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Scanning Tunneling Microscopy of Template-Stripped Au Surfaces and Highly Ordered Self-Assembled Monolayers

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Template stripping of Au films in ultrahigh vacuum (UHV) produces atomically flat and pristine surfaces that serve as substrates for highly ordered self-assembled monolayer (SAM) formation. Atomic resolution scanning tunneling microscopy of template-stripped (TS) Au stripped in UHV confirms that the stripping process produces a flat, predominantly $\langle 111 \rangle$ textured, atomically clean surface. Octanethiol SAMs vapor deposited in situ onto UHV TS Au show a $c(4 \times 2)$ superlattice with $(\sqrt{3} \times \sqrt{3})R30^\circ$ basic molecular structure having an ordered domain size up to 100 nm wide. These UHV results validate the TS Au surface as a simple, clean and high-quality surface preparation method for SAMs deposited from both vapor phase and solution phase.

The self-assembly of organic molecules onto surfaces has produced rich science and technology, including new nanoscale lithography methods,¹ receptor–ligand dynamics,² and substrates for cell adhesion.³ More recently, the integration of biological molecules into powerful new chip-scale sensors¹ and medical diagnostic devices⁴ demands even more control over these inorganic/organic interfaces. Although self-assembled monolayers (SAMs) have been shown to produce locally well-ordered molecular structures via both solution phase⁵ and vapor phase⁶ deposition, in almost all cases, the longer range structural order in the SAM is limited by the surface roughness of the underlying substrate.^{7–11} Solution-deposited alkanethiol SAMs on the coinage metals Au, Ag, Pt, and Pd are among the best studied monolayer systems; it is well established that these molecular monolayers of 1–3 nm thickness are readily disordered by the 2–5 nm peak-to-valley roughness and grain boundaries typical of the metal surfaces. Ultraflat template-stripped (TS) metal surfaces^{12–15} have been shown to serve as a substrate for ordered molecular structures of solution-

deposited SAMs.^{16–19} Until now, however, no study has validated the TS surface preparation through in situ ultrahigh vacuum (UHV) investigations of the TS surface and the subsequently assembled molecular monolayer. In this paper, we report such a UHV scanning tunneling microscopy (STM) investigation of TS Au surfaces stripped in UHV, and octanethiol SAMs vapor-deposited in situ onto those surfaces. We find that the stripping process produces a flat $\langle 111 \rangle$ textured atomically clean surface. The octanethiol SAMs show a clear $c(4 \times 2)$ superlattice with $(\sqrt{3} \times \sqrt{3})R30^\circ$ molecular structure over large 100 nm regions. These data agree favorably with “gold-standard” SAMs on single crystal Au(111) also prepared under UHV conditions, and thus validate the TS Au as a much simpler, but clean and high-quality surface preparation method for many studies of vapor or solution-deposited SAMs.

The thin film layer structure and fabrication process for the TS Au is described in Figure 1. This process has been improved from our initial UHV study of TS metals^{14,15} to better control surface grain structure. In this improved process, Au thin films with a thickness of 500 nm were electron-beam deposited at 300 K onto a Si(001) template that had a 5 nm dry, thermally grown oxide layer. A 5 nm thick Ta layer followed by a 100 nm thick tungsten nitride (WN) layer was then deposited on Au thin films. Ta acts as an adhesion layer between WN and Au. Incorporation of a WN layer was found to improve layer transfer from template to substrate in the case of TS Ag and therefore was utilized for TS Au fabrication. STM images of TS Ag with WN and without WN are included in the Supporting Information. The Au/Ta/WN samples were annealed in air at 473 K for 2 h to obtain low defect density Au surfaces at the Au/SiO₂ interface. After annealing, a Si substrate was glued to the WN surface by silver epoxy, and a clasp was attached to the Si substrate for stripping in UHV.

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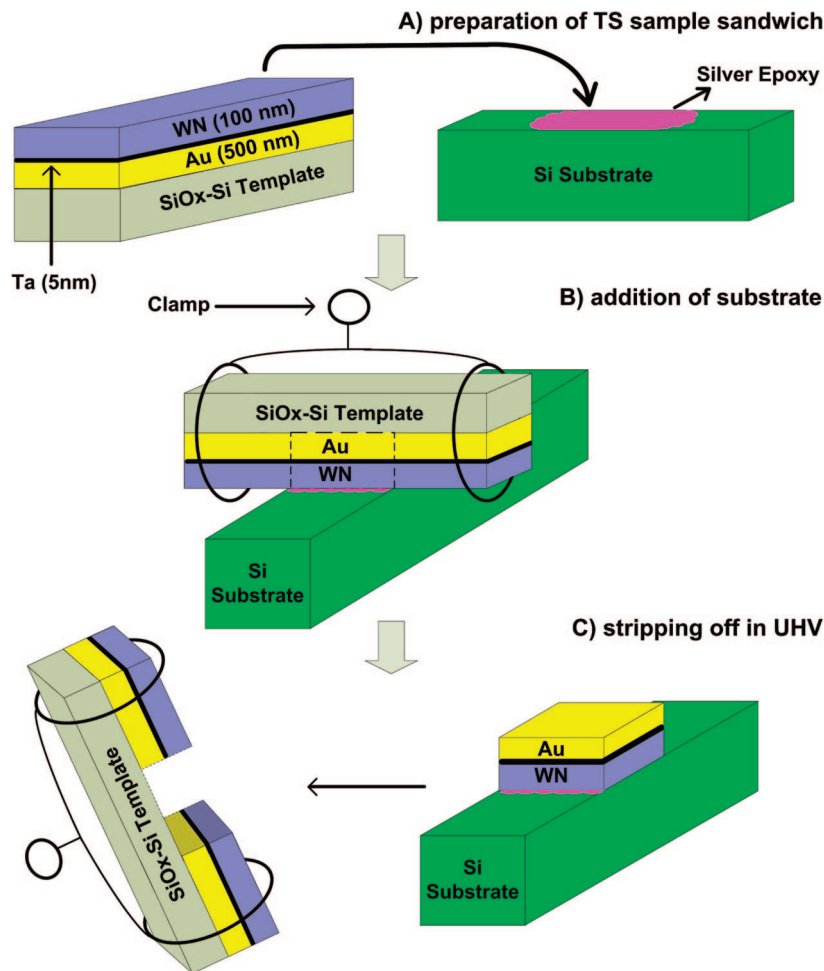


Figure 1. Schematic of a thin film layer structure and the in situ UHV template-stripping procedure. (a) 500 nm Au + 5 nm Ta + 100 nm WN thin films were deposited on a SiO_x template and then annealed at 473 K for 2 h. After, a Si substrate was attached to the WN surface by Ag epoxy. (b) A template clasp was attached to the sample for stripping in the UHV chamber. (c) The template was pulled off the substrate to expose the Au surface in UHV.

Figure 2a shows a $200 \text{ nm} \times 200 \text{ nm}$ STM image of a TS Au surface that was stripped in a UHV chamber with an Omicron VT STM/AFM system attached. Atomically flat terraces with a measured average terrace size $28 \text{ nm} \pm 8.3 \text{ nm}$ (1σ) are clearly resolved in the STM image. The average step height was measured as $0.284 \text{ nm} \pm 0.053 \text{ nm}$ (1σ), which corresponds to a single atomic step height on Au. The line profile of the white line in the Figure 2a, having a height range of 0.4 nm, shows only single atomic steps between terraces. Pits were observed in terraces of TS Au surfaces. Atomically resolved STM image analysis revealed that these pits have one atomic height difference from the nearby terrace. These atomic-scale pits can be considered as a characteristic of the TS Au surface, since similar pits were observed on a TS Au surface when mica was used as a template.¹⁶ Figure 2b shows a $10 \text{ nm} \times 10 \text{ nm}$ atomic resolution STM image of the TS Au surface. A Fourier transform (FT) pattern of Figure 2b, shown as an inset in the figure, was used to determine the nearest-neighbor spacing (nns) of Au atoms as $0.284 \text{ nm} \pm 0.011 \text{ nm}$ (1σ), which is in good agreement with the nns (0.288 nm) of an unrelaxed single crystal Au(111) surface. From this image, we confirm that the TS Au surface has a $\langle 111 \rangle$ textured structure. An alternating bright and dark striped pattern is also observed in Figure 2b. The periodicity of this feature was measured as 6.9 nm along the $[\bar{1}10]$ direction from the image in Figure S1 in the Supporting Information. Considering that the piezodrift of the STM scanner was calculated as approximately 0.04 \AA/s along

this direction, thereby leading to distortion of the measurement of up to 0.4 nm under the data acquisition conditions, the measured periodicity is in agreement with the periodicity of the herringbone reconstruction on Au(111) that is generally accepted as $23 \times \sqrt{3}$.²⁰ The herringbone reconstruction is characteristic of clean single crystal Au(111) in UHV after a surface cleaning process, for example, flame annealing or sputtering. The atomic resolution image of TS Au in Figure 2b was obtained without any surface cleaning process. Thus the template-stripping method was used to obtain a pristine Au $\langle 111 \rangle$ textured surface that can be produced via a simple and fast procedure.

Au(111) is one of the prevalent substrates for the self-assembly of (bio)molecular layers. In order to characterize the domain size and molecular packing structure of SAMs on TS Au, 500 Langmuir (L) of octanethiol was deposited from the vapor-phase onto TS Au. The deposition was performed in a chamber with a base pressure of 10^{-9} Torr that was connected to the UHV STM chamber. Dosing pressures were typically 1×10^{-7} Torr. After deposition, the sample was transferred to the STM chamber and annealed at approximately 310 K for 1 h. Figure 3a is a $200 \text{ nm} \times 200 \text{ nm}$ STM image of octanethiol on a TS Au surface. The packing structure of the octanethiol SAMs is composed of large ordered domains and comparably smaller disordered regions. Figure 3b shows this structure more clearly. The ordered domain

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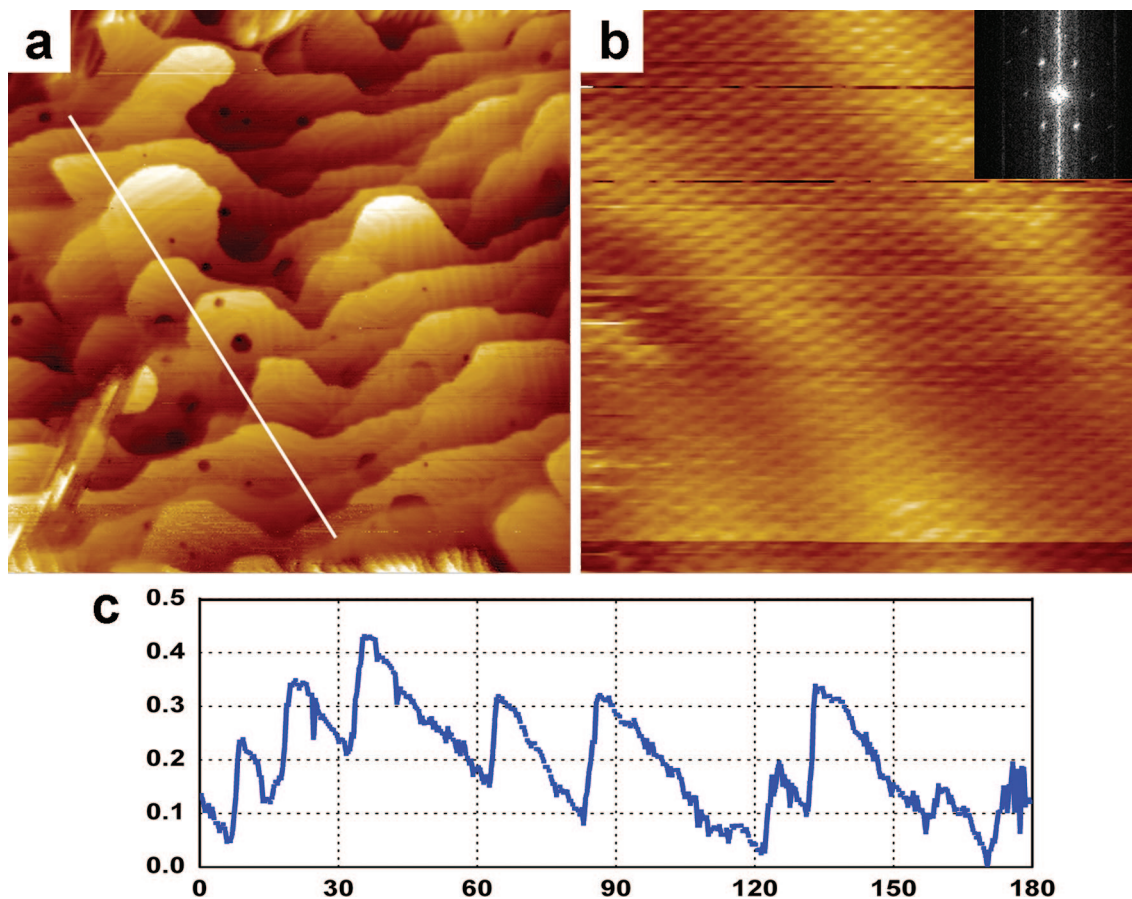


Figure 2. STM images of a TS Au surface having (a) $200 \text{ nm} \times 200 \text{ nm}$ and (b) $10 \text{ nm} \times 10 \text{ nm}$ image sizes. (c) A line profile of the white line in panel a. The inset in panel b shows an FT of the image. Both STM images were taken at room temperature. (Sample bias: (a) -2.0 V , (b) -0.658 V ; feedback current: (a) 0.658 nA , (b) 1.16 nA .)

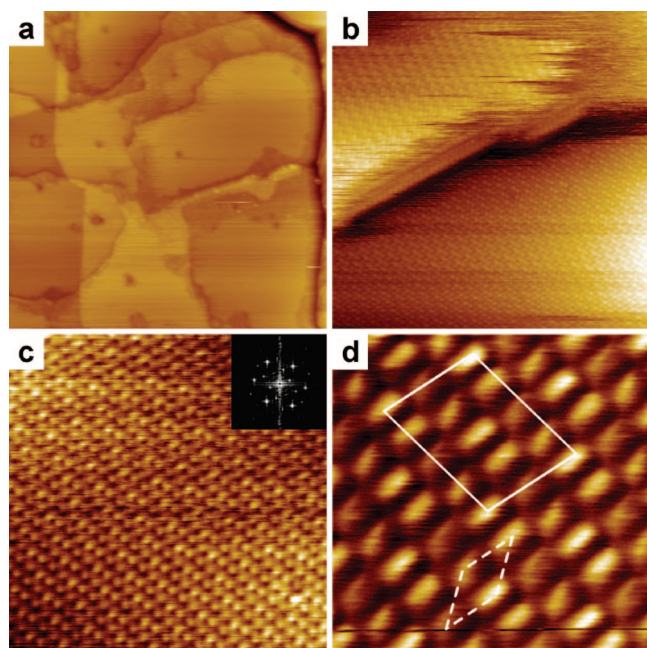


Figure 3. (a) $200 \text{ nm} \times 200 \text{ nm}$ (b) $35 \text{ nm} \times 35 \text{ nm}$ (c) $15 \text{ nm} \times 15 \text{ nm}$ and (d) $5 \text{ nm} \times 5 \text{ nm}$ STM images of TS Au dosed with 500 L of octanethiol. Inset in panel c shows an FT pattern of the image. (Sample bias: -2.0 V ; feedback current: 50 pA .)

size of the SAMs ranges from 40 to 100 nm. In comparison, SAMs on single crystal Au(111) show a complex network of ordered domains that are separated by disordered domain

boundaries and vacancy islands along the boundary.²¹ The ordered domain size of SAMs on single-crystal Au(111) ranges from 5 to 15 nm.^{22,23} Thus, SAMs on TS Au surfaces have a remarkable 1 order of magnitude larger domain size than SAM domains on single-crystal Au(111). The large domain size on TS Au may be attributed to the presence of a large number of single atomic steps that can act as attachment sites for Au adatoms and sinks for vacancies on the surface that result as the more densely packed herringbone surface reconstruction relaxes to the bulk lattice structure during SAM assembly.²⁴ On single-crystal Au(111), vacancy islands form during SAM assembly as Au atoms are ejected from the surface due to relaxation of the herringbone reconstruction.²⁵ Vacancy island defects pin SAM domain boundaries, thereby limiting SAM domain size on single-crystal Au(111).²¹ Yet the formation of vacancy islands is not correlated with SAM assembly on TS Au. Approximately the same numbers of atomic-scale pits, which have the same appearance as a vacancy island, are observed on the TS Au surface before (Figure 2a) and after SAM deposition (Figure 3a). Furthermore, in contrast to single-crystal Au(111), the pits are found in the middle of SAM domains on TS Au rather than on domain boundaries as on Au(111), indicating that pits do not limit domain size on TS Au. Step edges also appear less meandering after SAM deposition,

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thus Au adatoms may prefer kink sites for attachment on step edges. The presence of single atomic steps on TS surfaces, as observed in the line profile of Figure 2c, versus step bunching may also contribute to the larger SAM domain size; terraces expand as Au adatoms attach to step edges. The root-mean-square (rms) roughness of the TS Au surface was measured as 0.149 nm over a $1\ \mu\text{m} \times 1\ \mu\text{m}$ region. Since the value of the rms roughness is dependent on the number of steps between terraces, the low rms roughness value indicates a low probability of finding multiple atomic steps between terraces (step bunching) on TS Au surfaces. For example, a previous STM study of TS Pt versus single-crystal Pt(111) surfaces also showed that, while the terraces on single-crystal Pt were larger, there was a higher frequency in the appearance of step bunching on Pt(111) than on TS Pt. The rms roughness was 0.27 nm for TS Pt, whereas 2.97 nm for single-crystal Pt.¹⁴ The lack of step bunching exhibited by a low rms roughness value may prove to be very important in regard to SAM assembly on metal surfaces.

Molecular resolution images of the octanethiol SAMs are shown in Figure 3c,d. The inset of Figure 3c shows the FT pattern calculated from the image. The hexagonal symmetry of the outmost shell of the FT pattern shows that the SAM adopts the symmetry of the TS Au surface. The molecular nns was determined as $0.502\ \text{nm} \pm 0.022\ \text{nm}$ (1σ), which is $\sqrt{3}$ times the nns of Au atoms on the TS surface and corresponds to a $(\sqrt{3} \times \sqrt{3})R30^\circ$ basic molecular packing structure. In the center of the FT pattern, two additional periodicities are present, which are rotated 90° with respect to each other and represent a periodicity of 4 nns and 2 nns of the TS Au surface. Thus, the $c(4 \times 2)$ superlattice structure observed on SAMs on single-crystal Au(111)²¹ is also present on SAMs on TS Au. The basic packing unit and the superlattice are indicated in Figure 3d with dashed lines and solid lines, respectively.

In conclusion, we have successfully fabricated atomically flat and clean TS Au surfaces and used this TS Au as a substrate for

vapor phase assembly of octanethiol SAMs. STM images of TS Au showed atomic resolution of $28 \pm 8.3\ \text{nm}$ terraces with an ultraflat rms roughness of 0.149 nm over $1\ \mu\text{m}^2$. Octanethiol SAMs on TS Au show molecular resolution with 40–100 nm highly ordered domains of $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure with a $c(4 \times 2)$ superstructure. While this local structure is consistent with the best SAMs on single-crystal Au, most significant assembly on TS Au on average yields much larger ordered molecular domains. The template-stripping method is a simple and fast procedure, well suited for both vapor and solution SAM growth. The UHV control study presented here demonstrates that template stripping produces high quality Au surfaces that can be utilized for highly ordered molecular assembly as a superior alternative to both single crystal and thin-film deposited Au surfaces.

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Supporting Information Available: STM images of TS Au surface that exhibit herringbone reconstruction. STM images of TS Ag surfaces showing the effect of WN layer between Ag and Si substrate. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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