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## Self-Assembled Monolayers on Oxidized Metals. 4. Superior *n*-Alkanethiol Monolayers on Copper

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Self-assembly (SA) of long-chain alkanethiols on copper was studied. Two factors were found to have substantial influence on the SA process: (i) the chemical reactivity of Cu toward substances present in the adsorption solution, particularly the solvent, and (ii) surface pretreatment, which influences the amount of oxide and the surface morphology. Both factors are less important in the case of SA onto gold because of its chemical inertness. Monolayers of octadecanethiol (C18SH) were adsorbed from different solvents (ethanol, toluene, and bicyclohexyl) at various thiol concentrations onto Cu surfaces pretreated in several different ways. The monolayers were characterized by contact-angle measurements, grazing-incidence Fourier transform infrared spectroscopy, and scanning force microscopy. Ethanol, the most common solvent for alkanethiol SA, is found to have a negative effect on monolayer SA apparently because of its chemical reactivity toward copper. With toluene as a solvent, better oriented and more crystalline monolayers are obtained provided that a higher thiol concentration is used to compensate for the higher solubility of thiols in toluene. Treatment of the Cu surface prior to SA is shown to significantly improve the SA by reducing the amount of surface oxide and the surface corrugation. The effect of the solvent is more critical than surface oxidation; hence, high-quality monolayers are formed in the presence of thin oxide layers on Cu surfaces. Superior C18SH monolayers, in terms of organization and crystallinity, are obtained by SA from toluene onto Cu surfaces sputtered-annealed in high vacuum, even when the Cu surface is subjected to short exposure to air before SA.

### Introduction

The study of self-organization of amphiphilic molecules on solid surfaces goes back to 1946 when Zisman and co-workers published their work on oleophobic monolayers.<sup>1</sup> Over the past decade, concurrently with the development of surface analytical methods, self-assembled monolayers and multilayers have been extensively studied, predominantly for their potential application as new materials for advanced technologies.<sup>2</sup> The early work of Allara and Nuzzo,<sup>3</sup> as well as several other groups, gave rise to a large number of studies concerning the self-assembly (SA) of organosulfur compounds to form organized monolayers. In particular, alkanethiol monolayers on Au substrates have attracted the most attention. They are prepared by a relatively simple and highly reproducible procedure to form well-organized, closely packed, and stable monolayers.<sup>4,5</sup> Gold has the unique advantage of chemical inertness, which is a major reason for its becoming the most common substrate for the SA of organosulfur compounds.<sup>6</sup> Nevertheless, it was also demonstrated that alkanethiols form closely packed monolayers on active metal surfaces such as silver,<sup>4,5</sup> copper,<sup>7–11</sup> nickel,<sup>12</sup> and iron,<sup>13</sup> which, in contrast to Au, oxidize under ambient conditions.

Although the SA of *n*-alkane amphiphiles is a molecular-scale phenomenon, the effect of the monolayer can be observed

on the macroscale, e.g., on the wetting properties of the solid substrate, as Zisman and co-workers first realized.<sup>1</sup> These authors were intrigued by the fact that the walls of a Pyrex flask, which contained a dilute solution of eicosyl alcohol (C<sub>20</sub>H<sub>41</sub>OH) in *n*-hexadecane, were not wetted by the solution. As part of their study, monolayers that comprised various *n*-alkane amphiphiles such as *n*-eicosyl alcohol, primary *n*-octadecanamine, and *n*-nonadecanoic carboxylic acid were self-assembled from dilute solutions (in hexadecane) onto glass and metal surfaces (including copper). It was found that the monolayers were oleophobic (unwetted by hexadecane), as well as hydrophobic (unwetted by water), and therefore emerged dry from the adsorption solution. By now it is well established that the methyl surface formed by SA of *n*-alkane amphiphiles is a low free-energy surface, which explains the poor wetting of these surfaces.<sup>6</sup> Our experience, as well as that of others,<sup>5</sup> is that it is essential for an *n*-octadecanethiol (C18SH) monolayer self-assembled on evaporated Au to emerge dry from a 1 mM solution in ethanol to be considered a “high-quality” monolayer.

In contrast to Au, when *freshly evaporated* Cu surfaces undergo alkanethiol SA in identical ethanolic solutions under identical conditions, the adsorbed surfaces emerge wet from the adsorption solution. It is reasonable to assume that the inertness of Au compared to the reactivity of Cu surfaces may explain the difference in the SA results and in particular the rapid oxidation of Cu under ambient conditions.

Whitesides and co-workers<sup>7</sup> compared the wetting properties of alkanethiol monolayers adsorbed from ethanol onto Cu<sup>14</sup> and Au. It was shown that water advancing contact angles (CAs)

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measured on a C18SH monolayer on Cu are higher than those measured on Au, while the receding CAs are lower; i.e., the hysteresis on Cu is higher. The hysteresis in hexadecane CAs is also higher on Cu surfaces than on Au. On the basis of this wetting behavior, it was suggested that the Cu surface is rougher than that of Au. These authors also found that, unlike with Au, the thickness of alkanethiol monolayers adsorbed onto Cu, determined from ellipsometric measurements, is higher than the theoretical length of the adsorbed molecule. However, *the most acute complication concerning the study of SA of alkanethiols on Cu is the poor reproducibility of the films*, as shown by the above characterization methods, as well as by grazing incidence Fourier transform infrared (GI-FTIR) spectroscopy. X-ray photoelectron spectroscopy (XPS) measurements reveal that alkanethiol monolayers self-assembled onto Cu that was exposed to ambient environment are actually adsorbed on an oxide layer. Laibinis et al.<sup>9</sup> proposed that the uncontrolled oxidation of the Cu surface may explain the poor reproducibility of thiol monolayers on Cu.

The above suggestion is strongly supported by our previous study,<sup>15,16</sup> where it was demonstrated that *n*-alkanethiols form closely packed monolayers on oxidized Au. Gold does not spontaneously oxidize under ambient conditions, but it is possible to oxidize Au to various extents (e.g., by oxygen plasma or UV/ozone) in a controlled manner. This provided a unique method for studying the effect of surface preoxidation on the characterization of the adsorbed monolayer.<sup>15</sup> Differences in the ellipsometric and CA results on oxidized Au, compared with characterization of similar monolayers on reduced Au, showed good correlation with the amount of oxide present on the Au surface prior to SA. The calculated ellipsometric "thickness" of the monolayer increased gradually with the amount of Au oxide, to values far above the theoretical length of the molecule constituting the monolayer. Advancing water CAs increased while those of bicyclohexyl (BCH) and hexadecane (HD) decreased with the extent of preoxidation. Furthermore, the hysteresis in the BCH and HD CAs increased with the amount of oxide. Similar to the case of organic solvents, water showed hysteresis increase with the degree of preoxidation, but at a certain point a decrease in the hysteresis was noticed. The latter, as well as the other results in refs 15 and 16, clearly indicated that the oxidized Au surface is rough compared to reduced Au and that the roughness increased with the amount of oxide present prior to SA. A later study<sup>17</sup> confirmed this conclusion, using scanning force microscopy (SFM) on Au surfaces oxidized to different levels. It should be emphasized that the preoxidized Au surfaces emerged *wet* from the ethanolic adsorption solution and that the water advancing CAs increased as a function of surface oxidation to values higher than 140°.

As part of their thorough study, Laibinis et al.<sup>7</sup> compared the properties of *n*-alkanethiol monolayers adsorbed onto freshly evaporated Cu from thiol solutions in two different solvents, isooctane and ethanol. It was found that the reproducibility in the case of isooctane was better, which was attributed by the authors to the higher solubility of the thiol in isooctane. However, the solubility explanation is problematic in light of SA studies on Au under varying solubility conditions. Bain et al.<sup>6</sup> studied the effect of various solvents (ethanol, toluene, CCl<sub>4</sub>, with different thiol solubilities) on the monolayer wetting and its thickness, determined from ellipsometric measurements, for *n*-hexadecanethiol (C16SH) monolayers self-assembled onto Au; the results obtained for Cu upon using different solvents<sup>7</sup> were not obtained in the case of Au.<sup>6</sup> This difference between Au and Cu suggests that in addition to the interaction between the

thiol and the Cu, there might be a significant interaction between ethanol and the Cu surface as well.

Underpotentially deposited (UPD) Cu layers on Au substrates were used for SA of alkanethiols by Jennings and Laibinis.<sup>18</sup> C18SH monolayers were prepared in this way from 1 mM solutions in ethanol or isooctane. As we show below, the adsorption conditions used by these authors are far from ideal for SA on Cu surfaces, which may explain, for example, the large contact-angle hysteresis for water and hexadecane.<sup>18</sup>

Cu is a known catalyst for the conversion of methanol and ethanol to aldehydes.<sup>19,20</sup> Sexton<sup>21</sup> showed by high-resolution electron energy loss measurements that the mechanism for the conversion of these alcohols to aldehydes involves formation of stable methoxy and ethoxy intermediates, respectively. The latter intermediates are bound chemically to Cu and are decomposed only above 370 K. It was also claimed by Sexton, as well as by others,<sup>22</sup> that the chemisorption of alcohols onto Cu occurs *through interaction with chemisorbed oxygen*.

Freshly evaporated Cu surfaces are usually oxidized prior to their introduction into the adsorption solution. First, the Cu is exposed to air while the substrate is transferred from the evaporation chamber to the adsorption solution;<sup>9</sup> possibly even more important is the relatively long time the samples are left to cool after the evaporation in a typical vacuum of 10<sup>-6</sup> Torr, allowing surface oxidation by residual water and oxygen in the evaporation chamber.

One may expect that suitable conditions for ethanol chemisorption on Cu are met during SA of thiols from ethanolic solutions. The concentration of ethanol in a 1 mM ethanolic solution of a thiol is more than 4 orders-of-magnitude higher than the thiol concentration; hence, the differences in the monolayers formed on Cu by SA from ethanol compared to isooctane are probably due to the different interactions of the solvents with the Cu surface. While ethanol is chemisorbed on the Cu surface, as discussed above, alkanes are only physisorbed.<sup>23</sup>

Upon a review of the literature concerning SA of *n*-alkanethiols (with methyl or other  $\omega$ -terminating groups) on Cu, it becomes clear that the effects of the solvent, the thiol concentration, and the surface quality on the monolayer properties have not yet been fully recognized and understood. SA on Cu has been performed arbitrarily in ethanol,<sup>18,24-27</sup> isooctane,<sup>7-9,18</sup> and heptane.<sup>28</sup> The present study is aimed at demonstrating proper conditions for reproducibly obtaining superior *n*-alkanethiol monolayers on Cu, primarily under ambient conditions, and at resolving the effect of ethanol as a solvent from the effect of substrate surface properties for thiol SA on active metals.

## Experimental Section

**Materials.** *n*-Octadecanethiol (C18SH) (Sigma, AR) and *n*-octadecanol (C18OH) (Fluka, >97%) were purified by recrystallization from ethanol (Merck, AR). *n*-Dodecanethiol (C12SH) (Merck, >98%) was distilled under reduced pressure. Toluene (Biolab, 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 nitrogen (99.999%), argon (99.996%), and dry purified air.

**Sample Preparation.** Evaporated {111}-textured Au surfaces were prepared and pretreated as previously described.<sup>16</sup> Cu films were prepared in a diffusion-pumped resistive evaporator. Samples of 1000 Å Cu (99.999%) were evaporated from

**TABLE 1: Contact Angles (Advancing and Receding) of C18SH and C12SH Monolayers Adsorbed for 24 h (Unless Otherwise Specified)**

monolayer preparation procedure		contact angle [deg]					
		H <sub>2</sub> O		BCH		HD	
		adv	rec	adv	rec	adv	rec
1	C18SH on freshly evaporated Au, adsorbed from 1 mM solution in ethanol (as in Figure 1a)	110	108	53	52	46	46
2	C18SH on freshly evaporated Cu, adsorbed from 1 mM solution in ethanol (as in Figure 1b, dashed line)	114	102	47	37	41	28
3	C18SH on freshly evaporated Cu, adsorbed from 20 mM solution in toluene (as in Figure 1b, solid line)	111	109	45	43	40	37
4	C12SH on freshly evaporated Cu, adsorbed from 40 mM solution in toluene	108	106	45	45	40	39
5	C18SH on freshly evaporated Cu, adsorbed from 20 mM solution in BCH	110	110	46	45	40	39
6	C18SH on evaporated Cu kept in air 24 h prior to SA from 20 mM solution in toluene (as in Figure 1c)	111	110	44	42	36	22
7	C18SH on evaporated Cu kept in ethanol 24 h prior to SA from 20 mM solution in toluene	114	102	40	32	32	22
8	C18OH on freshly evaporated Cu, adsorbed from 20 mM solution in toluene (as in Figure 1d, solid line)	105	90	34	26	25	15
9	sample 8 after 48 h in 20 mM C18SH solution in toluene (as in Figure 1d, dashed line)	114	103	40	35	30	24
10	C18SH on evaporated Cu sputtered-annealed in UHV, adsorbed from 20 mM solution in toluene (as in Figure 1e, solid line)	110	109	46	45	41	40
11	C18SH on evaporated Cu sputtered-annealed in UHV, adsorbed from 1 mM solution in ethanol (as in Figure 1e, dashed line)	113	107	47	40	40	33

a tungsten boat at  $5 \times 10^{-6}$  Torr at a rate of  $5 \text{ \AA/s}$  onto quartz (when the Cu was annealed prior to SA) as well as onto glass slides. The substrate surface was cleaned with acetone followed by glow discharge for 5 min (with air) in the evaporation chamber. After the samples were cooled in a vacuum, the evaporation chamber was backfilled with dry nitrogen.

**Monolayer Preparation on Freshly Evaporated Cu.** C18SH and C12SH monolayers were prepared by immersion of the freshly evaporated sample in the adsorption solution for 24 h. C12SH was assembled from a 40 mM solution in toluene. C18SH monolayers were assembled from 1 mM C18SH solution in ethanol or from 20 mM C18SH in toluene. The adsorption solutions were deoxygenated by bubbling Ar for 15 min prior to SA. After removal from the adsorption solution, the samples were rinsed three times with chloroform and ethanol and dried under a stream of dry purified air.

**Monolayer Preparation on Copper Pretreated in Ultra-high Vacuum (UHV) and XPS Measurements.** The sample (1000 Å Cu on quartz) was introduced into a commercial KRATOS AXIS-HS XPS system equipped with an Ar ion gun. The Cu surface was cleaned ( $9 \times 9 \text{ mm}^2$  rastering area) by using 4 keV argon ion bombardment. Sputtering was followed by annealing the sample at  $320^\circ\text{C}$  for 3 h and subsequently cooling it to  $40^\circ\text{C}$  under UHV conditions ( $10^{-9}$  Torr). All treatment stages were followed by XPS analysis, using an Al K $\alpha$  monochromatized source and a normal take-off configuration. The total period of exposure to air of the treated substrate prior to the SA was ca. 2 min.

**Contact-Angle (CA) Measurements.** Contact angles (advancing and receding) of H<sub>2</sub>O, BCH, and HD were measured immediately (<10 min) after removal of the slides from the adsorption solution. Measurements at three different spots on the surface were carried out with each solvent using a Rame-Hart NRL model 100 contact-angle goniometer.

**Grazing Incidence Fourier Transform Infrared (GI-FTIR) Spectroscopy.** 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  $80^\circ$ , focused on the sample with a  $f/4.5$  lens. A liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector was used.

The spectra were taken at  $2 \text{ cm}^{-1}$  resolution. The instrument was programmed to run 150 scans with the reference (evaporated Cu or Au (for the respective samples), treated by UV/ozone) and then 150 scans with the sample, averaging 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<sub>3</sub>N<sub>4</sub> tip attached to a cantilever with a spring constant of 0.38 N/m. The SFM images were analyzed using the NanoScope III software.<sup>29</sup>

## Results and Discussion

### C18SH Monolayers on Evaporated, Unannealed Copper.

*Effect of Solvent and Concentration on the Contact Angles of Alkanethiol Monolayers on Cu.* Typical contact angles (CAs) for a closely packed well-oriented C18SH monolayer on an evaporated Au surface, self-assembled from a 1 mM solution in ethanol for 24 h, are shown in row 1 of Table 1. It is well established that the low hysteresis in the CAs correlates with the fact that the methyl surface that is formed emerges dry from the adsorption solution.<sup>5,6</sup> However, as noted before, when a freshly evaporated Cu surface is immersed in the same adsorption solution for the same amount of time, the adsorbed surface emerges wet from the ethanolic solution. Indeed, the hysteresis in the CAs for water, BCH, and HD seen in row 2 of Table 1 is high (cf. row 1 of Table 1) and is similar to that observed for C18SH monolayers prepared on UPD Cu from 1 mM solutions in ethanol or isooctane.<sup>18</sup> The difference in CAs measured on Au and on Cu was attributed to the increased corrugation of the Cu surface<sup>7,8</sup> associated with the presence of Cu oxide underneath the adsorbed monolayer.

In full agreement with the above, when a freshly evaporated Cu surface emerges dry from 20 mM C18SH in toluene (24 h adsorption), low hysteresis in the CAs is observed, as shown in row 3 of Table 1. The roughness effect on the CAs, evident when the monolayer is adsorbed onto Cu from ethanol (row 2 of Table 1), is reduced, and the hysteresis is now comparable



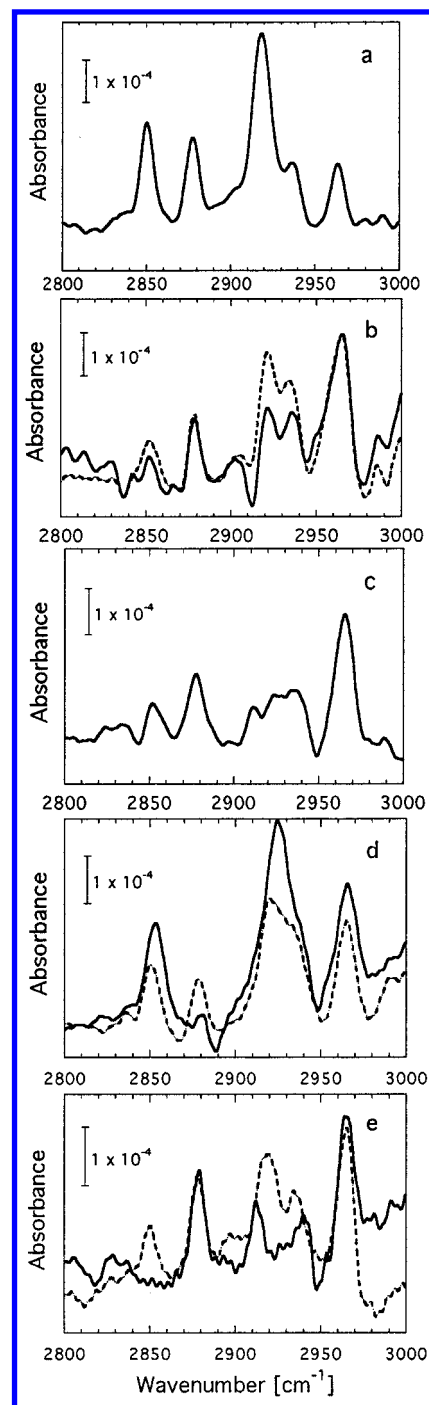
to that on Au. The wetting properties in row 3 of Table 1 indicate that the monolayer is well organized and closely packed. In addition, these results are remarkably reproducible, unlike the results reported in the literature for SA on freshly evaporated Cu under ambient conditions.<sup>7,8</sup> In fact, the CA values observed in numerous SA experiments of C18SH on freshly evaporated Cu from the 20 mM C18SH in toluene lie within the precision of the CA measurements, i.e.,  $\pm 2^\circ$ . The results in row 4 of Table 1 show that similar CAs are obtained for C12SH monolayers adsorbed under ambient conditions onto freshly evaporated Cu from 40 mM solution in toluene. The similar wetting properties obtained for C18SH and C12SH monolayers strongly suggest that for both monolayers a similar methyl surface is formed as a result of the formation of a well-organized, closely packed *n*-alkanethiol monolayer. Note that this is similar to the behavior of *n*-alkanethiols adsorbed onto Au.<sup>6</sup>

The CAs for BCH and HD measured for C18SH monolayers adsorbed from toluene (row 3 of Table 1) are somewhat lower than the corresponding CAs measured for C18SH monolayers on Au (row 1 of Table 1). A similar effect was reported when a C16SH (hexadecanethiol) monolayer was assembled onto Au from hexadecane,<sup>6</sup> where it was suggested that the decrease in the CAs is due to incorporation of solvent molecules in the monolayer. We could not detect incorporation of toluene in the C18SH monolayer by FTIR measurements. Note that similar CAs were measured for C18SH monolayers adsorbed from 20 mM solution in BCH (row 5 of Table 1).

The concentration of the amphiphile in an SA solution plays an important role in the properties of the monolayer obtained. Maoz and Sagiv,<sup>30</sup> in their study of wetting (among other properties) of *n*-alkane monolayers with various film-to-surface binding groups, self-assembled on different substrates, concluded that "adsorption from solutions below a certain critical concentration, characteristic of each particular system, produces incomplete monolayers with lower density and poor orientation of their molecular constituents". Bain et al.<sup>6</sup> studied the effect of concentration on the kinetics of C18SH monolayer formation. It was found that SA on Au from low-concentration solutions in ethanol produced only imperfect monolayers after 1 week. The solubility of C18SH in toluene is far greater than in ethanol; thus, in order to construct organized monomolecular structures, it is necessary to increase the thiol concentration in toluene relative to ethanol. The poor CAs and reproducibility observed when C18SH monolayers were adsorbed onto Cu from 1 mM solutions in isooctane<sup>7,18</sup> may be attributed to the concentration of thiol in the solution, which may be lower than the critical concentration for that system.

**GI-FTIR Measurements of C18SH Monolayers Assembled onto Au and Cu from Ethanol.** Parts a and b (dashed line) of Figure 1 present reflection-absorption infrared spectra of C18SH monolayers SA from 1 mM solution in ethanol onto Au and Cu, respectively. The high-frequency region of the vibrational mode assignment for the alkane chains of C18SH monolayers on Cu and Au is listed in Table 2. As seen in rows 1 and 2 of Table 2, the symmetric and asymmetric methyl and methylene vibrations in parts a and b (dashed line) of Figure 1 appear at about the same frequencies in the case of Au and Cu. Still, the methylene vibration intensities ( $\nu_a(\text{CH}_2)$  around 2920  $\text{cm}^{-1}$  and  $\nu_s(\text{CH}_2)$  around 2850  $\text{cm}^{-1}$ ) are considerably lower than those of the methyl ( $\nu_a(\text{CH}_3, \text{ip})$  around 2965  $\text{cm}^{-1}$  and  $\nu_s(\text{CH}_3)$  around 2878  $\text{cm}^{-1}$ ) for a C18SH monolayer on Cu compared to Au.

According to the surface selection rule introduced by Greenler,<sup>31</sup> only the perpendicular component of a dipole in the



**Figure 1.** GI-FTIR spectra of (a) C18SH monolayer on Au, assembled from 1 mM solution in ethanol for 24 h (as in row 1 of Table 1), (b) C18SH monolayer, assembled from 20 mM solution in toluene for 24 h onto freshly evaporated Cu (as in row 3 of Table 1) (solid line), and C18SH monolayer, assembled from 1 mM solution in ethanol for 24 h onto freshly evaporated Cu (as in row 2 of Table 1) (dashed line), (c) C18SH monolayer, assembled from 20 mM solution in toluene for 24 h onto evaporated Cu exposed to air 24 h prior to SA (as in row 6 of Table 1), (d) C18OH monolayer, assembled from 20 mM solution in toluene for 24 h onto freshly evaporated Cu (as in row 8 of Table 1) (solid line), and C18SH monolayer, assembled from 20 mM solution in toluene for 48 h onto the Cu/C18OH sample (as in row 9 of Table 1) (dashed line), (e) C18SH monolayer, assembled from 20 mM solution in toluene for 24 h onto evaporated Cu, sputtered-annealed in UHV prior to SA (as in row 10 of Table 1) (solid line), and C18SH monolayer, assembled from 1 mM solution in ethanol for 24 h onto evaporated Cu, sputtered-annealed in UHV prior to SA (as in row 11 of Table 1) (dashed line).

**TABLE 2: Infrared Mode Assignment, Peak Positions, and Methylene/Methyl Vibration Intensity Ratio  $I(\nu_s(\text{CH}_2))/I(\nu_s(\text{CH}_3))$  for C18SH and C18OH Monolayers, Adsorbed for 24 h (Unless Otherwise Specified)<sup>a</sup>**

	monolayer preparation procedure	-CH <sub>2</sub>		-CH <sub>3</sub>			$I(\text{CH}_2)/I(\text{CH}_3)$
		$\nu_s$ (cm <sup>-1</sup> )	$\nu_a$ (cm <sup>-1</sup> )	$\nu_{a(\text{ip})}$ (cm <sup>-1</sup> )	$\nu_s$ (cm <sup>-1</sup> )	$\nu_{s(\text{FR})}$ (cm <sup>-1</sup> )	
1	C18SH on freshly evaporated Au, adsorbed from 1 mM solution in ethanol (as in Figure 1a)	2850	2919	2964	2878	2936	1.18
2	C18SH on freshly evaporated Cu, adsorbed from 1 mM solution in ethanol (as in Figure 1b, dashed line)	2852	2921	2965	2878	2934	0.68
3	C18SH on freshly evaporated Cu, adsorbed from 20 mM solution in toluene (as in Figure 1b, solid line)	2848	2918	2965	2878	2936	0.50
4	C18SH on Cu kept in air 24 h prior to SA, adsorbed from 20 mM solution in toluene (as in Figure 1c)	2852	2922	2965	2878	2936	0.57
5	C18OH on freshly evaporated Cu, adsorbed from 20 mM solution in toluene (as in Figure 1d, solid line)	2853	2924	2965	2880	2936	5.27
6	sample 5 after 48 h in 20 mM C18SH solution in toluene (as in Figure 1d, dashed line)	2851	2920	2965	2878	2935	1.23
7	C18SH monolayer on Cu sputtered-annealed in a vacuum prior to SA, adsorbed from 20 mM solution in toluene (as in Figure 1e, solid line)	p	2912	2965	2878	2940	q
8	C18SH monolayer on Cu sputtered-annealed in a vacuum prior to SA, adsorbed from 1 mM solution in ethanol (as in Figure 1e, dashed line)	2850	2919	2965	2878	2936	0.54

<sup>a</sup> Definitions: s, symmetric; a, asymmetric; ip, in-plane; FR, Fermi resonance components; p, not observed; q, cannot be determined.

proximity of a metallic surface can be excited, since the component parallel to the surface is canceled by its image dipole. This selection rule provides helpful structural information.<sup>32,33</sup> In a fully extended alkane chain oriented perpendicular to the surface the methylene groups would have their vibrational dipoles parallel to the surface, while the methyl group would have dipole components perpendicular to the surface. It is therefore expected that methylene vibrational dipole intensities would decrease significantly with respect to those of the methyl group when the alkane chain is oriented closer to the surface normal. A qualitative indication of the monolayer orientation may thus be found in the intensity ratio between the methylene symmetric vibration,  $\nu_s(\text{CH}_2)$ , and the methyl symmetric vibration,  $\nu_s(\text{CH}_3)$ , denoted  $I(\text{CH}_2)/I(\text{CH}_3)$ . This ratio, derived from the spectra in parts a and b (dashed line) of Figure 1 (rows 1 and 2 of Table 2), indicates that the alkane chains in C18SH monolayers are oriented closer to the surface normal when adsorbed onto Cu than onto Au.

Allara and Nuzzo<sup>34,35</sup> introduced a quantitative analysis for determining a monolayer structure by reflection-absorption infrared spectroscopy, based on a comparison between a calculated and a measured absorption spectrum of the monolayer. GI-FTIR spectra of C18SH monolayers adsorbed onto Au and Cu were analyzed using the above method,<sup>7</sup> showing that the alkane chains in the C18SH monolayers are tilted 27° and 12° from the surface normal for Au and Cu, respectively. Despite some experimental differences, the spectra obtained in the present study (parts a and b (dashed line) of Figure 1) are very similar to the corresponding spectra in Figure 4 of ref 7. Thus, it can be reasonably argued that the orientation of the alkane chains in the C18SH monolayer adsorbed onto Au and Cu from ethanol in this study is similar to that of the corresponding monolayers obtained by Laibinis et al.<sup>7</sup>

**GI-FTIR Measurements of C18SH Monolayers Assembled onto Cu from Toluene.** The wetting properties of a C18SH monolayer adsorbed onto Cu from 20 mM C18SH solutions in toluene (row 3 of Table 1) indicated that better organized monolayers were formed compared with adsorption from ethanol. As shown below, the GI-FTIR results support this conclusion. The spectrum of a C18SH monolayer adsorbed onto freshly evaporated Cu from 20 mM solution in toluene is

presented in Figure 1b (solid line); it can be compared with the spectrum of C18SH adsorbed onto freshly evaporated Cu from 1 mM solution in ethanol (Figure 1b, dotted line). In Figure 1b the methylene vibration intensities ( $\nu_a(\text{CH}_2)$  around 2920 cm<sup>-1</sup> and  $\nu_s(\text{CH}_2)$  around 2850 cm<sup>-1</sup>) are considerably lower when the C18SH monolayer is assembled from toluene (Figure 1b, solid line) than from ethanol (Figure 1b, dotted line). Note that the methyl asymmetric and symmetric vibration intensities ( $\nu_a(\text{CH}_3, \text{ip})$  at 2965 cm<sup>-1</sup> and  $\nu_s(\text{CH}_3)$  at 2878 cm<sup>-1</sup>) are similar in both spectra in Figure 1b. The  $I(\text{CH}_2)/I(\text{CH}_3)$  ratio indicates that the alkane chains in the monolayer adsorbed from toluene are oriented more perpendicular to the surface.

The symmetric and asymmetric methylene vibrations listed in rows 2 and 3 of Table 2 are shifted to lower frequencies when the C18SH monolayer is adsorbed from toluene rather than from ethanol (2848 and 2918 cm<sup>-1</sup> compared with 2852 and 2921 cm<sup>-1</sup>, respectively). On the basis of the work of Snyder et al.,<sup>36</sup> the shift of the methylene vibrations is commonly assumed to reflect an increase in the intermolecular interactions and consequently in the crystallinity of the monolayer. A similar shift to lower frequencies, reported by Tao<sup>37</sup> for the methylene vibrations of *n*-alkanoic acid monolayers on silver upon increasing the chain length, was attributed to improvement in monolayer crystallinity. This, therefore, indicates improved long-range order for C18SH monolayers adsorbed onto Cu from toluene.

It may be concluded, on the basis of the CA results and the spectroscopic evidence (the  $I(\text{CH}_2)/I(\text{CH}_3)$  ratio as well as the shift of the methylene peaks), that SA of alkanethiols onto freshly evaporated Cu from toluene using appropriate thiol concentrations gives rise to better orientation and improved periodicity of the monolayers compared to similar monolayers adsorbed from ethanol.

**Effect of Surface Oxides and Ethanol on the SA of C18SH Monolayers on Freshly Evaporated Copper.** As suggested by Laibinis and Whitesides,<sup>9</sup> the thiol is actually adsorbed onto oxidized Cu (Cu<sub>2</sub>O; see below). The CA results (row 6 of Table 1) and the FTIR spectrum (Figure 1c) illustrate the effect of the surface oxide on the SA of thiols on Cu using preferred adsorption conditions. The thiol was adsorbed onto an evaporated Cu surface exposed to air for 24 h prior to adsorption

from 20 mM solution in toluene. (To minimize adsorption of sulfur-containing air contaminants, the evaporated Cu surface was kept in a closed vial in a desiccator for 24 h.) The wetting properties (row 6 of Table 1) are relatively little affected compared to SA from an identical solution onto freshly evaporated Cu (row 3 of Table 1). Similar wetting properties were obtained when the evaporated Cu was exposed to air for 3 days prior to SA from toluene.

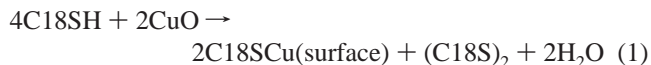
On the other hand, the methylene vibration frequencies of a C18SH monolayer SA on "aged" Cu are shifted to higher frequencies compared with those of SA onto freshly evaporated Cu (rows 4 and 3 of Table 2, respectively). Combined with the difference in the  $I(\text{CH}_2)/I(\text{CH}_3)$  value, this indicates a decreased order in the monolayer adsorbed onto "aged" Cu.

It should be emphasized that comparison between  $I(\text{CH}_2)/I(\text{CH}_3)$  for the spectra in Figure 1b (dashed line) and those in Figure 1c (rows 2 and 4 of Table 2) as well as the respective CAs (rows 2 and 6 of Table 1) shows that the monolayer on "aged" Cu, adsorbed from 20 mM solution in toluene, is better organized than the corresponding monolayer adsorbed onto freshly evaporated Cu from ethanol. The effect of exposure to ethanol vs oxygen on monolayer CAs was further tested as follows. A freshly evaporated Cu surface was dipped in ethanol for 24 h prior to SA of a C18SH monolayer from 20 mM toluene solution. Evidently, pretreatment in ethanol induces a much higher disorder in the resulting monolayer (row 7 of Table 1) compared with the surface oxide formed during the same period of time by exposure to air (row 6 of Table 1).

To emphasize the effect of alcohol adsorption on Cu, *n*-octadecanol (C18OH) was adsorbed onto freshly evaporated Cu from 20 mM solution in toluene. A monolayer is formed on the copper, though of a poor quality, as can be deduced from the relatively low CAs and the high hysteresis (row 8 of Table 1). The high  $I(\text{CH}_2)/I(\text{CH}_3)$  ratio observed in the GI-FTIR spectrum (Figure 1d, solid line) and the shift of the methylene frequencies to higher values compared to a C18SH monolayer adsorbed on freshly evaporated Cu (rows 5 and 3 of Table 2, respectively) support this conclusion.

When such a Cu surface with a C18OH monolayer was introduced into a 20 mM solution of C18SH in toluene for 48 h, a clear trend toward higher CAs and lower hysteresis was observed, as shown in row 9 of Table 1. GI-FTIR measurements (Figure 1d, dashed line) also indicate improvement in the alkane chain orientation, showing a lower  $I(\text{CH}_2)/I(\text{CH}_3)$  ratio and a shift of the methylene vibration frequencies to lower values (rows 5 and 6 of Table 2). Yet, the wetting properties and the infrared spectrum show that the monolayer obtained after 48 h in C18SH solution in toluene is of poorer quality compared to the monolayer obtained after exposing the Cu surface to air prior to SA (row 9 of Table 1; Figure 1d, dashed line; row 6 of Table 2 compared to row 6 of Table 1; Figure 1c; row 4 of Table 2).

As shown above, air oxidation of a Cu surface prior to SA is less harmful to the monolayer than immersion in ethanol. This is not surprising considering the chemical interaction between metal oxides and thiols, the latter being strong reducing agents. Wallace,<sup>38</sup> who studied the catalytic effect of metal oxides in the conversion of thiols to disulfides, demonstrated that thiols reduce metal oxides, including cupric oxide (CuO), upon oxidation to disulfides. In addition, Keller et al.<sup>28</sup> who studied the SA of thiols on Cu, suggested that the oxide formed on a Cu surface in ambient environment is reduced to metallic Cu upon oxidation of thiols to disulfides, as presented in eq 1 (taken from ref 28):



As mentioned above, Cu<sub>2</sub>O is the more relevant oxide when freshly evaporated thin layers of Cu are considered.<sup>39</sup> The replacement of oxygen by the thiolate is then described by eq 2:



The exchange of metal oxide by thiol upon adsorption of the latter was previously suggested by Ron et al.<sup>15,16</sup> for the SA of thiols on oxidized Au, as well as by Mukaiyama for the reduction of lead oxides by thiols.<sup>40</sup> Equations 1 and 2 respectively describe the SA of thiols on CuO that may be present on heavily oxidized Cu surfaces and that on Cu<sub>2</sub>O, which is the dominant oxide on freshly evaporated Cu films.

As discussed above, the surface roughness (manifested by the contact angles) is substantially lower when the monolayer is assembled from toluene compared to SA from ethanol (rows 2 and 3 of Table 1), a phenomenon not completely understood at this point. It is conceivable, however, that the reduction of the oxide by thiols gives rise to surface reorganization (i.e., smoothing), evident in the case of SA from toluene. This effect may be less pronounced when the thiols are adsorbed from ethanol, owing to two possible reasons: (i) the different water content (0.2% (87 mM) and 0.03% (14 mM) water in ethanol and toluene, respectively), resulting in competition between monolayer SA and surface oxidation (by water or oxygen); (ii) the competing chemisorption of ethanol on Cu, which may create complex morphologies.

The improvement in the monolayer properties after immersion of the Cu/C18OH monolayer in C18SH solution (rows 8 and 9 of Table 1; rows 5 and 6 of Table 2) suggests that at least part of the adsorbed C18OH monolayer (present as C18OCu) is exchanged by the C18SH molecules. It may similarly be argued that ethoxy species chemically adsorbed onto the Cu surface during SA of thiols from ethanol are exchanged with thiol molecules. Thus, we suggest that when a C18SH monolayer is adsorbed from toluene onto Cu surfaces oxidized in the ambient, the adsorption proceeds by replacement of oxide, as given by eq 2 (or eq 1). However, when the SA is performed in ethanol, monolayer formation proceeds largely by the less thermodynamically favored replacement of chemisorbed ethoxy moieties.

It may be concluded that while Au exhibits strong preferential reactivity toward organosulfur compounds, the reactivity of Cu is less selective. While Cu does strongly adsorb organosulfur compounds, it also adsorbs many other substances. Therefore, adsorption conditions for Cu must be chosen much more carefully.

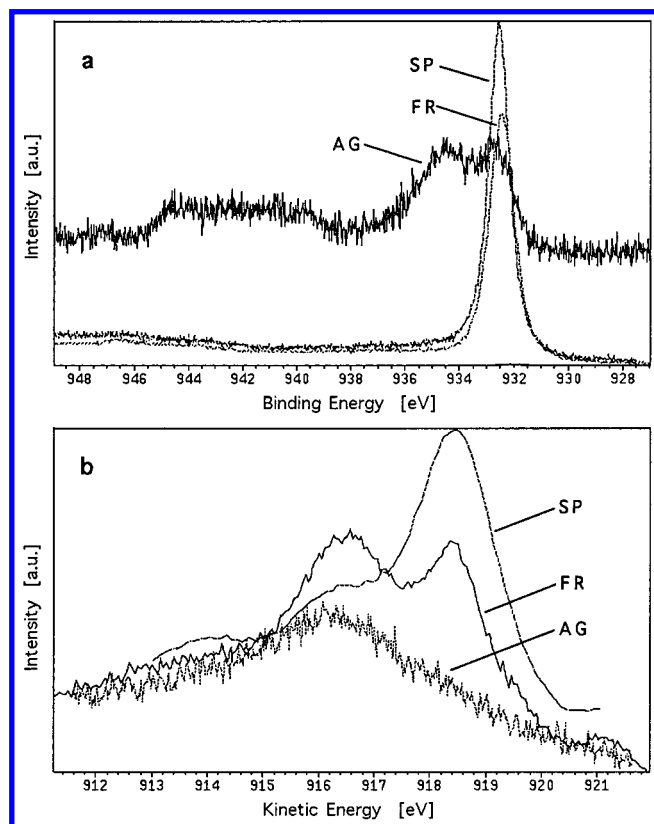
**C18SH Monolayers on Evaporated Copper, Sputtered-Annealed in High Vacuum Prior to SA.** Better-defined Cu surfaces for monolayer SA are obtained by sputtering and subsequent annealing under ultrahigh vacuum (UHV) conditions. This is a well-established procedure used in adsorption studies on Cu surfaces.<sup>20</sup> It should be realized that the surface, cleaned in the UHV chamber, is reoxidized to some extent during its transfer to the adsorption solution (the same amount of time, ca. 2 min, was required for the transfer of freshly evaporated Cu to the adsorption solution). Note that a certain amount of carbonic contamination was found on all substrates, even in the UHV sputtered-annealed ones (developed in the latter case during the annealing stage). Table 3 presents XPS results aimed



**TABLE 3: Atomic Concentrations of Copper, Oxygen, and Carbon (in atom %) and Calculated Oxide Thickness (See Text) from XPS Results of Cu Surfaces**

	Cu surface pretreatment prior to XPS measurement	% Cu	% O		% C	average oxide thickness [Å]
			As CuO <sub>x</sub>	contamination		
1	aged in air, untreated	6.4	31.0	10.0	52.6	>25 <sup>a</sup>
2	freshly evaporated, exposed to air for 2 min	32.3	26.1	6.5	35.1	10–15
3	sputtered-annealed in UHV	89.2	1.6	0.3	8.9	<1 <sup>b</sup>
4	sputtered-annealed, exposed to air for 2 min	64.5	10.0	2.2	23.4	5–10

<sup>a</sup> A more accurate estimate could not be achieved because of the considerable surface roughness. <sup>b</sup> Below a monolayer of oxide.



**Figure 2.** Narrow-scan XPS spectra of the Cu(2p<sub>3/2</sub>) line (a) and the Cu(LMM) Auger line (b) for the following Cu surfaces: “aged” (AG); freshly evaporated (FR); sputtered-annealed, reexposed to air for 2 min (SP). The “aged” Cu signal is magnified because of its lower intensity, attributed mainly to the existence of a contamination layer on the aged sample.

at providing quantitative characterization of the surface oxide layers, created under various preparation conditions.

As shown in Figure 2a, the Cu(2p<sub>3/2</sub>) line of the “aged” substrate consists of several pronounced shake-up features (around 940–945 eV), characteristic of the Cu(II) oxidation state, attributed here to the formation of a Cu(OH)<sub>2</sub> layer. The sputtered-annealed (reexposed to air) sample shows a spectrum very similar to that of the freshly evaporated substrate in this range (the minor differences around 946 eV correspond to the excitation of plasmons), with no indication of Cu(II). Since the binding energies of Cu(I) and metallic copper (932.5 and 932.6 eV, respectively)<sup>41</sup> are not easily distinguishable, the Auger Cu(LMM) spectrum was also examined (Figure 2b), where marked differences between the samples are observed.

The freshly evaporated sample shows a relatively small signal for metallic Cu (918.5 eV) and a large signal for Cu(I) (916.5 eV), attributed to Cu<sub>2</sub>O, whereas the sputtered-annealed (reexposed) sample shows the opposite trend. The Auger line of the “aged” sample comprises a distribution of Cu oxidation states, with a maximum corresponding to Cu(OH)<sub>2</sub>. This analysis is fully supported by the O(1s) spectrum; the results are quantitatively summarized in Table 3. As seen in the table, the O(1s) line was deconvoluted into a copper oxide signal and a complementary line associated with substrate contamination (mainly as CO<sub>x</sub>). The above is in agreement with the previously observed stoichiometry change from Cu(I) to Cu(II) in thicker copper oxide films.<sup>39</sup>

Owing to the complex (nonplanar) morphology of the oxide, several complementary methods were used to evaluate the oxide layer thickness: (i) calculation of intensity ratios (e.g., O(1s) vs Cu(2p)), assuming exponential attenuation of the escaping photoelectrons,<sup>9</sup> with inelastic mean-free-path factors  $\lambda_i^j$ , assumed to be roughly proportional to  $\sqrt{Ek_i}$  (where  $Ek_i$  is the kinetic energy of the photoelectron  $i$ ), while  $j$  is the index of the medium;<sup>42</sup> (ii) angle-dependent measurements; (iii) depth profiling using Ar<sup>+</sup> sputtering.

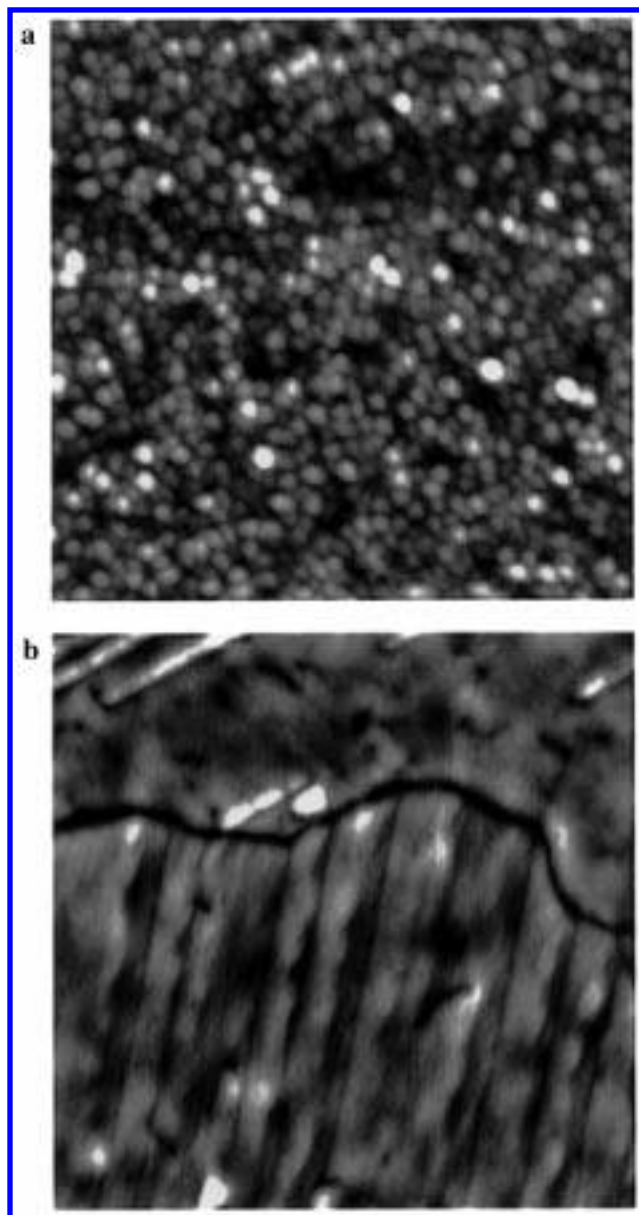
As can be expected, the sputter-annealing pretreatment effectively removes the oxide layer (row 3 of Table 3); its effect remains significant even when the Cu substrate is reexposed to air (rows 2 and 4 of Table 3).

Figure 1e shows GI-FTIR spectra of C18SH monolayers SA on sputtered-annealed Cu from 20 mM solution in toluene (solid line) and from 1 mM solution in ethanol (dotted line). It is clear from the  $I(\text{CH}_2)/I(\text{CH}_3)$  ratio and from the position of the methylene vibration frequencies that the monolayer adsorbed from ethanol onto a sputtered-annealed surface is more ordered and oriented closer to the surface normal compared with the monolayer adsorbed from ethanol onto freshly evaporated Cu (cf. rows 8 and 2 in Table 2). It is also evident that the hysteresis in the CAs is decreased, as shown in row 11 of Table 1, compared with row 2 of Table 1. Although the sputter-annealing treatment induced some improvement in the monolayer characteristics, it is clear that SA on freshly evaporated Cu from toluene results in better monolayers than SA from ethanol on sputtered-annealed Cu.

The CAs measured on C18SH monolayers adsorbed onto sputtered-annealed and freshly evaporated Cu from toluene are similar (rows 3 and 10 of Table 1), while the GI-FTIR spectra are remarkably different. A substantial shift in the asymmetric methylene vibration to lower frequency is observed for the C18SH monolayer adsorbed from toluene onto a sputtered-annealed substrate (2912 and 2918 cm<sup>-1</sup>, respectively). Furthermore, the symmetric methylene vibration in Figure 1e is too weak to be distinguished from the background.

It is evident from the above that the sputter-anneal pretreatment has a markedly favorable effect on the monolayer characteristics, even after short reexposure to air prior to SA. This is largely attributed to a different surface morphology obtained as a result of the sputter-anneal process and the oxide removal. The different surface morphologies were observed by contact-mode scanning force microscopy (SFM) imaging of the monolayer-covered Cu surfaces. Figure 3a shows an image of a C18SH monolayer prepared by 24 h adsorption onto a freshly evaporated Cu surface from a 20 mM C18SH solution in toluene, while Figure 3b shows an image of a C18SH monolayer adsorbed under identical conditions onto a sputtered-annealed Cu surface. The comparison reveals that the morphology is changed dramatically by the sputter-anneal treatment.





**Figure 3.** SFM images (960 nm scan) taken in air in contact mode ( $z$ -range: 10 nm) for (a) freshly evaporated Cu surface coated with a C18SH monolayer, adsorbed from 20 mM solution in toluene, (b) sputtered-annealed Cu surface coated with a C18SH monolayer, adsorbed from 20 mM solution in toluene. Figure 3a shows numerous grains, whereas Figure 3b shows a single boundary between two grains.

Although the corrugation rms is the same for both surfaces, the UHV surface treatment increases the average grain size (lateral dimension) by a factor of  $>30$  over that of the freshly evaporated, untreated surface, resulting in the much smoother-looking surface in Figure 3b.

The oxide removal and the substantial reduction in surface corrugation resulting from the sputter-annealing are related, since surface oxidation tends to increase the surface roughness. The end result is a marked improvement in the organization and crystallinity of thiol monolayers SA on Cu from either ethanol or toluene. The reactivity of Cu toward ethanol reduced the effect of the pretreatment compared with the much greater effect observed when the SA is done in toluene. Hence, when C18SH is assembled onto sputtered-annealed Cu from 20 mM solution in toluene, superior monolayers are obtained displaying unusual organization and orientation.

## Conclusions

For alkanethiol monolayers on metal surfaces, the surface wettability is a simple and effective indication of monolayer quality. Thus, a major objective of this study was to produce, *in a reproducible manner*, an oleophobic as well as hydrophobic surface by SA of  $n$ -alkanethiols under ambient conditions on evaporated Cu surfaces. Practically, we aimed at deriving a procedure by which the adsorbed Cu surface would emerge dry from the adsorption solution, as in the case of C18SH monolayers on Au. Two strategies were adopted: (i) replacing ethanol with a solvent that does not interact chemically with Cu (an inherent issue here is the appropriate thiol concentration for the chosen solvent) and (ii) reducing the surface corrugation and the amount of oxide on the Cu surface prior to SA.

The results clarified the role of two major factors that control the structure of monolayers formed by SA on Cu: (i) chemical interactions between Cu and substances present in the adsorption solution other than the thiol (the solvent should be chosen particularly carefully, since it is present at the highest concentration, while the thiol concentration should be adjusted according to its solubility in the chosen solvent) and (ii) pretreatment of the surface, which affects the amount of oxide and the surface morphology. Both factors are of lesser significance when thiols are assembled onto Au because of the inertness of the latter and its preferential reactivity toward organosulfur compounds.

The major conclusions of the present study, with respect to SA of alkanethiols on Cu surfaces, are the following.

1. As in the case of Au, Cu surface oxidation induces an increase in surface roughness, which influences the SA process. Monolayer adsorption from toluene reduces the surface roughness, while SA from ethanol does not show this effect. The oxide layer and the surface corrugation can be reduced using sputter-anneal treatment under UHV conditions.

2. Ethanol as a solvent causes the formation of low-quality monolayers probably because of chemical interactions with Cu; much better results are obtained when toluene is used. In the latter case, however, higher thiol concentrations have to be used because of the higher solubility of alkanethiols in toluene.

3. The presence of a thin oxide film on the Cu surface does not prevent the formation of high-quality C18SH monolayers, provided that other conditions are met, particularly concerning the solvent and the thiol concentration. The effect of chemical interactions with the solvent is more important than the presence of a thin oxide layer, since high-quality monolayers displaying superior CAs ( $1-2^\circ$  hysteresis) and GI-FTIR spectra (very low  $I(\text{CH}_2)/I(\text{CH}_3)$ ) are obtained *reproducibly* by adsorption from concentrated alkanethiol solutions in toluene onto Cu surfaces covered with thin  $\text{Cu}_2\text{O}$  films.

4. Alkanethiol monolayers of unusual quality are prepared on evaporated Cu pretreated by sputter-annealing in UHV, which reduces both the amount of oxide and the surface corrugation. These monolayers show a very high degree of orientation and crystallinity, observed even when the SA process is carried out after short exposure to air.

The conclusions reached here concerning SA of alkanethiols on Cu are expected to apply to other active metals as well as to other types of monolayers.

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