Formation and photooxidation of *n*-dodecanethiol self-assembled monolayers on Au(111): 'pits' formed during chemisorption disappear upon oxidation

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UV photolysis in air of self-assembled *n*-dodecanethiol monolayers (SAMs) on Au(111) quantitatively oxidizes the adsorbed thiol to its corresponding sulfonate and completely destroys the ordered structure of the SAM without exposing the underlying gold surface; STM images indicate that the etch pits which appear to form during chemisorption of the thiol are lost when the thiol is oxidized.

Self-assembled monolayers (SAMs) have attracted widespread interest because of their potential for practical applications.[1] One of the most studied and best understood group of SAMs is prepared by adsorbing alkanethiols on to Au(111).[2] Surprisingly little is known with certainty about the chemisorption and self-assembly processes, but it is generally accepted[3] that the sulfur atoms adopt a ($\sqrt{3} \times \sqrt{3}$)$R30°$ surface structure† and that the chains are extended into space with the same *all-trans* conformation observed in crystalline paraffins and polyethylene.[4] Recent STM experiments[3b–i] also suggest that chemisorption of the thiol is accompanied by the formation of small (30–100 Å), one-gold-atom-deep, 'etch pits' in the Au(111) surface.

As part of an effort to examine the reactivity of pitted Au(111) surfaces, we attempted to prepare pitted Au(111) surfaces by photochemically removing these alkanethiol monolayers. Our procedure, which has been used previously to produce micron scale features from polycrystalline gold supported alkanethiol monolayers,[5] was expected to produce clean gold surfaces with small, randomly distributed pits. Here, we report that quantitative removal of an *n*-dodecanethiol SAM from Au(111) does indeed produce a clean gold surface, but that the surface does not contain etch pits.

Thin gold films were grown epitaxially by thermal evaporation (1 Å s^{-1}) on scratch-free mica (Asheville-Schoomaker AV-STM grade) at 2.5×10^{-7} mbar and 300 °C until 1000 Å of gold had been deposited. Immediately prior to use, these films were flame annealed with a small butane torch to clean the surface and facilitate crystallization of the gold. This method regularly produces surfaces with large (1500 × 1500 Å) areas of defect-free [111] oriented gold. An STM image‡ of a typical gold substrate used in our work is shown in Fig. 1.

Immersion of a gold substrate in an ethanol solution of *n*-dodecanethiol (2 mmol dm^{-3}, 1.5–2.5 h) produced a well ordered SAM after rinsing with ethanol and drying in a stream of nitrogen. As illustrated by the STM images in Fig. 2 the thiols react with the surface to produce a SAM with the expected ($\sqrt{3} \times \sqrt{3}$)$R30°$ lattice and small, uniformly distributed pits. These pits, which have dimensions on the nanometre scale and must involve nearly 100 gold atoms, are remarkably uniform in diameter (*ca.* 33 Å) and distribution; they account for approximately 10–15% of the area on a typical surface.

UV photolysis of a gold supported thiol monolayer in air quantitatively oxidizes the thiol to its corresponding sulfonate, which can be rinsed from the surface with water or ethanol to expose clean gold surfaces.[5] In the case of *n*-dodecanethiol SAMs, UV photolysis§ completely destroys the ordered structure of the starting SAM without exposing the underlying gold surface. A typical STM image of the photooxidized SAM is shown in Fig. 3. Although the surface is covered by a monolayer of oxidized thiol molecules,[5] features such as step edges are easily discernible. It is quite clear from Fig. 3, which exhibits no features attributable to pits in the underlying gold surface, that the pits formed during chemisorption of the thiol are lost when the thiol molecules are oxidized. Upon rinsing with water, ethanol, or dilute acetic acid in ethanol (0.4% *v*/*v*), the oxidized thiol was completely removed from the gold to afford well ordered regions of Au(111).¶ STM images of the resulting gold surface showed no evidence for the presence of the etch pits which appeared to form during chemisorption of

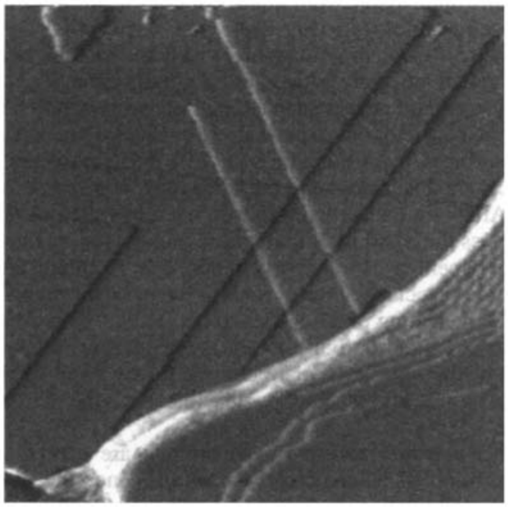

Fig. 1 Differentiated STM image (2050 × 2050 Å) of a typical Au(111) substrate recorded at 0.35 V and 1.0 nA

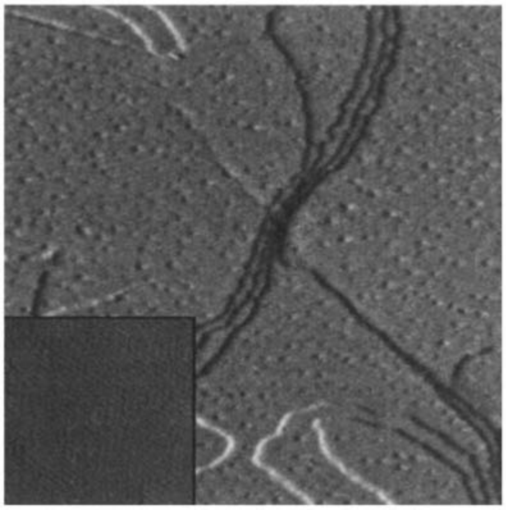

Fig. 2 Differentiated STM image (2050 × 2050 Å) of a dodecanethiol SAM on Au(111) recorded at 0.40 V and 1.0 nA. Inset: Differentiated STM image (65 × 65 Å) of a dodecanethiol SAM on Au(111) recorded at 1.01 V and 0.6 nA.

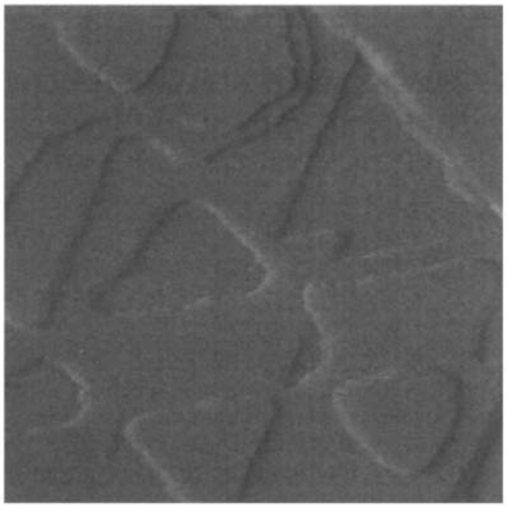

Fig. 3 Differentiated STM image (2050 × 2050 Å) of a photooxidized dodecanethiol SAM on Au(111) recorded at 0.30 V and 1.2 nA

the thiol. In fact, the images obtained after removal of the SAM were indistinguishable from images of gold substrates that were unexposed to thiol! (*e.g.* Fig. 1).

Surface diffusion of gold atoms is well known, but the barrier to diffusion on pure Au(111) is high enough at room temperature that features such as 33 Å etch pits would be stable during the course of our experiments.[6–8] Electrolyte solutions[6,7] and adsorbates from the atmosphere[8] can dramatically accelerate surface diffusion—and the same may be true for oxidized thiol SAMs—but adsorbed thiols do not allow the migration of gold unless the SAM is a liquid phase monolayer.[3h] (Even then, Ostwald ripening is relatively slow.)[9] It is interesting that defect-free *n*-octadecylthiol SAMs have been prepared on Au(111) by heating pitted SAMs to 350 K.[10,11] However, great care was taken during our photolysis experiments to avoid any heating of the sample. We are confident that a simple thermal annealing process is not responsible for the effects we observe.

Neither the mechanism by which pits are created during chemisorption of alkanethiols on Au(111), nor the details of SAM photooxidation and removal are well known. What is clear, however, is that the pits formed on a gold supported alkanethiol SAM represent a large fraction of the surface which must undergo rapid and surprisingly uniform changes to account for the apparently reversible changes observed during chemisorption and subsequent photooxidation of the alkanethiol. We are currently examining the formation and photooxidation of alkanethiol SAMs in real time to determine the mechanistic details of pit formation and loss.

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Footnotes

† The ($\sqrt{3} \times \sqrt{3}$)R30° structure adopted by adsorbed thiols is hexagonal. Its lattice constant is $\sqrt{3}$ × the lattice constant for Au(111), and it is rotated by 30° relative to the underlying hexagonally close-packed gold surface.

‡ A Besocke type STM operating in air under ambient conditions with etched Pt tips was used for imaging. All data was recorded in constant current mode, but the images are displayed with signal differentiation. The STM was calibrated in the x–y directions by measuring line scans of Au(111). For the z direction, Au(111) step edges were used for calibration. Numerous current/bias combinations produced stable images, but the data shown were obtained under conditions which resulted in the clearest, most detailed images.

§ Photooxidation of n-$C_{12}H_{25}SH$ monolayers was performed in air using a Stromart HBO 200 W high-pressure Hg vapour lamp. Light from the lamp was passed through an IR filter and then focused on a 1.5 cm^2 area at a distance of 25 cm. The photolysis time was typically 10–12 min.

¶ Water, ethanol, and dilute acetic acid in ethanol (0.4% *v*/*v*) have no noticeable effect on either Au(111) or SAMs produced by chemisorption of *n*-dodecanethiol.

References

1 (*a*) B. R. Heywood and S. Mann, *Chem. Mater.*, 1994, **6**, 311; (*b*) I. Rubenstein, S. Stienberg, Y. Tor, A. Shanzer and J. Sagiv, *Nature*, 1988, **332**, 426; (*c*) N. L. Abbott, J. P. Folkers and G. M. Whitesides, *Science*, 1992, **257**, 1380; (*d*) G. M. Whitesides, J. P. Mathias and C. T. Seto, *Science*, 1991, **254**, 1312; (*e*) J. Zak, H. Yuan, M. Ho, L. K. Woo and M. D. Porter, *Langmuir*, 1993, **9**, 2772; (*f*) T. T.-T. Li and M. J. Weaver, *J. Am. Chem. Soc.*, 1984, **106**, 6107; (*g*) A. Dhirani, M. A. Hines, A. J. Fisher, O. Ismail and P. Guyot-Sionnest, *Langmuir*, 1995, **11**, 2609.

2 (*a*) C. Schönenberger, J. Jorritsma, J. A. M. Sondag-Huethorst and L. G. J. Fokkink, *J. Phys. Chem.*, 1995, **99**, 3259; (*b*) K. Edinger, A. Gölzhäuser, K. Demota, Ch. Wöll and M. Grunze, *Langmuir*, 1993, **9**, 4; (*c*) R. G. Nuzzo, B. R. Zegarski and L. H. Dubois, *J. Am. Chem. Soc.*, 1987, **109**, 733; (*d*) A. Kumar, N. L. Abbott, E. Kim, H. A. Biebuyck and G. M. Whitsides, *Acc. Chem. Res.*, 1995, **28**, 219; (*e*) M. Mrksich and G. M. Whitesides, *Trends Biotechnol.*, 1995, **13**, 228; (*f*) L. H. Dubois and R. G. Nuzzo, *Annu. Rev. Phys. Chem.*, 1992, **43**, 437; (*g*) M. D. Porter, T. B. Bright, D. L. Allara and C. E. D. Chidsey, *J. Am. Chem. Soc.*, 1987, **109**, 3559; (*h*) C. D. Bain, E. B. Troughtman, Y.-T. Tao, J. Evall, G. M. Whitesides and R. G. Nuzzo, *J. Am. Chem. Soc.*, 1989, **111**, 321; (*i*) W. L. Jorma, A. Virtanen and R. M. Penner, *J. Phys. Chem.*, 1994, **98**, 11751; (*j*) T. Takami, E. Delamarche, B. Michel, Ch. Gerber, H. Wolf and H. Ringsdorf, *Langmuir*, 1995, **11**, 3876; (*k*) L. F. Rozsnyai and M. S. Wrighton, *Langmuir*, 1995, **11**, 3913.

3 (*a*) C. A. Widrig, C. A. Alves and M. D. Porter, *J. Am. Chem. Soc.*, 1991, **113**, 2805; (*b*) C. E. D. Chidsey, G.-Y. Lui, P. Rowntree and G. Scoles, *J. Chem. Phys.*, 1989, **91**, 4421; (*c*) N. Camillone, C. E. D. Chidsey, G.-Y. Lui, T. M. Putvinski and G. Scoles, *J. Chem. Phys.*, 1991, **94**, 8493; (*d*) M. G. Samant, C. A. Brown and J. G. Gordon, *Langmuir*, 1991, **7**, 437; (*e*) N. Camillone, C. E. D. Chidsey, P. Eisenberger, P. Fenter, J. Li, K. S. Liang, G.-Y. Lui and G. Scoles, *J. Chem. Phys.*, 1993, **99**, 744; (*f*) L. H. Dubois, B. R. Zegarski and R. G. Nuzzo, *J. Chem. Phys.*, 1993, **98**, 678; (*g*) G. E. Poirier and M. J. Tarlov, *Langmuir*, 1994, **10**, 2853; (*h*) G. E. Poirier, M. J. Tarlov and H. E. Rushmeier, *Langmuir*, 1994, **10**, 3383; (*i*) C. Schönenberger, J. A. M. Sondag-Huethorst, J. Jorritsma and L. G. J. Fokkink, *Langmuir*, 1994, **10**, 611.

4 D. L. Dorset, *J. Polym. Sci.: Polym. Phys. Ed.*, 1986, **24**, 79.

5 J. Huang, D. A. Dahlgren and J. C. Hemminger, *Langmuir*, 1994, **10**, 626.

6 D. J. Trevor and C. E. D. Chidsey, *J. Vac. Sci. Technol. B*, 1991, **9**, 964.

7 I. C. Oppenheim, D. J. Trevor, C. E. D. Chidsey, P. L. Trevor and K. Sieradzki, *Science*, 1991, **254**, 687.

8 D. R. Peale and B. H. Cooper, *J. Vac. Sci. Technol. A*, 1992, **10**, 2210.

9 G. E. Poirier and M. J. Tarlov, *J. Phys. Chem.*, 1995, **99**, 10966.

10 J.-P. Bucher, L. Santesson and K. Kern, *Langmuir*, 1994, **10**, 979.

11 O. Cavalleri, A. Hirstein and K. Kern, *Surf. Sci.*, 1995, **340**, 1960.

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