level of preload, the film is fully compressed. It should be noted that, based on the tip radius and a Hertzian analysis,  $1.4 \mu\text{N}$

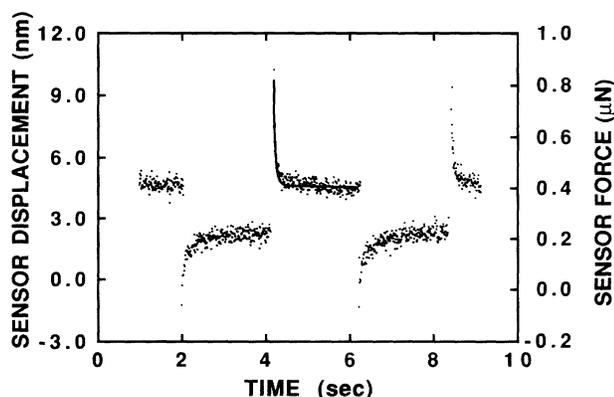


FIG. 2. Sensor-displacement behavior under a square-wave modulation of the sample position (without force-feedback control). The sample-displacement amplitude is 6 nm and the frequency is 0.5 Hz. Positive-going forces represent displacements toward the tip. The scale on the right represents the force applied to the film by the sensor displacement (sensor force constant of 100 N/m). The solid curve represents a single exponential fit to the data for a relaxation time constant of 0.08 s.

produces a surface stress near 3.0 GPa which is considerably larger than that used in the surface-force experiments cited in Ref. [6]. This difference may partly explain the differences in the relaxation time constants observed in the two experiments.

As a result of the foregoing discussion, we propose that the forces that are responsible for the initial monolayer self-assembly are also responsible for the observed anelastic response. In contrast, AFM studies on the loading of related Langmuir-Blodgett (LB) films show that these layers undergo permanent plastic deformation [5]. The important differences between the two systems are (1) the  $n$ -alkanethiol films are chemisorbed to the substrate, and (2) ordering in these films results from an intermolecular van der Waal's interaction and is *spontaneous*; i.e., the self-assembled configuration is the lowest-energy state [7]. For LB films, ordering requires an *externally* applied force during assembly. For a film that has been compressed between tip and substrate, spontaneous self-assembly would result in the eventual strain recovery of the film. The time-dependent recovery arises from the kinetics of the self-assembly process. During compression, the alkane backbones are forced closer to the surface and probably become disordered and entangled with one another. The subsequent reorganization of the film requires concerted chain motions and a significant period of time.

To support the contention that the time-dependence results from the self-assembly process, we have measured the mechanical response of a  $\text{C}_9\text{H}_{19}\text{SH}$  monolayer and observe *no* hysteresis in the strain recovery. Since it is known from polymer studies that the mobility of long chains scale as  $N^3$  (where  $N$  is the number of monomer units) [15], the shorter-chain  $n$ -alkane thiols may have much faster relaxation times. Future experiments on longer-chain thiols should permit more definitive scaling relationships to be established.

Since it represents an energy loss in the system, the hysteresis associated with anelasticity has important consequences for adhesion and tribology. The energy expended during loading is not fully recovered upon unloading. Unlike losses due to other mechanisms, such as plastic deformation, anelastic losses induce no permanent wear or surface deformation. Since anelasticity can produce a negative branch in the loading rate versus applied force behavior, a mechanical instability can result giving rise to stick-slip behavior in friction and adhesion [16].

In summary, we have measured the interfacial forces between a microscopic W tip and a Au film covered by self-assembled monolayers of  $n$ -alkanethiols. The results show that (1) there is a negligible adhesive interaction between the W tip and the methyl-terminated molecular surfaces; (2) the film responds anelastically to mechanical deformation with recovery after load release having an effective relaxation time of approximately 0.08 s; and (3) after the film is compressed to about 20% of its initial

thickness, it becomes very stiff and higher compressive forces do not result in the residual tip-Au-surface adhesion even for compressive loads up to  $3 \mu\text{N}$ .

The authors thank A. J. Ricco (SNL) for many helpful discussions. S.A.J., J.E.H., and T.A.M. acknowledge support by the Office of Basic Energy Sciences, Division of Materials Sciences, U.S. Department of Energy under Contract No. DE-AC04-76DP00789. R.M.C. and R.T. acknowledge the support of the Office of Naval Research (Young Investigation Program).

- 
- [1] F. P. Bowden and D. Tabor, *The Friction and Lubrication of Solid Surfaces* (Clarendon, Oxford, 1986), Chaps. 9-12.
  - [2] D. Y. C. Chan and R. G. Horn, *J. Chem. Phys.* **83**, 5311 (1985).
  - [3] J. B. Pethica and W. C. Oliver, *Phys. Scr.* **T19**, 61 (1987).
  - [4] N. A. Burnham and R. J. Colton, *J. Vac. Sci. Technol. A* **7**, 2906 (1989).
  - [5] G. S. Blackman, C. M. Mate, and M. R. Philpott, *Phys. Rev. Lett.* **65**, 2270 (1990).

- [6] Y. L. Chen, C. A. Helbard, and J. N. Israelachvili, *J. Phys. Chem.* **95**, 10736 (1991).
- [7] R. G. Nuzzo and D. L. Allara, *J. Am. Chem. Soc.* **105**, 4481 (1983); C. D. Bain, E. B. Troughton, Y.-T. Tao, J. Evall, G. M. Whitesides, and R. G. Nuzzo, *J. Am. Chem. Soc.* **111**, 321 (1989), and references therein; C. E. D. Chidsey and D. N. Loiacoro, *Langmuir* **6**, 682 (1990), and references therein.
- [8] S. A. Joyce and J. E. Houston, *Rev. Sci. Instrum.* **62**, 710 (1991).
- [9] J. Vancea, G. Reiss, F. Schneider, K. Bauer, and H. Hoffman, *Surf. Sci.* **108**, 218 (1989).
- [10] S. A. Joyce, J. E. Houston, and T. A. Michalske, *J. Appl. Phys.* (to be published).
- [11] H. Hertz, *Hertz's Miscellaneous Papers* (MacMillan, London, 1896), Chaps. 5 and 6.
- [12] T. T. Tsong, *Atom-Probe Field Ion Microscopy* (Cambridge Univ. Press, New York, 1990), Chap. 2.
- [13] N. A. Burnham and R. J. Colton, *J. Vac. Sci. Technol. A* **7**, 2906 (1989).
- [14] A. S. Nowick and B. S. Berry, *Anelastic Relaxation in Crystalline Solids* (Academic, New York, 1972).
- [15] P. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell Univ. Press, Ithaca, NY, 1979).
- [16] D. Maugis, *J. Mater. Sci.* **20**, 3041 (1985).