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Investigating a Surface Science Mystery: The Case of the Disappearing Monolayer

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A recent X-ray photoemission spectroscopy (XPS) and scanning tunneling microscopy (STM) investigation of an alkylsilane-based monolayer has yielded intriguing chemical and physical phenomena. In particular, oxidation of an octylsilane (C₈H₁₇SiH₃) monolayer chemisorbed to Au(111) via ambient atmosphere exposure yields two surprising results. First, the Au(111)-23×√3 surface reconstruction typical of a clean gold surface spontaneously regenerates underneath the oxidized (alkylsiloxane) monolayer. Furthermore, the physisorbed alkylsiloxane monolayer is completely transparent to STM imaging.

Frequently, the STM image contrast mechanism of organized organics—such as alkanethiols—on Au(111) is explained as a consequence of hydrocarbon chain crystallization and/or variations in chain angle or orientation. Similarly, subtle variations in alkyl chain angle or orientation may yield differing apparent heights of alkylsilane monolayer features as observed by STM. However, a recent XPS and STM investigation of an alkylsilane monolayer prior to and following oxidation suggests the alkyl chains are “transparent” to STM imaging and impart a negligible contrast contribution to the STM images.

A STM image of clean Au(111) displays the parallel striped features intrinsic to the 23×√3 surface reconstruction (**Figure 1a**). Monolayer formation via exposure of Au(111)-23×√3 to a saturating gaseous pressure of octylsilane (C₈H₁₇SiH₃) in ultrahigh vacuum (UHV) yields a complex pattern of interwoven, sinuous ridge features containing numerous interstitial Au islands 20 – 40 Å in diameter (**Figure 1b**). The presence and quantity of the Au islands (~7% area coverage in **Figure 1b**) indicates the underlying 23×√3 surface reconstruction has fully relaxed to the unreconstructed Au(111)-1×1

Authors (top photo, from left) Kevin S. Schneider and Bradford G. Orr, (bottom photo, from left) Thomas M. Owens, Mark M. Banaszak Holl, and Daniel R. Fossnacht.



phase.

Oxidation of the octylsilane monolayer via ambient atmosphere exposure results in the disappearance of monolayer features from the STM image (**Figure 1c**). The resulting substrate terraces are indistinguishable from clean Au(111)-23×√3 (having identical lateral and vertical dimensions) under the imaging conditions em-

ployed. STM image features of the exposed monolayer do not vary with changes in tunneling current (0.01 – 2 nA) or applied sample bias (± 2 V). However, exposure to additional octylsilane does not regenerate the image shown in **Figure 1b**. Instead, an image identical to clean Au(111)-23×√3 remains (**Figure 1d**). Therefore, the “clean gold” surface displayed in **Figure 1c** does not have iden-

tical chemical properties of the authentic clean gold surface illustrated in **Figure 1a**. On the basis of STM data alone, this set of results was mysterious!

Direct chemical analysis of oxidized sample surfaces have been performed using soft X-ray photoemission spectroscopy (SXPS) at beamline U8B at the National Synchrotron Light Source at Brookhaven National Laboratory. Beamline U8B is perfectly suited to obtain the high-resolution Si 2p core-level needed for this study as well as the valence band region. Note that due to the presence of an Au plasmon trailing the Au 4f core level, conventional XPS of the Si 2p core-level for these monolayers provides no information. Following exposure to ambient atmosphere,

the Si 2p core level of the unoxidized octylsilane monolayer (**Figure 2a**) shifts by 2.3 eV to higher binding energy and the peak full width at half-maximum (fwhm) increases (**Figure 2b**). The binding energy shift and peak broadening indicate formation of a cross-linked RSiO_3 and/or $(\text{ROSiO}_{1.5})_n$ network. The C 2s features arising from the octyl chain are retained in the valence band data (-12 to -20 eV), indicating the presence of intact alkyl chains in the oxidized monolayer (**Figure 2d**). In summary, the XPS data indicate exposure to ambient atmosphere effectively oxidizes the silicon head-groups; however, all of the silicon and alkyl chains are retained within the oxidized monolayer. Thus, the STM image displayed in **Figure 1c** does indeed have the monolayer present, albeit

it in an oxidized form.

The combination of SXPS and STM data suggest the original octylsilane monolayer image in **Figure 1b** is the result of significant mixing of Au and Si states. Oxidation of the Si head-groups removes this interaction, causing the underlying substrate to regenerate the $\text{Au}(111)\text{-}23\times\sqrt{3}$ surface reconstruction, and leaving only the Au states to image. In this case, the alkyl chains are "transparent" in both **Figures 1b** and **1c** and it is only the Au-Si interaction that changes upon oxidation. Since monolayer oxidation severs all Au-Si bonds, a completely "transparent" physisorbed alkylsiloxane layer remains on top of the reconstructed $\text{Au}(111)\text{-}23\times\sqrt{3}$ surface.

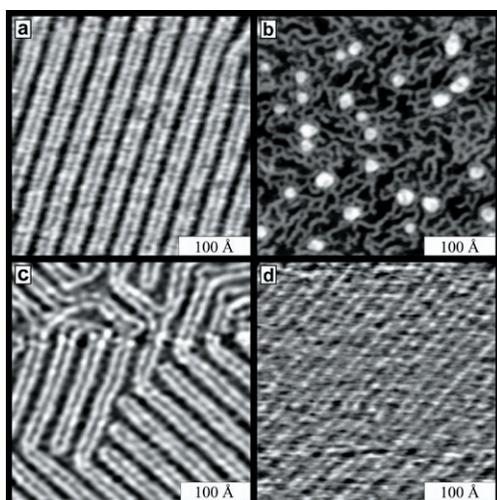


Figure 1. UHV-STM images of the same $\text{Au}(111)$ sample (different sample areas), following successive experimental steps. All images are $35\text{ nm} \times 35\text{ nm}$. (a) Clean $\text{Au}(111)\text{-}23\times\sqrt{3}$. (b) Chemisorbed octylsilane monolayer formed on (a) following exposure to 50 L ($L = \text{langmuir} = 1 \times 10^{-6}\text{ torr}\cdot\text{s}$) gaseous octylsilane in UHV. (c) Oxidized physisorbed alkylsiloxane monolayer formed following exposure of (b) to ambient atmosphere for 15 minutes. (d) Oxidized physisorbed alkylsiloxane monolayer in (c) following exposure to 50 L gaseous octylsilane in UHV.

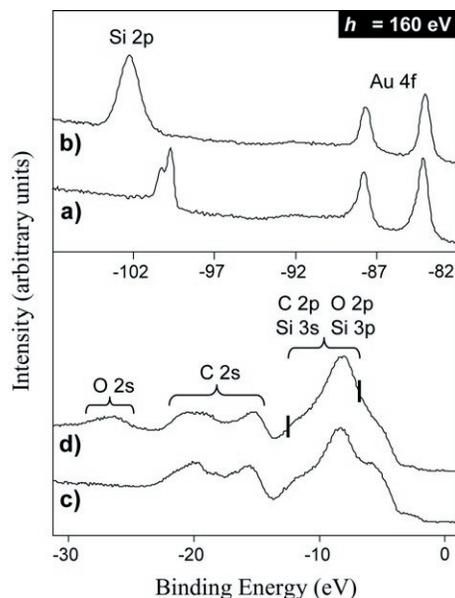


Figure 2. Soft X-ray photoemission spectra. (a) Si 2p and Au 4f core level spectra of an octylsilane monolayer on $\text{Au}(111)$. (b) Si 2p and Au 4f core level spectra of the monolayer in (a), following exposure to ambient atmosphere for 15 minutes. (c) Valence band spectrum of an octylsilane monolayer on $\text{Au}(111)$. (d) Valence band spectrum of the octylsilane monolayer in (c) following exposure to ambient atmosphere for 15 minutes.