

# Si/SiO<sub>2</sub>-Templated Formation of Ultraflat Metal Surfaces on Glass, Polymer, and Solder Supports: Their Use as Substrates for Self-Assembled Monolayers

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This paper describes the use of several methods of template stripping (TS) to produce ultraflat films of silver, gold, palladium, and platinum on both rigid and polymeric mechanical supports: a composite of glass and ultraviolet (UV)-curable adhesive (optical adhesive, OA), solder, a composite of poly(dimethyl siloxane) (PDMS) and OA, and bare OA. Silicon supporting its native oxide layer (Si/SiO<sub>2</sub>) serves as a template for both mechanical template stripping (mTS), in which the metal film is mechanically cleaved from the template, and chemical template stripping (cTS), in which the film–template composite is immersed in a solution of thiols, and the formation of the SAM on the metal film causes the film to separate from the template. Films formed on all supports have lower root-mean-square (rms) roughness (as measured by atomic force microscopy, AFM) than films used as-deposited (AS-DEP) by electron-beam evaporation. Monolayers of *n*-dodecanethiolate formed by the mTS and cTS methods are effectively indistinguishable by scanning tunneling microscopy (STM); molecularly resolved images could be obtained using both types of surfaces. The metal surfaces, before being cleaved, are completely protected from contact with the atmosphere. This protection allows metal surfaces intended to support SAMs to be prepared in large batch lots, stored, and then used as needed. Template stripping thus eliminates the requirement for evaporation of the film immediately before use and is a significant extension and simplification of the technology of SAMs and other areas of materials science requiring clean metal surfaces.

## Introduction

This paper describes the preparation and structural characterization of ultrasoft films of silver, gold, palladium, and platinum on a range of mechanical supports: glass, solder, ultraviolet (UV)-curable adhesive (optical adhesive, OA), and poly(dimethyl siloxane) (PDMS). It also explores the use of these films as substrates for self-assembled monolayers (SAMs) of *n*-alkanethiolate molecules. Ultraflat metal substrates<sup>1–20</sup> have

a lower root-mean-squared (rms) roughness and larger, flatter grains than films characterized as-deposited by electron beam (e-beam) evaporation (AS-DEP films, see Figure 1). These substrates, produced with a well-developed general method called “template stripping” (TS),<sup>7,16</sup> have proven to be useful in the study and application of well-ordered SAMs.<sup>1–6,9,10,18,21</sup> Our objective in this work was to integrate the TS procedure with materials that would facilitate the production of (i) ultraflat substrates (Au, Ag, Pt, and Pd) for SAMs to be used in electrical and optical studies, (ii) ultraflat films that are flexible, (iii) multiple samples having ultraflat surfaces, in a parallel preparative process, and (iv) films in which the backing materials had a range of electrical and optical properties (e.g., conducting or insulating; transparent or opaque).

We evaporated the metal onto a silicon wafer supporting a native oxide layer (Si/SiO<sub>2</sub>, the ultraflat “template”<sup>1,4,7,8,10–13,16–19,21,22</sup>), attached a mechanical support, either a composite of a glass slide and OA (glass/OA), a composite of PDMS and OA (PDMS/OA), bare OA, or a drop of solder, to the top of the evaporated metal film, and then cleaved the metal film, mechanically or chemically, from the template to expose the face of the film that had been adjacent to the Si/SiO<sub>2</sub> surface. The particular procedures that we employ here have four desirable features: (i) Mechanical supports comprising glass/OA, bare OA, or solder are chemically stable to ethanol, the solvent most commonly used in the formation of SAMs of alkanethiolates, even for extended periods of exposure (>24 h) at elevated temperatures (50 °C).<sup>23</sup> This aspect of film

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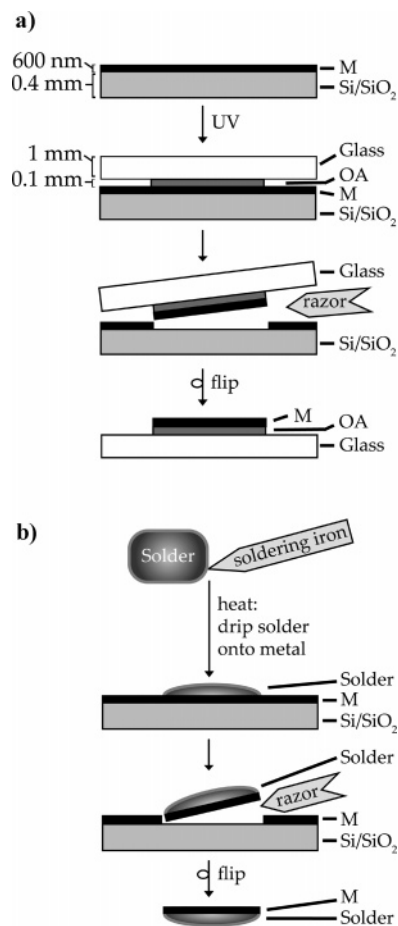
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**Figure 1.** (a) Schematic diagram of the procedure for template stripping using the composite of glass/OA as a mechanical support: (i) We deposited a metal onto an Si/SiO<sub>2</sub> substrate by evaporation with an e-beam. (ii) OA attached a glass slide to the surface of the metal. (iii) We cured the OA by exposing it to UV light for 1 h. (iv) In the case of mechanical template-stripping, we used a razor to cleave the glass/OA/metal composite manually from the Si/SiO<sub>2</sub> template to expose the smooth surface of the metal that was at the metal/SiO<sub>2</sub> interface. (b) For the procedure where solder was the mechanical support, a drop of solder, melted with a soldering iron onto the metal surface, replaced the glass/OA backing.

preparation is an improvement over procedures that use thermally cured epoxy,<sup>4,11–13,16,20</sup> which degrades in the presence of many organic solvents (including ethanol), or a mercaptosilane adhesion layer,<sup>24</sup> which has only been demonstrated to work with gold, and whose bond to the gold could be displaced by thiols in solution. (ii) These procedures are fast: once the metal is evaporated onto the template, we can generate the ultrasurface in 1 h for the glass/OA, PDMS/OA, or bare OA supports, or a few minutes for the solder support. (iii) We can produce ultraflat, flexible metal substrates by using an elastomeric polymer, here, PDMS, as a mechanical support or ultraflat electrodes that can be incorporated directly into a circuit by using solder as a mechanical support. (iv) Many independent, separated ultraflat metal surfaces can be formed simultaneously by using a patterned support (such as a PDMS support).

The TS method produces, as a precursor to the ultrasurface film, a “sandwich structure” that is composed of the template, the film, and the mechanical support (for example, Si/SiO<sub>2</sub>/Ag/OA/glass). In this sandwich structure, the template protects the

functional surface of the metal film from environmental contaminants and from oxidation. We can separate the TS film from the template by immersing it in an ethanolic solution of thiol (chemical template stripping, cTS) such that the film never comes into contact with O<sub>2</sub>. We believe that this capability will make it possible to prepare SAMs on metals whose reactivity toward O<sub>2</sub> has previously prevented their use.

We are able to store the metal films on the Si/SiO<sub>2</sub> template for at least 2 months (the longest interval we have examined) between the evaporation of the film and its use (or structural characterization), without contamination of its surface.<sup>10,16,17</sup> This capability to prepare and store metal films in a form that allows an ultraflat, uncontaminated metal surface to be generated on-demand is, in our opinion, a significant extension in the convenience with which metal surfaces and metal-supported SAMs are formed. In particular, it makes it possible to carry out evaporative deposition of metal films separately from their use. The clean metal films needed for SAMs can, thus, be prepared, backed (with a mechanical support), shipped, and stored; the formation of the SAM can then be separated in place and time from the formation of the metal film without concern for contamination of the metal surface. The stability of the metal films, before separation from the template, extends the ability to work with SAMs to laboratories that do not have access to the equipment needed to carry out metal evaporations.

## Results and Discussion

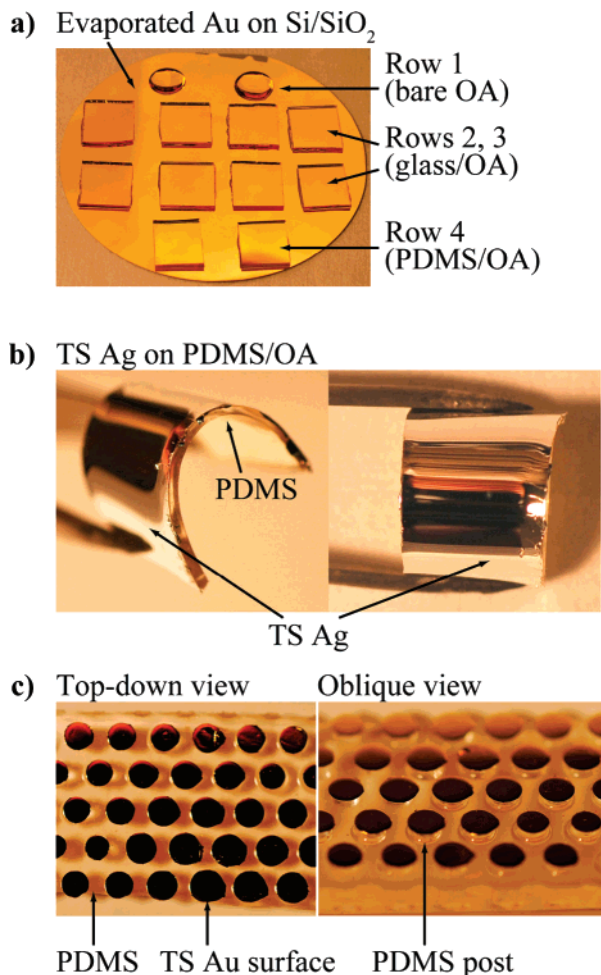
**Preparation of the Sandwich Structures: Si/SiO<sub>2</sub>/Metal/Mechanical Support.** *Glass/OA as the Mechanical Support.* Figure 1a shows the procedure used to prepare the sandwich structure with a glass/OA composite as the mechanical support. Using an e-beam evaporator, we deposited a metal film (Au, Ag, Pd, or Pt, 600 nm) onto a clean Si/SiO<sub>2</sub> wafer that had been rinsed with ethanol and acetone, and dried in a stream of nitrogen.<sup>25</sup> These films were 600 nm thick to ensure that there were no cracks or pinholes through which the OA or solder could penetrate. (We have not tried the procedure with thinner films, although it is possible that they would be sufficient.) We applied a drop (25 μL) of OA (Norland, no.61) to the metal film and placed on top of the OA a glass slide that had been rinsed with ethanol and acetone, dried in a stream of N<sub>2</sub>, and exposed to plasma oxidation for 5 min. Under the weight of the glass slide, the OA (uncured) spread over nearly the entire area of the metal film that was covered by the glass slide (without any additional pressure). A 25-μL drop of OA covered an area of ~2 cm<sup>2</sup> with a uniform thickness of ~0.1 mm. Curing the OA through the glass under an UV light (long-wave mercury lamp, 100 W) for 1 h attached the glass to the metal film. A long exposure to UV light helped to minimize un-cross-linked material that might diffuse from the backing to the surface of the metal through cracks or pinholes in the metal film.

*Solder as the Mechanical Support.* Figure 1b shows the procedure for preparing the sandwich structures with solder as the mechanical support. We melted and spread ~0.5 mL of a low-melting (mp = 70 °C) solder (LMA-158: an alloy of 50% Bi, 27% Pb, 13% Sn, 10% Cd, Small Parts, Inc.) onto an evaporated film of metal with a soldering iron. The solder cooled and hardened immediately.

(25) We used Si/SiO<sub>2</sub> (rather than mica) as the template because sheets of mica frequently adhered to the metal surface when we cleaved the glass/OA/metal composite from the template. The presence of the mica film was not visually apparent, but could be identified from (i) a lack of conductivity across the surface of the sample; (ii) X-ray photoelectron spectroscopy (XPS) measurements, which revealed the presence of potassium, aluminum, and silicon atoms; and (iii) contact angle measurements, which showed that the surface remained hydrophilic after exposure to a solution of alkanethiol.

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**Figure 2.** (a) Photograph of an array of sandwich structures prepared using a single Si/SiO<sub>2</sub> template onto which we had evaporated 600 nm of gold. Row 1: Si/SiO<sub>2</sub>/Au/bare OA; Rows 2 and 3: Si/SiO<sub>2</sub>/Au/OA/glass slide; Row 4: Si/SiO<sub>2</sub>/Au/OA/PDMS. (b) Photographs of a TS silver surface on a flexible PDMS/OA support. Bending the film causes some cracking at its edges (see Figure 9). (c) Photograph of a section of an array of gold surfaces on PDMS posts (0.8 mm high, 1.6 mm in diameter): top-down and oblique views. A thin layer of OA attaches the gold to the PDMS. Some curling of the OA/gold film can be seen around the edges of the posts. The surfaces are slightly different sizes due to variance in spreading of the OA at the interface between the PDMS posts and the evaporated gold surface.

**Bare OA and PDMS/OA as Mechanical Supports.** The procedures for preparing sandwich structures with bare OA and PDMS/OA as mechanical supports are nearly the same as that used with glass/OA: For the bare OA support, we cured the OA without covering it with a glass slide. For the PDMS/OA support, we exposed an ~4-mm-thick slab of cured PDMS<sup>26</sup> to oxygen plasma for 60 s, covered the OA with the PDMS, and then cured the OA as described previously.

Figure 2a shows an array of sandwich structures with different mechanical supports (bare OA, glass/OA, and PDMS/OA) all formed with the same Si/SiO<sub>2</sub> template onto which we had evaporated 600 nm of gold. The samples can be stored in these sandwich structures and used (one or many at a time) as needed. Figure 2b is a pair of photographs of a silver film (~600 nm thick) supported on PDMS/OA that had been cleaved mechanically from a Si/SiO<sub>2</sub> template; the sample readily bends (as shown)

with cracking only along the edges of the film (see the section on “The Effects of Bending the Metal Films”).

**Parallel Preparation of Multiple Samples of Ultraflat Metal Film.** In order to prepare multiple supported ultraflat surfaces simultaneously (Figure 2c), we molded PDMS into a 4-mm-thick slab with 0.8-mm-high (and 1.6-mm-diameter) posts (spaced by ~1 mm) by pouring the uncured PDMS over a 0.8-mm-thick sheet of stainless steel with an array of 1.6-mm-diameter holes. (The metal grid rested on an Si/SiO<sub>2</sub> wafer that had been exposed to a vapor of (tridecafluoro-1,1,2,3,-tetrahydrooctyl)-1-trichlorosilane for 1 h in a vacuum desiccator to prevent the PDMS from sticking to the wafer.) We then cured the PDMS at 70 °C for 2 h and peeled the molded PDMS away from the metal grid. (This step is facilitated by the use of a metal, rather than plastic, grid, because cured PDMS tends to adhere to plastic molds.) We treated the PDMS with oxygen plasma for 60 s, placed the PDMS (posts down) on top of a layer of OA that had been spun-coat onto a Si/SiO<sub>2</sub> wafer (5 s at 500 RPM and 30 s at 3000 RPM) to coat the tops of the posts, and placed the adhesive-coated PDMS (posts down) on top of a gold film. With no additional pressure applied to the PDMS, the OA cured through the PDMS under a UV light for 1 h to form the Si/SiO<sub>2</sub>/gold/OA/PDMS multi-surface sandwich structure.

#### Separation of the Metal Films from the Si/SiO<sub>2</sub> Template.

Three methods easily separated the metal film from the template. The first method, “mechanical template stripping” (mTS), involved cleaving the metal film mechanically from the Si/SiO<sub>2</sub> substrate in air. We ran the edge of a razor blade around the perimeter of the support/metal composite at the interface between the OA and the metal or the solder and the metal, and then gently pried the support from the Si/SiO<sub>2</sub> to expose the metal surface that had been in contact with the Si/SiO<sub>2</sub> template (Figure 1). We then either (i) immediately characterized the bare metal film (exposing it to air for ≤2 min before loading it into a vacuum chamber in the case of X-ray photoelectron spectroscopic (XPS) measurements) or (ii) immediately (within 30 s) submerged the metal film in a solution of hexadecane thiol (1 mM in 10 mL of anhydrous ethanol that had been purged of oxygen with a steady flow of argon gas for >30 min) and left the sample under positive pressure of argon gas until use.<sup>27</sup>

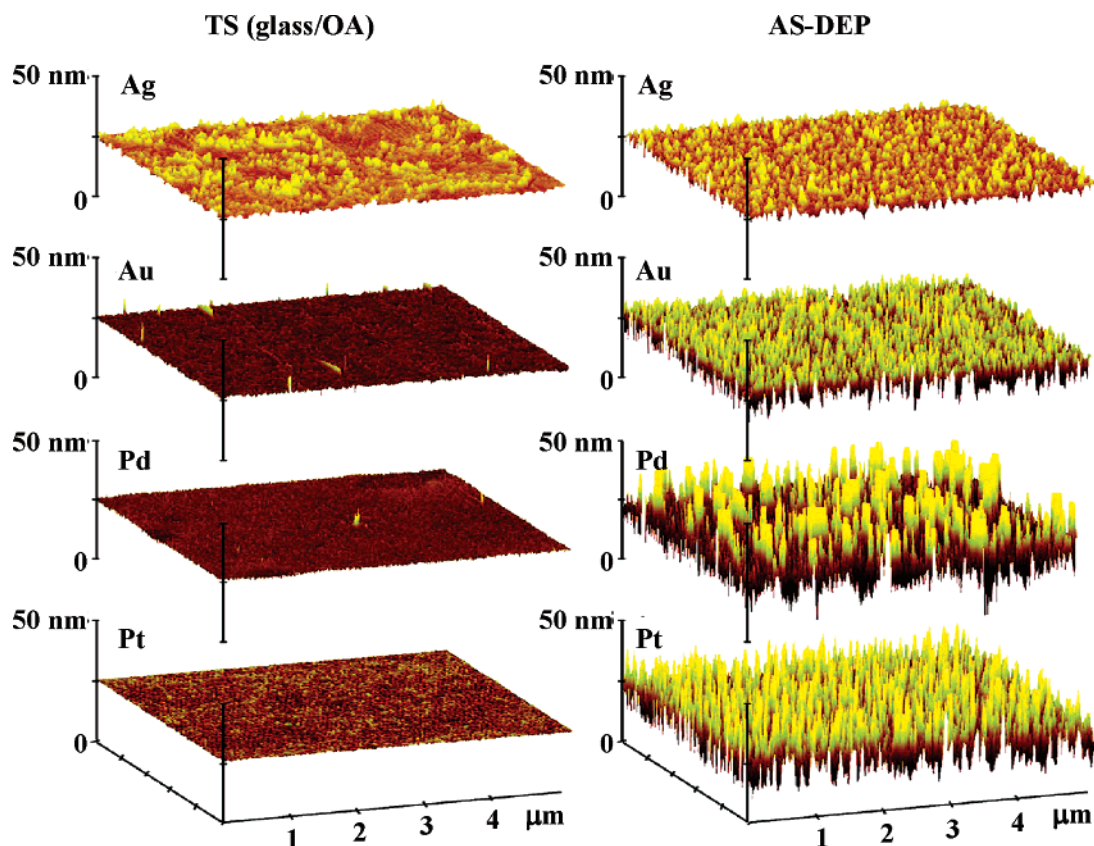
For the second method, we placed the sandwich structure into a deoxygenated ethanolic solution of hexadecane thiol and mechanically cleaved the metal film from the template (as described in the preceding paragraph) under solution (which was exposed to air during the cleaving process (~1 min)).

For the third method, “chemical template stripping” (cTS), we submerged the sandwich structure in the deoxygenated solution of hexadecane thiol. After 12 h (still under the thiol solution), we applied gentle pressure to the mechanical support, in the direction parallel to the plane of the surface, while holding the Si/SiO<sub>2</sub> wafer with a pair of tweezers; the metal film slid off of the Si/SiO<sub>2</sub> template easily. In both the second and third methods, after the template was removed from the solution, we maintained the sample under positive pressure of argon gas until use.

**Atomic Force Microscopy (AFM) Indicates that TS Films Are Smoother than AS-DEP Films.** We characterized all of the bare metal surfaces using AFM. For the metal films on supports comprising glass/OA or solder, we used contact mode. For the metal films on bare OA or PDMS/OA, we used tapping mode because (at least in the case of PDMS/OA) the contact mode

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(27) We also tried mTS after submerging the uncleaved samples under liquid N<sub>2</sub> (77 K) for 30 s (Figure S1) or annealing the evaporated metal films in an oven (Figure S2) or flame (Figure S3) before forming the sandwich structures; these methods produced rougher surfaces than those cleaved in air.



**Figure 3.** Contact-mode AFM micrographs of the topography of the template-stripped (TS, left column) and as-deposited (AS-DEP, right column) surfaces of silver, gold, palladium, and platinum. The TS samples have a glass/OA support. The rms roughnesses of the surfaces (total area =  $25 \mu\text{m}^2$ ) are: TS Ag, 1.2 nm; TS Au, 0.6 nm; TS Pd, 0.5 nm; and TS Pt, 0.2 nm; AS-DEP Ag, 5.1 nm; AS-DEP Au, 4.5 nm; AS-DEP Pd, 7.6 nm; AS-DEP Pt, 6.2 nm.

image seemed unrealistically smooth, probably because the tip exerted enough force on the PDMS to deform it as the image was recorded. The surfaces of silver, gold, palladium, and platinum, evaporated onto and mechanically cleaved from the Si/SiO<sub>2</sub> template (using a glass/OA support), have lower rms roughness than AS-DEP surfaces (Figure 3). Films of Pd and Au on a bare OA support and a PDMS/OA support (Figure 4) have a similar rms roughness to Pd and Au films on a glass/OA support. Figure 5 shows an AFM image of a film of Ag on a solder support (oblique and top-down views). The rms roughness (1.2 nm) is equal to that of the film of Ag on the glass/OA support.

**The mTS and cTS Procedures Form Similarly Ordered SAMs: Scanning Tunneling Microscopy (STM).** We confirmed that SAMs of alkanethiolates were present on the AS-DEP, mTS, and cTS Ag surfaces by reflection-absorption infrared spectroscopy (RAIRS), as detailed in the Supporting Information (Table S1 and Figure S4). In order to more directly obtain a detailed picture of the structure of the SAM on the various surfaces, we obtained scanning tunneling microscopy images of the surfaces of bare Ag, SAMs of *n*-hexadecanethiolate (SC<sub>16</sub>) on AS-DEP Ag, and SAMs of *n*-dodecanethiolate (SC<sub>12</sub>) on Ag (mTS and cTS) under ultrahigh vacuum (base pressure  $\sim 2 \times 10^{-10}$  mbar) using a commercial variable-temperature AFM/STM (Omicron Nanotechnology, Taunusstein, Germany) in constant current mode.

As has been observed previously,<sup>28,29</sup> images of bare mTS Ag showed atomically flat terraces (which correspond to the {111} plain) separated by monatomic steps (Figure 6a). The features were stable to repeated scanning even at low tunneling resistance

(5 GΩ). Figure 6b shows a low-resolution image of a SAM of SC<sub>16</sub> on AS-DEP Ag. We could not obtain high-resolution images of these SAMs due to the combination of relatively small grain size (<10 nm) and the steep surface curvature of each grain in these samples.

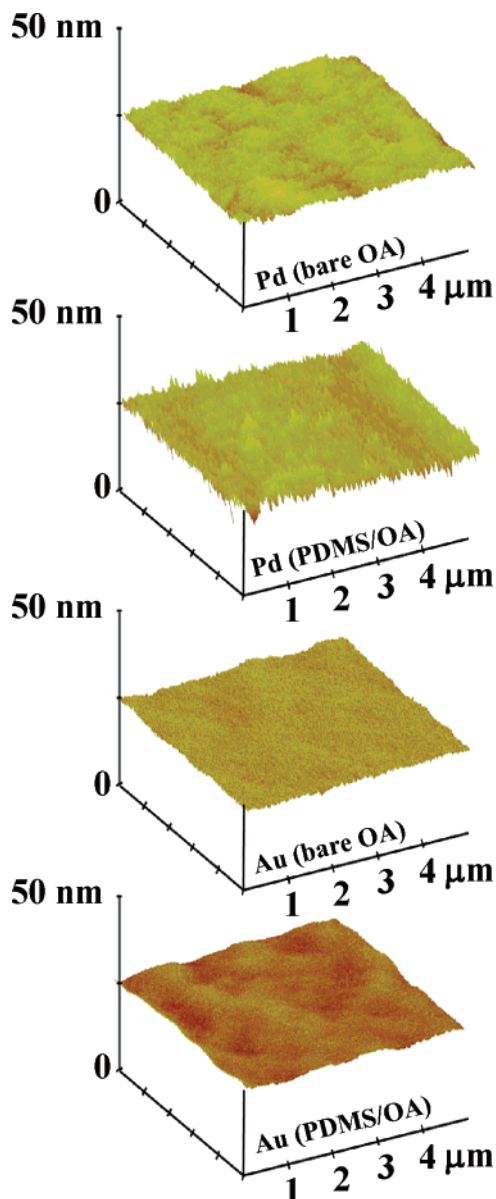
We imaged the SAMs of SC<sub>12</sub> on mTS and cTS Ag with a tunneling resistance of 100–160 GΩ (tunneling current = 0.015 nA) and a gap voltage of 1.5–2.4 V. We used SC<sub>12</sub> instead of the potentially better-ordered SAM of SC<sub>16</sub> because the SC<sub>16</sub> molecules were too resistive to obtain images at high resolution. It has been observed that, in order to maintain molecular resolution, the minimal tunneling resistance must be monotonically increased with the number of methylene units in the alkane chains (by a factor of 10 to 100 for every five units), because increased resistance results in a larger distance between tip and surface; this distance is necessary for nondestructive imaging of the SAM.<sup>29,30</sup> The fact that we could obtain molecular resolution only by using a tunneling resistance of 100 GΩ provides direct proof that there were molecules present in the tunneling gap in our experiments.<sup>30</sup> When using lower tunneling resistances ( $\sim 5$  GΩ) the tunneling behavior appeared erratic and irreproducible because the molecules detached from the surface and attached to the STM tip.

Images of the SAMs of SC<sub>12</sub> on both mTS and cTS Ag showed two major types of topography: ordered monolayers on flat {111}

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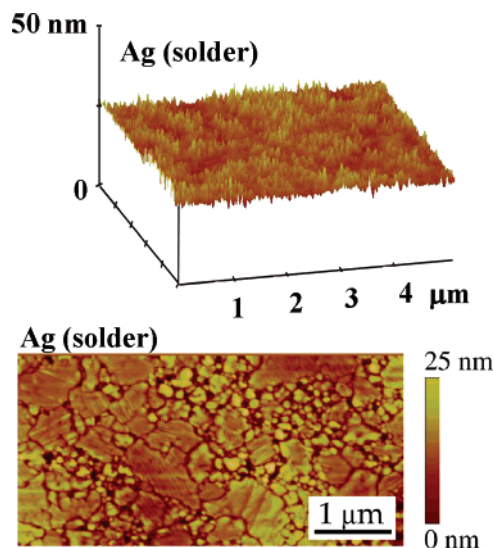
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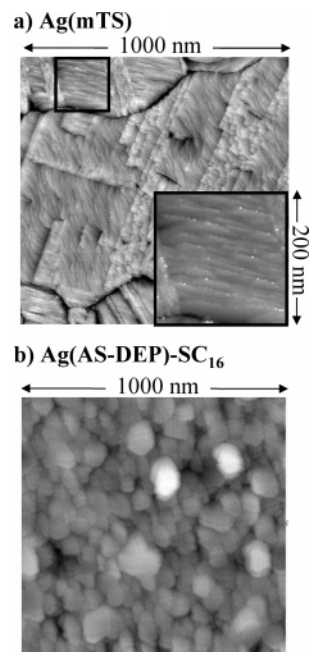
**Figure 4.** Tapping-mode AFM micrographs of: a TS Pd film on a bare OA support (rms roughness = 0.5 nm), a TS Pd film on a PDMS/OA support (rms roughness = 0.7 nm), a TS Au film on a bare OA support (rms roughness = 0.5 nm), and a TS Au film on a PDMS/OA support (rms roughness = 0.6 nm). All rms roughnesses were calculated over an area of  $25 \mu\text{m}^2$ .

planes oriented nearly parallel to the surface of the sample (Figure 7a) and disordered monolayers on terraces from grains that were tilted approximately 20% or more from the horizontal  $\{111\}$  planes (Figure 7c).

**Structure of the SAM on Flat Terraces.** In general, the SAMs of  $\text{SC}_{12}$  on the flat  $\{111\}$  planes of mTS Ag were indistinguishable from those on the flat  $\{111\}$  planes of cTS Ag by STM. The smooth  $\{111\}$  terraces oriented parallel to the surface of the sample were covered by a large number of elevated (by a single atomic step) island structures (approximately 10–20 nm in diameter, Figure 7a) that did not appear in the images of bare Ag (Figure 6). These island structures, which we were sometimes stacked on top of one another, are typical features in images of SAMs of alkanethiolates on Ag.<sup>29,31</sup> Formation of islands is a mechanism for relieving the stress at the interface between the Ag and the SAM; this stress exists because the lattice structure



**Figure 5.** Contact-mode AFM micrograph of a TS Ag film on a solder support (oblique and top-down views). The rms roughness of this film was equal to that on the glass/OA support (1.2 nm over an area of  $25 \mu\text{m}^2$ ).

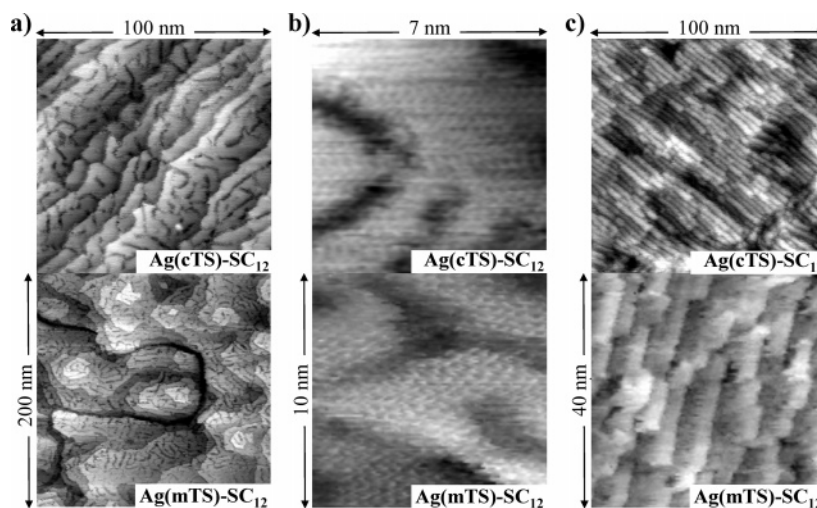


**Figure 6.** (a) STM image of a bare surface of mTS Ag obtained with a tunneling current of 1 nA, and a gap voltage of 2 V. The scanning speed depended on the size of the image (i.e., for a  $200 \text{ nm} \times 200 \text{ nm}$  image, the scanning speed was 200 nm/s). The  $z$  ranges (total differences in height between the lowest and highest points in the images) are 20 nm for the  $1000 \text{ nm} \times 1000 \text{ nm}$  image, and 5 nm for the  $200 \text{ nm} \times 200 \text{ nm}$  inset. (b) STM images of a SAM of  $\text{SC}_{16}$  on AS-DEP Ag obtained with a tunneling current of 0.015 nA, a gap voltage of 1 V, and a scanning speed of 2000 nm/s. The  $z$  range is 20 nm.

of the SAM (dictated by van der Waals interactions between the alkane chains) is incommensurate with the lattice structure of the underlying Ag substrate (which has a lattice constant of  $\sim 0.29 \text{ nm}$ <sup>28,30</sup>). Alkanethiolate molecules, still attached to a single atom or two atoms of Ag,<sup>32</sup> are mobile enough to reorganize into island structures because the ionic Ag–S bond is stronger than the Ag–Ag bond.<sup>31</sup> For longer-chain  $n$ -alkanethiolates ( $\text{S}(\text{CH}_2)_{n-1}\text{CH}_3$ )

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**Figure 7.** STM images of  $\text{SC}_{12}$  SAMs on cTS (row 1) and mTS (row 2) Ag, obtained with a tunneling current of 0.015 nA, and gap voltages of 1.5–2.4 V. The scanning speed depended on the size of the image (i.e., for a 200 nm  $\times$  200 nm image, the scanning speed was 200 nm/s). Moving from left to right, the z-ranges for these images are 0.98, 0.59, and 1.90 nm for the top row, and 2.05, 0.66, and 0.93 nm for the bottom row.

with  $n > 3$ , this reorganization results in a tilt angle of 10–15° from the surface normal,<sup>28</sup> and in a lattice that is more like that of the bulk alkane, and distorted from that of the underlying  $\text{Ag}\{111\}$ .<sup>29</sup>

The terraces, including the island structures, were covered by densely packed, ordered domains of molecules. We could obtain molecular resolution of these ordered SAMs in the case of both mTS and cTS samples (Figure 7b). Depressions were visible throughout the ordered regions (Figure 7a). The depth of these depressions was, on average, 0.325 nm; they are therefore probably grain boundaries in the SAM, rather than missing rows of molecules (which would leave  $\sim 1.5$ -nm-deep depressions).<sup>29</sup> We presume, from information gathered from diffraction studies on SAMs of long-chain alkanethiolates on  $\text{Ag}\{111\}$ ,<sup>29,31</sup> but cannot prove from these images that these depressions separate hexagonally packed arrays of the SAM that are tilted by 21°–24° from each other. High-resolution images of the ordered regions of the SAM (middle) on both the mTS and cTS samples show a lattice of molecules with a nearest-neighbor distances of 0.43–0.51 nm, on average. This range of values agrees well with the 0.46-nm spacing expected for a crystalline SAM of long-chain alkanethiolates.<sup>31</sup> Far from domain boundaries, the height variations of nearest neighbor molecules are  $< 0.12$  nm.

**Structure of the SAM on Highly-Tilted Terraces and Non- $\{111\}$  Planes.** Approximately 60% of the surface was covered by regions where the individual crystallite orientation deviated from that of the planar  $\{111\}$  grains (Figure 7c). We could not obtain molecular resolution of the SAM in these regions. High-resolution imaging of the region of the SAM on a flat  $\{111\}$  plane immediately adjacent to the “tilted” region (a “twinning” plane, usually a  $\{511\}$  orientation) was commonly observed; this observation suggests the tunneling conditions were adequate for obtaining molecular-scale resolution, but that the SAM on the twinning plane was not as ordered as the SAM on the  $\{111\}$  plane.

Though we could not directly observe individual molecules or ordered arrays in the “tilted” regions of the surface, two observations strongly indicated that the tilted planes were, in fact, covered with alkanethiolate molecules: (i) For a given gap voltage (typically 1.5–2.4 V) and magnification, the tunneling currents required to image the flat or tilted regions of the SAM of  $\text{SC}_{12}$  were similar ( $\leq 30$  pA), whereas that required for imaging the bare surface of Ag was  $\geq 1$  nA. This observation indicates

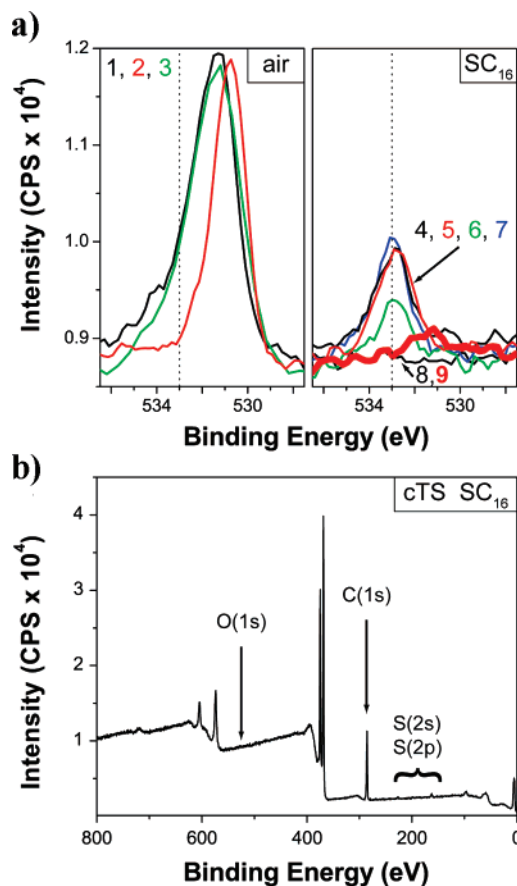
that the Ag surface could be imaged reproducibly with the tip positioned much closer to the surface than could the SAM. (ii) The traces of current ( $I$ ) vs voltage ( $V$ ) measured by the STM tip within these regions were similar in shape and in the magnitude of  $I$  to those recorded on the flat  $\{111\}$  planes (which were covered by ordered SAM) for both mTS and cTS samples and were different in shape and in the magnitude of  $I$  from those taken on the bare Ag surface (Figure S5).

We believe that a number of factors precluded the growth of well-ordered SAMs in the regions where the  $\{111\}$  planes were tilted or where  $\{111\}$  planes contacted non- $\{111\}$  planes. These factors included (i) small grains in the Ag substrate (only  $\sim 7$  to 10 nm wide), (ii) different strengths of substrate-molecule binding on different crystal planes, and (iii) roughness caused by boundaries between crystal planes.

In summary, the mTS and cTS procedures both produce similarly ordered SAMs with a high degree of coverage of the Ag substrate, but also a high degree of heterogeneity: each surface is split about evenly into regions where  $\text{Ag}\{111\}$  planes, oriented parallel to the surface of the sample, support a well-ordered SAM, and regions where highly tilted  $\{111\}$  planes, or planes of a different crystal orientation, support poorly ordered SAM. Structurally, there does not appear to be any obvious advantage of the cTS procedure over the mTS procedure that can be detected by STM. As discussed in the next section, the SAMs produced by these two methods do, however, have different chemical compositions.

**The TS Method Minimizes Exposure of the Metal Films to Oxygen: X-ray Photoelectron Spectroscopy (XPS).** Figure 8a shows the XP spectra acquired for the O(1s) core-level binding energy of TS and AS-DEP thin films of silver and films of silver with a SAM of  $\text{SC}_{16}$ ; Table 1 lists the methods used to prepare each of these films. We prepared these films by either separating them from the template mechanically (mTS) in air or under the thiol solution or allowing them to separate from the template chemically (cTS). Figure 8b shows a survey spectrum of a thin film of silver bearing a SAM of  $\text{SC}_{16}$ , chemically cleaved from a Si/SiO<sub>2</sub> template.

The O(1s) XPS peaks of the bare silver surfaces (**1**, **2**, and **3**) are best fit with a sum of three Gaussian functions with peak positions, relative amplitudes, and full-width at half max (fwhm) given in Table 1. Spectrum **1**, which corresponds to the sample that was cleaved mechanically in air after being in the sandwich



**Figure 8.** (a) XP spectra, after 3-point smoothing, acquired for the O(1s) core-level binding energy of a thin film of silver, prepared as described in Table 1. (b) A survey spectrum of a thin film of silver bearing a SAM of SC<sub>16</sub>, chemically template-stripped (cTS) from the Si/SiO<sub>2</sub> template.

structure for 1 day, is, overall, shifted to higher energy than are **2** (the sample that was cleaved mechanically in air after being in the sandwich structure for 2 months) and **3** (the AS-DEP surface). The overall fwhm of the band in spectrum **2**, the 2-month-old mTS sample, is about 0.75 that of the other two bare Ag samples. Reported binding energies of oxygen for uncontaminated Ag<sub>2</sub>O range from 528.1 to 529.2 eV.<sup>33–35</sup> Carbonate species, or other oxygen-containing carbon contamination that forms during exposure to air, shift the peak to higher energies (530.0–531.5 eV), as do adsorbed water (532.4 eV) and sulfur oxides (532.5–533.5 eV).<sup>33</sup> The component of spectra **1**, **2**, and **3** at ~530.5 eV is probably from oxygen-containing carbon contamination from the air. The simplest explanation for the differences in energy and line-shape between spectra **1** and **2** is a larger contribution from adsorbed water in spectrum **1** than in spectrum **2**; contamination from water probably occurred between the time when the surface was cleaved and the time the XPS chamber was put under vacuum. The spectrum of the AS-DEP sample (**3**) appears to have the greatest contribution from Ag<sub>2</sub>O (hence the greater line width and overall shift toward lower energy as compared to spectrum **2**). The AS-DEP surface was exposed directly to air for 24 h (compared to minutes for the mTS surfaces), so the bare mTS Ag surfaces were somewhat protected from oxidation in the sandwich structures.

The mTS and AS-DEP samples with a SAM of SC<sub>16</sub> on them (**4**, **5**, **6**, and **7**) can all be adequately fit with a single Gaussian

**Table 1.** Method of Preparation of Ag Surfaces for Characterization by XPS and Line Shape Parameters for Gaussian Fits to the XP Spectra

label	preparation	medium <sup>a</sup>	age <sup>d</sup> (days)	SAM <sup>e</sup>	line shape parameters <sup>f</sup>	
					binding energy (amp.)	fwhm
1	mTS	air	1	none	530.9 (1)	1.0
					531.5 (4.5)	1.8
					532.9 (3.5)	4.1
2	mTS	air	67	none	530.8 (6)	1.3
					532.2 (1)	1.3
					534.8 (1)	3.1
3	AS-DEP	air <sup>b</sup>	1	none	530.5 (14)	1.8
					531.7 (11)	3.3
					537.2 (1)	1.6
4	mTS	air <sup>c</sup>	1	SC <sub>16</sub>	533.1	1.6
5	mTS	air <sup>c</sup>	67	SC <sub>16</sub>	532.9	1.6
6	AS-DEP	air <sup>b</sup>	1	SC <sub>16</sub>	533.0	1.7
7	mTS	solution	1	SC <sub>16</sub>	533.0	1.6
8	cTS	solution	1	SC <sub>16</sub>	no peak	
9	cTS	solution	67	SC <sub>16</sub>	531.5	1.2

<sup>a</sup> TS samples were template stripped in air or under thiol solution. <sup>b</sup> AS-DEP samples were prepared in air. <sup>c</sup> Samples were transferred from air into solution within 30 s. <sup>d</sup> TS: the length of time the sample remained in its sandwich structure prior to template stripping. AS-DEP: the length of time between evaporation and characterization. <sup>e</sup> SAMs of *n*-hexadecanethiolate (SC<sub>16</sub>) formed for 12 h in 1 mM C<sub>16</sub>SH in EtOH, under Ar. <sup>f</sup> The parameters are binding energy, in eV, followed by the amplitude of the component (amp., in parentheses, normalized to the amplitude of the smallest component), and the full-width-at-half-max of the band, fwhm, in eV.

function centered at ~533 eV, a binding energy that probably reflects the presence of sulfur oxides, and possibly contamination from adsorbed ethanol and carbon compounds, although it is difficult to differentiate between the contributions of these contaminants. The cTS samples (**8** and **9**) show less contamination by oxygen than the other samples.

From the XPS data, we conclude the following: (i) The cTS procedure effectively excluded oxygen from the SAM, even when the sample was left in the un-cleaved sandwich structure for more than 2 months (**9**). (ii) The sandwich structures protect the bare Ag surfaces from oxidation (to form Ag<sub>2</sub>O), but the bare surfaces (both AS-DEP and TS) are vulnerable to contamination by oxygen-containing carbon compounds and water once cleaved. (iii) The SC<sub>16</sub> molecules appear to displace some of the oxygen from the silver film upon formation of the SAM: curves **4**–**9** have smaller intensities than curves **1**–**3**, even though curve **6** corresponds to an AS-DEP surface that was exposed to laboratory atmosphere for 2 days.

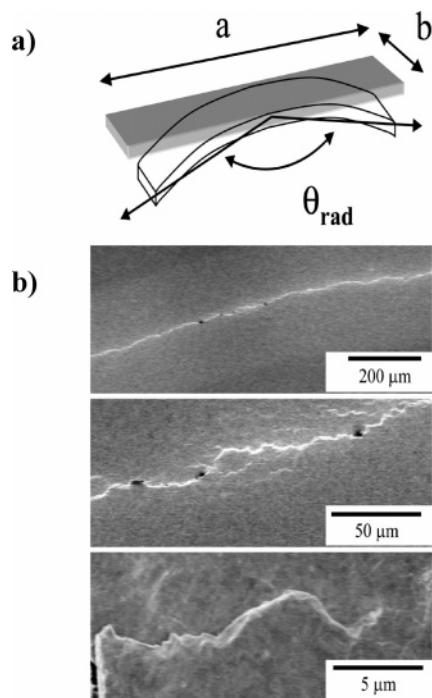
The XP spectra of these samples also show, conclusively, that the OA does not contaminate the surface of the sample during the SAM-formation process, Figure S6: There is no perceptible nitrogen (which is clearly present in the spectrum of OA) in any of the samples of AS-DEP or TS surfaces of Ag (with or without a SAM). Sulfur is present in the silver samples that contain a SAM, but we detected no sulfur in the bare silver samples.

**The Effects of Bending the Metal Films on PDMS/OA Supports: SEM and AFM.** Figure 9a is a diagram that defines the radial angle,  $\theta_{\text{rad}}$ , at which we bent the TS Ag film on a PDMS/OA support. Figure 9b shows SEM images of the cracks that formed when we bent the sample to  $\theta_{\text{rad}} = 100^\circ$ . These visible cracks formed only along the edges of the sample that were parallel to the direction of bending (the edges parallel to dimension “a”), and the cracks themselves all ran approximately parallel to dimension “b”. The cracks were 10–500  $\mu\text{m}$  long

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**Figure 9.** (a) Definition of the radial angle,  $\theta_{\text{rad}}$ , at which we bent the TS Ag film on a PDMS/OA support. (b) SEM images of the cracks that formed at the edges of the Ag film after bending it at  $\theta_{\text{rad}} = 100^\circ$ . The images were taken at an electron beam energy of 3 keV and a working distance of 7 mm. These features were not present in the interior of the film after bending or anywhere in the film before bending (see Figure S7).

(most were closer to  $10 \mu\text{m}$  long). Figure S7a is an SEM image of a representative region of the interior of the silver film after bending and shows that no cracks formed in the interior of the film.

AFM images of the TS silver surfaces on PDMS/OA supports (Figure S7b) show that the surface roughens slightly after bending the substrate at  $\theta_{\text{rad}} = 160^\circ$ . (We could not bend the sample further because it would not then return to a state that was flat enough for the AFM tip to stay in contact with the surface.) The rms roughness of the surface (over a  $25 \mu\text{m}^2$  area) was 0.8 nm before bending and 1.1 nm after bending: both of these numbers are less than the rms roughness of the silver surface on a glass/OA support.

## Conclusions

**Summary.** This paper describes methods for preparing ultraflat metal surfaces for use as supports for SAMs (and for other applications in surface science). This method consists of electron-beam evaporation of metal onto an ultraflat Si/SiO<sub>2</sub> surface (a polished silicon wafer), covering this film with a mechanical support, and then cleaving it off, mechanically (mTS) or chemically (cTS), when the metal surface was needed. This method forms films of metal (e.g., silver, gold, palladium, and platinum) on supports of optical adhesive (OA, glass/OA, and PDMS/OA), and solder; template-stripped films are smoother and have larger grains (by atomic force microscopy, Figures 3–5) than films used as-deposited (AS-DEP) by e-beam evaporation.

Scanning tunneling microscopy (Figure 7) indicates that the set of features present, the high degree of coverage, and the overall order of the SAMs were similar when formed using mTS and cTS procedures. Using STM, we were able to obtain high-resolution images that showed formation of island structures and

the molecular lattice characteristic of well-ordered SAMs of alkanethiolates on Ag{111} on the TS films (Figure 7). It appears that the reorganization of the Ag surface into island structures did not take place in the AS-DEP films, probably because the small size and high degree of curvature in the grains of Ag impeded the long-range interactions among the alkane chains that cause this reorganization.

**Comparison to Other Methods of Template Stripping.** The methods of template stripping that use either thermally cured epoxy<sup>4,11–13,16,20</sup> or a SAM of mercaptosilane molecules<sup>24</sup> as the adhesion layer between the metal film and the mechanical support, and the method of cold welding<sup>36,37</sup> have also been shown to produce ultraflat metal films on rigid and elastomeric substrates. Our TS procedures utilize solder and OA, which, unlike thermally cured epoxy, are stable to ethanol, which is commonly used to form SAMs. Both mTS and cTS appear to induce very little mechanical stress on the metal films (as shown by AFM and STM, Figures 3–7), whereas high pressures applied to the metal films during cold welding<sup>36,37</sup> can cause them to crack. The method that uses a mercaptosilane adhesion layer<sup>24</sup> has been successfully applied only to the production of films of gold, whereas we have utilized template stripping to produce films of platinum, palladium, and silver as well.

### The Unique Advantages of the Template Stripping Method.

**Creation of High-Quality, Storable, Transportable Substrates.** The ability to store the metal surfaces in a form where they are protected from the atmosphere (as shown by XPS, Figure 8a) for long periods of time is an important attribute of the template stripping method. Samples of metal film can be prepared, stored, and shipped in the un-cleaved (Si/SiO<sub>2</sub>/Ag/mechanical support) structures, and clean surfaces can be generated (by cleaving the Ag film from the Si/SiO<sub>2</sub>) when needed. The storable “supply” of clean surfaces will enable researchers who do not have access to a metal evaporator to carry out experiments that use SAMs.

**Applications for Template-Stripped Surfaces.** Template stripping is a versatile method: we can produce ultraflat metal films for a variety of applications by changing the material(s) used as the mechanical support. For example, solder is electrically conductive; ultraflat metal films formed on solder could be incorporated directly into electronic circuits or used as substrates for the formation of SAMs for applications in molecular electronics. The glass/OA, bare OA, and PDMS/OA supports are transparent and insulating; SAMs formed on these supports could be used in molecular electronics or in biological assays that employ surface plasmon resonance (SPR) and other optical techniques. The bare metal films could function as electrodes for organic field effect transistors, mirrors for oscillator cavities, and electrodes for solar cells and light-emitting diodes (LEDs). In addition, we have shown that we can simultaneously produce many ultraflat surfaces for these applications by molding the mechanical support.

We have shown (in a separate publication<sup>23</sup>) that the range of current densities ( $J$ ) measured through SAMs of *n*-alkanethiolates using an Hg-drop as a top-contact shrinks dramatically (by several orders of magnitude, depending on the length of the alkane chain) on going from AS-DEP substrates to TS substrates (all were mTS). Measurements of  $J$ , which are extremely sensitive to structural inhomogeneity in the SAM because tunneling current depends exponentially on the thickness of the insulating layer, still yield a range of values of approximately 2 orders of magnitude using TS substrates. The distribution of  $J$  values can, however,

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be fit with a Gaussian function and explained using a well-characterized set of defects for SAMs of alkanethiolates on Ag, whereas the set of  $J$ -values collected on the same SAMs using AS-DEP substrates is too broad and distributed too randomly to yield any physical insight into relationships between structure (of the individual molecules or of the SAMs) and electrical function. Furthermore, junctions incorporating alkanethiolates on TS substrates were less susceptible to failure (due to amalgamation of the Hg with the Ag through defects in the SAM) than were AS-DEP junctions.

The TS surfaces have proven to be an invaluable tool for the formation and characterization of large-area (i.e., more than a few molecules) junctions. Their use mitigates the contribution of defect-mediated current to the observed current and is therefore a significant step toward using SAMs for both fundamental studies

of conduction through molecules and construction of molecule-based electrical devices.

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**Supporting Information Available:** Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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