

# Self-Assembled Monolayers of *n*-Alkanethiolates on Copper Are Barrier Films That Protect the Metal against Oxidation by Air<sup>1</sup>

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**Abstract:** Self-assembled monolayers (SAMs) derived from adsorption of *n*-alkanethiols onto the surfaces of copper slow the oxidation of the copper surface by reaction with atmospheric dioxygen. Angstrom-level changes in the thickness of the monolayer result in readily observable differences (by X-ray photoelectron spectroscopy, XPS) in the rates of oxidation of the copper and adsorbed thiolates. The rates of oxidation of the copper and the thiolates can be decreased by ~50% by increasing the length of the adsorbate, and thus of the SAM, by four CH<sub>2</sub> units. The species present on the oxidized interface—both alkanesulfonate and Cu(II)—are replaced when the assemblage is exposed to solutions of alkanethiols, and the resulting SAMs resembled those that were present before the oxidation, although the supporting surface is rougher.

## Introduction

This paper reports the ability of self-assembled monolayers to act as barrier films that retard the oxidation of a copper surface. Self-assembled monolayers (SAMs) formed by adsorption of alkyl thiols and disulfides from solution onto gold surfaces<sup>2,3</sup> have been used in studies of wetting,<sup>3,4</sup> adhesion,<sup>5,6</sup> X-ray-induced damage,<sup>7</sup> and electron transfer.<sup>8</sup> Under ambient conditions, gold does not oxidize and these SAMs have limited potential in studies of corrosion; electrochemical methods have been used to oxidize the adsorbate and result in its desorption from the surface.<sup>9</sup> Recently,

(1) This research was supported in part by the Office of Naval Research and by the National Science Foundation (Grant CHE-88-12709). XPS spectra were obtained using instrumental facilities purchased under the DARPA/URI program and maintained by the Harvard University Materials Research Laboratory.

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Table I. Binding Energies of Cu(2p) and O(1s) XPS Peaks for Various Copper-Containing and Related Compounds

| compd               | binding energy (eV)    |       | refs       |
|---------------------|------------------------|-------|------------|
|                     | Cu(2p <sub>3/2</sub> ) | O(1s) |            |
| Cu                  | 932.6                  |       | 15, 16     |
| Cu <sub>2</sub> O   | 932.6                  | 530.4 | 16, 17     |
| Cu <sub>2</sub> S   | 932.7                  |       | 16         |
| CuO                 | 933.8 <sup>a</sup>     | 529.5 | 16, 17     |
|                     | 940.5 <sup>b</sup>     |       | 15         |
|                     | 943.5 <sup>b</sup>     |       | 15         |
| Cu(OH) <sub>2</sub> | 935 <sup>a,c</sup>     | 531.0 | 15, 17, 18 |
|                     | 941.0 <sup>b</sup>     |       | 15         |
|                     | 943.5 <sup>b</sup>     |       | 15         |
| CuCO <sub>3</sub>   | 935.0 <sup>a</sup>     |       | 18         |
|                     | 941 <sup>b</sup>       |       | 17         |
|                     | 943 <sup>b</sup>       |       | 17         |
| H <sub>2</sub> O    |                        | 532.2 | 15         |

<sup>a</sup>Line widths of Cu(2p<sub>3/2</sub>) peaks for Cu(II) species (~2.5 eV) are approximately twice those of Cu and Cu<sub>2</sub>O due to multiplet splitting (Gupta, R. P.; Sen, S. K. *Phys. Rev. B* **1975**, *12*, 15-19). <sup>b</sup>Shake-up peak. <sup>c</sup>Binding energies of 935.1 and 934.4 eV have been reported in refs 15 and 17, respectively.

we<sup>10</sup> reported that *n*-alkanethiols adsorb from solution onto copper surfaces and from densely packed, oriented SAMs.<sup>11</sup> The adsorbed species in this type of SAM is a thiolate,<sup>10,12</sup> and the hydrocarbon chain is primarily trans-extended and is oriented close to the surface normal (cant angle = ~12° from the surface normal).<sup>10</sup> When formed under controlled, anaerobic conditions, the copper surface contained no Cu(II) species. In this paper, we survey the rates of oxidation of these assemblies by exposure to air as a function of the time of exposure and of the chain length of the adsorbates, and the effect of the resulting oxidation on the stability of these SAMs.<sup>13</sup> *The most significant result of this*

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(11) For earlier studies of the adsorption of long-chain organosulfur compounds on copper, see: (a) Blackman, L. C. F.; Dewar, M. J. S.; Hampson, H. J. *Appl. Chem.* **1957**, *7*, 160-171. (b) Blackman, L. C. F.; Dewar, M. J. S. *J. Chem. Soc.* **1957**, 171-176.

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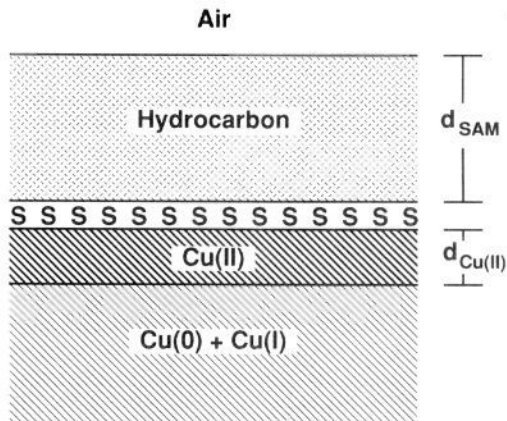
(13) Related to this topic, Allara et al. have reported that an *n*-octadecanethiolate SAM on GaAs retards the oxidation of the GaAs to the level of ~3% of a monolayer of oxide after 2-day exposure to the atmosphere (Sheen, C. W.; Shi, J.-X.; Mårtensson, J.; Parikh, A. N.; Allara, D. L. *J. Am. Chem. Soc.* **1992**, *114*, 1514-1515). In this study, an isolated example was reported; the present work examines the timescales of formation of the oxidation products on copper substrates and how they are affected by the chain length of the adsorbate.

work is the demonstration that the thin (1–3 nm) hydrocarbon layer of the SAM can provide significant protection against oxidation to a metal surface. This demonstration is based on the observation that the rate of oxidation becomes slower as the *n*-alkanethiols used to make the SAM become longer. We hypothesize that the SAM is sufficiently densely packed that it provides a low-permeability barrier that hinders access of O<sub>2</sub> to the metal.

### Method of Analysis

We used X-ray photoelectron spectroscopy (XPS) to monitor the changes in the copper and in the SAM after the SAM had been exposed to atmospheric dioxygen.

XPS is well-suited for these studies: it can provide elemental composition, can differentiate between oxidation states of many elements, and is sensitive to the presence of very thin films of material (<10 Å). To ensure that we monitored the products of oxidation, we relied on changes in the Cu(2p) and S(2p) spectral regions rather than changes in the O(1s) peak: the former peaks reflect products of oxidation; changes in the O(1s) peak could reflect reactions due to other oxygenated species (for example, H<sub>2</sub>O and CO<sub>2</sub>) (see Table I). Copper is one of the metals whose corrosion has been most studied using XPS as an analytical tool.<sup>14</sup> XPS does, however, have limitations in multicomponent systems as complex as that examined here. Given a system composed of one species, XPS can readily determine its identity (for example, Cu versus Cu<sub>2</sub>O versus CuO); when more than one species is present, however, determination of the identity and the relative abundance of the various species is often complicated by the inability to resolve individual peaks. For example, in the Cu(2p<sub>3/2</sub>) spectral region, Cu<sub>2</sub>O is shifted from Cu(0) by only 0.1 eV, and these two species are thus not distinguishable (see Table I).<sup>15–19</sup> These oxidation states can be distinguished by using the most intense component of the L<sub>3</sub>M<sub>4,5</sub>M<sub>4,5</sub> Auger transition (<sup>1</sup>G; Δ versus Cu(0): Cu<sub>2</sub>O, 2.3 eV; CuO, 1.0 eV).<sup>20,21</sup> This region of the spectrum also contains other Auger transitions, and the differentiation of oxidation states and their quantitation is difficult when more than one oxidation state is present.<sup>22,23</sup> The main peak due to CuO is shifted by ~1.2 eV from Cu(0) and Cu<sub>2</sub>O in the Cu(2p<sub>3/2</sub>) spectral region, and, although readily identifiable, it overlaps with the peaks due to Cu(0) and Cu<sub>2</sub>O.<sup>15–17</sup> The most diagnostic feature in the copper spectrum is the pronounced satellite structure in the 2p region for Cu(II) species; these peaks are separated from the 2p<sub>3/2</sub> peaks of Cu(0) and Cu(I) by ~10 eV.<sup>15–18,24</sup> These satellites, so-called “shake-up” peaks,<sup>25</sup> arise



**Figure 1.** Schematic illustration of a SAM on a copper film that has oxidized. The specific domains given for the different oxidation states of copper reflect the assumptions we use to derive eqs 1 and 2.

from the simultaneous excitation of outer-shell 3d electrons during the ejection of core 2p electrons and, for copper, are present only for the +2 oxidation state. Because the relative XPS intensity of Cu(II) species can be unequivocally determined from the shake-up peaks, we relied on them as our principal measure of oxidation.<sup>26</sup>

Relating any XPS intensity to a composition requires a model. The model that we use here assumes that the oxidation occurs homogeneously over the entire surface and that the most oxidized copper species, Cu(II), are present near the Cu/SAM interface (Figure 1).<sup>27</sup> The relative intensity of the XPS peaks due to the Cu(II) species can be described by eq 1,

$$\% \text{ Cu(II)} = 1 - \exp(-d_{\text{Cu(II)}}/\lambda \cos \phi) \quad (1)$$

where % Cu(II) is the percentage of the integrated peak area of the Cu(2p<sub>3/2</sub>) spectral envelope that is due to Cu(II) species (both the primary and shake-up peaks),<sup>28</sup>  $d_{\text{Cu(II)}}$  is the thickness of the layer that contains Cu(II) species,  $\lambda$  is the inelastic mean free path of Cu(2p<sub>3/2</sub>) photoelectrons through the CuO layer,<sup>29</sup> and  $\phi$  is the angle at which the detector is positioned relative to the surface normal (so-called “take-off angle” = 55°). Rearrangement of eq 1 yields an expression that relates the XPS data to the thickness of the Cu(II) layer (eq 2).

$$d_{\text{Cu(II)}} = -\lambda \cos \phi \ln [1 - \% \text{ Cu(II)}] \quad (2)$$

We note that this treatment is not rigorous. For example, an implicit assumption in this derivation is that the values of  $\lambda$  through Cu, Cu<sub>2</sub>O, and CuO are the same; their values have not been

(14) McIntyre, N. S. In *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*; Briggs, D., Seah, M. P., Eds.; Wiley: Chichester, 1983; Chapter 10.

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(16) Larson, P. E. *J. Electron Spectrosc. Relat. Phenom.* **1974**, *4*, 213–218.

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(18) Wagner, C. D.; Gale, L. H.; Raymond, R. H. *Anal. Chem.* **1979**, *51*, 466–482.

(19) Briggs, D., Seah, M. P., Eds. *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*; Wiley: Chichester, 1983; pp 495–497 and references therein.

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(21) <sup>1</sup>G, the most intense signal in the spectral envelope of the L<sub>3</sub>M<sub>4,5</sub>M<sub>4,5</sub> Auger transition, accounts for ~60% of the transition's intensity for Cu; in addition, a fit to this envelope requires five peaks (Dubot, P.; Jousset, D.; Pinet, V.; Pellerin, F.; Langeron, J. P. *Surf. Interface Anal.* **1988**, *12*, 99–104).

(22) Although distinct changes occurred in the shape of the spectral envelope containing the various L<sub>3</sub>MM Auger transitions, the complexity of this region did not allow us to quantitate with any confidence the relative amounts of Cu(0), Cu(I) and Cu(II).<sup>23</sup>

(23) The L<sub>3</sub>M<sub>4,5</sub>M<sub>4,5</sub> Auger transition has been used to quantitate the composition of mixtures of Cu and Cu<sub>2</sub>O (Speckmann, H. D.; Haupt, S.; Strehblow, H.-H. *Surf. Interface Anal.* **1988**, *11*, 148–155); however, this method cannot be used when CuO is also present.

(24) (a) Schön, G. *Surf. Sci.* **1973**, *35*, 96–108. (b) McIntyre, N. S.; Cook, M. G. *Anal. Chem.* **1975**, *47*, 2208–2213.

(25) (a) Rosenzwaig, A.; Wertheim, G. K.; Guggenheim, H. J. *Phys. Rev. Lett.* **1971**, *27*, 479–481. (b) Vernon, G. A.; Stucky, G.; Carlson, T. A. *Inorg. Chem.* **1976**, *15*, 278–284.

(26) Although our discussion centers on the differences in the Cu(2p<sub>3/2</sub>) spectra of Cu, Cu<sub>2</sub>O and CuO, the shake-up peaks due to Cu(II) species should always be well separated from the primary Cu(2p<sub>3/2</sub>) peaks for most counterions of Cu(I) and Cu(II).<sup>19</sup> The lone exception would be CuF<sub>2</sub>: Cu(2p<sub>3/2</sub>), BE = 937.0 eV.<sup>18</sup> As no signal due to fluorine is observed in any of our XPS spectra, we conclude that the integrated intensity of the shake-up peaks that we assign to the various Cu(II) species that are present in our samples (oxides, hydroxides, carbonates, etc.) reflect only the intensity of the shake-up peaks.

(27) We do not know whether the oxidation process occurs in localized areas or uniformly over the sample. Our model assumes that the oxidation proceeds by a uniform process, and underestimates the quantity of Cu(II) species if the process is instead localized. The mechanism of oxidation (localized or uniform) should be the same on all of our samples, and the model we have chosen does not change our data or our phenomenologically-based conclusion that changes in the chain length of the *n*-alkanethiol affect the rate of oxidation of the copper substrate.

(28) We quantitate the intensity of the shake-up peaks and relate them to the sum of the intensities of the primary and shake-up peaks. The shake-up peaks comprise ~31% of the Cu(2p<sub>3/2</sub>) spectrum for CuO.<sup>15,16</sup>

(29) The value of  $\lambda$  for Cu(2p<sub>3/2</sub>) photoelectrons (kinetic energy = 550 eV) through Cu has been calculated to be 10.7 Å (Tanuma, S.; Powell, C. J.; Penn, D. R. *Surf. Interface Anal.* **1988**, *11*, 577–589); the values of  $\lambda$  for Cu(2p<sub>3/2</sub>) photoelectrons through CuO and Cu(OH)<sub>2</sub> are expected to be similar ( $\pm 1$  Å).<sup>30</sup>

determined experimentally but are expected to differ by less than 10%.<sup>30</sup> A more complex model, using different values of  $\lambda$  for each of the different layers, would probably be no more accurate; it is too difficult to quantify the intensities of overlapping peaks due to different oxidation states, and to determine the uncertainty in the actual values of  $\lambda$ . We note that the use of eq 2 does not change any of our conclusions regarding the relative abilities of the various SAMs to retard the oxidation of the copper; we only use it to provide approximate values of the thicknesses of the oxidized layers examined in this paper.

Since the sulfur atoms exist as a single layer on the SAM and the attenuation of the intensities of the different species of sulfur by the alkyl layer is the same, relating the XPS intensities of the peaks due to sulfur to a composition is straightforward: the relative intensities of peaks due to the different oxidation states equals the relative composition of the different species of sulfur.

## Results and Discussion

**Oxidation of Cu/S(CH<sub>2</sub>)<sub>n</sub>CH<sub>3</sub>.** Copper films (99.99%, 2000 Å) were prepared by electron beam evaporation onto chromium-primed silicon wafers. The evaporation chamber was backfilled with Ar, and the wafers were transferred without exposure to O<sub>2</sub> to deoxygenated 1 mM isooctane solutions of various *n*-alkanethiols. After 1-h exposure to the solutions, the wafers were rinsed with hexanes and blown dry in a stream of N<sub>2</sub>.<sup>10</sup> Further details are given in the Experimental Section. The resulting SAMs were characterized by wetting and X-ray photoelectron spectroscopy (XPS), and again after being exposed to the ambient atmosphere (temperature = ~20 °C; relative humidity ≤ 30%) for various intervals of time. Figure 2, a and b, displays XPS spectra of the Cu(2p) and Cu L<sub>3</sub>MM Auger spectral regions for SAMs derived from hexadecanethiol, both immediately after formation and after various lengths of exposure to the atmosphere. With continued exposure, peaks due to Cu(0) decrease in intensity in both sets of spectra;<sup>22</sup> changes in the Cu(2p) spectra demonstrate that Cu(II) species form during the oxidation. From the position of the new peak in the O(1s) spectra in Figure 2c, we assign the Cu(II) species that is formed to be primarily Cu(OH)<sub>2</sub>.

Figure 2d shows corresponding XPS spectra of the S(2p) region for these SAMs. For samples minimally exposed to the atmosphere, the S(2p) spectral region displayed a single peak that could be fit well as a spin-orbit doublet; this peak has been identified as a thiolate.<sup>10</sup> Upon exposure to the atmosphere, the spectral envelope of the thiolate broadened and could no longer be fit within the constraints of a spin-orbit doublet for S(2p) (line width ≈ 1.2 eV; separation between S(2p<sub>3/2</sub>) and S(2p<sub>1/2</sub>) peaks = 1.15 eV).<sup>31</sup> This broadening and apparent shift (by ~1 to 2 eV) may reflect the oxidation of some of the thiolates<sup>32</sup> or may suggest that the local environment of the thiolates becomes more heterogeneous. With extended exposure, the adsorbed thiolates oxidize and are transformed into a species we believe to be a sulfonate.<sup>33</sup> In the spectra obtained on samples that have been exposed to atmosphere for >300 h, we observe that the primary species on the surface are the thiolate and the sulfonate; discernible peaks due to sulfur having intermediate oxidation states are not observed on any sample that we have examined, although they probably exist at

(30) The relation between two inelastic mean free paths can be derived from Seah and Dench's expression for  $\lambda$  (Seah, M. P.; Dench, W. A. *Surf. Interface Anal.* 1979, 1, 2-11) to be

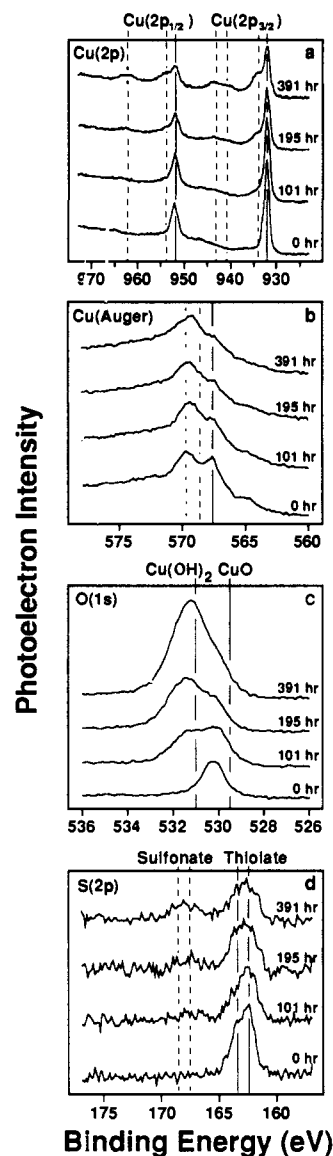
$$\lambda_1/\lambda_2 = \sqrt{A_1/\rho_1} / \sqrt{A_2/\rho_2} \quad (i)$$

where  $A_n$  is the mean atomic weight of the matrix atoms in compound  $n$  (for example, for Cu<sub>2</sub>O,  $A = 143.08/3$  or 47.69), and  $\rho_n$  is the density of compound  $n$ . Using eq 1, the value of  $\lambda_{Cu_2O}$  is estimated to be ~6% greater than  $\lambda_{Cu}$ , the value of  $\lambda_{CuO}$  to be ~7% lower than  $\lambda_{Cu}$ , and the value of  $\lambda_{Cu(OH)_2}$  to be ~10% lower than  $\lambda_{Cu}$ .

(31) Salaneck, W. R.; Lipari, N. O.; Paton, A.; Zallen, R.; Liang, K. S. *Phys. Rev. B* 1975, 12, 1493-1500.

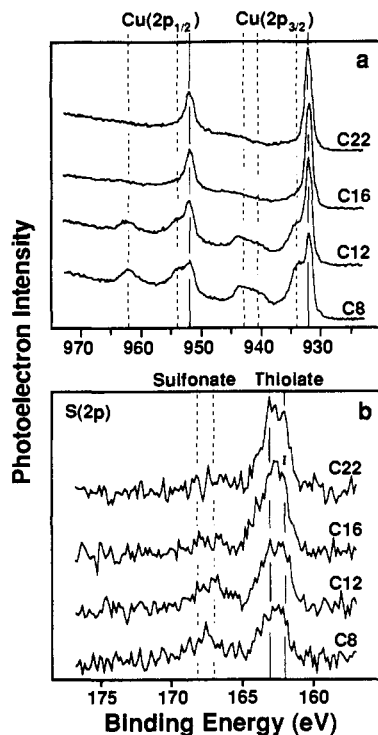
(32) The binding energy of the S(2p<sub>3/2</sub>) peak for an *n*-alkanethiol is 163.6 eV; for an *n*-alkanethiolate SAM on Cu, Ag, or Au, it is 162.1 ± 0.2 eV.<sup>10</sup>

(33) The binding energy of the S(2p<sub>3/2</sub>) peak for a SAM derived from an alkyl sulfonic acid on Ag<sub>2</sub>Ag<sub>2</sub>O is 167.4 eV.<sup>10</sup>



**Figure 2.** XPS spectra of the Cu(2p), Cu(L<sub>3</sub>MM Auger), O(1s), and S(2p) spectral regions of a *n*-hexadecanethiolate SAM on copper after various lengths of exposure to atmosphere. (a) The solid lines note the position of peaks due to Cu(0) and Cu(I) species; the dashed lines note the position of the peaks due to Cu(II) species. In our analysis (Figure 4), we rely on the intensities of the Cu(2p<sub>3/2</sub>) satellites (~942 eV) to quantitate the extent of oxidation. (b) The solid, dotted, and dashed lines note the positions of the most intense peak of the L<sub>3</sub>MM Auger envelope for Cu, Cu<sub>2</sub>O, and CuO, respectively. The intensity at any of these markers provides qualitative information to the changes in the composition of the copper surface (see text). (c) The solid lines denote the position of the O(1s) peak for pure samples of CuO and Cu(OH)<sub>2</sub>. (d) The solid lines note the positions of S(2p) peaks due to a thiolate; the dashed lines note the positions of S(2p) peaks due to a sulfonate. The left and right lines of each pairing reflect the positions of the two components, S(2p<sub>1/2</sub>) and S(2p<sub>3/2</sub>), respectively, of the S(2p) spectral envelope.

concentrations below those that we can detect. The spectra clearly show that the oxidation of the thiolates does not proceed in a stepwise manner with all the thiolates being converted to an intermediate oxidation state (for example, a sulfinate) before conversion to a higher oxidation state (for example, a sulfonate). This coexistence of thiolates and sulfonates may suggest that the oxidation of these samples does not occur uniformly but rather at specific localized areas (presumably, near defects in the SAM). In the numerous spectra that we have obtained, spectra that contained peaks due to sulfonates typically also showed peaks due to Cu(II) species. This observation suggests that the oxidation



**Figure 3.** XPS spectra of the Cu(2p) and S(2p) spectral regions of a SAMs on copper derived from *n*-alkanethiols ( $C_nH_{2n+1}SH$ ) after 101-h exposure to the atmosphere. Lines identifying the spectral positions of the various species are the same as those given in Figure 2.

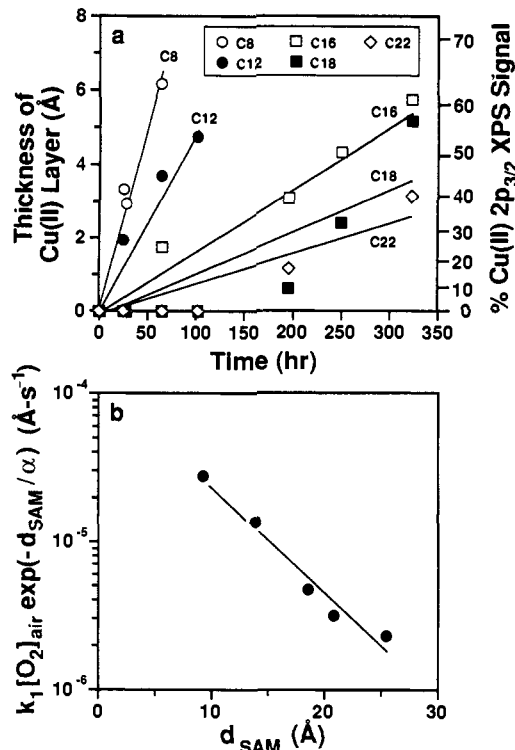
of the copper and the thiolates are related.

**Importance of the Thickness of the Hydrocarbon Layer of the SAM in Retarding Oxidation.** SAMs derived from *n*-alkanethiols of different chain lengths were allowed to oxidize under similar conditions. XPS spectra of the Cu(2p) region indicated that the thicker SAMs retarded the oxidation of copper better than did thinner SAMs (Figure 3a). The oxidation of thiolates to sulfonates also proceeded more slowly on the thicker SAMs (Figure 3b). The longer SAMs could be exposed to atmosphere for longer periods of time than the shorter SAMs before peaks due to Cu(II) species and to sulfonates were present in the XPS spectra.

Figures 4 and 5 summarize the XPS results from the oxidation of SAMs derived from *n*-alkanethiols of various lengths. Figure 4a presents XPS data for the oxidation of the copper to Cu(II) species; the thickness of the Cu(II) layer was derived from the XPS data using eq 2. The increased effectiveness of the longer SAMs in retarding the oxidation of the copper substrate is clearly evident from the XPS data. To quantitate the differences in the oxidation rates of the copper by the different adsorbates, we must make some assumptions regarding the mechanism of oxidation. *One weakness of our analysis is that we ignore Cu(I) species because of the difficulties in quantifying their concentration (vide supra).* As the oxidation probably proceeds by a similar route regardless of the length of the SAM (albeit one slower with some adsorbates), the amount of Cu(I) species on any sample is probably related to the amount of Cu(II) species that is present; thus, as our conclusions are based on differences in the rates of oxidation, we expect that our conclusions would change little if we could also measure the amount of Cu(I) species.

We have assumed a mechanistic model in which the rate of formation of the Cu(II) layer is limited, at steady state, by the concentration of  $O_2$  that penetrates through the hydrocarbon layer and reaches the copper surface. Other models might also be compatible with the data (for example, rate expressions that incorporate water in them as  $Cu(OH)_2$  is the primary oxidation product that we observe), but we have not explored alternatives in any detail. With this assumed model, the thickness of the Cu(II) layer can be described by eq 3

$$d_{Cu(II)} = k_1 t [O_2]_{air} \exp(-d_{SAM}/\alpha) \quad (3)$$



**Figure 4.** Extent of oxidation of the copper surface for *n*-alkanethiolate SAMs on copper as a function of exposure time to the atmosphere. (a) Relative intensity of the Cu(II) peaks in the Cu(2p<sub>3/2</sub>) spectral region; XPS data were related to thicknesses by eq 1. This treatment assumes that Cu(II) species are present at the copper/SAM interface. Lines represent linear least-squares fits of the data to eq 3 and were constrained to intersect the origin; the slopes of these lines are used in the lower panel. Data are from two independent experiments. We estimate the error in the ordinate to be  $\pm 5\%$ . (b) Relation between the zeroth-order rate constants for formation of Cu(II) species and the thickness of the hydrocarbon layer of the SAM; to convert the units of the ordinate from Å of Cu(II) species/s to moles of Cu(II) species/cm<sup>2</sup>·s, multiply the plotted values by  $8 \times 10^{-10}$ . The line represents a linear least-squares fit of the data to eq 5 and gives a value of  $\alpha$  of 6 Å.

where  $k_1$  is the rate constant for the reaction between the copper surface and  $O_2$ ,  $t$  is time in hours,  $[O_2]_{air}$  is the concentration of  $O_2$  at the SAM/air interface and is taken to be a constant,  $\alpha$  is the thickness of hydrocarbon required to decrease the concentration of  $O_2$  at steady state by a factor of  $1/e$ ,<sup>34</sup> and  $d_{SAM}$  is the thickness of the hydrocarbon layer of the thiolate SAM. Most of the data in Figure 4a are adequately fit by lines whose slope describes the rate of formation of Cu(II) species. Whether the apparent induction period observed for  $C_{18}$  and  $C_{22}$  SAMs is real or due to fluctuations in the data has not been established. In Figure 4b, we show that the rates of formation of Cu(II) species depend on the chain length of the adsorbate by applying eq 4

$$\ln \left[ \frac{d(d_{Cu(II)})}{dt} \right] = -\frac{d_{SAM}}{\alpha} + \ln(k_1 [O_2]_{air}) \quad (4)$$

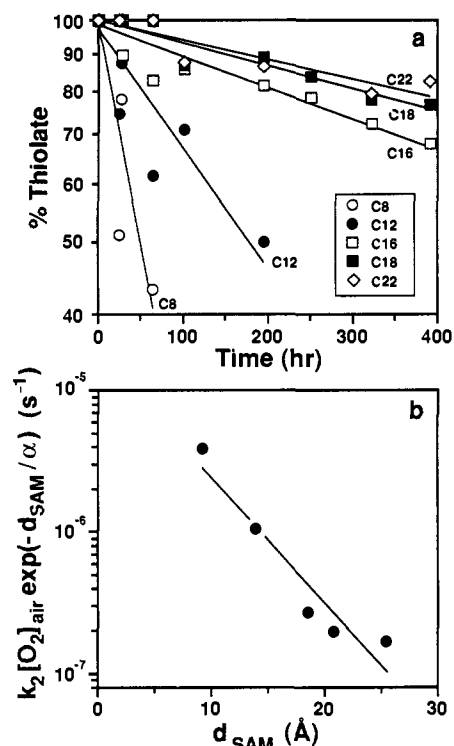
The value of  $d_{SAM}$  was calculated using eq 5,

$$d_{SAM} = 1.27n \cos \phi \quad (5)$$

where 1.27 Å is the incremental distance per  $CH_2$  group in a trans-extended hydrocarbon chain,<sup>35</sup>  $n$  is the number of carbon

(34) It has been suggested that the transport of small molecules (like  $O_2$ ) through lipid layers involves kinks (i.e., gauche defects) in the layer (Träuble, H. J. *Membr. Biol.* 1971, 4, 193–208. Pace, R. J.; Chan, S. I. *J. Chem. Phys.* 1982, 76, 4241–4247). Given an average probability of finding a methylene present in the SAM in a gauche conformation, we therefore expect that there might be an exponential chain length dependence on the relative rates of oxidation.

(35) Abrahamsson, S.; Larsson, G.; von Sydow, E. *Acta Cryst.* 1960, 13, 770–774.



**Figure 5.** Extent of oxidation of the thiols for *n*-alkanethiolate SAMs on copper as a function of exposure time to atmosphere. (a) Relative intensity of the S(2p) peak due to thiolate in the S(2p) spectral region; data are modelled as a first-order decay. Lines are exponential least-squares fits of the data to eq 6 and were constrained to intersect the ordinate at 100% thiolate. Data are from two independent experiments. We estimate the error in the ordinate to be  $\pm 10\%$ . (b) Relation between the first-order rate constants for formation of the sulfonates and the thickness of the hydrocarbon layer of the SAM. The line represents a linear least-squares fit of the data to eq 7 and gives a value of  $\alpha$  of 5 Å.

atoms in the adsorbate, and  $\phi$  is the angle the chain is canted from the surface normal ( $=13^\circ$ ).<sup>10</sup> From these data, we obtain a value of  $\alpha$  of 5 Å.

In Figure 5, we examine the oxidation of the sulfur atoms of the SAMs in a related manner. Unlike copper, the amount of sulfur present in the system is limited to a monolayer. We model the loss of thiolate as a first-order process (eq 6),

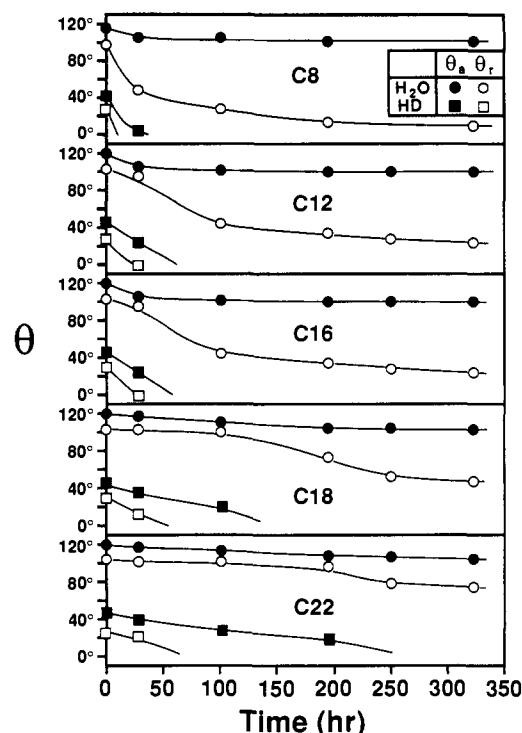
$$\frac{[\text{thiolate}]}{[\text{thiolate}]_{t=0}} = \exp[-k_2 t [\text{O}_2]_{\text{air}} \exp(-d_{\text{SAM}}/\alpha)] \quad (6)$$

where  $[\text{thiolate}]_{t=0}$  is the concentration of thiols present on the surface prior to exposure to the atmosphere, and  $k_2$  is the rate constant for the reaction between the thiols and  $\text{O}_2$ . In a similar manner, we derive eq 7 to describe the effectiveness of the hydrocarbon layer in retarding the oxidation of the thiols.

$$\ln \left[ - \frac{d \ln \left\{ \frac{[\text{thiolate}]}{[\text{thiolate}]_{t=0}} \right\}}{dt} \right] = - \frac{d_{\text{SAM}}}{\alpha} + \ln (k_2 [\text{O}_2]_{\text{air}}) \quad (7)$$

The value of  $\alpha$  that we obtain by this analysis of the data in Figure 5 is 6 Å and agrees well with the value we obtained from the copper data. The similarity of the value of  $\alpha$  obtained from the Cu(2p) data with the value obtained from the S(2p) data seems to validate our assumption that we could use the Cu(II) data to represent, in a relative manner, the amount of oxidation to the copper surface.

The data in Figures 4 and 5 establish firmly that thicker SAMs inhibit the oxidation of the copper surface better than thinner SAMs. We note that the difference in thickness between the SAMs derived from the shortest ( $\text{C}_8$ ) and longest ( $\text{C}_{22}$ ) alkane-

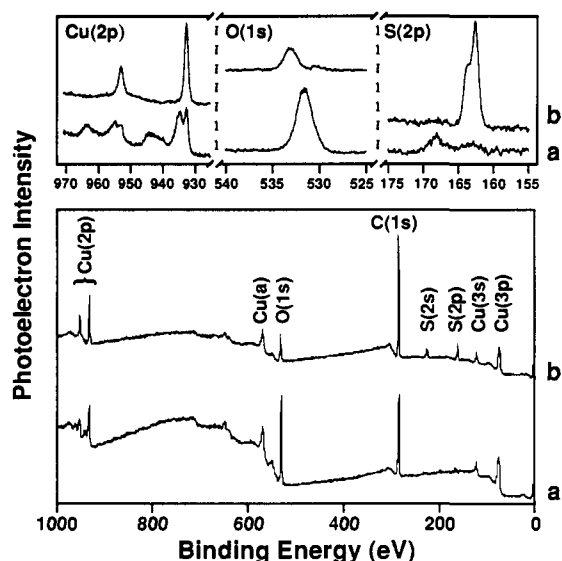


**Figure 6.** Wetting data for *n*-alkanethiolate SAMs on copper ( $\text{C}_n\text{H}_{2n+1}\text{S}/\text{Cu}$ ) as a function of their length of exposure to the atmosphere. Lines are provided as guides to the eye. HD = hexadecane.

thiols is  $\sim 18$  Å. This difference translates into a difference of a factor of  $\sim 20$  ( $\sim e^{18/6}$ ) in the rates of oxidation of the underlying copper and the thiols. The differences in the rates of oxidation are readily detected, even though the difference in the thicknesses of the SAMs is of only a few angstroms.

**Changes in Wetting.** To assess the structural integrity of the monolayers after they had been exposed to atmosphere, we examined their wetting by water and hexadecane (HD) as a function of exposure time (Figure 6). The wetting properties of the SAMs exposed to atmosphere changed in two ways. First, the advancing and receding contact angles of HD,  $\theta_a(\text{HD})$  and  $\theta_r(\text{HD})$ , respectively, decrease with exposure. The lower values of  $\theta_a(\text{HD})$  and  $\theta_r(\text{HD})$  suggest that the SAMs no longer present a surface consisting of densely packed methyl groups. Second, the contact angles of water decrease and the hysteresis in the contact angles of water ( $\Delta\theta = \theta_r - \theta_a$ ) increase on the SAMs upon their exposure to the atmosphere; the decrease is greater for  $\theta_r(\text{H}_2\text{O})$  than for  $\theta_a(\text{H}_2\text{O})$ .  $\theta_a(\text{H}_2\text{O})$ ,  $\theta_r(\text{H}_2\text{O})$ ,  $\theta_a(\text{HD})$ , and  $\theta_r(\text{HD})$  are lower on SAMs derived from alkyl sulfonic acids than from alkyl thiols,<sup>36</sup> and we believe that the decreases in the contact angles reflect the conversion of some fraction of the thiols to sulfonates. The increased hysteresis in the contact angles of water on the oxidized samples probably reflects an increase in the heterogeneity of the SAM, presumably due to the presence of alkyl thiols and alkyl sulfonates. The increased hysteresis may reflect an increase in the roughness of the samples upon oxidation (vide infra) although samples established by XPS to be highly oxidized had the same "rolling hills" morphology<sup>10</sup> by scanning electron microscopy (SEM) as samples minimally exposed to atmosphere. The increased hysteresis could be due to the presence of increased roughness on a scale below the resolution of SEM ( $\sim 200$ – $500$  Å).<sup>37</sup>

(36) The contact angles of water and HD are lower on SAMs derived from alkyl sulfonic acids than from thiols: for  $\text{C}_{16}\text{H}_{33}\text{SO}_3\text{H}$  adsorbed on  $\text{Ag}/\text{Ag}_2\text{O}$ :  $\theta_a(\text{H}_2\text{O}) = 96^\circ$ ,  $\theta_r(\text{H}_2\text{O}) = 61^\circ$ ,  $\theta_a(\text{HD}) < 15^\circ$ ,  $\theta_r(\text{HD}) \approx 0^\circ$ ; for  $\text{C}_{18}\text{H}_{37}\text{SH}$  adsorbed on Cu, Ag, or Au, the values are ( $\pm 4^\circ$ ):  $\theta_a(\text{H}_2\text{O}) = 116^\circ$ ,  $\theta_r(\text{H}_2\text{O}) = 103^\circ$ ,  $\theta_a(\text{HD}) = 48^\circ$ ,  $\theta_r(\text{HD}) = 36^\circ$ .<sup>10</sup> Using these values, the hysteresis in  $\theta(\text{H}_2\text{O})$  for SAMs derived from alkyl sulfonic acids is approximately twice that of SAMs derived from alkyl thiols.



**Figure 7.** XPS spectra of the Cu(2p) and S(2p) spectral regions. (a) A SAM on copper derived from undecanethiol exposed to atmosphere for 295 h. (b) Sample as in (a) exposed to a 1 mM ethanolic solution of 11-hydroxyundecanethiol for 1 min. Upon treatment with the thiol, the shapes of the Cu(2p) and S(2p) spectral regions revert to those obtained on copper samples that have been derivatized with an *n*-alkanethiol and minimally exposed to the atmosphere (see Figure 2).

The changes in the wetting properties of SAMs derived from shorter chain *n*-alkanethiols occurred on shorter timescales than with SAMs derived from longer *n*-alkanethiols. This trend is the same as that observed above with the oxidation of the copper and thiolate. Although these two techniques, wetting and XPS, probe different features of the assembly, they together suggest that, upon oxidation, the SAM becomes more heterogeneous.

We have compared the data in Figures 4, 5, and 6, and we note two correlations. First, the films that contain even small amounts of sulfonates (detected by XPS) are typically wet by HD ( $\theta_c(\text{HD}) \approx 0^\circ$ ). When the extent of oxidation of the thiolates was low, the contact angles of H<sub>2</sub>O on these samples were often similar to those obtained on the freshly prepared SAMs. These observations suggest that the films that contain sulfonates expose some methylene groups at the SAM/liquid(air) interface,<sup>38</sup> and are therefore less ordered than the SAMs that contain only thiolates. Second, with continued exposure to the atmosphere, peaks due to Cu(II) species were observed by XPS, and  $\theta_c(\text{H}_2\text{O})$  had a value more than 40° lower than that measured on the freshly prepared SAMs; the decrease in  $\theta_c(\text{H}_2\text{O})$  was responsible for the increased hystereses observed on these samples.<sup>39</sup> The changes in the wetting properties and in the Cu(2p) XPS spectra from those of the freshly prepared SAMs occurred over the same time interval for a SAM derived from a particular *n*-alkanethiol. As the receding contact angles of H<sub>2</sub>O on these surfaces are lower than that measured for SAMs derived from an alkyl sulfonate,<sup>36</sup> the oxidation of the copper surface may form a roughened SAM/

liquid(air) interface and be responsible for the increased hysteresis in the contact angles of H<sub>2</sub>O.<sup>37</sup>

**Exposure of an Oxidized Sample of Cu/S(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub> to HS-(CH<sub>2</sub>)<sub>11</sub>OH.** Figure 7a shows survey and high resolution XPS spectra for a SAM on copper derived from undecanethiol after 295-h exposure to atmosphere. The SAM was exposed for 1 min to a 1 mM solution of 11-hydroxyundecanethiol (HUT) in ethanol and was characterized by XPS (Figure 7b). A number of differences between the two sets of spectra exist. First, the XPS spectra in Figure 7b resemble those of the SAM as formed initially (Figure 2) and demonstrate that the sulfonates are replaced by thiolates.<sup>40</sup> The timescale under which the adsorbed sulfonates are replaced with thiols is rapid compared to the replacement of thiolates with thiols.<sup>41</sup> Second, the loss of peaks due to Cu(II) in the Cu(2p) region illustrates that the thiol is able to reduce (or displace) the Cu(II) species formed during the oxidation. Beecher has observed similar results using aromatic thiols and unfunctionalized, oxidized copper surfaces.<sup>12b</sup> Third, the reduction (or displacement) of oxidized copper species is also illustrated by the reduction in the intensity of the O(1s) peak upon treatment with the thiol. Lastly, in the oxidized sample, the C(1s) spectral region contains a peak that can be assigned to a carbonate (not shown); upon treatment with the thiol, the C(1s) region no longer contains this peak. The carbonate peak presumably arises from the reaction of CO<sub>2</sub> with the copper hydroxides or oxides; the adsorbed copper carbonate is displaced by the thiol.

The adsorbed layer that results from treatment of the oxidized sample with HUT is different from the SAM that forms on a freshly evaporated copper surface: the C(1s), S(2p), and S(2s) peaks in Figure 7b are more intense, relative to the copper peaks, than for a SAM on freshly evaporated copper derived from HUT. The S(2p) peak in Figure 7b is for a single species, and suggests that all of the sulfurs present in the film exist as thiolates that are presumably coordinated to the copper surface. The differences in the intensities of the XPS peaks between SAMs of HUT formed on oxidized copper and on freshly evaporated copper can be explained by hypothesizing that the thiolates are adsorbed on a copper surface that is substantially roughened on the scale of the length of the HUT molecule ( $\approx 15$  Å). This hypothesis is compatible with the changes observed in the wetting properties of the oxidized SAMs by water (Figure 6).

## Conclusions

Self-assembled monolayers (SAMs) derived from the adsorption of *n*-alkanethiols onto freshly evaporated copper surfaces protect the metal from oxidation. The kinetics of oxidation is compatible with (but does not rigorously demand) a model in which the SAM provides a barrier to the transport of O<sub>2</sub> to the copper surface. Increases in the length of the adsorbate decrease the rates of oxidation of the copper surface and of the adsorbed thiolates; angstrom-level changes in the thickness of the SAM result in decreases in the rate of oxidation that are easily detected by XPS (an increase in the thickness of the SAM by  $\sim 6$  Å results in a decrease in the rate of oxidation by  $\sim 60\%$ ). The oxidation proceeds with a roughening of the copper surface and a transformation of the adsorbed thiolates into sulfonates. The sulfonates and Cu(II) species are rapidly displaced when the sample is exposed to an alkanethiol.

## Experimental Section

**Materials.** Copper (99.99+%), chromium (99.99+%), and isooctane were obtained from Aldrich. Isooctane was percolated twice through a column of neutral alumina (EM Science) prior to use; hexanes were obtained from Fisher and used as received. Si(100) wafers (Silicon Sense) were rinsed with absolute EtOH (Quantum Chemical) and dried

(37) We have previously examined SAMs that express alkyl surfaces that are molecularly rough and have found that the hysteresis in the contact angles of H<sub>2</sub>O is greater on these surfaces than on SAMs on the same substrates that express methyl surfaces. For examples, see: (a) Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989**, *111*, 7164–7175. (b) Laibinis, P. E.; Fox, M. A.; Folkers, J. P.; Whitesides, G. M. *Langmuir* **1991**, *7*, 3167–3173. (c) Folkers, J. P.; Laibinis, P. E.; Whitesides, G. M. *Langmuir* **1992**, *8*, 1330–1341. (d) Laibinis, P. E.; Nuzzo, R. G.; Whitesides, G. M. *J. Phys. Chem.* **1992**, *96*, 5097–5105.

(38) Methyl and methylene surfaces are wet differently by H<sub>2</sub>O and HD: CH<sub>3</sub> surface,  $\theta_{\text{eq}}(\text{H}_2\text{O}) = 112^\circ$ ,  $\theta_{\text{eq}}(\text{HD}) = 43^\circ$ ;<sup>2c</sup> CH<sub>2</sub> surface,  $\theta_{\text{eq}}(\text{H}_2\text{O}) = 102^\circ$ ,  $\theta_{\text{eq}}(\text{HD}) = 0^\circ$  (Holmes-Farley, S. R.; Reamey, R. H.; McCarthy, T. J.; Deutch, J.; Whitesides, G. M. *Langmuir* **1985**, *1*, 725–740).  $\theta_{\text{eq}}$  = equilibrium contact angle.

(39) The oxidation rate of copper surfaces that had been treated with derivatives of benzotriazole (which forms an adherent polymeric coating of Cu(I)-benzotriazole) is lower on those samples that exhibit lower values of  $\theta_c(\text{H}_2\text{O})$  (Thomas, R. R.; Brusica, V. A.; Rush, B. M. *J. Electrochem. Soc.* **1992**, *139*, 678–685).

(40) Exposure of an anaerobically or aerobically manipulated copper surface to a solution containing equimolar concentrations of an alkanesulfonic acid to an alkanethiol in isooctane results in a monolayer derived, within the detection limits of XPS, exclusively from the alkanethiol. Laibinis, P. E.; Folkers, J. P.; Whitesides, G. M. Unpublished result.

(41) For examples of rates of exchange of thiolates with thiols, see: (a) Reference 8d. (b) Reference 8f. (c) Collard, D. M.; Fox, M. A. *Langmuir* **1991**, *7*, 1192–1197. (d) Reference 37b.

prior to placement in the evaporation chamber.

**Preparation of Cu/S(CH<sub>2</sub>)<sub>n</sub>CH<sub>3</sub>.** Chromium (200 Å) and copper (2000 Å) were evaporated in sequence at 5 Å/s onto Si(100) wafers in a cryogenically-pumped chamber (base pressure ≈ 8 × 10<sup>-8</sup> Torr; operating pressure ≈ 1 × 10<sup>-6</sup> Torr) using an electron beam; the resulting copper films are polycrystalline but have a predominant crystallographic orientation that is (111).<sup>10</sup> After evaporation, the chamber was backfilled with argon (Med-tech; 99.998%, <5 ppm O<sub>2</sub>), and the wafers were transferred under a positive flow of argon to 1 mM deoxygenated iso-octane solutions of the *n*-alkanethiols that were brought into the evaporation chamber. The available area between the opened chamber door and the chamber itself for diffusion of air into the chamber was reduced to the minimum needed for transfer of adsorption solutions into the chamber by blocking these regions with sheets of polyethylene; this procedure minimized the oxidation of the copper films prior to their placement into the solutions containing the thiols.<sup>42</sup> After 1 h in solution, the wafers were removed from solution, rinsed with hexanes, and blown dry with N<sub>2</sub>; we have described the procedure used in forming these SAMs previously.<sup>10,43</sup> After various intervals of exposure of the wafers to atmosphere (temperature = ~20 °C; relative humidity ≤30%), two slides (~1 × 3 cm<sup>2</sup>) were cut from the wafer, and one each was characterized by wetting and XPS.

**Wetting.** Advancing and receding contact angles,  $\theta_a$  and  $\theta_r$ , respectively, were measured using a Ramé-Hart goniometer on both sides of

(42) Related experiments using copper films prepared in a diffusion-pumped evaporation chamber (base pressure ≈ 1 × 10<sup>-6</sup> Torr) by resistive heating of a copper-coated tungsten filament and less rigorous procedures for the transfer of the copper films to the adsorption solution resulted in SAMs that were not as ordered as the SAMs used in this study. The ability of these less ordered SAMs to retard the oxidation of the copper surface was diminished by the disorder (by >50%). The longer SAMs did, however, slow the oxidation of the copper better than the shorter SAMs.

(43) Laibinis, P. E.; Bain, C. D.; Whitesides, G. M. *J. Phys. Chem.* **1991**, *95*, 7017-7021.

static drops that had been caused to advance or recede using a Matrix Technologies electro-pipette (~1 μL/s); the pipet tip remained in the drop during the measurements. Data in Figure 6 are typically the average of three drops (six measurements).

**X-ray Photoelectron Spectroscopy (XPS).** XPS spectra were obtained with a Surface Science X-100 spectrometer using a monochromatized Al K $\alpha$  X-ray source (spot diameter = 600 μm) and a concentric, hemispherical analyzer (pass energy = 100 eV). Samples were mounted with metal clips onto a stage and rotated sequentially into the X-ray beam under computer control. Under these conditions, the spectral focus of the sample could not be assured; the spectra presented in Figures 2 and 3 have been sized vertically for presentation purposes. Our analysis did not require the samples to be in optical focus as we rely on the relative intensities of peaks having similar binding energies. Copper and sulfur spectra were accumulated over ~30 min (10 scans; 50-eV window) and ~1 h (40 scans; 20-eV window), respectively. The spectra were fitted by using symmetrical 70% Gaussian/30% Lorentzian profiles and a Shirley background.<sup>44</sup> Previous reports have observed reduction of oxidized copper species during the XPS measurement (exposure times as short as 30 min) using nonmonochromatized X-ray sources.<sup>45</sup> We examined sequential spectra obtained on highly oxidized samples in our spectrometer and found little reduction occurring in our samples over the timescale of our accumulations. We believe this difference is due to our use of a monochromatized X-ray source that does not contain the Bremstrahlung associated with nonmonochromatized sources.<sup>7</sup>

**Registry No.** Cu, 7440-50-8; C<sub>16</sub>H<sub>34</sub>, 544-76-3; Si, 7440-21-3; CH<sub>3</sub>-(CH<sub>2</sub>)<sub>21</sub>SH, 7773-83-3; Cr, 7440-47-3; CH<sub>3</sub>(CH<sub>2</sub>)<sub>10</sub>SH, 5332-52-5; HO(CH<sub>2</sub>)<sub>11</sub>SH, 73768-94-2; CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>SH, 112-55-0; CH<sub>3</sub>(CH<sub>2</sub>)<sub>12</sub>SH, 2917-26-2; CH<sub>3</sub>(CH<sub>2</sub>)<sub>17</sub>SH, 2885-00-9; CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>SH, 111-88-6.

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## Radiation-Induced Conductivity in Polymerized and Nonpolymerized Columnar Aggregates of Phthalocyanine

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**Abstract:** Upon pulsed irradiation, long-lived, highly mobile charge carriers have been found in columnar stacks of thermotropic liquid-crystalline monomer octakis(dodecyloxy)phthalocyanine, Pc12, and polymeric octakis(octyloxy)phthalocyanine, [Si(Pc8)O]<sub>n</sub>. The sum of the charge-carrier mobilities in the solid phase of Pc12 lies between 0.04 × 10<sup>-4</sup> and 1.3 × 10<sup>-4</sup> m<sup>2</sup>/(V s) at room temperature. At the transition from the solid phase to the mesophase, a decrease in the mobilities by a factor of 8 is found. The activation energies associated with the mobilities are very small, on the order of 0 ± 0.05 eV, in both the solid phase and the mesophase. The conductive properties of the liquid-crystalline polymer change gradually over the temperature range studied, from -100 to +200 °C, and coincide with those of the monomer in its mesophase.

### Introduction

The phthalocyanine ring system can be modified in several ways. Incorporation of a central metal atom, substitution around the periphery of the ring, and polymerization can bring about significant changes in the physical properties. In general, the phthalocyanine macrocycle, Pc, has a tendency to organize itself, forming stacks in which there is an interaction between the large  $\pi$ -systems of adjacent rings. As has been recognized, this results in a most interesting and varied group of organic materials which are capable of behaving as one-dimensional semiconductors.<sup>1-4</sup>

It has been established that phthalocyanines which are peripherally octasubstituted with long hydrocarbon chains form thermotropic liquid-crystalline materials in which the Pc macrocycles stack into hexagonally arranged columns.<sup>5-11</sup> The in-

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