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Chemically-Sensitive Interfacial Force Microscopy: Contact Potential Measurements of Self-Assembling Monolayer Films

by

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Chemically-Sensitive Interfacial Force Microscopy: Contact Potential Measurements of Self-Assembling Monolayer Films

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We report contact potential difference (CPD) measurements of *n*-alkanethiol self-assembling monolayers (SAMs)[1-3] adsorbed to Au substrates using an organomercaptan-modified Au probe. Our results demonstrate for the first time the feasibility and importance of controlling the chemical properties of force microscope probe surfaces. Moreover, control over the chemical characteristics of the probe provides a basis for distinguishing between chemically distinct surface features with nanometer resolution in force microscopy. We show that CPD values obtained using Au probes modified with methyl-terminated SAMs are stable and reproducible, whereas identical unmodified probes yield highly variable data. Our experimentally determined CPD values are in qualitative agreement with calculated CPDs for several ω-terminated SAMs.

We have previously used the interfacial force microscope (IFM)[4] to obtain detailed information about the mechanical properties of methyl-terminated *n*-alkanethiol SAMs adsorbed to Au substrates.[5-8] In the present work, we use the IFM to determine local CPDs that arise between an organomercaptan-modified Au probe and various SAM-modified Au substrates (Scheme I).[9] The CPD is defined as the work function difference between these modified Au surfaces, which we view as tightly bound dipole sheets that shift the work functions of each modified Au surface.[10] For example, the work function is increased relative to bare Au for

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dipoles having their negative end pointing away from the modified Au surface. We perform experiments by applying a triangular-sweep voltage between the sample and probe, which is held at ground, while measuring the resulting electrostatic force. The force-feedback capability of the IFM is used to keep the probe/sample distance rigidly fixed, which allows us to directly measure the electrostatic force at a constant interfacial separation. The CPD is determined by measuring the applied potential necessary to null the electric field and eliminate the interfacial force between the two surfaces.[11]

Figure 1 shows force-versus-substrate-potential data obtained using a $HS(CH_2)_{11}CH_3$-modified Au probe. In these plots, negative forces are attractive and the shape is parabolic since the electrostatic force is proportional to the square of the bias voltage.[12] The solid line represents a second-order polynomial fit of the data. In Figure 1a, the probe and the sample are both $HS(CH_2)_{11}CH_3$-modified Au substrates that should have identical work functions and therefore the same CPD. The measured CPD value of 0.050 V deviates slightly from zero, which is probably the result of differences in surface packing and coverage for each SAM-modified surface. By increasing the work function of the modified Au substrate with molecules having dipole moments of different magnitudes that point away from the surface, the applied potential required to null the electric field becomes more positive. These CPD differences provide a basis for mapping the chemical characteristics of the surface.

Table I summarizes CPD results for each SAM relative to nominally identical $HS(CH_2)_{11}CH_3$-modified Au probes, tip A and tip B. The CPD data in this table represent an average of results obtained from several different locations on each substrate over a period of several weeks. The data show that organomercaptan-modified Au probes are both stable and reproducible. In contrast, experiments using either bare Au or W probes yield data that varies by several hundred millivolts for CPD measurements of the same samples. We also found that CPDs of methyl-terminated and perfluorinated substrates did not change appreciably over a one month period, whereas CPDs for hydroxyl- and carboxylic acid-terminated SAMs drifted substantially over the same period. For example, the CPD values for "aged" carboxylic acid-terminated surfaces shifted negative by several hundred millivolts relative to freshly prepared samples. Subsequent experiments performed in a system that was evacuated to 10^{-4} mmHg and then backfilled with N_2 usually gave CPDs close to their initial values, but there was considerable variation in the results of these experiments. Clearly, these high energy carboxylic acid-terminated SAMs adsorb hydrocarbon contaminants, which decreases their work functions in a non-reproducible manner. In contrast, CPD values obtained for the low surface energy methyl-terminated SAMs in vacuum were reproducible and essentially identical to values obtained in air.

The CPD estimates given in Table I are calculated in terms of the relative CPD shifts for each SAM terminal group, which are proportional to the electric dipole magnitude normal to the surface ($\mu_\perp$), eq 1:

$$\Delta\mathrm{CPD} = \mu_\perp / (\varepsilon_\circ A) \qquad (1)$$

where $\varepsilon_\circ$ is the permittivity of free space and A is the area per molecule.[10] We approximate $\mu_\perp$ using a vectorial addition method that relies on experimentally determined bond and group moments,[13] along with previously published orientation and surface coverage data.[14,15] Our calculation only considers the dipole of the SAM end groups, since Au/S interactions between the probe and sample cancel and C-H dipoles between adjacent methylene units also cancel since the molecules extend in an all-trans configuration. These approximations also hold for the perflourinated SAM. The qualitative agreement between the calculated and measured values for $HS(CH_2)_{11}CH_3$, $HS(CH_2)_{11}OH$, and $HS(CH_2)_2(CF_2)_7CF_3$ monolayer films gives us confidence that we are measuring work function differences between the terminal groups of these SAMs.

The overestimated CPD value for the carboxylic acid-terminated SAM reflects uncertainty in our approximation of $\mu_\perp$, which we estimate by assuming a 32° tilt angle and a 55° twist angle of the carbon backbone relative to the surface normal.[14] We also assume that the carboxylic acid group is rigidly oriented and configured to minimize steric interactions between adjacent methylene groups. However, our calculation does not consider intramolecular hydrogen bonding, which occurs and affects the dipole magnitude and orientation.[16] Our results indicate that the net electric dipole of the carboxylic acid group is oriented at a larger angle relative to the surface normal as a result of these intermolecular interactions.

To determine the effect of different types of Au substrates on CPD data, we performed experiments with SAMs adsorbed on Au/Cr/Si(100), Au/Ti/Si(100), and single-crystal Au(111) surfaces. If appreciable amounts of either Cr or Ti diffuse to the Au surface, we would expect to observe a finite CPD relative to single-crystal Au(111), since the work function for both of these metals is at least 0.6 V less positive than Au.[17] As shown in Table I, the CPD data are not sensitive to the different Au adhesion layers, even though Cr and Ti are known to diffuse through Au.[18] Although we do not fully understand this result at the present time, we speculate that the organomercaptans may complex and remove metal surface contaminants from the Au surface during self assembly.[19]

To summarize, we have demonstrated that Au probes modified with methyl-terminated organomercaptan SAMs provide surfaces that are sufficiently stable and reproducible that they can be used to distinguish between different SAM terminal groups. By controlling the chemical properties of the probe surface, we are also able to estimate CPDs that are in qualitative agreement with experimentally measured values. Discrepancies that arise between calculated and measured CPD values reflect uncertainties in our approximation of $\mu_{\perp}$. Our results demonstrate the importance of understanding the chemical properties of interfacial probes used for studying molecular interactions between two surfaces, and provide a basis for imaging chemical inhomogeneities by force microscopy.

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(12) The electrostatic force is given by the equation, $F = C'V^2/2$, where C' is the derivative of the probe/sample capacitance with respect to interfacial separation. In the more common Kelvin probe method for CPD measurements, the probe/sample capacitance is biased by an applied potential, V_0, while the distance between the probe and sample is periodically modulated at a frequency, *f*. This produces a displacement current, $i(t) = fC'(V_0+CPD)\cos ft$, which goes to zero when $V_0 = -CPD$. The force scheme used here has the advantages that it does not require

motion between the sample and probe and it produces higher signal levels unless the Kelvin probe is operated in the GHz regime.

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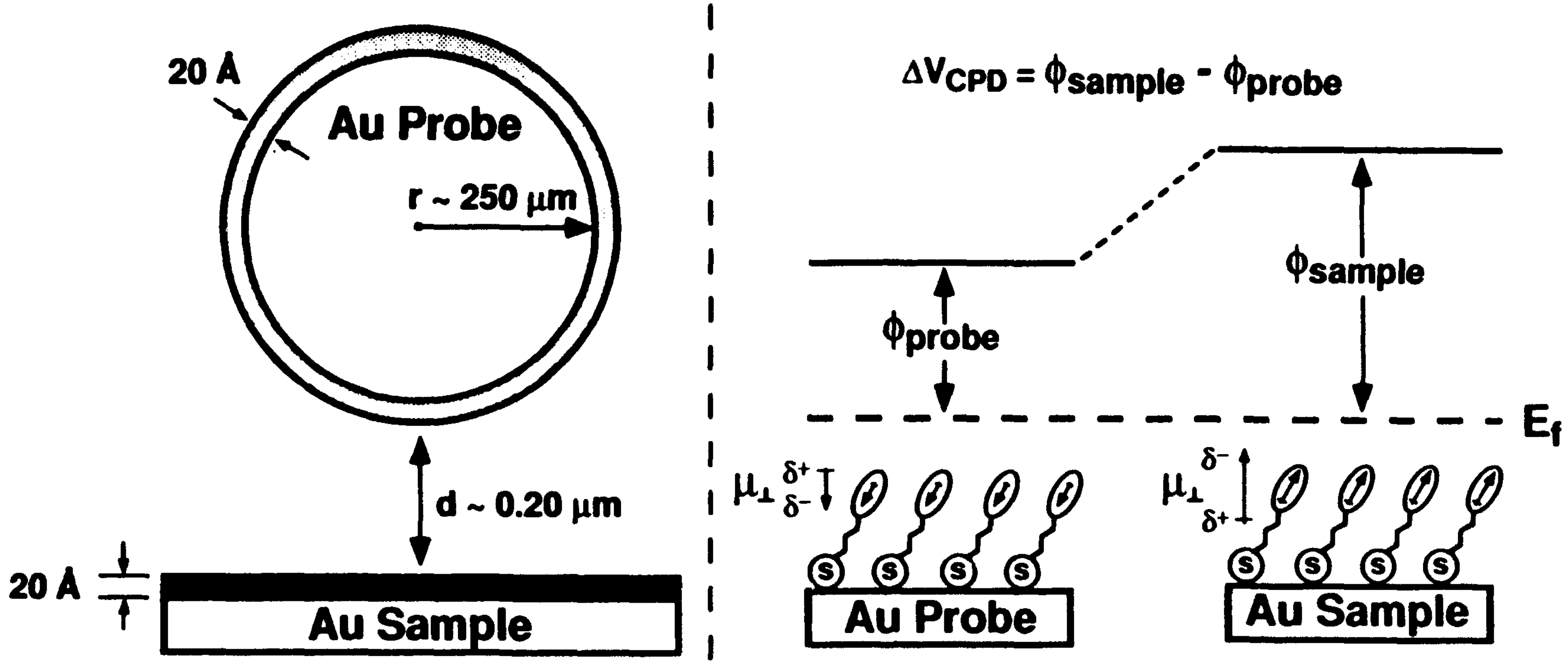
TABLE I: CPDs of SAM-modified Au substrates with respect to $HS(CH_2)_{11}CH_3$ -modified Au probes[a]

SAM	Experimental CPD (V) Tip A	Experimental CPD (V) Tip B	Calculated CPD (V)
$HS(CH_2)_{11}CH_3$	0.057 ± 0.021	0.010 ± 0.007	0.00
	0.008 ± 0.034[b]	0.028 ± 0.030[b]	
	0.050 ± 0.006[c]	0.011 ± 0.022[c]	
$HS(CH_2)_{11}OH$	0.587 ± 0.041	0.567 ± 0.070	0.542
$HS(CH_2)_{10}COOH$	0.533 ± 0.045	0.418 ± 0.157	1.69
$HS(CH_2)_2(CF_2)_7CF_3$	1.68 ± 0.018	1.63 ± 0.032	1.91

[a] All samples were prepared on Au/Ti/Si(100) unless noted. Other supporting substrates were [b] Au/Cr/Si(100) and [c] single crystal Au(111).

Figure Caption

Figure 1. Interfacial force-versus-substrate-potential curves between a spherical, $HS(CH_2)_{11}CH_3$-modified Au probe with a 250 μm radius of curvature and organomercaptan modified Au samples. The probe was held at ground while biasing the sample with a triangular-sweep voltage. Negative forces are attractive. The data points were fit with a second-order polynomial. Average standard deviations of curve fits were ~0.020 V. The CPD is determined at the applied potential at which the force goes through its minimum value. The data in this figure are typical of our results, but several such data sets were used to generate the average values given in Table I.



Scheme I / Thomas et al.

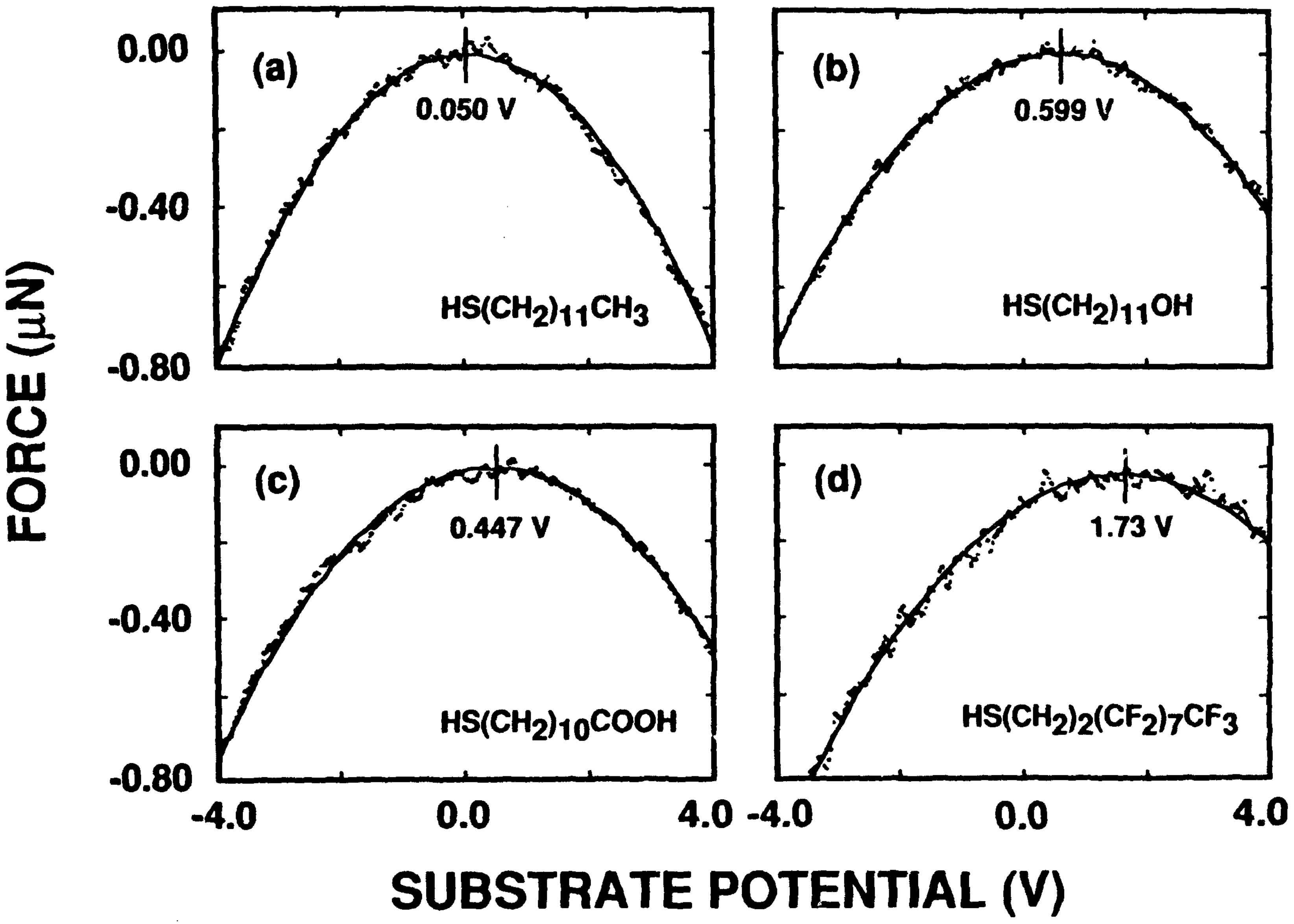


Figure 1 / Thomas et al.