High-Resolution Chemical Mapping of Surface Bound Functional Groups with Tapping-Mode Scanning Force Microscopy

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Figure 1. Schematic of partial bilayers formed at Au(111). For a stearic acid (SA) top layer, X = −CH$_2$CH$_3$. For a hexadecanedioic acid (HDDA) top layer, X = −CO$_2$H.

One of the recent, exciting advancements in scanning probe microscopy is the development of contrast mechanisms which yield surface compositional information.[1,2] We demonstrate here for the first time the ability of tapping-mode scanning force microscopy (TM-SFM)[3] to distinguish between segregated domains of functional groups. We show that the phase shift of an oscillating cantilever is sensitive to the surface functional groups that are interacting with the tip. These efforts are motivated by our interest in the compositional mapping of chemically modified electrodes and polymer interfaces, a challenging prospect in contact mode SFM (i.e., friction contrast) because of tip-induced sample deformation and topographic convolution in frictional signals.

The ability of TM-SFM to distinguish between regions of varying chemical composition was assessed by imaging partial bilayer structures formed by exposing gold substrates to an ethanolic solution containing both mercaptohexadecanoic acid (MHA, HS(CH$_2$)$_{16}$CO$_2$H) and stearic acid (SA, CH$_3$(CH$_2$)$_{16}$-CO$_2$H) as described previously.[2] A schematic is shown in Figure 1 where X = −CH$_2$CH$_3$ for SA. A surface composed of domains of CH$_3$ and CO$_2$H groups differing in height can be formed by allowing the second layer to only partially form.[2]

The images in Figure 2 provide the basis for our conclusions. Parts A and B of Figure 2 present 600 × 600 nm constant amplitude topographic (Figure 2A) and phase contrast (Figure 2B) TM-SFM images collected simultaneously at a location on top of a flat Au(111) terrace.[4] As illustrated in the image and in the cross-sectional profile of Figure 2A, the topography of these samples is comprised of segregated domains exhibiting heights that range from 1.5 to 2.0 nm consistent with the height expected for a fully extended layer of SA.[5]

The image in Figure 2B provides the initial evidence for chemical sensitivity in phase contrast TM-SFM of partial bilayer interfaces. The observed contrast reflects phase angle shifts (Δφ) of the oscillating cantilever as the tip interacts with the surface relative to its phase while oscillating freely. As shown in both the image and the cross-sectional profile in Figure 2B, a significant change in Δφ is detected between the different levels of the partial bilayer samples. Quantitatively, Δφ at the top of the SA layer is typically advanced by 2−5° relative to
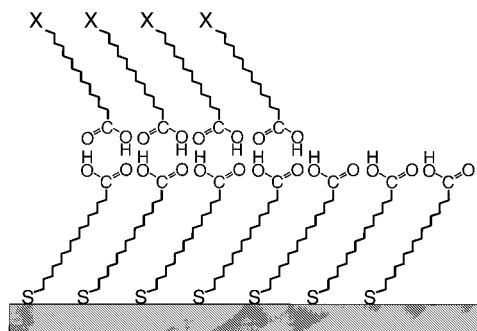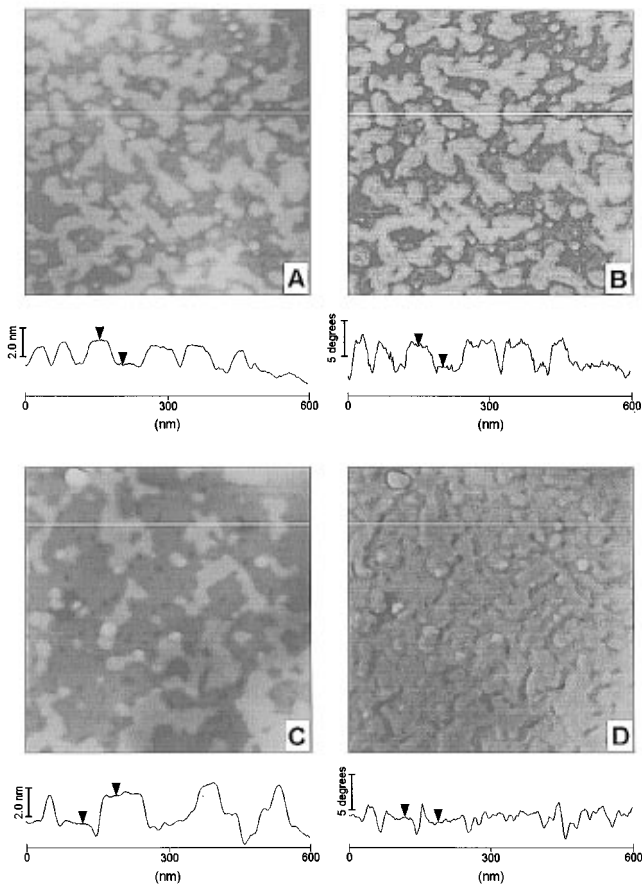

Figure 2. (A) Topographic (z-scale = 10 nm) and (B) phase contrast (z-scale = 20°) tapping-mode SFM images (600 × 600 nm) of a MHA/SA partial bilayer. (C) Topographic (z-scale = 15 nm) and (D) phase contrast (z-scale = 20°) images of a MHA/HDDA partial bilayer. The cross-sectional profiles correspond to the line traversing each image.

the top of the MHA layer.[6] We estimate a lateral resolution of 15 nm in terms of both the smallest domain resolved and the distance clearly separating two regions of different phase. It is tempting, because of the controlled design of our samples, to correlate the contrast in Figure 2B with differences in the functional groups exposed at each region (i.e., CH$_3$ and CO$_2$H). However, because a number of recent reports have linked contrast in phase images to surface elasticity and viscoelasticity,[7−9] the observations in Figure 2B alone are insufficient to associate the contrast solely with chemical composition.

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(1) See, for example: (a) Overney, R. M.; Meyer, E.; Fromemr, J.; Brodbeck, D.; Lüthi, R.; Howald, L.; Güntherodt, H.-J.; Fujihira, M.; Takano, H.; Gotoh, Y. *Nature* **1992,** *359,* 133. (b) Frisbie, C. D.; Rozsnyai, L. F.; Noy, A.; Wrighton, M. S.; Lieber, C. M. *Science* **1994,** *265,* 2071. (c) Wilbur, J. L.; Biebuyck, H. A.; MacDonald, J. C.; Whitesides, G. M. *Langmuir* **1995,** *11,* 925.

(2) Green, J.-B.; McDermott, M. T.; Porter, M. D.; Siperko, L. M. *J. Phys. Chem.* **1995,** *99,* 10960.

(3) Zhong, Q.; Innis, D.; Kjoller, K.; Elings, V. B. *Surf. Sci. Lett.* **1993,** *290,* L688.

(4) All images in this work were collected with a Nanoscope III MultiMode scanning force microscope operated in the ambient and Si tapping-mode cantilevers (Digital Instruments, Santa Barbara, CA). Images were acquired with the cantilever oscillating at an amplitude of 50−70 nm.

(5) Tao. Y.-T. *J. Am. Chem. Soc.* **1993,** *115,* 4350.

(6) This phase shift corresponds to imaging amplitudes of 50−60% of the free oscillation amplitude. The magnitude of the contrast increases to ~20° for low imaging amplitudes (e.g., 10% of the free oscillation amplitude).

(7) Tamayo, J.; Garcia, R. *Langmuir* **1996,** *12,* 4430.

To ensure the contrast in Figure 2B is not based on variations in the mechanical properties of the bilayer as a result of, for example, differences in packing between the first and second layers, we designed control samples in which a partial second layer was formed at a MHA/Au(111) monolayer from hexadecanedioic acid (HDDA, $HO_2C(CH_2)_{14}CO_2H$). This type of surface consists of segregated regions of different heights but identical interfacial chemistry (Figure 1, X = $-CO_2H$).[10] Figure 2, images C and D, respectively, presents 600 × 600 nm topographic and phase contrast images of a partial MHA/HDDA bilayer. Similar to the MHA/SA system, the topographic profile reveals domains differing in height by 1.8−2.2 nm.[11] However, relative to Figure 2B, Figure 2D exhibits negligible phase shift between the top of the second layer relative to the top of the first.[12] Importantly, this observation argues that any variations in mechanical properties between the top and bottom layers in our partial bilayers are negligible in terms of generating phase differences. This provides compelling evidence that the phase contrast observed at the MHA/SA system (Figure 2B) is predominantly due to differences in surface chemistry.

Confining the image areas in Figure 2 to atomically flat Au(111) terraces permits the assessment of chemical mapping without the influence of substrate topography. However, we believe the real utility of chemically sensitive SFM techniques will be demonstrated by their ability to probe technologically relevant materials (e.g., polymers and electrodes) which often exhibit surfaces with rough, ill-defined topography. The influence of topographic variations on SFM frictional signals has been demonstrated[13] and may ultimately limit the applicability of chemical mapping with contact mode SFM. Figure 3A is a 5 × 5 μm TM-SFM topographic image of a partial bilayer sample assembled on a gold film sputter coated onto mica at room temperature. The phase image in Figure 3B reveals contrast apparently unrelated to the gross substrate topography of the randomly sized gold crystallites. Images at lower lateral scales indicate that the regions in Figure 3B exhibiting an increased $\Delta\phi$ correspond to areas covered by the SA layer (i.e., CH_3 groups) and that the regions of lower $\Delta\phi$ correspond to CO_2H moieties. Figure 3 thus demonstrates the applicability
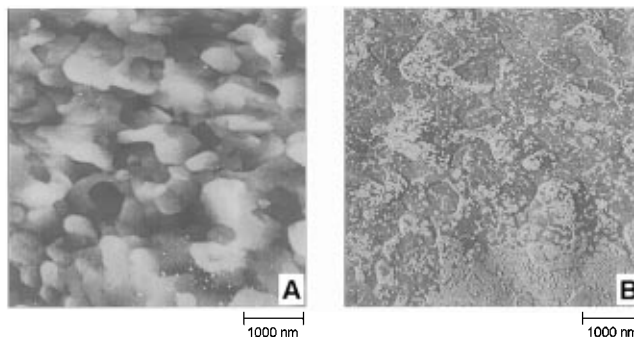

Figure 3. TM-SFM images (5 × 5 μm) of a MHA/SA partial bilayer (A) topography (z-scale = 30 nm) and (B) phase contrast (z-scale = 30°).

of phase contrast TM-SFM for the chemical imaging of relatively rough surfaces.

We believe the chemical sensitivity of phase contrast imaging involves a mechanism based on adhesive differences between the Si tip and surface functional groups.[7,14] Considering surface free energy arguments and recent reports, the adhesion between the hydrophilic Si−OH groups on the tip and CO_2H groups is expected to be higher than that between the tip and CH_3 groups.[16] Studies treating a tapping tip/cantilever assembly as a damped oscillator predict that adhesive interactions will result in retarded phase shifts and darker contrast in phase images.[7,8c,15] An adhesion mechanism is further supported by our observed dependence of $\Delta\phi$ on imaging amplitude. The tip−sample contact time (t_c) is directly related to the imaging amplitude where lower amplitudes correspond to higher t_c.[7] In the limit of the short contact times involved in TM-SFM (microsecond range) the number of adhesive interactions between the tip and sample is expected to increase the longer the tip is in contact. Consistent with the proposed adhesion mechanism, we observe an increase in the magnitude of $\Delta\phi$ between CH_3 and CO_2H groups as t_c is increased.

In conclusion, we have shown that phase contrast TM-SFM can produce chemical maps of surfaces based on differences in tip−sample adhesion without significant convolution of topography. We caution, however, that our samples were designed to test the *chemical* sensitivity of TM-SFM. More complex surfaces will likely exhibit a combination of mechanical and chemical differences which will complicate interpretation of phase images.

(8) (a) Leclère, Ph.; Lazzaroni, R.; Brédas, J. L.; Yu, J. M.; Dubois, Ph.; Jérôme, R. *Langmuir* **1996**, *12*, 4317. (b) Magonov, S. N.; Elings, V.; Papkov, V. S. *Polymer* **1997**, *38*, 297. (c) Magonov, S. N.; Elings, V.; Whangbo, M.-H. *Surf. Sci.* **1997**, *375*, L385.

(9) (a) Anczykowski, B.; Krüger, D.; Fuchs, H. *Phys. Rev. B* **1996**, *53*, 15485. (b) Winkler, R. G.; Spatz, J. P.; Sheiko, S.; Möller, M.; Reineker, P.; Marti, O. *Phys. Rev. B* **1996**, *54*, 8908. (c) Burnham, N. A.; Behrend, O. P.; Oulevey, F.; Gremaud, G.; Gallo, P.-J.; Gourdon, D.; Dupas, E.; Kulik, A. J.; Pollock, H. M.; Briggs, G. A. D. *Nanotechnology* **1997**, *8*, 67.

(10) Multilayer formation was inhibited by restricting immersion times to <4 h.

(11) We do not believe the consistent difference in height observed for the HDDA layer compared to the SA layer arises from differences in packing. Our preliminary infrared spectroscopic characterizations indicate that both layers are crystalline. The height differences may be a result of the differences in surface chemistry. The influence of surface properties on TM-SFM topographic measurements has been reported.[9c]

(12) A small variation in $\Delta\phi$ is apparent at the edges of the HDDA domains, as a result of either packing differences at the edge or torsional bending of the cantilever between layers.

(13) (a) Baselt, D. R.; Baldeschwieler, J. D. *J. Vac. Sci. Technol., B* **1992**, *10*, 2316. (b) Haugstead, G.; Gladfelter, W. L.; Weberg, E. B.; Weberg, R. T.; Weatherill, T. D. *Langmuir* **1994**, *10*, 4295. (c) McDermott, M. T.; Green, J.-B.; Porter, M. D. *Langmuir* **1997**, *13*, 2504.

(14) Chernoff, D. A. *Proc. Microscop. Microanal.* **1995**, 888.

(15) For a tip/cantilever assembly interacting with a surface $\Delta\phi$ is expected to scale with the derivative of the sum of the forces acting on the tip, $\partial F/\partial z$, where z corresponds to the axis normal to the surface.[8c] For the imaging amplitudes applied here, the overall force between the tip and sample is likely repulsive due to compression of the layers. Attractive interactions at the CO_2H groups will offset some of the repulsive forces, resulting in a lower overall repulsive force and a retarded phase shift at the CO_2H groups.