

# Self-Assembled *n*-Alkanethiolate Monolayers on Underpotentially Deposited Adlayers of Silver and Copper on Gold

G. Kane Jennings and Paul E. Laibinis\*

Contribution from the Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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**Abstract:** This paper describes the use of gold films that contain underpotentially deposited (upd) metal layers of copper or silver as substrates in the generation of self-assembled monolayers (SAMs). The assembly of alkanethiols to form SAMs is compatible with the presence of the upd layer and forms a system that contains an interlayer of the upd metal that is between the gold substrate and the adsorbed organic monolayer. The assembly on these substrates can accommodate both polar and nonpolar tail groups, and the resulting SAMs span the range of wettabilities ( $\theta_{\text{a}}(\text{H}_2\text{O}) = <15^\circ$  to  $113^\circ$ ). The SAMs on the upd substrates have highly organized structures that are distinct from those that form on the parent bulk metal surfaces. In addition, the upd metal has a more noble redox potential than the corresponding bulk metal and allows an expanded potential window in cyclic voltammetry. For example, ferrocene-terminated alkanethiols—despite having redox potentials that are positive of bulk silver—can be assembled onto silver upd substrates and form stable electroactive SAMs. The presence of the upd layer improves the stability of alkanethiolate monolayers against both desorption at elevated temperatures and molecular exchange within thiol-containing solutions.

## Introduction

Advances in materials chemistry rely on the ability to tailor the structure and composition within the bulk and at interfaces at the nanoscopic level.<sup>1</sup> Indeed, the ability to generate systems with higher levels of organization and structural complexity is a focus of many areas of current research. Supramolecular assemblies,<sup>2</sup> self-assembled structures,<sup>3</sup> heteroelement composites,<sup>4</sup> and bimetallic catalysts<sup>5</sup> are examples where molecular (or atomic-scale) engineering has produced species with novel architectures, synthetic flexibility, and tailored properties.

At metal surfaces, two strategies—the formation of self-assembled monolayers (SAMs)<sup>6</sup> and the process of underpotential deposition (upd)<sup>7</sup>—have provided useful means for

functionalizing the surface and tailoring its properties. These methods functionalize the surface with a highly organized single layer of material, where the composition of the layer is readily controlled. The difference between these methods is that the self-assembly method produces a thin organic layer on the metal surface and the upd procedure coats the metal surface with a one-atom-thick layer of a dissimilar metal.

Self-assembled monolayers (SAMs) form by the spontaneous adsorption of organic molecules onto a metal or metal oxide surface.<sup>6</sup> Various systems are presently available, with the assembly of *n*-alkanethiols onto copper,<sup>8,9</sup> silver,<sup>8–12</sup> and (particularly) gold<sup>6,8,13</sup> being the most investigated. On these metals, the thiols form a densely packed, oriented monolayer and the hydrocarbon chains pack in a trans-zigzag-extended structure.<sup>8,10</sup> The assemblies are the product of strong metal–sulfur interactions that are also responsible for the robust nature of the SAM in liquid and vacuum environments. A notable feature of these assemblies is their ability to accommodate a wide range of polar and nonpolar functionalities in the tail group of the adsorbate.<sup>9,13</sup> This flexibility in their synthesis has allowed the formation of tailored organic surfaces for studies of wetting,<sup>9,12,14</sup> adhesion,<sup>15</sup> biocompatibility,<sup>16</sup> friction,<sup>17</sup> and interfacial electron transfer.<sup>18</sup>

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The SAMs on copper, silver, and gold surfaces differ in structure: on gold, the axis of the hydrocarbon chain tilts  $\sim 30^\circ$  from the surface normal ( $\sim 5.0\text{-}\text{\AA}$  spacing),<sup>6,8</sup> whereas it tilts  $\sim 13^\circ$  from the surface normal on silver and copper ( $\sim 4.7\text{-}\text{\AA}$  spacing).<sup>6,8,10,11</sup> These differences in adsorbate packing density are a result of the bonding characteristics between the metal surface and the ligating sulfur atoms, particularly their tendency to occupy specific sites on the metal surface.<sup>6</sup> Efforts for controlling the molecular packing density within SAMs have relied on the use of adsorbates that contain bulky substituents,<sup>19</sup> rigid architectures,<sup>20</sup> or multiple ligating functionalities<sup>21</sup> and often require lengthy syntheses. The development of methods that can manipulate the surface chemistry of the substrate—particularly at the sub-monolayer level—may offer a more flexible, synthetically simpler strategy for controlling the packing density, structure, and properties of these adsorbed films.

Underpotential deposition is an electrochemical process whereby a single metal adlayer is electroplated onto a dissimilar metal.<sup>7,23–26</sup> The process is driven by the formation of substrate–adatom interactions that are stronger than the adatom–adatom interactions that form during bulk electrodeposition. This

difference in interaction allows easy preparation of adlayers with coverages no greater than a monolayer. Many substrate/adlayer combinations are known, and they have been characterized by a wide range of techniques, including surface scattering and diffraction methods (LEED, SEXAFS, etc.),<sup>23,24</sup> Auger and X-ray photoelectron spectroscopies,<sup>23</sup> and more recently various scanning probe microscopies.<sup>7,25</sup> In many cases, the upd layer forms a highly ordered, epitaxial layer on the underlying substrate and the coverage of the upd layer (and its structure) is dictated by factors that limit access of the predeposited adlayer metal ions to the electrode surface.<sup>27</sup> The flexibility and control afforded by the upd technique allows access to a broad hierarchy of well-defined surface architectures. Of the various substrates that can be used for underpotential deposition, gold has been the most popular due to its general inertness, its resistance toward chemical oxidation, and the large number of elements that can form a upd layer on it.<sup>28</sup>

Self-assembled monolayers and underpotentially deposited layers share the common feature that they can form highly organized adlayers on the surface of an underlying material. To date, these highly structured monolayer-based systems, despite their functional similarities and analytical reliance on a common set of surface techniques (XPS, Auger, LEED, STM, AFM, etc.), have remained separate areas of research. Our work aims to determine whether the synthetic flexibility afforded by these two methods could be used together to generate a new class of self-assembled structures with possibly superior properties and attributes. In this paper, we have focused our work on polycrystalline gold films as these substrates are widely used in the SAMs area and have direct analogs in device fabrication.<sup>29</sup> We have also selected copper and silver for the upd layers as these systems have been widely investigated as upd layers on both crystalline<sup>7,25</sup> and polycrystalline<sup>7,26,30</sup> gold substrates and a wide variety of alkanethiols are known to form SAMs on surfaces of these bulk metals.<sup>9</sup> The result of our work is that underpotentially deposited films of copper and silver on polycrystalline gold substrates provide a new type of substrate for the self-assembly of adsorbed alkanethiolate monolayers. These substrates offer the high degree of synthetic flexibility associated with the assembly of thiols onto gold surfaces while providing a higher level of structural hierarchy to the assemblage and the ability to produce supported SAMs with properties that are superior to those formed on gold. The strategies employed in this paper should be generalizable for many of the metals that can be underpotentially deposited on gold<sup>7,28</sup> and other substrates.<sup>7</sup>

## Results and Discussion

**Au/upd/SAM Formation.** In a two-step procedure, we functionalized the surface of a polycrystalline gold substrate first with a submonolayer amount of copper or silver (upd) and then with a self-assembled organic monolayer to form the structures schematically illustrated in Figure 1;<sup>29,30</sup> all manipulations of the gold substrate were conducted in the laboratory

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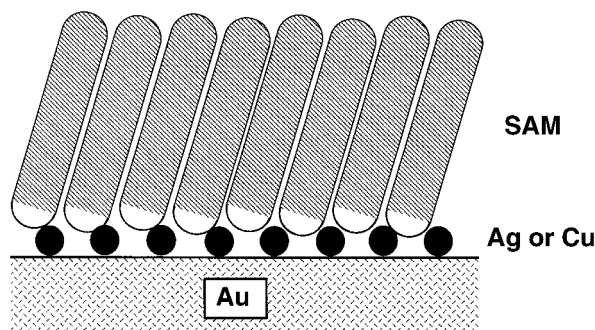
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(27) The structure and coverage of the upd layer can be selected by choice of counterion with bulkier anions yielding upd layers that have lower coverages and more open structures.<sup>7,25</sup>

(28) The following metals are known to form upd layers on gold: Ag, Bi, Cu, Hg, Li, Pb, Pd, Sb, Sn, Tl, and Zn (ref 7a and the following: Gofer, Y.; Barbour, R.; Luo, Y.; Tryk, D.; Scherson, D. A.; Jayne, J.; Chottiner, G. *J. Phys. Chem.* **1995**, *99*, 11739–11741).

(29) Evaporated films of copper, silver, and gold are predominately (111) in texture.<sup>9</sup>

(30) In this study, we focus on upd films of copper and silver prepared from H<sub>2</sub>SO<sub>4</sub> solutions. Under these conditions at medium coverages, copper forms a ( $\sqrt{3} \times \sqrt{3}$ )R30° overlayer on Au(111) while silver forms an expanded 3 × 3 overlayer.<sup>25a,b</sup>



**Figure 1.** Schematic illustration of a gold/silver or copper (upd)/SAM assembly.

**Table 1.** XPS Binding Energies and Coverages for Ag and Cu Adlayers on Au

sample	Ag		Cu	
	binding energy (eV) <sup>a</sup>	coverage <sup>c</sup>	binding energy (eV) <sup>a</sup>	coverage <sup>c</sup>
bulk metal	368.0		932.0	
Au/upd metal	367.4 <sup>b</sup>	0.64	931.3 <sup>b</sup>	0.92
Au/upd metal + C <sub>18</sub> H <sub>37</sub> SH	367.8 <sup>b</sup>	0.59	931.8 <sup>b</sup>	0.90

<sup>a</sup> Binding energies of Ag (3d<sub>5/2</sub>) and Cu(2p<sub>3/2</sub>) peaks. <sup>b</sup> Binding energies referenced to Au(4f<sub>7/2</sub>) at 84.0 eV. <sup>c</sup> Coverages are ±10%.

ambient. Evaporated films of gold supported on silicon supports were functionalized with a layer of copper or silver atoms in a sulfuric acid solution (aqueous) of copper or silver sulfate, respectively. The gold substrates were first electrochemically cycled in these solutions as both a cleaning procedure and a means to provide information about the upd process on the substrate. During the second cathodic scan of this cycle, the potential was held just negative of the upd peak. The resulting derivatized gold substrates were emersed from the electrochemical cell under potential control, rinsed with ethanol, blown dry in a stream of nitrogen, and transferred through air to a 1 mM solution of the alkanethiol. Upon removal from the adsorbate solution, the slides were rinsed with fresh solvent and blown dry in a stream of nitrogen prior to characterization. We observed that adsorption times between 5 min and 1 day in the thiol-containing solutions produced SAMs with similar properties; we typically used an adsorption time of 40 min.

**X-ray Photoelectron Spectroscopy (XPS).** Table 1 displays the results from X-ray photoelectron spectroscopy (XPS) for the upd layers of silver and copper deposited onto the polycrystalline gold films and after their exposure to octadecanethiol. The untreated upd adlayers exhibit binding energies that are lower than those for the corresponding bulk metals due to their electronic equilibration with the underlying gold substrate.<sup>31</sup> The coverages of the copper and silver adlayers on the gold surface were sub-monolayer, based on coulometric<sup>32</sup> and XPS results, and exhibited good reproducibility across independent preparations. Upon assembly of the alkanethiol, XPS revealed that the copper and silver upd layers survive the assembly of the organic layer. The coverages of the upd layers exhibited little (or no) change upon adsorption of the thiol (Table 1), and we observed only slight decreases in coverage (<10%) during continued exposure to the thiol solution (5 days). These observations are in contrast with reports that the assembly of

alkanethiols onto gold occurs with etching of the metal substrate.<sup>33</sup> The lack of change in the coverage of the upd layer (as derived from the relative XPS intensities of gold and copper or silver—see eq 1) during the assembly of the SAM suggests that the upd layers are not readily displaced by the thiol treatment, they remain at the gold/sulfur interface, and the upd metals do not diffuse into the gold substrate under our experimental conditions.

Upon adsorption of the thiol onto the upd substrates, the primary peaks of the adlayer elements shift to higher binding energies (Table 1), and the S(2p<sub>3/2</sub>) peak occurs at 162 eV indicating the presence of an adsorbed thiolate;<sup>6,8</sup> the binding energy data suggest that the adsorption of the thiol involves an oxidative-addition process at the upd metal surface. Such mechanisms have been suggested for the assembly of thiols onto copper, silver, and gold surfaces;<sup>6</sup> however, the presence of the oxidized metal species produced by this process could not be verified for these systems as its signals could not be distinguished from those due to the bulk metal. The monolayer-level coverages of the upd metals allow direct observation of these surface-level redox changes to the metals.

The XPS spectra for the Au/Ag(upd)/SAM samples exhibited no signals due to oxygen. As the unfunctionalized Au/Ag(upd) substrate was exposed to air prior to adsorption of the thiol, the absence of oxygen signals suggests that the Au/Ag(upd) substrate is not prone to oxidation in air—the redox potential of the Ag(upd) layer is ~520 mV positive of Ag<sup>+0</sup>—or that the thiol reduces any oxidized species that do form. On the Au/Cu(upd) substrate, we regularly detected signals due to oxygen by XPS as well as trace signals in the Cu(2p) spectral region due to Cu(II) species.<sup>8,9</sup> The Au/Cu(upd) substrate is more prone to oxidation than the Au/Ag(upd) substrate; however, the properties of the resulting Au/Cu(upd)/SAMs were only moderately affected by the oxidation (noted by slightly larger hystereses in wetting, vide infra). The quality of the SAMs formed on the Au/Cu(upd) substrate formed in air were almost as good as those for SAMs formed on evaporated films of copper that were handled under anaerobic conditions<sup>8</sup> and superior to those for copper films handled in air.<sup>34</sup> In this latter case, the assembly produces poorly organized multilayers or low-quality thin films.<sup>34</sup> Although the redox potential of the Au/Cu(upd) substrate is only ~150 mV positive of Cu<sup>+0</sup>, the superior properties of this substrate in air to those of bulk copper probably reflect that oxidation of this substrate is limited to a maximum of one layer of copper.

**Ellipsometry and Wetting Measurements.** The organic films formed from the assembly of *n*-alkanethiols onto copper and silver upd substrates exhibited properties similar to those produced on gold. For example, films formed on the copper and silver upd substrates and on gold with use of C<sub>18</sub>H<sub>37</sub>SH had similar ellipsometric thicknesses (23 ± 3, 23 ± 2, and 21 ± 3 Å, respectively) and wettabilities (Table 2). The thickness of the SAM on the upd substrates could be varied by choice of adsorbate (Figure 2). The slope of the line in Figure 2 for silver upd samples derivatized with a series of *n*-alkanethiols is 1.4 Å/CH<sub>2</sub> and is comparable to the value for alkanethiols assembled onto bulk films of gold<sup>13</sup> and silver.<sup>10a</sup> We obtained data (not shown) with similar levels of reproducibility using copper upd substrates that also gave a slope of 1.4 Å/CH<sub>2</sub>. The ellipsometric data confirm that the alkanethiols form monolayer films on the silver and copper upd substrates.

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(32) Coverages determined by averaging the cathodic and anodic charges for the upd peaks are 0.41 ± 0.05 for silver upd and 0.45 ± 0.05 for copper upd on gold. Coulometric measurements frequently underestimate surface coverage.<sup>25b</sup>

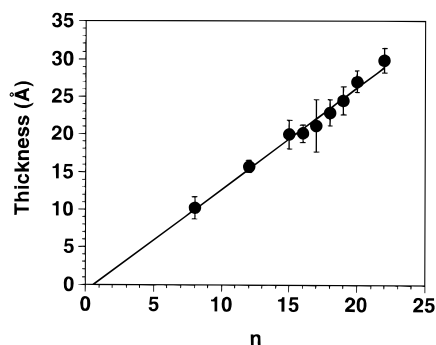
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**Table 2.** Static Wetting Properties of Water and Hexadecane on Films Formed on Gold and upd Substrates

adsorbate	contact angles (advancing, receding; in deg) <sup>a</sup>					
	Au		Au/Ag(upd)		Au/Cu(upd)	
	H <sub>2</sub> O	HD	H <sub>2</sub> O	HD	H <sub>2</sub> O	HD
HS(CH <sub>2</sub> ) <sub>11</sub> OCH <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	109, 102	69, 63	111, 104	71, 66	110, 103	73, 66
HS(CH <sub>2</sub> ) <sub>17</sub> CH <sub>3</sub>	111, 102	46, 41	113, 103	48, 42	112, 98	45, 35
HS(CH <sub>2</sub> ) <sub>11</sub> OCH <sub>3</sub>	81, 70	30, 20	80, 70	28, 18	81, 71	33, 22
HS(CH <sub>2</sub> ) <sub>11</sub> OH	15, —	<5, —	17, —	<5, —	20, —	<5, —
HS(CH <sub>2</sub> ) <sub>10</sub> COOH	<10, —	<5, —	<10, —	<5, —	<10, —	<5, —

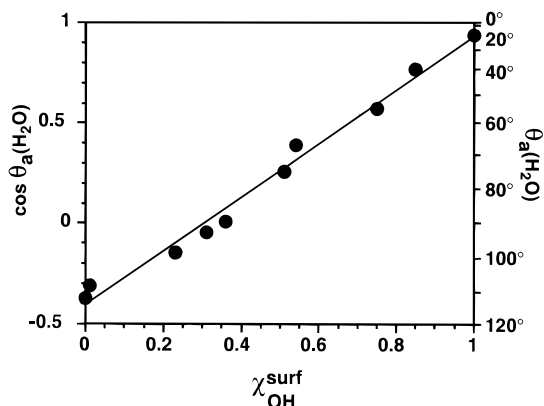
<sup>a</sup> HD = hexadecane. A dash (—) indicates a receding angle for a contacting liquid that could not be removed from the surface. For these systems,  $\theta_r = 0^\circ$ .



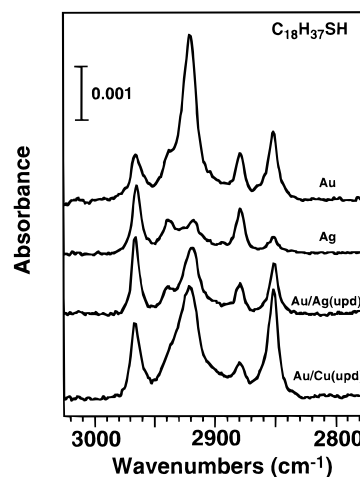
**Figure 2.** Ellipsometric thickness for SAMs of *n*-alkanethiols (CH<sub>3</sub>(CH<sub>2</sub>)<sub>*n*-1</sub>SH) adsorbed onto evaporated gold films containing an underpotentially deposited layer of silver. The line is a least-squares fit to the data and has a slope of 1.4 Å/CH<sub>2</sub>. Thickness were calculated by using a refractive index of 1.46.

Table 2 displays the wetting properties of SAMs prepared from alkanethiols that terminate in either polar or nonpolar tail groups. The SAMs on the upd substrates exhibited wettabilities by water and hexadecane that were similar to those for SAMs formed from the same adsorbates on gold surfaces. This similarity indicated that the tail groups of the adsorbates were localized at the SAM/air(liquid) interface in a densely packed state. The wetting results indicate that the assembly on the silver and copper upd substrates can accommodate both polar and nonpolar tail groups in the adsorbate and suggest that this system may have the synthetic flexibility associated with the thiols on the gold system. Contact angle hystereses were comparable on the silver upd substrates and gold and slightly greater for SAMs on the copper upd substrates. The greater levels of hystereses on the copper upd substrates might reflect a greater sensitivity of the bare copper upd substrates to oxidation in air as less hysteresis was observed when the transfer time between the electrochemical cell and the adsorption solution was minimized. We note that the level of hysteresis on the copper upd substrate is much lower than for assembly of these adsorbates onto freshly evaporated copper films that had been similarly exposed to air prior to monolayer assembly.<sup>34</sup>

The ability to form high- and low-energy organic surfaces on these substrates by selection of the tail group allows the generation of organic surfaces that span the range of wettability. Using 1 mM mixtures of HS(CH<sub>2</sub>)<sub>11</sub>OH and HS(CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub>, we prepared mixed SAMs on Au/Ag(upd) substrates that varied in surface composition between those for the pure SAMs. Figure 3 displays the wetting properties of the mixed SAMs and demonstrates the ability to tailor their composition and properties. The surface compositions of the mixed SAMs were determined from XPS by comparing the intensity of the O(1s) peak for the hydroxyl group to its intensity in a SAM derived from HS(CH<sub>2</sub>)<sub>11</sub>OH. In Figure 3, the relationship between wettability and surface composition on the upd substrates is the



**Figure 3.** Advancing contact angles of water on mixed monolayers prepared from binary mixtures of CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>SH and HO(CH<sub>2</sub>)<sub>11</sub>SH (1 mM total concentration in ethanol). The *x*-axis represents the mole fraction of the polar component on the surface, as determined by XPS.



**Figure 4.** Grazing incidence polarized infrared spectra for SAMs of octadecanethiol adsorbed onto evaporated gold and silver surfaces and onto evaporated gold films that contain an underpotentially deposited layer of silver or copper. The approximate positions of the methylene modes are 2918 (asym) and 2850 (sym) cm<sup>-1</sup>, and those for the methyl modes are 2964 (asym), 2935 (sym, Fermi resonance), and 2879 (sym) cm<sup>-1</sup>. The spectra have been offset vertically for clarity.

same as that observed with use of mixed SAMs of these adsorbates on evaporated films of copper, silver, and gold.<sup>9</sup>

**Reflectance Infrared Spectroscopy.** Figure 4 displays reflectance infrared spectra for SAMs derived from octadecanethiol on Au, Ag, Au/Ag(upd), and Au/Cu(upd) substrates. In the upper three spectra of Figure 4, the asymmetric methylene peaks appeared at  $\sim 2918$  cm<sup>-1</sup>, indicative of a primarily trans-zigzag extended hydrocarbon chain containing few gauche conformers.<sup>35</sup> The spectra demonstrate the ability to form highly crystalline monolayers by the assembly of alkanethiols onto

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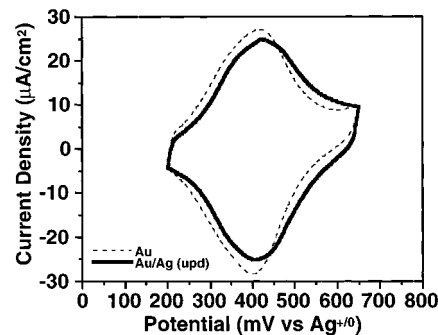
these three substrates. For the various substrates, the intensities of the methylene peaks are greatest for SAMs on gold, the least intense for SAMs on silver, and intermediate for the upd substrates. The differences in intensity reflect different canted orientations for the polymethylene chains on these surfaces, with the tilts of the chains on upd substrates of silver and copper being intermediate ( $\sim 20^\circ$  from the surface normal) between those found for alkanethiolate SAMs on gold ( $\sim 30^\circ$ ), silver ( $\sim 13^\circ$ ), and copper ( $\sim 13^\circ$ ).<sup>6,8,10,11</sup> The tilt of the hydrocarbon chain in SAMs is a result of the packing arrangement of the adsorbates on the metal surface, and the presence of the upd layer must alter the structural arrangement of the adsorbate on the upd surface from those on the parent metal surfaces.

On Au/Ag(upd),  $\nu_a(\text{CH}_2)$  appears at  $2918\text{ cm}^{-1}$ , suggesting that the hydrocarbon chains in the SAM are primarily trans-zigzag extended and contain few gauche conformers. The spectrum for the adsorbed layer on the Au/Ag(upd) sample exhibits a lower dichroic ratio for the methylene absorption modes ( $\nu_a(\text{CH}_2)/\nu_s(\text{CH}_2)$ ) and a less intense symmetric methyl peak than the spectra for films on gold and silver. These two features in the spectrum provide evidence that the SAM on the Au/Ag(upd) substrate has a structure that is not a composite of the structures that form on gold and silver (as might form if the surface were composed of islands of gold and silver), but instead has a structure that is distinct from those that form on the corresponding bulk metals.<sup>36</sup>

The SAMs formed on Au/Cu(upd) were less well defined, with  $\nu_a(\text{CH}_2)$  appearing at  $2921\text{ cm}^{-1}$ . This position suggests that the SAMs produced under our assembly conditions are structurally better ordered than SAMs formed on air-exposed copper, but include a higher degree of gauche defects within the SAM than on the Au/Ag(upd) substrate. As with the SAM on Au/Ag(upd), the  $\nu_a(\text{CH}_2)$  peak had intermediate intensity to those for the octadecanethiolate SAMs on gold and copper. The greatest difference between the spectrum for the Au/Cu(upd) substrate and the other metals was that the dichroic ratio for the methylene absorption modes ( $\nu_a(\text{CH}_2)/\nu_s(\text{CH}_2)$ ) was  $\sim 1$  (vs 1.5 on Au/Ag(upd) and 2 to 2.5 on copper, silver, and gold). These results are indicative of a different structure that forms on the Au/Cu(upd) surface.

In general, the use of upd layers may provide a means for controlling and manipulating the structure of SAMs. The relationships between the monolayer structure—crystallinity, canted orientation, chain twist, and packing density—and the composition and coverage of the upd layer in these two systems are presently being investigated and will be reported shortly.

**Electroactive SAMs.** As the redox potential for the Au/Ag(upd) substrate is  $\sim 520\text{ mV}$  positive of  $\text{Ag}^{+/0}$ , this substrate offers useful applications for the formation of electroactive SAMs. Figure 5 displays cyclic voltammograms for SAMs prepared by chemisorption of  $\text{FcCO}(\text{CH}_2)_{10}\text{SH}$  (Fc = ferrocenyl) onto Au and Au/Ag(upd) substrates. The curves display the expected peaks corresponding to the oxidation of ferrocene and the reduction of ferrocenium, with the broadness of the peaks being comparable to that observed by others for SAMs of  $\text{FcCO}_2(\text{CH}_2)_{11}\text{SH}$  and related adsorbates on gold.<sup>37,38</sup> The durability of the substrates modified with  $\text{FcCO}(\text{CH}_2)_{10}\text{SH}$  is sufficiently great that routine electrochemical characterization is possible. The coverages obtained by coulometry for the



**Figure 5.** Cyclic voltammograms in 0.1 M  $\text{HClO}_4$  of monolayers prepared from  $\text{FcCO}(\text{CH}_2)_{10}\text{SH}$  (1 mM, ethanol). Scan rate = 100 mV/s.

ferrocenyl species were  $4.3$  and  $4.5 \times 10^{-10}$  ( $\pm 10\%$ )  $\text{mol}/\text{cm}^2$  on Ag(upd) and gold, respectively, and are comparable to those of prior studies for similar ferrocenyl-based adsorbates.<sup>37,38</sup> It is important to note that voltammetry for this monolayer cannot be performed on a bulk silver electrode at room temperature as the ferrocene<sup>+0</sup> redox potential for this adsorbate is  $\sim 400\text{ mV}$  positive of that for silver oxidation and electrochemical cycling results in the anodization of silver and loss of the SAM.<sup>39</sup> XPS spectra for the SAM on the Au/Ag(upd) substrate both before and after electrochemical cycling displayed signals for silver and demonstrated that the Ag upd layer survives the assembly of the monolayer and the redox cycling of the surface-attached ferrocene couple. By depositing the silver layer on gold underpotentially, we have increased the  $\text{Ag}^{+/0}$  redox potential on this modified electrode by  $\sim 520\text{ mV}$  over that for a bulk silver electrode, and thus, we are able to observe ferrocene redox behavior.

In Figure 5, the potential of the SAM-modified Au/Ag(upd) electrode was ramped to  $650\text{ mV}$ —a value that is positive of the  $\text{Ag}^{+/0}$  redox potential for silver upd on gold; however, silver oxidation was not observed in the cyclic voltammogram, and XPS results indicated that the silver coverage on the SAM-coated electrode did not change after being cycled to  $650\text{ mV}$ . We attribute this added stability of the upd layer to the presence of the SAM. Chidsey et al. have shown that an adsorbed organic monolayer can reduce electron transfer rates and thus lead to the requirement of more positive potentials to drive an oxidation process.<sup>40</sup> The cyclic voltammograms of a nonelectroactive monolayer (not shown) prepared from  $\text{C}_{16}\text{H}_{33}\text{SH}$  on Au/Ag(upd) showed no evidence of silver oxidation until the potential reached  $\sim +800\text{ mV}$ .

**Effect on Stability.** The incorporation of an atomic interlayer at the gold/sulfur interface can alter the level of interaction between the organic monolayer and the metal support and may provide a means to stabilize the adsorbed monolayer.<sup>41</sup> Figure 6 displays the effect of a Ag upd layer to stabilize a SAM against its desorption into a branched hydrocarbon solvent at  $84^\circ\text{C}$ . Under these conditions, the SAM on gold desorbs from the surface with a half-life of about 3 h. The SAM on the Au/Ag(upd) surface exhibits a greater stability to these conditions. We attribute the enhanced stability of the Au/Ag(upd) substrate to a stronger interaction between S and Ag versus that of S and Au.<sup>41</sup> With longer exposure to these conditions or to higher temperatures, the SAM could eventually be completely desorbed

(36) The spectra for the Au/Ag(upd) and Au/Cu(upd) samples cannot be obtained by summing a weighted average of the spectra taken on the bulk metals.

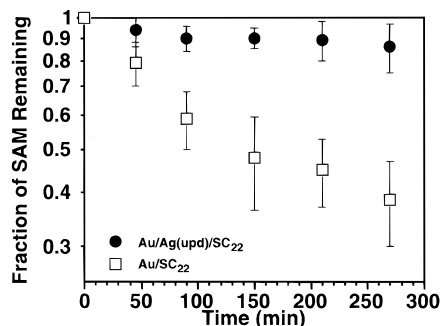
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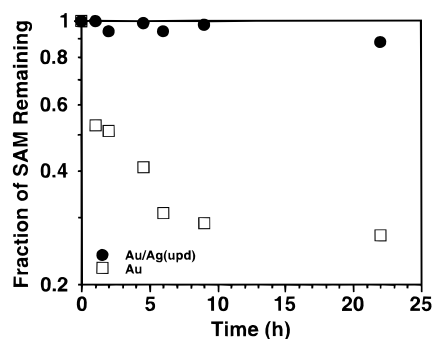
(39) The redox behavior of ferrocene has been observed at a silver electrode at 170 K and below where the rate of electron transfer to ferrocene becomes faster than the anodization of silver (Curtin, L. S.; Peck, S. R.; Tender, L. M.; Murray, R. W.; Rowe, G. K.; Creager, S. E. *Anal. Chem.* **1993**, *65*, 386–392).

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**Figure 6.** Thermal desorption of SAMs of *n*-C<sub>22</sub>H<sub>45</sub>SH on Au and Au/Ag(upd) surfaces at 84 °C into decahydronaphthalene (DHN). The surface coverages of the SAMs were obtained *ex situ* by ellipsometry and are plotted normalized to the thickness of an initially formed SAM on the respective substrate.



**Figure 7.** Time dependence for the surface coverage of SAMs derived from FcCO(CH<sub>2</sub>)<sub>10</sub>SH on Au and Au/Ag(upd) electrodes upon exposure to a 1 mM ethanol solution of *n*-C<sub>12</sub>H<sub>25</sub>SH. The data were normalized to the coverages of an initially formed SAM on the respective substrate.

from the upd-modified surface. Examination of the surface by XPS showed that the upd layer of silver was still present on the gold substrates at roughly 80% ( $\pm 10\%$ ) of its initial coverage. This observation suggests that the monolayer desorbs by cleavage of the sulfur/metal interaction rather than loss of the SAM as silver thiolates.

As the gold–sulfur interaction is not a fully covalent one, SAMs undergo exchange when contacted with alkanethiol solutions.<sup>37,38,42,43</sup> Figure 7 displays the compositions of ferrocene-terminated SAMs on gold and Au/Ag(upd) that were contacted with a non-electroactive alkanethiol. Under these conditions, the gold substrate exhibits much faster loss of the ferrocenyl species than does the Au/Ag(upd) substrate. Whereas the gold substrate loses  $\sim 70\%$  of its ferrocene coverage after 9 h of exposure to a 1 mM ethanolic solution of C<sub>12</sub>SH, the Au/Ag(upd) substrate exhibited no change (10%) from its initial condition after 22 h, within experimental error. Recent efforts to produce patterned SAMs—notably with use of microcontact printing<sup>44</sup>—rely on a physical stamp to localize thiols onto gold and use a subsequent step to adsorb a second thiol. During this second step, exchange processes can influence the integrity of the initially stamped regions as the SAMs are placed in direct contact with the solution containing the second thiol. As the number of patterning steps increases, exchange processes become a more important factor for disrupting the homogeneous nature of the patterned regions. The use of a upd coating on the gold—particularly the use of silver based on the stability of the Au/Ag(upd) substrate against oxidation—would provide

superior control over the homogeneity of the patterned SAMs that rely on sequential adsorption steps.

## Conclusions

We have developed a new class of self-assembled monolayers that relies on the use of underpotential deposition techniques for manipulating the surface chemistry of metal substrates. The methods are straightforward and flexible in their synthesis and can provide an additional strategy for controlling the structures and properties of supported organic assemblies. Both underpotentially deposited layers of copper and silver on gold survive the adsorption of alkanethiols and allow the formation of both hydrophilic and hydrophobic SAMs. The presence of the upd layer yields SAMs that are structurally distinct from those formed on copper, silver, or gold surfaces. Importantly, the presence of the upd layer is compatible with the formation of electroactive SAMs—including those with redox potentials positive of the metal—as the redox properties of the upd layer are less prone to oxidation than in their bulk form. The upd layer can provide additional stability to the SAM, against both its desorption at elevated temperatures and its exchange with thiols in a contacting solution.

## Experimental Section

**Materials.** Gold shot (99.99%) and chromium-coated tungsten filaments were obtained from Americana Precious Metals Co. (East Rutherford, NJ) and R. D. Mathis (Long Beach, CA), respectively. Silicon(100) wafers (Silicon Sense, Nashua, NH) were rinsed with ethanol and dried with nitrogen prior to use in the evaporator. Octane, dodecane, and octadecane thiols (Aldrich) were distilled under vacuum prior to use. All other *n*-alkanethiols were prepared from the corresponding alkyl bromides (Aldrich) by nucleophilic displacement with thioacetate followed by solvolysis in HCl/MeOH. 11-Hydroxyundecanethiol,<sup>13</sup> mercaptoundecanoic acid,<sup>45</sup> 11-(2,2,3,3,3-pentafluoropropoxy)undecanethiol,<sup>9</sup> and octadecanethiol-*d*<sub>37</sub><sup>14c</sup> were prepared according to literature procedures. 11-Methoxyundecanethiol<sup>14f</sup> was a gift from Seok-Won Lee (MIT). 11-Ferrocenylundecanethiol was available from previous studies.<sup>38</sup> Ethanol (95%, Pharmco), isooctane (EM Science), and hexadecane (Aldrich) were used as received. Deionized water was purified with a Millipore-Q system.

**Preparation of Assemblies.** Chromium (100 Å) and gold (1000 Å) were evaporated in sequence at 1.5 and 4 Å/s, respectively, onto 100-mm silicon wafers in a diffusion-pumped chamber with a base pressure of  $8 \times 10^{-7}$  Torr and an operating pressure of  $2 \times 10^{-6}$  Torr. The gold-coated wafers were cut into 1 cm x 3 cm samples and were used for underpotential deposition and/or SAM formation within 3 days of evaporation. Copper and silver were underpotentially deposited onto evaporated gold surfaces in a glass cell with use of a supported gold film as counter electrode, a copper or silver wire as a reference electrode, and a computer-controlled PAR Model 263A potentiostat. The exposed area of the working electrode was either  $\sim 0.8$  cm<sup>2</sup> for samples characterized by XPS, ellipsometry, and wetting or  $\sim 5$  cm<sup>2</sup> for samples characterized by IR. Before deposition, the gold film was electrochemically cycled at 20 mV/s in a 0.1 M H<sub>2</sub>SO<sub>4</sub>(aq) solution of 0.6 mM Ag<sub>2</sub>SO<sub>4</sub> or 1.0 mM CuSO<sub>4</sub>·5H<sub>2</sub>O between 200 and 650 mV vs reference for silver or between 50 and 550 mV vs reference for copper. On the cathodic scan, the potential was held at a value just negative of the upd peak (460 mV for silver and 110 mV for copper). The electrode was emersed under potential control, rinsed with ethanol,<sup>46</sup> blown dry in a stream of N<sub>2</sub>, and transferred rapidly through air to 1 mM isooctane or ethanol solutions of the alkanethiols for 40 min. The resulting SAMs were rinsed with ethanol and blown dry with N<sub>2</sub> prior to characterization.

Mixed monolayers expressing methyl and hydroxyl termini were formed by immersing silver upd substrates into ethanolic solutions

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(46) By XPS, we found that an ethanol rinse removed residual electrolyte from the emersed electrode but did not change the coverage of the upd layer.

containing mixtures of dodecanethiol and 11-hydroxyundecanethiol for 40 min. The mole fractions of the two thiols were varied while the total concentration of thiol in solution was held constant at 1 mM. The mole fraction of the hydroxyl-terminated component in the SAM was determined by normalizing the intensity of the O(1s) peak in the XPS spectrum to the peak obtained for a SAM composed solely of the hydroxyl-terminated species.<sup>9</sup> The SAM prepared from dodecanethiol on Au/Ag(upd) exhibited no O(1s) peak.

**Ellipsometry.** The thicknesses of the SAMs were determined by using a Gaertner L116A automatic ellipsometer equipped with a He-Ne laser ( $\lambda = 6328 \text{ \AA}$ ) at an incident angle of  $70^\circ$  and a refractive index for the organic film of 1.46. Samples were rinsed with ethanol and blown dry with  $N_2$  before measurements were taken. Baseline values for upd assemblies were measured on unfunctionalized upd substrates within 2 min after emersion from the electrochemical cell. The reported thicknesses are the average of at least five independent experiments where each sample was characterized by ellipsometry at three different locations on its surface; the averages of three measurements made at each location on the sample were used to calculate thicknesses.

**Wetting Measurements.** Advancing contact angles were measured on static drops of water or hexadecane with a Ramé-Hart manual goniometer equipped with video camera and computer monitor for viewing the drops. Contacting liquids were advanced or retreated ( $1 \mu\text{L/s}$ ) prior to measurement with a Micro-Electrapette syringe (Matrix Technologies, Lowell, MA). The pipet tip remained in the drop during measurement. Both sides of  $\sim 5\text{-}\mu\text{L}$  drops were measured at three different locations on a sample, with the reproducibility across a sample being  $\pm 2^\circ$ .

**X-ray Photoelectron Spectroscopy (XPS).** XPS spectra were obtained with a Surface Science Instruments Model X-100 spectrometer with use of a monochromatized Al K $\alpha$  X-ray source (elliptical spot of  $1.0 \text{ mm} \times 1.7 \text{ mm}$ ) and a concentric hemispherical analyzer (pass energy = 150 eV). The detector angle with respect to the surface parallel was  $35^\circ$ . Peak positions were referenced to Au( $4f_{7/2}$ ) = 84.00 eV, and peaks were fit with 80% Gaussian/20% Lorentzian profiles and a Shirley background. Coverages of the upd adlayer component ( $\phi_{\text{upd}}$ ) were calculated from measured intensities of the adlayer ( $I_{\text{upd}}$ ) and substrate ( $I_{\text{Au}}$ ) peaks with use of eq 1 (see Supporting Information for derivation):<sup>47</sup>

$$\phi_{\text{upd}} = \left\{ \left( \frac{I_{\text{Au}}}{I_{\text{upd}}} \right) \left( \frac{I_{\text{upd}}^0}{I_{\text{Au}}^0} \right) C_{\text{SAM}} \left[ 1 - \exp \left( \frac{-a_{\text{upd}}}{\lambda_{\text{upd(KE}_{\text{upd}})} \cos \Theta} \right) \right] + \left[ 1 - \exp \left( \frac{-a_{\text{upd}}}{\lambda_{\text{upd(KE}_{\text{Au}})} \cos \Theta} \right) \right] \right\}^{-1} \quad (1)$$

where  $a_{\text{upd}}$  is the diameter of the adatom (2.56 and 2.89  $\text{\AA}$  for copper and silver, respectively);  $\lambda_{\text{upd(KE}_i)}$  is the inelastic mean free path through the upd adlayer for electrons of kinetic energy (KE) from the upd layer or the gold substrate ( $\lambda_{\text{Cu}}$  for Au( $4f_{7/2}$ ) and Cu( $2p_{3/2}$ ) photoelectrons are 21 and 11  $\text{\AA}$ , respectively;  $\lambda_{\text{Ag}}$  for Au( $4f_{7/2}$ ) and Ag( $3d_{5/2}$ ) photoelectrons are 18 and 15  $\text{\AA}$ , respectively),<sup>48</sup>  $\Theta$  is the angle of the detector to the surface normal, and  $I_{\text{upd}}^0$  and  $I_{\text{Au}}^0$  are sensitivity factors for the adlayer atoms and substrate atoms, respectively. Equation 2 gives the attenuation of the adlayer and substrate electrons by the SAM or adventitious carbonaceous material  $C_{\text{SAM}}$

$$C_{\text{SAM}} = \frac{\exp \left( \frac{-d_{\text{SAM}}}{\lambda_{\text{SAM(KE}_{\text{upd}})} \cos \Theta} \right)}{\exp \left( \frac{-d_{\text{SAM}}}{\lambda_{\text{SAM(KE}_{\text{Au}})} \cos \Theta} \right)} \quad (2)$$

where  $\lambda_{\text{SAM(KE}_i)}$  is the attenuation length through the SAM for electrons of kinetic energy (KE) from the upd layer or the gold substrate ( $\lambda_{\text{SAM}}$  for Au( $4f_{7/2}$ ), Ag( $3d_{5/2}$ ), and Cu( $2p_{3/2}$ ) photoelectrons are 40, 34, and

21  $\text{\AA}$ , respectively),<sup>49</sup> and  $d_{\text{SAM}}$  is the thickness of the hydrocarbon layer for the SAM ( $d_{\text{SAM}} = nd \cos \alpha$  where  $n$  is the number of methylene groups in the adsorbate,  $d$  is the incremental contribution of a methylene group to the length of an  $n$ -alkyl chain ( $d = 1.27 \text{ \AA}$ ),<sup>50</sup> and  $\alpha$  is the angle the hydrocarbon chain is canted relative to the surface normal as determined by IR (on gold,  $\alpha \approx 30^\circ$ , on the upd systems,  $\alpha \approx 20^\circ$ ). For unfunctionalized upd samples, the thickness of adventitious carbonaceous material on the surface was quantified by comparing the attenuated intensity of the Au( $4f_{7/2}$ ) peaks for these samples with that for a substrate coated with octanethiol. This treatment assumed that the attenuation lengths through this carbonaceous material and the SAM are similar.

**Reflectance Infrared Spectroscopy.** IR spectra were obtained in a single reflection mode with a Bio-Rad FTS 175 infrared spectrometer and Universal Reflectance Attachment. The p-polarized light was incident at  $80^\circ$  from the surface normal. The reflected light was detected with a narrow-band MCT detector cooled with liquid nitrogen. Spectral resolution was  $2 \text{ cm}^{-1}$  after triangular apodization. Spectra were referenced to those of SAMs prepared on the corresponding substrates from octadecanethiol- $d_{37}$ , and 1024 scans of both the sample and the reference were collected to obtain good signal-to-noise ratios. Samples were rinsed with ethanol and blown dry with  $N_2$  prior to characterization.

**Electrochemistry.** Cyclic voltammetry of ferrocene-terminated SAMs was performed in a glass cell with use of a supported gold film as the counter electrode, a silver wire as the reference electrode, and a PAR Model 263A potentiostat. A solution of 0.1 M  $\text{HClO}_4$ , prepared immediately before use with purified water (Millipore), served as the electrolyte. The exposed area of the working electrode was  $\sim 0.4 \text{ cm}^2$ . The potential was cycled between 200 and 650 mV at a scan rate of 100 mV/s. The amount of charge passed between the electrode and the monolayer was determined by averaging the faradaic contributions to the anodic and cathodic peaks.

**Thermal Desorption Experiments.** Docosanethiolate ( $\text{C}_{22}\text{H}_{45}\text{S}^-$ ) SAMs on gold and Au/Ag(upd) were exposed to decahydronaphthalene (DHN) at  $84^\circ\text{C}$  for various lengths of time. Upon removal from DHN, the samples were rinsed with hexane and ethanol, dried in a stream of  $N_2$ , and characterized by ellipsometry. The fraction of the SAM remaining on the surface was determined by ratioing the ellipsometric thickness of the partial SAM to the thickness of the initially prepared SAM.

**Exchange Studies.** Gold and Au/Ag(upd) samples were functionalized with  $\text{FcCO}(\text{CH}_2)_{10}\text{SH}$  (1 mM, ethanol) for at least 12 h. After removal from solution, the samples were rinsed with ethanol and dried in a stream of  $N_2$ . The resulting assemblies were exposed to 1 mM solutions of  $n\text{-C}_{12}\text{H}_{25}\text{SH}$  in ethanol for various periods of time. After removal from solution, the samples were rinsed with ethanol, dried in a stream of  $N_2$ , and characterized by cyclic voltammetry. The coverage of the ferrocene-terminated SAM was determined by ratioing the average integrated charge of the partially exchanged SAM to that of a freshly prepared  $\text{FcCO}(\text{CH}_2)_{10}\text{S}^-$  SAM on the respective substrate.

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**Supporting Information Available:** Details for the derivations of eqs 1 and 2 for the calculation of surface coverage, cyclic voltammograms for polycrystalline gold films in 0.1 M  $\text{H}_2\text{SO}_4$  (aq) in the absence and presence of copper or silver ions, and X-ray photoelectron spectra for Au/Cu(upd) and Au/Ag(upd) substrates functionalized with octanethiol (6 pages). See any current masthead page for ordering and Internet access instructions.

JA962973Y

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