

Self-Assembled Monolayers on Oxidized Metals. 2. Gold Surface Oxidative Pretreatment, Monolayer Properties, and Depression Formation

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Self-assembly (SA) of organic monolayers onto gold surfaces has been known to be influenced by the surface conditions prior to monolayer adsorption. A new procedure is introduced for obtaining clean, reproducible Au surfaces, appropriate for monolayer self-assembly. The two-step procedure involves (i) exposure of the Au surface to UV/ozone (or O₂ plasma) treatment and (ii) immersion in pure ethanol. The organic contaminants present on the (aged) gold surface are oxidized in the first step to volatile products such as carbon dioxide and water, followed by the second step where gold oxide, formed on the Au surface during the UV/ozone treatment, is reduced (to Au) by reaction of the oxidized gold with ethanol (the most frequently used solvent for SA of alkanethiols). It is shown by scanning force microscopy (SFM) measurements that gold oxide which is not reduced prior to monolayer SA is encapsulated by the closely packed alkanethiol monolayer adsorbed onto the gold oxide. This enables convenient imaging of the (otherwise unstable) gold oxide on the surface. The efficiency of the pretreatment procedure is demonstrated by complete removal of an octadecanethiol (C18SH) monolayer (a simulated stubborn contamination) from a gold surface using the above procedure, followed by reconstitution of a similar monolayer. Ellipsometry, contact-angle measurements, and grazing-incidence FTIR spectroscopy show that the removed and the reconstituted C18SH monolayers are indistinguishable. The formation of a high density of small depressions in such pretreated Au surfaces, as well as in aged (unpretreated) Au surfaces, is shown by STM imaging and discussed in light of similar morphologies induced by alkanethiol self-assembly.

Introduction

Properties of gold surfaces have been the subject of considerable work.¹ Hence, the issue of whether a clean gold surface is hydrophilic or hydrophobic has been the focus of considerable controversy in the literature.^{2–4} Although it is widely accepted that clean gold is hydrophilic, Bernet and Zisman² as well as Smith⁴ were able to “wet” the gold surface (advancing contact angle, $\theta_{\text{water}} = 0^\circ$) only after careful and tedious cleaning processes. Notably, Smith cleaned the gold surface and measured the water contact angle in an ultrahigh-vacuum chamber. The reason is that the high surface free energy of gold is reduced by adsorption of organic molecules from the environment; hence, *complete wetting of gold cannot be achieved under ambient conditions*, as derived from the early work of Trapnell⁵ and later of Smith.⁴ Trapnell indicates that the heat of adsorption of C₂H₂ and C₂H₄ on Au is approximately 20 kcal/mol and that that of CO is 8 kcal/mol. By comparison with energies associated with chemisorption of alkanethiols on Au (ca. 40 kcal/mol⁶), one might expect a certain influence of preadsorbed molecules on the self-assembly (SA) process of thiols on Au. Bain et al.⁷ performed XPS measurements on freshly evaporated Au surfaces exposed to laboratory atmosphere

for several minutes. These measurements confirmed the presence of a carbon- and oxygen-containing contaminant layer of approximately 6-Å thick, which explains the water contact angles (advancing) of 30°–70° measured by Bain et al., as well as by our group, on freshly evaporated gold surfaces.

The importance of the cleanliness of the gold surface has been recognized by many groups working in the field of SA monolayers; hence, in most of the published studies a certain procedure of surface pretreatment is used. Yet, one can identify in the literature numerous different procedures for the same purpose. Most of the cleaning procedures involve Au surface oxidation: electrochemical oxidation,⁸ introduction into strong oxidizing solutions,^{9–11} a combination of the two,^{12,13} or exposure to reactive oxygen species formed by either UV irradiation or oxygen plasma.^{14,15} For single-crystal Au surfaces, surface pretreatment is usually carried out in ultrahigh vacuum. The present work concerns oxidative surface treatment of evaporated gold under ambient conditions.

Cleaning surfaces by exposure to UV/ozone has been known¹⁶ and used for Au surface treatment prior to SA.¹⁴ It is also known that gold surfaces oxidize upon exposure

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to ozone.^{15,17,18} Gold oxide is a strong oxidant which is inherently unstable and decomposes spontaneously under ambient conditions, most probably by oxidation of organic air contaminants, to form gold metal. Of special interest here is the fact that gold oxide is reduced by ethanol oxidation.¹⁵ Still, when *n*-alkanethiols are self-assembled from ethanol onto oxidized Au surfaces, the oxide is stabilized upon formation of the alkanethiol monolayer. A layer of oxide is encapsulated under the closely packed alkanethiol monolayer, thus preventing chemical and electrochemical reduction of the oxide. Contact angles (CAs) and ellipsometric parameters of alkanethiol monolayers adsorbed onto Au surfaces were shown to be highly sensitive to the presence of gold oxide under the monolayer.¹⁵ Furthermore, as demonstrated below, the encapsulation allows convenient detection of gold oxide in air by scanning force microscopy (SFM).

We present here a simple, effective and highly reproducible procedure for gold surface preparation for various possible applications. The first step involves exposure of the Au surface to UV/ozone (or O₂ plasma) treatment, effecting oxidative removal of organic contamination as well as oxidation of the Au surface itself. This is followed by immersion in ethanol, whereupon the gold oxide is reduced to metallic Au by reaction with ethanol, which is oxidized to acetaldehyde.¹⁹ The effectiveness of the procedure is tested by SA of octadecanethiol (C18SH) onto various contaminated/treated evaporated Au surfaces. The morphology of treated Au, as well as that of encapsulated gold oxide, is investigated by scanning probe microscopy.

Experimental Section

Materials. Octadecanethiol (C18SH) (Sigma, AR) was purified by recrystallization from ethanol (Merck, AR). Chloroform (Biolab, AR), bicyclohexyl (BCH) (Aldrich, AR), and hexadecane (HD) (Sigma, AR) were passed through a column of activated basic alumina (Alumina B, Akt. 1, ICN). Water was triply distilled. Ethanol (Merck, AR) was used as received. Gases used were argon (99.996%), oxygen (99.5%), and dry purified air.

Sample Preparation. {111} textured gold films were prepared in a cryogenically pumped resistive evaporator. Gold layers (1000 Å, 99.99%) were evaporated from a tungsten boat at 4×10^{-6} Torr at a deposition rate of 1 Å/s onto glass microscope cover slides (unless otherwise specified) and subsequently annealed in air at 250 °C for 180 min. The samples in Figure 5 only were similarly prepared by evaporation of 1000 Å of gold onto freshly cleaved mica and were then annealed in the same way.

UV/Ozone plus Ethanol Cleaning of Gold Surfaces. Gold surfaces were exposed for 10 min to radiation from a low-pressure quartz-mercury vapor lamp, which generates UV emission in the 254- and 185-nm range. The ozone is produced upon absorption of the 185-nm emission by atmospheric oxygen, while the organic moieties are excited and dissociated by the 254-nm radiation. The excited organic molecules react with ozone to form volatile products such as water and carbon dioxide. A UVOCS, Inc. model T10×10/OES/E ultraviolet ozone cleaning system was used. Immediately following the oxidation step the gold-coated samples were immersed in pure ethanol for 20 min with stirring.

Monolayer Self-Assembly. C18SH monolayers were prepared by immersion of the gold sample in a 1 mM C18SH solution in ethanol for 24 h.

Ellipsometry. Measurements were carried out before and immediately after monolayer adsorption. The refractive index used to calculate monolayer thickness was $n_f = 1.5$, $k_f = 0$.²⁰ A Rudolph Research Auto-EL IV ellipsometer with a monochro-

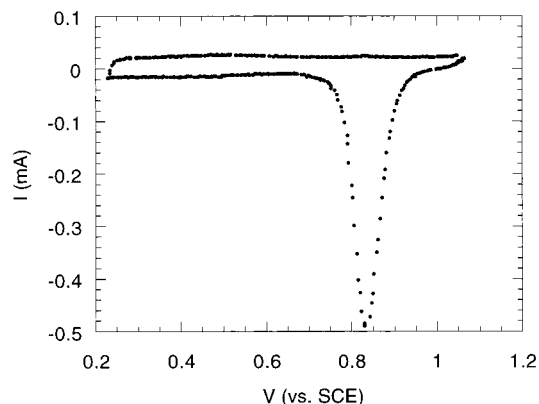


Figure 1. Cyclic voltammetry in 0.1 M H₂SO₄ for a gold-coated glass slide subjected to UV/ozone treatment for 10 min (scan rate, 0.1 V/s; electrode area, 1.75 cm²).

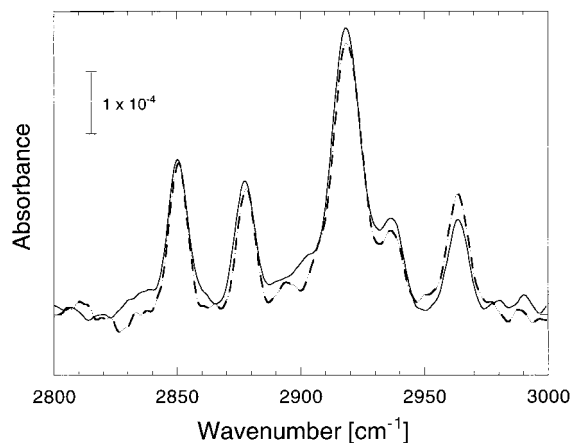


Figure 2. Grazing-incidence FTIR (GI-FTIR) spectra: C18SH monolayer on gold, as in Table 2, row 3 (full line); reconstituted C18SH monolayer on gold, as in Table 2, row 5 (dashed line).

mated tungsten-halogen light source was used, at an angle of incidence $\Phi = 70^\circ$ and a wavelength $\lambda = 632.8$ nm. The same three points were measured on the bare and the monolayer-covered slide. The thickness of the film is calculated from the change in the ellipsometric parameters Δ and Ψ measured before and after film deposition.²¹ In the case of nonabsorbing organic layers such as *n*-alkanethiol monolayers, the most notable change associated with film deposition is in the value of Δ , which decreases as a result of film formation.

Contact-Angle (CA) Measurements. Contact angles (advancing and receding) of H₂O, BCH, and HD were measured immediately (<10 min) after removal of the slides from the adsorption solution. Three measurements at different spots were carried out with each solvent, using a Rame-Hart NRL Model 100 contact-angle goniometer.

Electrochemical Stripping of Gold Oxide. Following exposure of the Au surface to UV/ozone treatment, the gold-coated glass slide was mounted as a working electrode in a three-electrode cell containing 0.1 M H₂SO₄. The gold oxide was reduced by applying a potential scan from +1.025 to +0.200 V (vs SCE) at 0.1 V/s, and the charge was calculated by integration of the oxide reduction peak. A home-computerized electrochemical system was used, comprising a Zenith 486 computer functioning as a wave-form generator as well as a data acquisition system, connected through a A/D + D/A converter to an analog potentiostat (Department of Chemistry, Technion, Haifa). The software for the computerized electrochemical system was written

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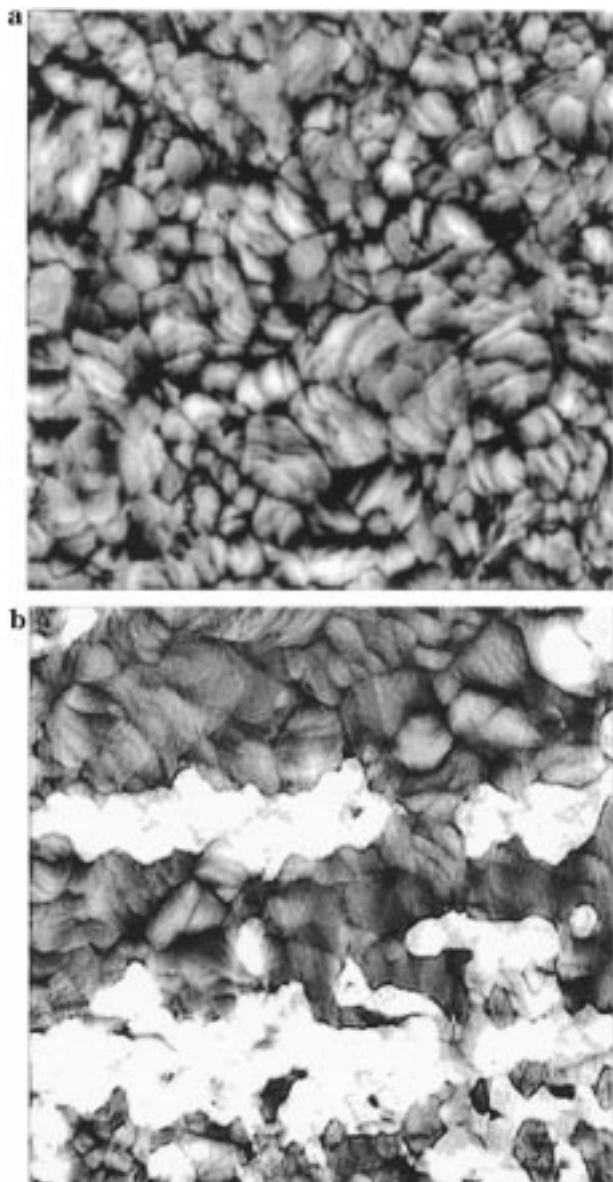


Figure 3. SFM images ($2\text{-}\mu\text{m}$ scan) taken in air in the contact mode: (a) gold surface pretreated by the UV/ozone plus ethanol dip procedure and then coated with a C18SH monolayer (z -range, 29 nm); (b) similar to part a, but skipping the ethanol dip (z -range, 53 nm).

by the Laboratory Computers Unit, Weizmann Institute of Science.

Grazing Incidence Fourier Transform Infrared Spectroscopy (GI-FTIR). The spectra were obtained using a nitrogen-purged Bruker IFS66 FTIR spectrometer operating in the reflection mode with the incident beam at an angle of 80° , focused on the sample with a $f/4.5$ lens. A liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector was used. Spectra were taken at 2-cm^{-1} resolution. The instrument was programmed to run 150 scans with the reference (gold substrate treated by UV/ozone) and then 150 scans with the sample, collecting altogether 10 such cycles.

Scanning Force Microscopy (SFM). SFM imaging was performed at room temperature in air using a Nanoscope IIIa microscope (Digital Instruments, Inc.). The samples were scanned in the contact mode using a commercial Si_3N_4 tip attached to a cantilever with a spring constant of 0.38 N/m. Images were acquired at the minimum force allowed by the feedback sensitivity to minimize possible damage to the sample by the tip.

Scanning Tunneling Microscopy (STM). STM imaging was performed at room temperature in air using a Nanoscope

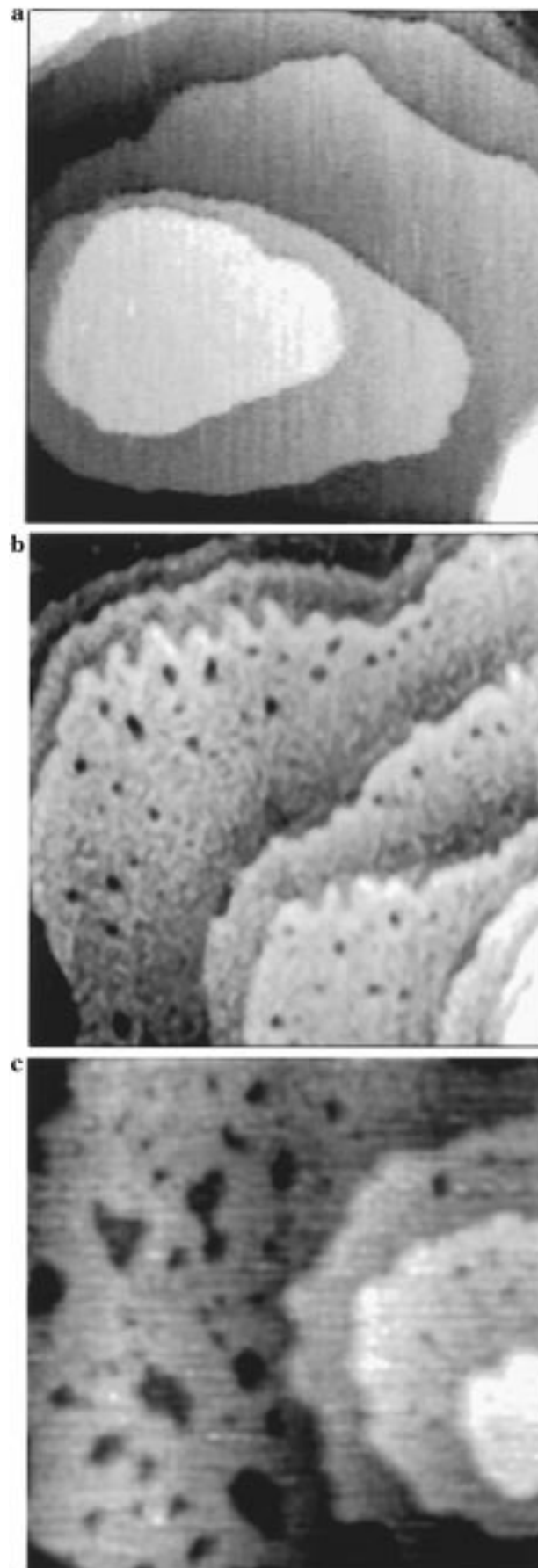


Figure 4. STM images ($0.1\text{-}\mu\text{m}$ scan) taken in air: (a) freshly evaporated, annealed gold; (b) similar to part a, after UV/ozone plus ethanol dip treatment; (c) similar to part a, aged 6 months in laboratory atmosphere.

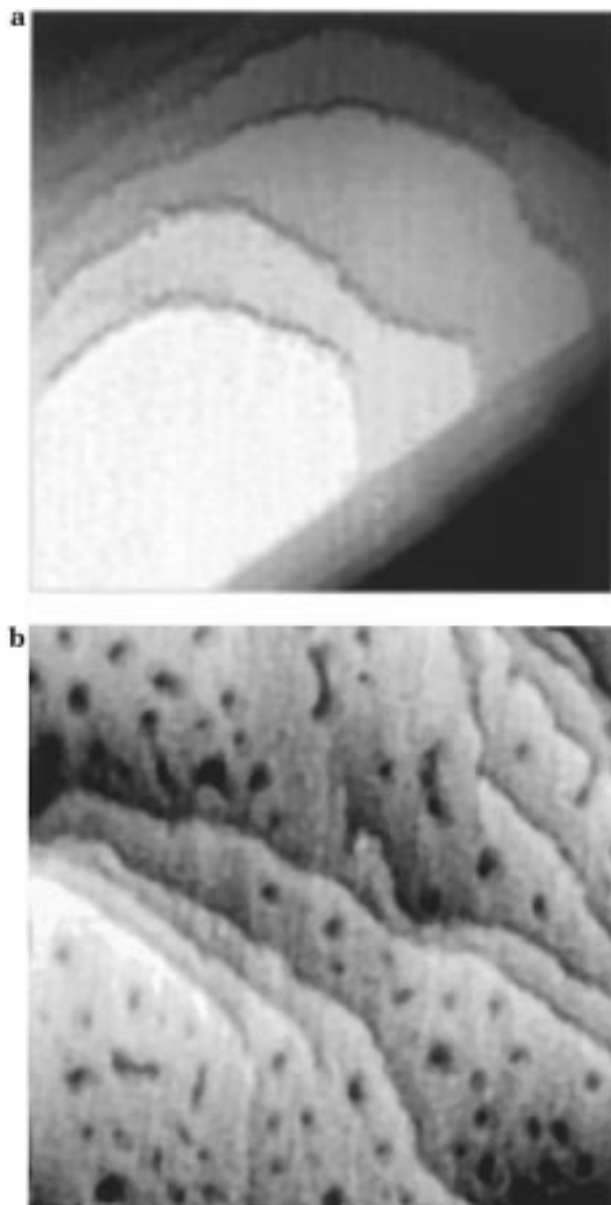


Figure 5. STM images (0.07- μm scan) taken in air: (a) freshly evaporated, annealed gold (on mica), kept 18 months in a vacuum; (b) similar to part a, kept 18 months in laboratory atmosphere.

IIIa microscope (Digital Instruments, Inc.). The samples were scanned in the constant current mode using a Pt/Ir tip. Low current (15 pA) and high bias (1 V) were applied to prevent the tip from contacting and damaging the sample.

Results and Discussion

Gold Surface Pretreatment. A gold-coated glass slide, postannealed in air, was kept for 4 months in a nonhermetically closed glass vial in laboratory atmosphere. The surface was then cleaned using the following two-step procedure: (i) exposure to UV/ozone treatment for 10 min and (ii) immersion in ethanol for 20 min. Ellipsometry and water CAs were measured before treatment and after each pretreatment step; the results are presented in Table 1. When Δ of the treated surface is compared with Δ prior to treatment (Table 1), it is evident that the two-stage procedure reduced the amount of contamination on the surface (see Experimental Section). Yet, advancing water CAs measured on the treated surface indicate the existence of some organic contamina-

Table 1. Variations in the Ellipsometric Parameters and Advancing Water Contact Angles (CAs) of a Gold Surface at the Various Stages of UV/Ozone plus Ethanol Dip Treatment

	pretreatment step	Δ (deg)	Ψ (deg)	water CA ^a (deg)
1	annealed in air; then kept in a vial for 4 months	109.26	43.73	90
2	subjected to UV irradiation in air for 10 min (step 1)	108.80	43.78	<10
3	dipped in ethanol for 20 min (step 2)	110.52	43.96	70

^a CA measurements were carried out on slides treated similarly to those used for the ellipsometric measurements.

tions following the overall procedure. It can be reasonably assumed that the original organic layer on the gold surface was effectively removed by the UV/ozone treatment; however, the surface was contaminated again, to a much lesser extent, upon exposure of the cleaned surface to ethanol and ambient conditions. The thickness of the initial contamination layer can be estimated from the data in Table 1 using the pretreated surface ellipsometric parameters (as the substrate), those of the surface before cleaning (as the covered surface), and a film refractive index ($n_f = 1.5$, $k_f = 0$). The thickness of the contamination layer is found to be approximately 10 Å.

Following the first pretreatment step (Table 1, row 2), Δ is decreased while the surface becomes completely wetted by water. This is somewhat surprising considering the effective removal of organic contaminations by the UV/ozone, expected to result in an increase in Δ . Furthermore, as discussed above, Smith⁴ demonstrated that gold surfaces cannot be completely wetted by water under ambient conditions. Therefore, the complete wetting (Table 1, row 2) indicates a change in the chemical nature of the gold surface, attributed to formation of gold oxide upon exposure to UV/ozone. A similar trend in the ellipsometric parameters was observed in a previous study¹⁵ where Δ was shown to decrease as a result of Au surface oxidation by O₂ plasma. It was also shown that gold oxide can be quantitatively detected by measuring the charge passed during voltammetric reduction of the oxide.¹⁵ Figure 1 shows a voltammogram used for measuring the amount of gold oxide formed upon exposure of a gold-coated electrode to UV/ozone treatment. The charge measured, 215 $\mu\text{C}/\text{cm}^2$, indicates that the surface is only partially oxidized under these conditions.²² These results are in agreement with the work of King,¹⁸ who detected gold oxide on surfaces treated by UV irradiation using XPS measurements. It is therefore clear that the complete wetting of the Au surface following UV/ozone treatment (Table 1, row 2) is due not only to removal of organic contaminants but mainly to the presence of a gold oxide layer on the surface.

Alkanethiol Self-Assembly. The theoretical thickness of a C18SH monolayer on a {111} gold surface, comprising fully extended alkyl chains tilted 30° from the surface normal,²³ is 22 Å. The ellipsometric thickness of a C18SH monolayer adsorbed onto freshly evaporated or UV/ozone-plus-ethanol-treated Au surfaces is 18–19 Å (Table 2, rows 1–3). As argued by Bain et al.,⁷ this consistent difference can be associated with a contamination layer formed after cleaning the gold at ambient conditions. This layer is removed upon alkanethiol SA but is measured by the ellipsometer prior to SA. This

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Table 2. Contact Angles (Advancing and Receding) and Ellipsometric Thicknesses of C18SH Monolayers

monolayer system		ellips thickness (Å)	contact Angle (deg)					
			H ₂ O		BCH		HD	
			adv	rec	adv	rec	adv	rec
1	C18SH, on freshly evaporated Au (no pretreatment)	19.3 ± 0.6	110	109	53	52	47	46
2	C18SH, on 4-month-aged Au pretreated by UV/ozone plus ethanol dip	18.8 ± 1.0	107	105	53	52	46	45
3	C18SH, on 1-day-old Au pretreated by UV/ozone plus ethanol dip	18.2 ± 0.2	110	108	53	52	46	46
4	(3), after monolayer removal by UV/ozone plus ethanol dip	—	70	50	<10	<10	<10	<10
5	(4), after C18SH readsorption	19.0 ± 0.5	109	108	53	52	46	46
6	C18SH, on Au pretreated by UV/ozone (no ethanol dip)	31.6 ± 1.7	112	106	46	30	39	32
7	C18SH, on 3-week-aged Au (no pretreatment)	17.0 ± 3.3	105	90	50	43	42	35

Table 3. GI-FTIR Characterization of C18SH Monolayers on Gold Surfaces

system	CH ₂		CH ₃		
	ν_s	ν_a	$\nu_{a(ip)}$	$\nu_s(FR)$	$\nu_s(FR)$
sample 3 in Table 2	2850	2919	2963	2935	2877
sample 5 in Table 2	2850	2919	2964	2935	2877

allows us to roughly estimate the thickness of the initially adsorbed contamination layer as ca. 3–4 Å.

Table 2, row 2 shows CAs and ellipsometric results for a C18SH monolayer SA on an aged/pretreated Au surface. When these results are compared with the results for similar monolayers adsorbed onto either freshly evaporated Au (Table 2, row 1) or Au pretreated 1 day after evaporation (Table 2, row 3), it is evident that the three monolayers are of similar quality (within experimental error), displaying ellipsometry and wettability properties usually attributed to high-quality monolayers. Similar results were obtained with Au surfaces pretreated after air exposure for various periods of time (from hours to months), illustrating the efficiency and reproducibility of the new pretreatment procedure. This may be compared with a C18SH monolayer SA on an aged but untreated Au surface (Table 2, row 7), where the results indicate a poor monolayer quality.

To further demonstrate the validity of the new procedure an experiment was carried out where a C18SH monolayer was used to simulate a substantial contamination layer. A gold-covered slide was pretreated as above, followed by SA of a C18SH monolayer. The monolayer was characterized by ellipsometry, CA measurements, and GI-FTIR. The results in Table 2, row 3 (CAs and ellipsometry) and Table 3 and Figure 2 (GI-FTIR) indicate that the C18SH monolayer is densely packed and crystalline-like with the alkyl chains in an all-trans conformation.^{7,24} Following characterization, the C18SH monolayer was removed by UV/ozone oxidation followed by immersion in ethanol for 20 min. The values in Table 2, row 4 show that the strongly adsorbed, highly organized C18SH monolayer is readily removed by UV/ozone, as also shown by Worley and Linton²⁵ using XPS measurements. C18SH was then readsorbed onto the cleaned Au surface, and the readsorbed monolayer was characterized using the same characterization techniques. It is clear from the CAs and ellipsometric values (Table 2, rows 3 and 5) and the GI-FTIR results (Table 3 and Figure 2) that the original and the readsorbed monolayers are indistinguishable.

Contrary to Worley and Linton's conclusions, gold oxide is formed on a Au surface upon exposure of the gold to UV/ozone treatment (as discussed above). This is highly significant in the preparation and characterization of SA monolayers. When the ellipsometry and CAs of a C18SH

monolayer adsorbed onto a Au surface pretreated by UV/ozone plus ethanol dip are compared with those of a similar C18SH monolayer adsorbed onto a Au surface oxidized by UV/ozone but not reduced by ethanol prior to SA (Table 2, rows 3 and 6), it is evident that the introduction of the oxidized sample into ethanol has a marked influence on the measured monolayer parameters. This agrees well with our previously published results¹⁵ on alkanethiol SA onto O₂ plasma-preoxidized Au surfaces without oxide removal. It was shown that the unusual ellipsometric and CA values obtained for the monolayers were due to the presence of oxidized Au under the monolayer. On the other hand, when the oxidized Au surface was reduced by ethanol prior to SA, normal values were always obtained (as in Table 2, rows 2 and 3).

SFM Imaging of Gold Oxide. The exceedingly effective stabilization of gold oxide achieved upon SA of an alkanethiol monolayer onto the oxide allows one to detect and image the inherently unstable gold oxide under ambient conditions. Figure 3a presents a SFM image of a gold surface cleaned by the UV/ozone plus ethanol dip procedure followed by SA of a C18SH monolayer. Figure 3b shows a SFM image of a similar system, where the ethanol dip was skipped and thus the gold oxide was not reduced prior to monolayer SA. The bright spots (with an average elevation of 4.6 nm) observed in Figure 3b, which are absent in Figure 3a, are attributed to gold oxide present under the monolayer. The oxide coverage and average height correlate well with the extent of oxidation.²⁶ (Careful examination of the image in Figure 3b reveals the typical morphology of the rudimentary reduced gold surface.) Note that gold oxide is rapidly reduced by ethanol;¹⁵ hence, it is evident that the oxide observed in Figure 3b is isolated from its surrounding by a C18SH monolayer.²⁶ The image in Figure 3b indicates that the UV/ozone oxidation forms a discontinuous oxide layer. Note that while organic contaminations are effectively removed from the Au surface during the pretreatment procedure, the surface is only partially oxidized by the UV/ozone. This conclusion is supported by the electrochemical measurement (Figure 1), where the amount of oxide reduced cathodically suggested that the surface is only partially oxidized upon exposure to UV/ozone for 10 min. It is noteworthy that discontinuous oxide layers similar to those shown in Figure 3b were observed by in-situ STM during the initial stage of electrochemical formation of gold oxide.^{27,28}

Morphological Changes in the Gold Surface. Although the overall structural features of Au surfaces pretreated by UV/ozone plus ethanol dip (Figure 3a) are similar to those of untreated Au surfaces immediately following evaporation/annealing, it is instructive to ex-

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amine the morphology in more detail using the STM. A freshly evaporated Au surface annealed at 250 °C exhibits atomically flat terraces of approximately 100 nm in diameter (Figure 4a). The image of a similar Au surface after UV/ozone plus ethanol dip treatment is shown in Figure 4b, and the image of an untreated Au surface, kept under ambient conditions for about 6 months, is shown in Figure 4c. It is clear that both the oxidation–reduction treatment and the long exposure to laboratory atmosphere induce formation of a dense population of depressions in the Au terraces, mostly one- to two-atoms deep. In both cases the depression size (from a few nanometers to a few tens of nanometers) as well as the shape of the terraces (from deeply indented lacelike (Figure 4b) to relatively smooth (Figure 4c)) varies from one sample to another.

To verify that the depressions seen in Figure 4c are formed as a result of Au surface atoms reacting with air contaminants, the following experiment was carried out: Freshly prepared evaporated/annealed Au samples from the same evaporation lot were subjected to three different treatments and examined after 18 months. (i) Each sample in the first group was sealed and kept under vacuum lower than 10^{-5} Torr. No depressions were found on the Au surface of these samples (Figure 5a). (ii) Each sample in the second group was sealed under absolute ethanol; here very few depressions were found (not shown). (iii) Each sample in the third group was kept under ambient conditions. A multitude of depressions fill the Au terraces (Figure 5b), similar to those seen in Figure 4c. Interestingly, samples kept under vacuum (Figure 5a) are indistinguishable from freshly evaporated/annealed samples (Figure 4a), indicating that no significant elastic strain is present in the Au layer. This implies that depressions formed on Au surfaces kept under ambient conditions are not related to contraction of the topmost layer during the reconstruction process. The similarity of Figures 4c and 5b also eliminates the possible effect of the underlying substrate (glass vs mica).

These results provide strong evidence for the contamination origin of the depressions. Also of interest is the reported depression formation in Au terraces found in freshly evaporated Au surfaces annealed at 400 °C.²⁹ This may be explained by assuming that the contamination-induced depression formation has a thermal activation barrier.

Especially relevant to the present work is the reported observation that alkanethiol monolayer assembly onto freshly evaporated/annealed (at 250 °C) Au surfaces leads to depression formation,^{30–32} namely to the same kind of morphology changes observed upon exposure of the Au

surface to prolonged ambient contamination or to UV/ozone plus ethanol dip treatment. It seems reasonable to assume that Au atoms are similarly removed from the surface as a result of interaction with either the sulfur in alkanethiols, air contaminants, or UV/ozone plus ethanol. This may provide an explanation for the fact noted above that C18SH monolayers assembled on the two types of surfaces presented in Figure 4a and b show identical CAs, ellipsometric thicknesses, and GI-FTIR spectra. It can therefore be concluded that whether one assembles the alkanethiol onto freshly evaporated Au or onto UV/ozone-plus-ethanol-dip-treated Au, the resultant fine structure of the Au surface and hence the monolayer properties are essentially the same.

Summary

A simple and effective pretreatment procedure for reproducible gold surface preparation was introduced and employed in the preparation of self-assembled alkanethiol monolayers. The method includes two steps: (i) removal of organic contaminations by exposure of the Au surface to UV/ozone for 10 min and (ii) removal of the resulting gold oxide layer by immersion in ethanol for 20 min. The significance of the second (oxide reduction) step was demonstrated by contact angle (CA) and ellipsometric measurements. It should be noted that similar results are obtained when step 1 (UV/ozone treatment) is replaced with mild O₂ plasma treatment,¹⁵ followed by step 2.

The effectiveness of the pretreatment procedure was demonstrated by the complete removal of a compact C18SH monolayer using the above procedure, followed by readsorption of a similar monolayer. The original and the reconstituted monolayers were indistinguishable with respect to ellipsometry, CAs, and grazing-incidence FTIR characterization.

STM imaging revealed a high density of small depressions on the Au surface, resulting from the UV/ozone plus ethanol dip treatment. This, however, seems not to affect monolayer properties when compared with similar monolayers adsorbed onto freshly evaporated, untreated Au, evidently due to the fact that a similar surface morphology is known to be generated by the SA process itself. It was also shown that similar depressions are formed as a result of exposure of a gold surface to random air contamination.

Effective stabilization of gold oxide is achieved when an alkanethiol monolayer is adsorbed onto the oxidized surface (with no ethanol dip). This can be exploited for obtaining SFM images of the (inherently unstable) gold oxide layer in laboratory air.

Although the emphasis in this work is on the use of the above procedure for monolayer SA, it may prove effective for various other applications requiring clean, reproducible gold surfaces.

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