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Effects of Metal Coating on Self-Assembled Monolayers on Gold. 1. Copper on Dodecanethiol and Octadecanethiol

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We report studies on the perturbations induced by the evaporation of copper metal overlayers on dodecanethiol and octadecanethiol self-assembled monolayers (SAMs). Monolayers were characterized after deposition on a gold substrate from an ethanolic solution, after heat treatment alone, after acid treatment alone, after physical evaporation of a submonolayer copper layer alone, and after deposition of an optically thick copper layer followed by stripping with a nitric acid solution. The monolayers were studied using cyclic voltammetry, grazing-angle IR spectroscopy and X-ray photoelectron spectroscopy. Cyclic voltammetry revealed that the gold electrodes are passivated by the formation of the monolayers. The degree of passivation does not decrease with exposure to <6 N nitric acid solutions or after copper deposition and removal with nitric acid. The IR studies indicate that the deposition of metal induced a reorganization, interpreted as increased disordering, of the monolayer, that is similar to heat treatment alone. X-ray photoelectron spectroscopy experiments showed no evidence of bond formation between carbon and copper upon deposition of the copper layer on the SAM.

1. Introduction

Self-assembled monolayers (SAMs) composed of organothiols on gold surfaces play an important role in many recent investigations of electrical conduction through organic molecules. A critical aspect of these studies is the type of interaction between a metal overlayer and the SAM. Perturbations induced by both the deposition process and the nature of the metallic film can play an important role in the charge transport behavior of the organic layer. In this paper we report studies aimed at characterizing the organization and close packing of the SAM before and after vacuum deposition of an optically thick metal film. Alkanethiol monolayers were chosen as model systems since they have been extensively characterized by both spectroscopic and structural probes.¹

This laboratory's investigation of metal overlayer effects on SAMs is motivated by past studies on copper-coated SAMs conducted in our laboratories.² In our previous work, we fabricated gold-conjugated oligomer SAM/copper junctions by self-assembly of thiol-terminated "molecular wires" on gold electrodes and subsequent evaporation of a copper film. We then investigated charge transport through this system via electrochemical oxidation of the copper overlayer and measured the barrier heights to charge injection at the SAM/metal contacts. The conclusions we reached depend strongly on the integrity and organization of the SAM after the evaporation process. Preliminary evidence presented in that work suggested the monolayer remained intact following evaporation of

the metal overlayer. However, its organization is not necessarily identical to that of the monolayer as deposited. The same issues are faced in any other measurement of conductivity through metal/SAM/metal junctions, whenever vacuum deposition of a metal is involved.^{3,4} Therefore, we undertook these studies in order to characterize the SAM after the copper coating process.

Prior studies on SAM/metal interfaces have been reported in the literature, and recent reviews have been published on this subject.^{5,6} The techniques applied to metal-coated SAMs have been primarily vacuum-based X-ray photoelectron spectroscopy (XPS) and ion-scattering spectroscopy (ISS), and these were applied to the investigation of modifications induced by an ultrathin metal overlayer (usually ≤ 1 nm). Metal penetration of the monolayers is a common observation in these studies. Different combinations of metals and terminal groups on the monolayer have been shown to produce different results in terms of reactivity and penetration of the metal through the organic monolayer, the trend being one of increasing penetration for decreasing reactivity.^{5,7,8} Metals such as Ti and Cr tend to react with the terminal groups, whereas Au, Ag, and Cu display lower reactivity. Methyl groups have been found to confer the lowest reactivity to the vacuum/SAM interface, whereas $-\text{COOH}$ and $-\text{CN}$ groups tend to react more easily with the metals. Furthermore, the rate of penetration depends also on temperature and on the tendency of the metal to form

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clusters.^{7,8} In the specific case of the HS(CH₂)₁₇CH₃/Cu combination, it was found that a 1 nm layer of Cu completely penetrates the SAM in 2 h at room temperature.⁷

These previous studies have been performed for ultrathin films and with very low deposition rates. The object of this work is to study the effect of vacuum deposition at high deposition rates of an optically thick layer of copper (suitable for establishing conventional electrical contacts) on dodecanethiol and octadecanethiol monolayers (abbreviated C₁₂SH and C₁₈SH, respectively), self-assembled on polycrystalline gold substrates. The main goals of this work are as follows: (a) to determine if the monolayer is still present after a rapid copper evaporation process; (b) to determine if the SAM has suffered any modifications; (c) to establish if these changes are reversible or not; (d) to determine whether increased electrical defects in the SAM result from evaporation; and (e) to draw conclusions on the nature of any changes induced by the metal coating. For this purpose, we characterized the organization and structure of the monolayer as deposited and after copper evaporation followed by removal of this layer using nitric acid. Cyclic voltammetry and FTIR-external reflectance spectroscopy were used for these experiments. X-ray photoelectron spectroscopy was also performed on the Au/SAM/Cu sample, following deposition of a thin copper layer.

2. Experimental Procedures.

Materials and Equipment Used. Nitric acid (Fisher Scientific), dodecanethiol (Aldrich), octadecanethiol (Aldrich), 100% ethanol (AAPER), sulfuric acid (Fisher Scientific), 30% hydrogen peroxide (Mallinckrodt), ferricyanide (Fisher Scientific), sodium sulfate (Fisher Scientific), and copper shot (99.999%; Puratronic) were all reagent grade and used without further purification. Aqueous solutions were prepared with deionized water. The substrates used for the IR studies were 100 nm thick evaporated gold films on a ~5 nm chromium layer and supported on glass slides. These substrates were purchased from Evaporated Metal Films Inc. (Ithaca, NY). The gold electrodes used for the electrochemical measurements were purchased from Bioanalytical Systems Inc.

Sample Preparation. For the IR experiments, the gold substrates were cleaned in piranha solution (1:3 H₂O₂/H₂SO₄. *Caution:* Exercise extreme caution when handling piranha solution) for ~1 min, rinsed in deionized H₂O and dried in a N₂ flow. The clean gold slides were transferred to an inert atmosphere drybox (Vacuum Atmospheres) and immersed in a ~1 mM solution of C₁₂SH or C₁₈SH in ethanol, and the monolayer was allowed to self-assemble at least overnight, with a typical deposition time of 20 h. After deposition, the samples were rinsed with ethanol and dried for 30 min in air or in a nitrogen flow. After drying they were immediately used for the characterization of the "as deposited" SAMs.

Evaporated copper layers were deposited by placing the sample in a home-built oil-free high-vacuum metal evaporation chamber. Copper was deposited at an approximate pressure of 2×10^{-5} Torr. Thick copper layers were evaporated by passing a 200 A current through a Mo boat for 20 s. The thickness of these layers was ~200 nm (measured by atomic force microscopy (AFM)), giving an approximate deposition rate of 10 nm/s. The temperature was monitored during the evaporation process by placing a J-type thermocouple on the back of the glass slide (the thermocouple was not positioned on the sample surface to avoid copper coating of the metal junction). The maximum temperature ever recorded during evaporation was 52 °C. Also thinner layers were evaporated to conduct studies at low copper coverages. The conditions for this type of deposition were 150 A for 5 s, yielding a thickness of ~5 nm (measured by AFM) obtained at an approximate rate of 1 nm/s. Copper layers were then removed by immersing the gold slides in a 0.5 N HNO₃ solution for 10 min. The samples thus obtained were rinsed in deionized H₂O, dried under N₂ flow, and characterized.

Sputtered copper layers were obtained by placing the SAMs in the sputtering chamber of a CrC-100 Sputtering System, by Plasma Sciences Inc. A 100 nm thick layer of copper was deposited at an Ar pressure of 5×10^{-3} Torr at an approximate rate of 7 nm/min. The copper removal was carried out following the same procedure as that for evaporated films.

The annealed samples were prepared in the evaporation chamber, and their purpose was to simulate an evaporation process without the contribution given by the impinging copper atoms. The SAM was placed in the sample holder at the same distance from the Mo boat as in the usual copper evaporation but without placing the copper shot in the boat. As the current was passed, the SAM was heated by the boat irradiation.

Samples for use in the electrochemical studies were prepared in a manner similar to that described above. Gold electrodes (BAS) were polished with a polishing film of 15, 3, 1, and 0.3 μm grain size (Fiber Instrument Sales) and then cleaned in fresh piranha solution for 5 min. The electrodes were submerged in a fresh 10 mM solution of C₁₂SH in ethanol for 4 h, followed by rinsing with ethanol and deionized water. These electrodes were used immediately for the electrochemical characterization of the "as deposited" SAM.

A layer of copper was then evaporated on to the same as deposited SAM-coated electrode which had undergone the electrochemical characterization above. The electrode was placed in the evaporation chamber, and 150 A were passed through the boat for 30 s, allowing an approximately 45 nm layer of copper to form onto the SAM-coated electrode. Following evaporative coating the electrode was removed from the vacuum chamber and submerged in a 3 N nitric acid solution for 5 min to remove the copper layer. These electrodes were immediately used for the electrochemical characterization of the SAM subjected to copper evaporation and removal.

The same electrodes were then placed in a fresh piranha solution for 5 min to remove the layer of C₁₂SH. These electrodes were used for the electrochemical characterization of gold electrodes without the C₁₂SH SAM present.

For the XPS measurements a piece of tantalum foil coated with a layer of sputtered gold was used as the substrate. This substrate was submerged overnight in a 2.5 μM ethanol solution of C₁₂SH in the inert atmosphere drybox. The sample was carefully rinsed in ethanol and dried under a stream of nitrogen and then immediately loaded into the XPS chamber.

FTIR Measurements. All spectra were obtained on a Mattson Infinity 60AR FTIR spectrometer, equipped with a grazing angle accessory manufactured by Specac, and an MCT wide-band detector. The unpolarized IR beam was incident at 84° on the gold substrates. For each sample 300 scans were collected (greater scan numbers did not yield further improvement to the signal quality), with a 2 cm⁻¹ resolution. A gold slide cleaned in piranha solution at the beginning of each measurement session was used as a background. Spectra were collected for both C₁₂SH and C₁₈SH samples that had undergone the following treatments: (a) as deposited SAM; (b) after deposition of the SAM and Cu evaporation at low coverage; (c) after deposition of the SAM, Cu evaporation and its removal with HNO₃; (d) after deposition of the SAM and immersion in HNO₃; (e) after multiple Cu evaporations and removal; (f) after deposition of the SAM and annealing in the evaporation chamber; (g) after Cu sputtering and its removal with HNO₃. Only the C-H stretching region of the spectra yielded reproducible peaks of good quality. The spectra were used after applying minimal offset and baseline corrections.

Electrochemical Measurements. Electrochemical measurements were performed on an EG&G Princeton Applied Research potentiostat model 263 under computer control. Cyclic voltammetry was performed in the presence of a redox active species, as a test of electrode passivation. The cyclic voltammetry was performed from +0.8 to -0.1 V vs SCE, at a scan rate of 10 mV/s, in a quiescent aqueous solution of 10 mM K₃Fe(CN)₆ with 1 M Na₂SO₄ supporting electrolyte which had been previously deoxygenated by bubbling nitrogen gas for 20 min. Nitrogen was allowed to flow over the surface of the electrolyte during the measurement. Three scans were taken for each electrode all in the same solution: after deposition of the monolayer, after copper evaporation and removal of the copper with nitric acid, and after removal of the monolayer by piranha solution.

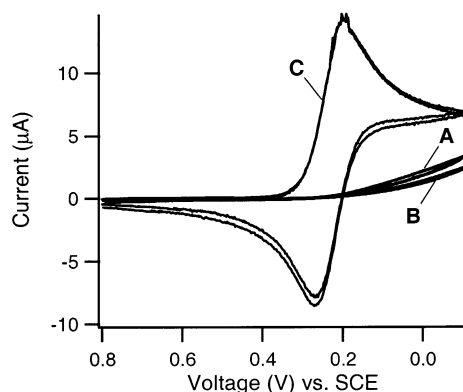


Figure 1. Cyclic voltammetry of $C_{12}SH$ -passivated electrode subjected to copper evaporation and copper dissolution with nitric acid. (A) $C_{12}SH$ monolayer; (B) $C_{12}SH$ monolayer subjected to copper evaporation and 3 N nitric acid; (C) gold electrode cleaned in piranha solution (see text for details).

An electrochemical study was performed to determine the resistance of $C_{12}SH$ SAMs to nitric acid. A polished gold BAS electrode with a $C_{12}SH$ monolayer was formed as above. The electrode was subjected to cycles of soaking in increasing concentrations of nitric acid for 5 min and cyclic voltammetry. For the last two concentrations the monolayer was re-formed due to damage sustained during the previous cycle of nitric acid. The nitric acid solutions were 0.0, 0.6, 1.2, 1.8, 3.0, 6.0, 9.0, 12.0, and 15.0 N.

XPS Measurements. The SAM-coated substrate was introduced into the XPS system (Omicron) using a loadlock to access the chamber without breaking vacuum. Data were collected by employing a hemispherical energy analyzer and the Mg $K\alpha$ source. The entrance and exit slits were set to 6×12 mm and 1×10 mm, respectively. To avoid the destruction of the organic layer, the data were collected keeping the energy delivered to the SAM to the minimum needed to obtain an acceptable signal. Therefore, the spectra reported in this work originate from the atoms that are closest to the SAM/vacuum interface. Spectra were collected from 289.0 to 281.0 eV, the region characteristic of the C 1s peak, and from 937.0 to 928.0 eV, the region where the Cu $2p_{3/2}$ peak is found, at steps of 0.050 eV with a dwell time of 0.300 s. A copper layer was vapor deposited onto the surface with a homemade copper doser located inside the vacuum chamber.⁹ The deposition time was 14 min and yielded an approximate coverage of 2 monolayers. The amount of copper deposited could not be determined with greater accuracy since a complete doser calibration had not been performed at that time. Following copper deposition the two spectra were acquired again. The values for the binding energy peaks were obtained by performing a Gaussian fit with a commercial data analysis software (Igor Pro 4.0).

3. Results and Discussion

Cyclic Voltammetry. Figure 1 shows a typical cyclic voltammogram performed at the $C_{12}SH$ monolayer coated gold electrode. Curve A in the figure was recorded with the monolayer as deposited and shows significant passivation of the electrode surface. Passivation of electrodes by alkanethiol monolayers is well-known and results from the impermeable nature of the monolayer, which blocks the access to the electrode surface from solvent, electrolyte, and redox active molecules. Curve B in the figure was recorded from the same electrode after deposition of an optically thick layer of copper at a rate of 1.5 nm/s for 30 s and removal of that copper layer by soaking in a 3 N nitric acid solution. While there is a slight decrease in the current compared to the first voltammogram, this electrode shows that the monolayer remains intact and continues

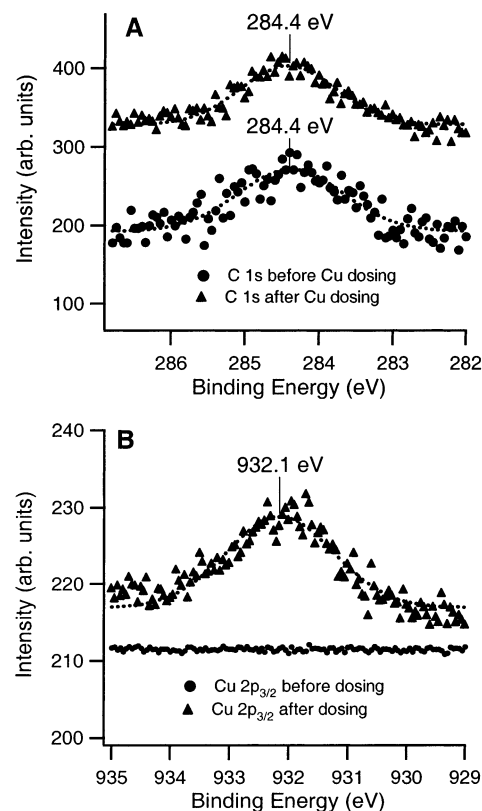


Figure 2. XPS of $C_{12}SH$ SAM before and after submonolayer Cu coverage with best-fit Gaussian curves. (A) C 1s region, before and after copper evaporation; (B) Cu $2p_{3/2}$ region, before and after copper evaporation.

to passivate the electrode surface. The third voltammogram, curve C, shows the electrode response after removal of the $C_{12}SH$ monolayer with piranha solution, leaving a clean gold electrode.

A series of experiments was conducted to determine the effects of nitric acid alone on electrochemical passivation by the monolayer. Our results showed that, for exposures of 5 min, nitric acid concentrations up to 6 N produced no measurable effects on the passivation of the electrode, as measured with a ferricyanide/ferrocyanide redox couple. Concentrations of 9 N and above reactivated the electrode under the same conditions.

From these studies, we conclude that nitric acid does not profoundly disturb the structure and coverage of the monolayer under the conditions used in the remainder of this paper and further that a rapidly evaporated copper layer does not damage the integrity of the monolayer. These experiments do not, however, provide direct information about the nature of any more subtle chemical changes to the terminal group or about a more subtle disordering of the monolayer. To examine these effects, XPS and grazing angle FTIR were used.

XPS Studies. Figure 2 shows XPS data for a monolayer of $C_{12}SH$ before and after deposition of 2 monolayers coverage of copper by slow evaporation at an approximate rate of 0.14 monolayer/min. Figure 2A shows the binding energy regions for the carbon 1s, and Figure 2B shows the copper $2p_{3/2}$ peaks, before and after the deposition of a partial monolayer of copper, along with the best Gaussian fits to the data. Signal-to-noise in these measurements is low because no more than two scans were averaged for fresh, unexposed monolayers to limit exposure of the monolayer to the X-ray source. Earlier experiments showed that the exposures necessary to produce high S/N

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XPS data resulted in at least partial degradation of the monolayer. Nevertheless, the position of the carbon peak in Figure 2A remains at 284.4 eV following evaporation, indicating that there is no observed change in the carbon oxidation state. The carbon XPS data are less informative about bonding than the copper XPS because XPS is a very surface-sensitive measurement; an overlayer of copper could obstruct the carbon atoms beneath it and obscure details of the underlying carbon oxidation state. The carbon XPS does, however, indicate that most of the surface in this experiment is exposed, indicating that aggregation of copper atoms to form clusters has occurred since the total dosage was higher than 1 monolayer.

The copper XPS in Figure 2B has its peak centered at 932.1 eV, very slightly less than the library value of 932.5 eV for metallic Cu. This is indicative of the presence of metallic copper, but, due to the surface sensitivity of XPS, this signal most likely originates from the outermost copper atoms of the copper clusters. We may conclude, therefore, that there is at least no positive evidence that chemical bonds are forming between the copper and the monolayer. We were unable to detect any signal from the sulfur atoms, as is expected for a well-ordered monolayer studied with a surface-sensitive technique.

IR Studies of Thermally- and Acid-Treated SAMs.

Our studies of copper-coated SAMs were performed mainly on rapidly deposited films formed in a homemade evaporator. We conducted a series of infrared absorption experiments on coated monolayers under different evaporation conditions in our chamber. At low flux, the radiative heating of the SAM-coated sample by the Mo boat was sufficient to partially desorb the SAM during evaporation. Samples removed from the chamber following low-flux evaporation were very hot to the touch. High-flux evaporation for 20 s resulted in samples that were only moderately warm when removed from the chamber and showed persistent SAM infrared spectra even after multiple cycles of evaporation and metal removal (see below). Thermocouple measurements made on the reverse side of the coated slides gave a maximum temperature of 52 °C for the high-flux evaporation condition. Most samples reached typical maximum temperatures of 40 °C during evaporation under the high-flux condition, measured at the backside of the 1 mm thick substrate.

Measurements on SAMs exposed to a thermal treatment equivalent to high-flux evaporation in the same chamber were made to determine what effects the thermal cycle alone would produce in the films. These thermal cycles were exact duplicates of deposition cycles, except that no copper was loaded into the Mo sample boat during the cycle. Infrared reflectance spectra of octadecanethiol samples prepared by this "fake evaporation" protocol are shown in Figure 3. The spectra of alkanethiol SAMs as deposited show five peaks that have been previously assigned in the literature as described in Table 1.^{1,10–12} A general trend observed in the heat-treated samples is that the infrared signature of the SAMs decreases with increasing numbers of heating cycles.

Data for C₁₂SH samples is similar to Figure 3, except that the loss of the spectrum is much more rapid. C₁₂SH films were almost completely lost after three fake evaporation cycles, while C₁₈SH films remained in place much longer. The loss of the infrared signature of the organic

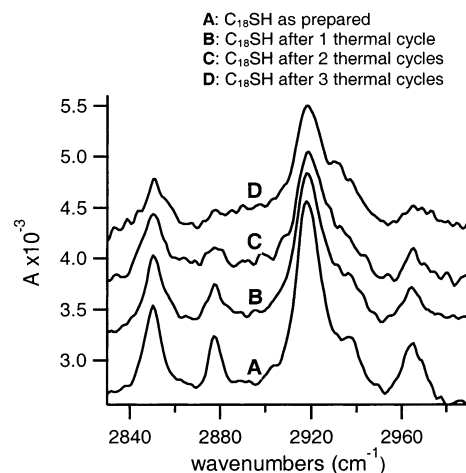


Figure 3. Infrared reflectance spectra of C₁₈SH SAM on Au as a function of thermal exposure equivalent to the copper evaporation process. Scan parameters: 300 scans at 84° incidence, 2 cm⁻¹ resolution. (A) C₁₈SH as prepared; (B) C₁₈SH after one thermal cycle; (C) C₁₈SH after two thermal cycles; (D) C₁₈SH after three thermal cycles. Curves are offset for clarity.

Table 1. Frequencies of the C–H Stretching Modes of C₁₂SH and C₁₈SH SAMs Appearing in the Infrared Reflectance Spectra of the SAMs as Prepared and Following Coating with a 200 nm Thick Layer of Copper via Rapid Thermal Evaporation at 10 nm/s and Stripping with 0.5 N Nitric Acid^a

assignm ¹³	peak freq (cm ⁻¹)			
	C ₁₂ SH SAMs as prepared	C ₁₂ SH SAM after Cu evaporation	C ₁₈ SH SAMs as prepared	C ₁₈ SH SAM after Cu evaporation
ν_a , ip (CH ₃)	2964	2966	2964	2965
ν_s , FR (CH ₃)	2937	-	2937	-
ν_a (CH ₂)	2918	2924	2918	2924
ν_s , FR (CH ₃)	2878	-	2877	-
ν_s (CH ₂)	2850	2852	2849	2852

^a ν = stretching mode; a = asymmetric; s = symmetric; ip = in plane; FR = Fermi resonance enhanced. The assignments for the IR peaks were taken from ref 13, Table 1.

film is thus attributed to gradual desorption of the film during the heat treatment, with C₁₂SH being lost more rapidly because of its higher vapor pressure.

A more subtle effect observed in the heated samples is the very rapid loss of the 2878 cm⁻¹ peak assigned as a Fermi-resonance-enhanced symmetric methyl stretching vibration¹³ and other associated changes in the spectrum. This 2878 cm⁻¹ peak decreases in intensity relative to the remaining SAM infrared absorbances. This phenomenon is irreversible and is associated with the increased disordering of alkanethiol monolayers because of a phase transition to a liquidlike state above 350 K.^{14,15}

Infrared reflectance measurements of acid-treated SAMs of C₁₂SH and C₁₈SH were performed to examine whether any subtle changes in the nature of the monolayers occurred that were not observed using cyclic voltammetry. No such changes were observed following exposure to 0.5 N nitric acid solutions used in the remainder of these studies.

Combined with the results of the cyclic voltammetry measurements, thermal effects associated with evapora-

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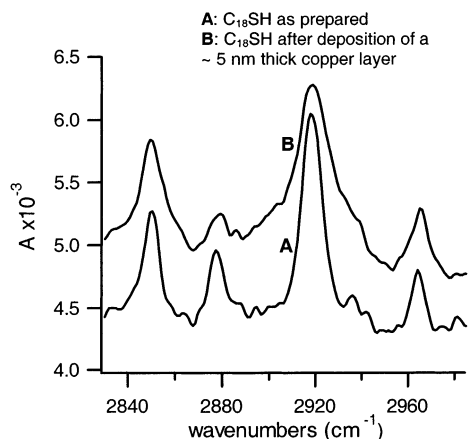


Figure 4. Infrared reflectance spectra of $C_{18}SH$ SAMs with a 5 nm (average thickness) copper overlayer deposited at 1 nm/s. Scan Parameters: 300 scans at 84° incidence, 2 cm^{-1} resolution. (A) $C_{18}SH$ as prepared; (B) $C_{18}SH$ after having deposited a copper layer ~ 5 nm thick. Curves are offset for clarity.

tion at high rates may induce a melting behavior of the monolayer that does not destroy its electrochemical passivation. Chemical treatment of the methyl-terminated alkanethiol SAMs with nitric acid at moderate concentrations does not, by itself, produce any significant effects on the chemical or structural nature of the SAM on gold.

Infrared Studies of Alkanethiol SAMs with Cu Overlayers. Infrared spectroscopy of SAMs that were overcoated with copper was measured for samples prepared in different ways. Low coverages of Cu were produced at a deposition rate of 1 nm/s for 5 s. This produced a film of copper through which infrared spectra of the monolayer were clearly visible. Optically thick overlayer films deposited for 20 s at a rate of 10 nm/s were produced and stripped with 0.5 N nitric acid so that the infrared spectra of the remaining monolayer could be observed.

Figure 4 shows infrared reflectance spectra of $C_{18}SH$ SAMs with a 5 nm (average thickness) copper overlayer. The only comparable data in the literature at present are reported in ref 6, in which methyl ester-terminated alkanethiols were copper coated with ultrathin films. The spectroscopy of samples prepared in this way showed that the 2878 cm^{-1} Fermi resonance peak was reduced in intensity, and other changes in peak positions and intensities are observed consistent with the effects of simple thermal treatment. The report of Jung and Czanderna⁶ used a SAM with no terminal methyl group, and thus no changes in the spectra associated with the terminal methyl group reported here were observed.

Figure 5 shows the changes induced by the evaporation of 200 nm of Cu on the IR spectra of $C_{12}SH$ and $C_{18}SH$ SAMs and stripping of the copper with 0.5 N nitric acid. After the evaporation process and the removal of the copper layer, the C–H stretching bands undergo changes in frequency, intensity, and width. Control experiments, some of which are reported above, demonstrate that neither the vacuum to which the SAM is exposed in the evaporation chamber nor the nitric acid solution used for removing the metal induce any changes by themselves on the monolayers. Therefore, these perturbations are introduced during the deposition process itself. As described below, these changes are irreversible and are consistent with thermal effects alone.

The most remarkable changes are observed for the peak at 2918 cm^{-1} , assigned to the asymmetric stretching of the CH_2 groups of the backbone chain. This peak broadens

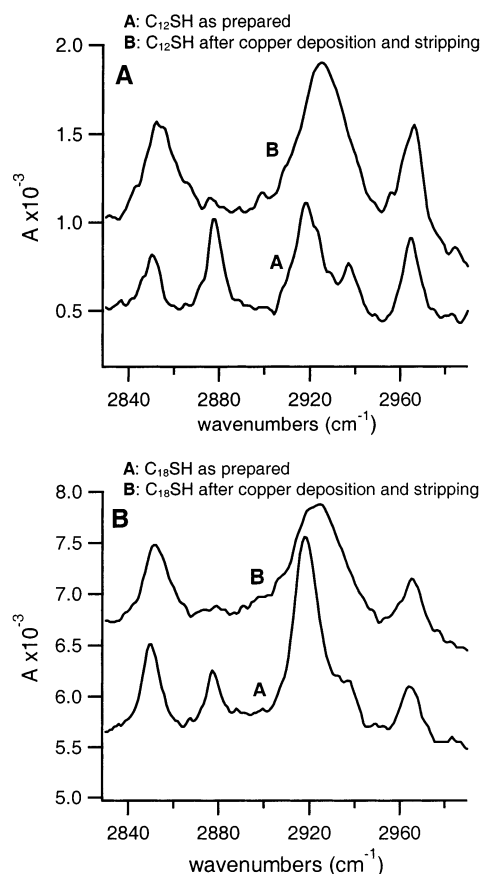


Figure 5. Infrared reflectance spectra of $C_{12}SH$ (A) and $C_{18}SH$ (B) SAMs following coating with 200 nm copper via rapid thermal evaporation at 10 nm/s and stripping with 0.5 N nitric acid. Scan Parameters: 300 scans at 84° incidence, 2 cm^{-1} resolution. (A) C_nSH as prepared; (B) C_nSH after having deposited a copper layer ~ 200 nm thick followed by copper stripping. Curves are offset for clarity.

considerably both in the case of $C_{12}SH$ and $C_{18}SH$ SAMs, and its frequency is shifted toward a higher value (see Table 1). Copper evaporation has a similar effect on the 2850 cm^{-1} mode, assigned to the symmetric stretching of the methylenes. $C_{12}SH$ and $C_{18}SH$ SAMs, however, show differences in the total integrated intensities of these two peaks. The $C_{12}SH$ SAM shows an increase in intensity of up to 50% for the symmetric stretching, and 300% for the asymmetric stretching. On the other hand, the $C_{18}SH$ SAM shows a decrease in intensity of $\sim 12\%$ for the symmetric stretching and no appreciable variation for the asymmetric stretching.

The frequencies of these two peaks provide information regarding the intermolecular interactions. It has been shown in previous work¹⁰ how these bands shift toward higher frequencies when going from the solid to the liquid state, and this shift has been explained by an increase in the population of gauche defects in the polymethylene chains.^{1,14–16} A greater amount of gauche defects is expected to enlarge the total integrated intensity of these bands as well. The presence of more gauche defects means that more CH_2 groups are randomly oriented with respect to the surface; therefore, more modes are in the right orientation to allow a vibrational transition than when the chains are all trans. This type of increase in the intensity has been observed when the IR spectra of alkanethiol monolayers are collected at temperatures

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above ~ 350 K as well.^{14,15} Therefore, the broadening and shift of these two peaks in the $C_{12}SH$ and $C_{18}SH$ spectra are compatible with a more liquidlike organization of the monolayer.

In the case of the $C_{18}SH$ SAMs the total intensity of the asymmetric stretching was consistently found to decrease upon copper evaporation, whereas the symmetric stretching intensity remained unaltered. This suggests that, concomitant with the increase in conformational freedom, another structural change that induces a decrease in the methylene bands intensities takes place. A possible explanation would be a decrease in the tilt angle of the chains that would orient the CH_2 associated modes more parallel to the surface, thus reducing the absorption intensity.^{15,17} This type of intensity loss has been studied for long-chain alkanethiols (C_nSH , $n \geq 15$) as a function of temperature.^{14,15} It is likely then that the copper evaporation induces an untilting of the chains, without any change in the packing of the sulfur atoms, that therefore decreases the chain density, allowing for greater conformational freedom and consequent population of gauche defects. These structural modifications have been suggested also for the order-disorder transition at about ~ 350 K, investigated both in experimental and theoretical works.^{14,15,18,19}

Another important effect of optically thick deposition of copper on the IR spectrum of the alkanethiol SAMs studied here is the disappearance of the symmetric methyl stretch at 2878 cm^{-1} . This mimics the behavior observed for simple thermal treatments and the behavior observed for 5 nm thick overlayers of copper reported above. This is in agreement with what has been previously observed when the monolayers undergo simply an increase in temperature.¹⁵

These observed spectral changes are irreversible, even after several hours of storage at room temperature and after up to 4 h of immersion in ethanol. It has been observed that monolayers of alkyl chains show similar variations in the methyl and methylene bands when heated and that these variations are reversible until the SAMs are heated above a transition temperature, usually found in the neighborhood of 350 K.^{14,15,20} This would suggest that the copper evaporation process induces a pseudo-melting-phase transition and that this melted state is quenched when the evaporation ends and the sample rapidly cools. This process is consistent with purely thermal effects and requires no special chemical or physical interaction with the overlayer. Previous annealing experiments monitored by STM and grazing incidence X-ray diffraction^{18,21,22} that appear to show increased domain size are not necessarily contradictory to this result, as these experiments measure long-range order, while the infrared absorption studies measure essentially intramolecular disorder.

To confirm that no decomposition of the monolayers occurs during our evaporation processes at high rates, we have also studied the effect of multiple copper evaporation and removal processes (up to 3 times) on the SAMs. Multiple coating and stripping cycles introduce no further changes in the infrared spectra, as shown in Figure 6. This implies that the copper evaporation reorganizes the

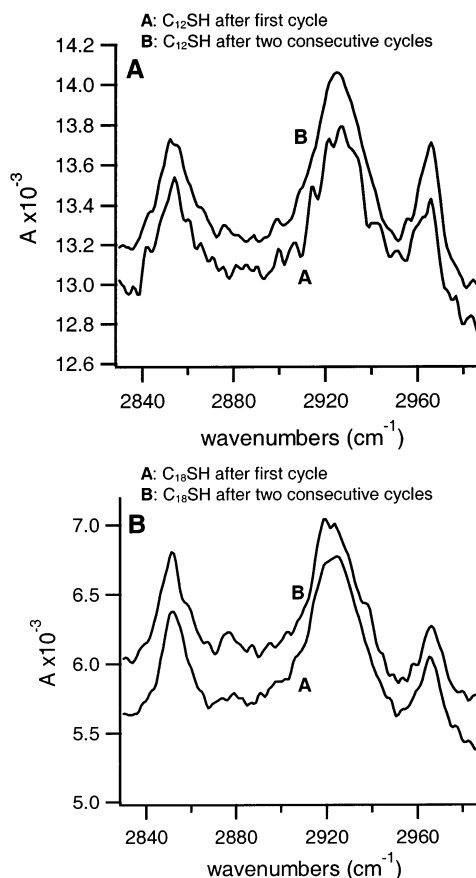


Figure 6. Infrared reflectance spectra of $C_{12}SH$ (A) and $C_{18}SH$ (B) SAMs following multiple copper-deposition-and-stripping cycles under rapid thermal evaporation conditions of 10 nm/s. Scan Parameters: 300 scans at 84° incidence, 2 cm^{-1} resolution. (A) C_nSH after the first cycle; (B) C_nSH after two consecutive cycles. Curves are offset for clarity.

monolayers, but after this first reorganization there is no additional disordering or desorption.

It is interesting to note that multiple "fake deposition" heating cycles using an empty Mo boat lead to progressive decrease in the overall IR signal, signaling desorption. This last effect was not observed when the copper was actually deposited on the organic layers even after three consecutive copper deposition and removals. An interpretation of this result is that the rapid coating process traps the monolayer and prevents its desorption.

Infrared Spectroscopy of SAMs Coated by Sputtering. Copper sputtering at ambient temperature was studied as a method for forming metal overlayers on SAMs. The C-H stretching region of the samples after removal of the copper by nitric acid showed no evidence of residual organic material. This was not unexpected, given the more energetic nature of this process as compared to evaporation.

4. Conclusions

Alkanethiol self-assembled monolayers on gold substrates are still present after being coated with an optically thick copper overlayer. Electrochemical techniques revealed that the degree of passivation of the gold electrodes does not change after coating the monolayers with copper. Therefore, the coverage and the amount of defects do not vary significantly as compared to the as deposited films.

The degree of order appears to change as demonstrated by IR spectra. There is evidence of an increased population of gauche defects as opposed to the all-trans conformation

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of the as deposited films. This greater number of groups in gauche conformations is also accompanied by an untilting of the chains, evidence of which was found in the case of the C₁₈SH SAMs. These changes are irreversible.

XPS reveals that copper evaporated on the monolayer under low-flux conditions does not form chemical bonds to the monolayer. The same conclusion is reached for high-flux conditions based on infrared spectroscopy.

The system chosen for study here is among the least reactive and, consistent with this description, we find that the observed changes in the form of the film are explicable as purely thermal in origin. While our thermocouple measurements under high-flux conditions suggest temperatures no greater than about 50 °C (323 K), these measurements were made on the reverse side of the substrate on which the SAM was deposited. Changes in the infrared spectrum suggest that the SAM temperature

exceeded 350 K during the measurement. Desorption observed during fake evaporation and the persistence of the infrared spectra of the SAM through multiple real high-rate evaporations suggests that even higher temperatures probably occur that are sufficient to desorb, though not to decompose, the SAM. The high-rate formation of a metal overlayer is found to trap the SAM beneath it and prevent its desorption.

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