

## Stability of Aliphatic Dithiocarboxylic Acid Self-Assembled Monolayers on Gold

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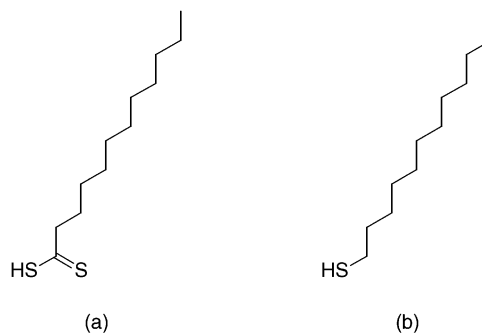
Self-assembled monolayers (SAMs) were prepared by the adsorption of aliphatic dithiocarboxylic acids (ADTCAs) onto the surface of gold. The films were characterized using a variety of analytical techniques: ellipsometry, contact angle goniometry, polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS), and X-ray photoelectron spectroscopy (XPS). These studies found that the ADTCAs attach to the surface of gold via equivalent binding of both sulfur moieties in the dithiocarboxylic acid headgroup. The stability of these highly orientated SAMs was examined at room temperature under a variety of atmospheric conditions (i.e., under argon, oxygen, air, and humid air) and compared to the stability of related SAMs derived from *n*-alkanethiols. The ADTCA-based SAMs were observed to decompose relatively rapidly via oxidation of the sulfur headgroups, as judged by XPS. The rate of desorption of the SAMs was observed to vary as a function of the atmospheric conditions as well as the chain length of the ADTCA adsorbates.

## Introduction

Self-assembled monolayers (SAMs) derived from the adsorption of organic molecules on solid substrates have been extensively studied over the past two decades.<sup>1</sup> These spontaneously adsorbed films have potential applications in many areas, such as biomaterials fabrication,<sup>2</sup> lithographic patterning,<sup>3,4</sup> and thin-film lubrication.<sup>5</sup> The most widely studied and easily prepared SAMs are those derived from the adsorption of normal alkanethiols on gold.<sup>6</sup> While the finite stability of such systems under ambient conditions represents a key obstacle for their use in many applications,<sup>7,8</sup> certain technologies (e.g., soft lithographic patterning) can potentially benefit from the use of a transient easily removable protective overlayer.<sup>9</sup>

Researchers have shown that the decomposition of alkanethiol-based SAMs on gold and silver typically arises from the oxidation of the sulfur headgroups, and that the rate and extent of the oxidation depends on several factors, including the initial film quality, the level of ozone, and the nature of the metal substrate.<sup>7</sup> Moreover, several studies have examined the relationships between the stability and the structure of other organosulfur-based SAMs on gold. The various classes of adsorbates examined include di-*n*-alkyl sulfides,<sup>10</sup> di-*n*-alkyl disulfides,<sup>11</sup> and various chelating dithiols.<sup>12–14</sup> These studies have shown that, in general, the di-*n*-alkyl sulfides form the least stable SAMs, while the di-*n*-alkyl disulfides form SAMs with stabilities indistinguishable from those derived from the corresponding normal alkanethiols, and the chelating dithiols form the most stable SAMs of all. The stability of the latter has been attributed to a combination of factors, including the chelate effect and ring strain associated with desorption as a cyclic disulfide.<sup>14</sup>

A few years ago, we reported a new type of chelating SAM generated by the adsorption of aliphatic dithiocarboxylic acids (ADTCAs) onto the surface of gold.<sup>15</sup> Figure 1 shows the general structure of ADTCAs and that of the corresponding



**Figure 1.** Structure of (a) ADTCA adsorbates and (b) normal alkanethiol adsorbates.

normal alkanethiols. In the present study, we evaluate the stability of ADTCA-based SAMs as a function of chain length and under various conditions by using ellipsometry, contact angle goniometry, polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS), and X-ray photoelectron spectroscopy (XPS). We also compare the stability of ADTCA SAMs to that of normal alkanethiol SAMs, which represent the current benchmark for organic thin films on gold and thus serve as an appropriate standard for comparison.

## Experimental Section

Many of the materials and experimental procedures in the present study have been described in detail in a previous report.<sup>15</sup> Consequently, we provide here a brief summary of certain pertinent and supplementary details.

**Materials.** Gold shot (99.99%) was purchased from Americana Precious Metals, and chromium rods (99.9%) were purchased from R. D. Mathis Co. Single-crystal silicon(100) wafers were purchased from Silicon Sense, Inc. and were rinsed with absolute ethanol before use. Hexadecane used for contact angle measurements was obtained with the highest purity from Aldrich Chemical Co. and was used without further purification. The ADTCA adsorbates were synthesized via the Grignard addition of alkylmagnesium bromides to carbon disulfide.<sup>15,16</sup>

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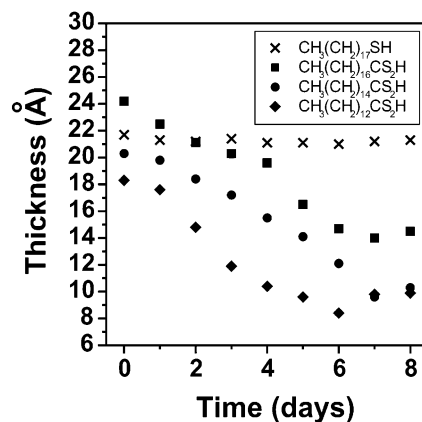
**SAM Preparation.** Silicon wafers were primed with 100 Å of chromium to promote the adhesion of gold to the surface.<sup>17</sup> Gold films, ~1000 Å thick, were prepared by thermal evaporation under vacuum ( $1 \times 10^{-5}$  Torr) at a rate of 1 Å/s. The wafers were cut into slides (~1 × 2 cm), washed with absolute ethanol, and blown dry with ultrapure nitrogen. The ellipsometric constants of the bare gold slides were then collected. Dilute solutions of the ADTCAs (1 mM in absolute ethanol) were prepared in glass weighing bottles, which had been cleaned by soaking in piranha solution (7:3 H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>) for 1 h followed by rinsing thoroughly with deionized water and absolute ethanol. *Caution! Piranha solution reacts violently with organic materials and should be handled carefully.* In forming the SAMs, the gold-coated silicon wafers were immersed in the ADTCA solutions for 48 h at room temperature. The SAM-coated slides were removed from solution, rinsed immediately with dichloromethane, toluene, and ethanol, and then blown dry with ultrapure nitrogen.

The stabilities of the SAMs were monitored under a variety of atmospheric environments (argon, air, and oxygen). Each SAM-coated wafer was sealed in a vial and purged with the various contacting atmospheres for 5 min. In certain trials, a few drops of water were added to the vials to examine the influence of humidity. The influence of ambient laboratory light was also examined. In these latter trials, certain vials were covered with aluminum foil to minimize exposure to light; other vials were placed inside a foil-coated box and directly exposed to a light source (Philips 60 W soft white bulb). In these studies, the ambient laboratory temperature varied between 22 and 23 °C, and the temperature under the light source varied between 25 and 26 °C. After exposure to the various stimuli, the SAM-coated slides exposed were exhaustively rinsed with dichloromethane, toluene, and ethanol and then dried with ultrapure nitrogen before analysis by ellipsometry, contact angle, and PM-IRRAS. For the XPS measurements, however, the slides were unwashed prior to analysis so that any decomposed physisorbed species could be detected and quantified along with the remaining unmodified chemisorbed species.

**Ellipsometric Thickness Measurements.** The thicknesses of the SAMs were measured with a Rudolph Research Auto El III ellipsometer equipped with an He–Ne laser (632.8 nm) set at a fixed incident angle of 70°. In these analyses, the ADTCA SAMs were assumed to possess a refractive index of 1.45. Unless specified otherwise, the data were averaged over two separate slides using three spots per slide for a given adsorbate. All measurements were performed at room temperature under ambient laboratory atmosphere, and the data were collected within 3 h after removing the slides from the vials.

**Contact Angle Measurements.** Hexadecane was used as a contact liquid and was dispensed and withdrawn with an electronic micropipet (Matrix Technologies) at the slowest possible speed (1 μL/s). Advancing and receding angles were measured on both edges of the drop with a Ramé-Hart model 100 goniometer. For a given sample, three drops per slide were averaged to obtain the data. All contact angle measurements were conducted at room temperature with the pipet tip in contact with the drop.

**Infrared Spectroscopy.** All spectra were collected immediately after removing the samples from solution and rinsing. For the time intervals indicated in the relevant figures, the kinetics of film decomposition were monitored by PM-IRRAS after exposure to the various stimuli and environments. These data were collected using a Nicolet MAGNA-IR 860 Fourier transform spectrometer equipped with a liquid-nitrogen cooled



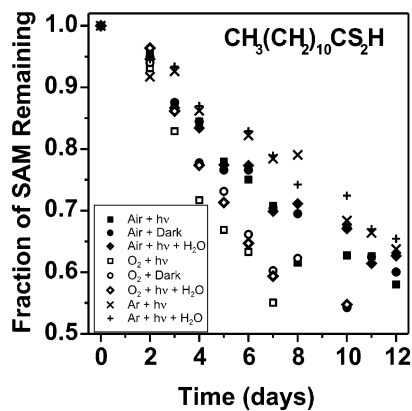
**Figure 2.** Ellipsometric thickness of various SAMs as a function of exposure to air and soft white light. Although the data show some degree of scatter ( $\pm 2$  Å), the relative order of the thicknesses and the slopes were reproducible from run to run. Data for the *n*-alkanethiol SAM were collected separately for the purpose of comparison.

mercury–cadmium–telluride (MCT) detector and a Hinds Instruments PEM-90 photoelastic modulator. The p-polarized light was incident at 80°, and the spectra were collected for 64 scans at a spectral resolution of 4 cm<sup>-1</sup>.

**X-ray Photoelectron Spectroscopy.** In these measurements, the SAMs were characterized using a PHI 5700 X-ray photoelectron spectrometer equipped with a monochromatic Al K $\alpha$  X-ray source ( $h\nu = 1486.7$  eV) incident on the surface. The spectrometer was configured to operate at high resolution with pass energy of 23.5 eV, a photoelectron takeoff angle of 45° from the surface, and an analyzer spot diameter of 1.1 mm. Spectra were collected at room temperature and a base pressure of  $2 \times 10^{-9}$  Torr. All binding energies were referenced to that of Au 4f at 84 eV. Standard curve-fitting algorithms were used to determine the peak intensities.<sup>18</sup>

## Results and Discussion

**Thickness Profiles.** Previous studies have shown that both UV light and oxygen (either directly or through the intermediacy of ozone) hasten the decomposition of SAMs on gold derived from normal alkanethiols.<sup>7,19,20</sup> Given the projected use of ADTCA SAMs in coatings and patterning applications, we wished to examine their stability upon exposure to common laboratory stimuli (i.e., ambient air and light). To this end, we utilized ellipsometric thickness measurements of the SAMs to estimate the initial quality of the films and to monitor the fraction of the SAMs remaining on the surface as a function of time under various conditions. In a first set of experiments, we examined a series of SAMs derived from three ADTCAs with chain lengths varying from C14 to C18. We exposed these SAMs to soft white light and an atmosphere of air and then monitored the film thickness over the course of ca. 2 weeks. Figure 2 illustrates the resultant stability profiles, which demonstrate, first of all, that the initial ellipsometric thicknesses of all three SAMs were consistent with those reported previously,<sup>15</sup> indicating that the SAMs prepared here correspond to uniform, densely packed monolayer films. The data further illustrate that all three SAMs underwent substantial desorption during the analyses, with the thinner films desorbing more readily than the thicker ones. Over the course of 8 days, for example, the C14 film lost ~50% in thickness while the C18 film lost ~40% in thickness.<sup>21</sup> In contrast, the thickness of the SAM derived from the normal alkanethiol was relatively constant during the entire interval of time.

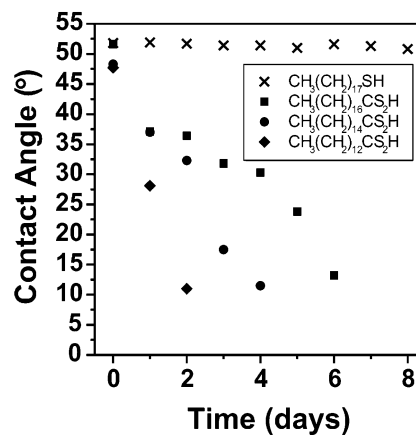


**Figure 3.** Ellipsometric thickness of SAMs derived from  $\text{CH}_3(\text{CH}_2)_{10}\text{CS}_2\text{H}$  as a function of the time of exposure to various conditions.

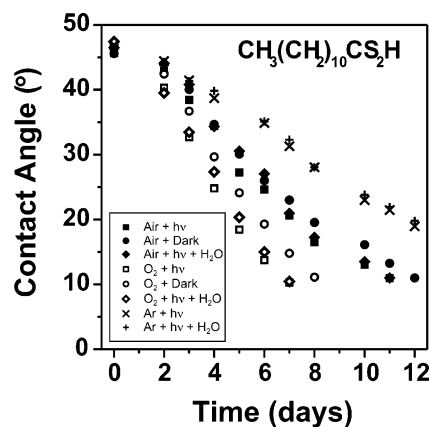
We also examined the ellipsometric thickness profiles of SAMs derived from  $\text{CH}_3(\text{CH}_2)_{10}\text{CS}_2\text{H}$  upon exposure to various atmospheric conditions and other stimuli. For these studies, we chose an ADTCA adsorbate having a relatively short chain length because preliminary studies had shown that thinner films were more readily susceptible to decomposition than thicker ones (e.g., see Figure 2); consequently, we anticipated that a systematic analysis of thinner films would be relatively less time-consuming. Two major trends can be gleaned from the data in Figure 3. First, the extent of desorption can be grouped into three general categories: (1) under argon, slowest desorption; (2) in air, intermediate desorption; (3) under oxygen, fastest desorption. These observations strongly suggest that oxygen plays a major role in the decomposition of these SAMs. The fact that the films under argon also underwent desorption can be rationalized given that they were routinely exposed to the ambient laboratory atmosphere during the ellipsometric analyses; moreover, it is likely that trace amounts of oxygen diffused into the septa-sealed vials during the exposure intervals. The second trend apparent from these data is that the exposure of ADTCA SAMs to soft white light and/or water appears to have little or no effect on the stability of the films.

**Wettability Profiles.** Contact angle measurements are sensitive to the composition, orientation, and conformational order of organic thin films.<sup>6</sup> In particular, hexadecane is a highly sensitive contacting liquid that can readily detect small differences in the orientation and order of thin films that possess tail groups composed exclusively of hydrocarbons.<sup>22</sup> We examined the contact angles of hexadecane on a series of ADTCA SAMs having three different chain lengths as a function of exposure to soft white light and an atmosphere of air. For all of these ADTCA SAMs, the contact angles decreased systematically with exposure time (see Figure 4, which represents the “contact angle” analogue to Figure 2). Moreover, the fastest decay occurred with ADTCA SAMs composed of adsorbates having the shortest chain lengths—an observation readily noted by comparing the slopes in the data for a given adsorbate as a function of time.<sup>23</sup> In contrast, the SAM generated from the normal alkanethiol exhibited no substantial variation in contact angle during the course of these experiments.

We also used contact angle measurements to compare the stabilities of SAMs exposed to a variety of stimuli and conditions (see Figure 5, which represents the “contact angle” analogue to Figure 3). For the reasons outlined in the previous section, we chose to examine SAMs derived from  $\text{CH}_3(\text{CH}_2)_{10}\text{CS}_2\text{H}$  in these experiments. Consistent with the ellipsometric data, the profiles in Figure 5 can be grouped into three general classes: (1) under argon, most stable; (2) in air, intermediate



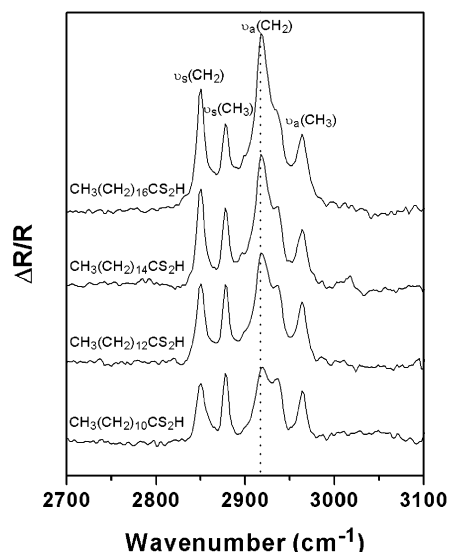
**Figure 4.** Advancing contact angles of hexadecane on various SAMs as a function of exposure to air and soft white light. Data are omitted for contact angles  $\leq 10^\circ$ , which we define as fully wettable surfaces. Data for the *n*-alkanethiol SAM were collected separately for the purpose of comparison.



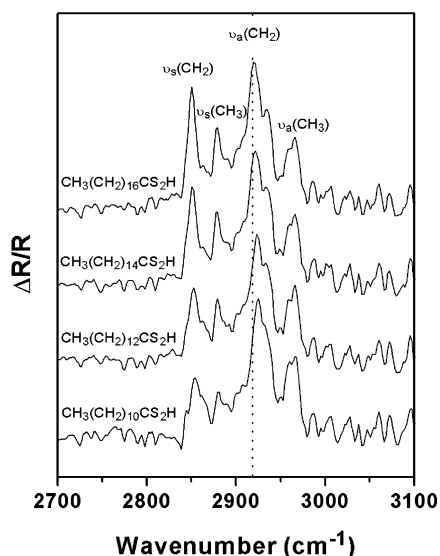
**Figure 5.** Advancing contact angles of hexadecane on SAMs derived from  $\text{CH}_3(\text{CH}_2)_{10}\text{CS}_2\text{H}$  as a function of the time of exposure to various conditions.

stability; (3) under oxygen, least stable. Moreover, it appears that neither water nor soft white light strongly influences the stabilities of these SAMs. Taken as a whole, these data strongly suggest that oxygen (or ozone)<sup>7</sup> is primarily responsible for the instability of ADTCA SAMs on gold.

**PM-IRRAS Analysis of Freshly Prepared and Partially Desorbed ADTCA SAMs.** Figure 6 shows the IR spectra of the C–H stretching region for freshly prepared ADTCA SAMs having chain lengths ranging from C12 to C18. We note that SAMs on gold derived from *n*-alkanethiols exhibit analogous spectra, but the relative intensities of the various bands are noticeably different than those shown here,<sup>24</sup> which suggests that the ADTCA SAMs adopt an orientation distinct from that of normal alkanethiol SAMs. While a detailed analysis of the orientation of ADTCA SAMs is not the objective of this paper, we nevertheless wish to highlight some structural features that can be inferred from the spectra. First, for all of the ADTCA SAMs, the relative intensities of the methyl stretching bands ( $\nu_s^{\text{CH}_3}$  vs  $\nu_a^{\text{CH}_3}$ ) suggest that the terminal methyl group is pointed roughly normal to the surface.<sup>22,25</sup> Second, the intensities of the  $\nu_s^{\text{CH}_2}$  and  $\nu_a^{\text{CH}_2}$  bands increase with increasing chain length of the adsorbates, reflecting their relative stoichiometry. Third, the position of antisymmetric methylene stretching band ( $\nu_a^{\text{CH}_2}$ ) at ca. 2918  $\text{cm}^{-1}$  indicates a fully trans extended conformation for these SAMs.<sup>26</sup> We note further that the  $\nu_a^{\text{CH}_2}$  band for the SAM derived from the shortest adsorbate,  $\text{CH}_3(\text{CH}_2)_{10}\text{CS}_2\text{H}$ ,



**Figure 6.** PM-IRRAS spectra of freshly prepared ADTCA SAMs on gold. The dashed line is positioned at  $2918\text{ cm}^{-1}$ .

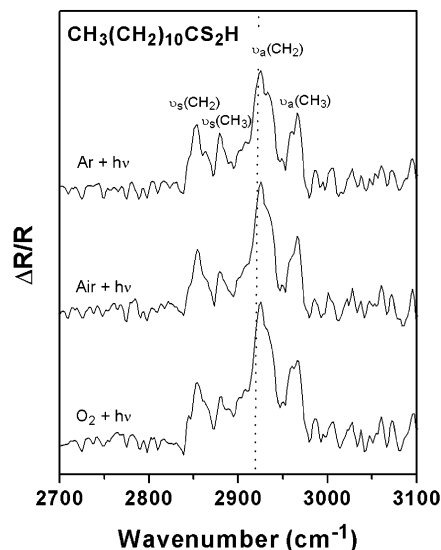


**Figure 7.** PM-IRRAS spectra of SAMs exposed to oxygen for 5 days. The dashed line is positioned at  $2918\text{ cm}^{-1}$ .

appears at a slightly higher wavenumber ( $2919\text{ cm}^{-1}$ ), reflecting a reduced conformational order for this film, which is consistent with studies of SAMs derived from *n*-alkanethiols in which adsorbates having less than  $\sim 10$  carbon atoms afford SAMs that are relatively disordered.<sup>26</sup>

Figure 7 shows the PM-IRRAS spectra of the ADTCA SAMs upon exposure to soft white light and an atmosphere of oxygen for a period of 5 days. For the chain lengths of C18, C16, C14, and C12, the position of the  $\nu_a\text{CH}_2$  band increases as follows:  $2920$ ,  $2921$ ,  $2923$ , and  $2926\text{ cm}^{-1}$ , respectively. Given that the initial band positions for these SAMs appeared at  $2918$ – $2919\text{ cm}^{-1}$ , these data suggest that the loss of conformational order is greater for SAMs having shorter chain lengths; moreover, the data are consistent with the ellipsometry and wettability data provided above, which indicate enhanced desorption (and thus diminished stability) for films having shorter chain lengths.

In separate studies, we used PM-IRRAS to evaluate the stability of these films as a function of exposure to various conditions and stimuli. Figure 8 shows the spectra of SAMs derived from  $\text{CH}_3(\text{CH}_2)_{10}\text{CS}_2\text{H}$ , upon exposure to soft white light and the following atmospheres: argon, air, and oxygen.



**Figure 8.** PM-IRRAS spectra of SAMs on gold derived from  $\text{CH}_3(\text{CH}_2)_{10}\text{CS}_2\text{H}$  and exposed to various conditions for 7 days. The dashed line is positioned at  $2918\text{ cm}^{-1}$ .

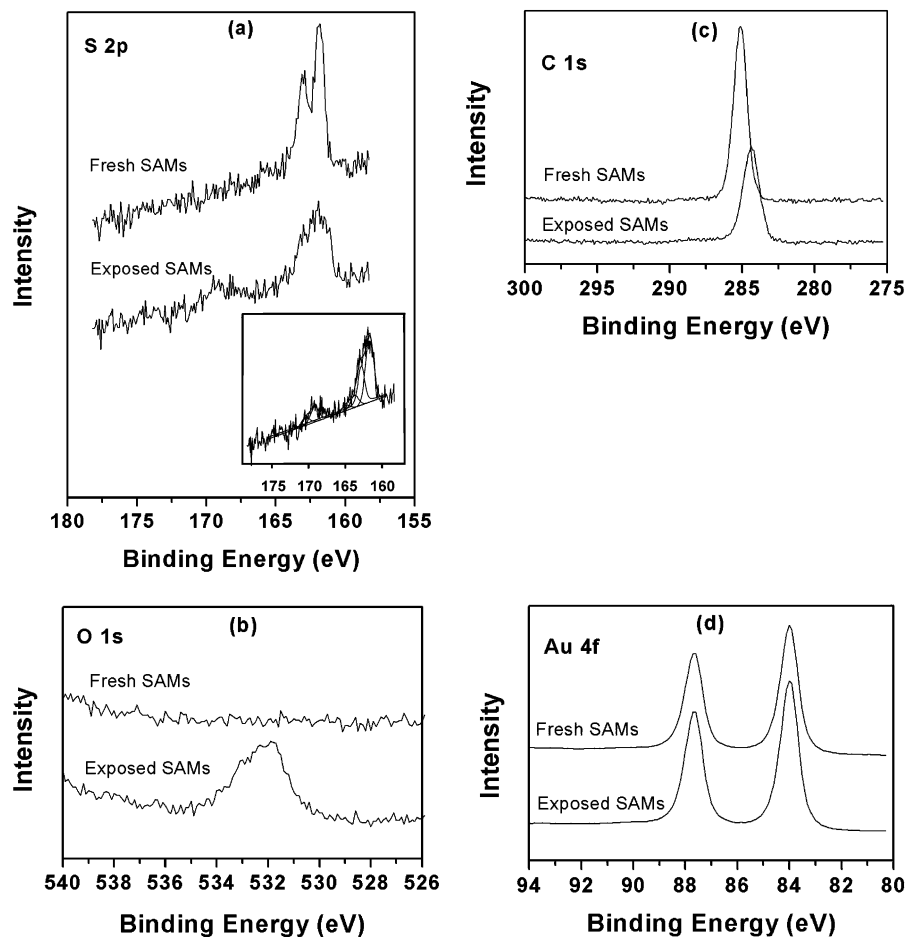
Despite the fact that the ellipsometry and wettability data presented above provided clear evidence that ADTCA film stability was most strongly influenced by oxygen, the PM-IRRAS data are inconclusive. We note, however, that it is likely that the analysis here is flawed because the initial films derived from this short chain adsorbate were disordered to begin with, and thus the PM-IRRAS technique fails to differentiate the precise degree to which the films become further disordered.

**XPS Analysis of Freshly Prepared and Partially Desorbed ADTCA SAMs.** XPS is commonly used to evaluate the atomic composition and chemical nature of organosulfur adsorbates on metal surfaces.<sup>20,24,25,27</sup> Furthermore, by comparison of the relative intensity of the signals for C, S, and Au of organosulfur-based SAMs on gold, the packing density of the alkyl chains on the surface can be determined.<sup>28</sup> Figure 9a shows the S 2p region for a freshly prepared ADTCA SAM on gold derived from  $\text{CH}_3(\text{CH}_2)_{14}\text{CS}_2\text{H}$  and the same SAM after exposure to soft white light and air for 2 weeks. For the freshly prepared SAM, the sulfur peak consists of a spin split doublet, where S  $2p_{3/2}$  and S  $2p_{1/2}$  are located at  $161.9$  and  $163.1\text{ eV}$ , respectively, with a ratio of areas equal to 2. These data indicate the presence of only one type of sulfur species on the surface,<sup>29</sup> which suggests that the ADTCA adsorbates coordinate to the surface equally through both sulfur atoms.

In Figure 9a, the S 2p spectrum of the partially desorbed SAM, which was analyzed after exposure to soft white light and air for 2 weeks, contains an additional peak at  $169\text{ eV}$ , which can be assigned to the presence of oxidized sulfur species.<sup>7</sup> Furthermore, the S  $2p_{3/2}$  and S  $2p_{1/2}$  peaks are broader than those of the freshly prepared SAM. We used standard curve fitting protocols to determine the position and intensity of each peak in the spectra. The data were then deconvoluted to reveal the percentages of the various sulfur species present on the surface (see Table 1). Given the fact that oxidized sulfur species are indeed present, it is reasonable to conclude that at least one pathway in the decomposition of ADTCA SAMs involves oxidation of the sulfur atoms prior to desorption of the adsorbates.

Additional evidence for a pathway involving oxidative loss is provided by analysis of the O 1s spectral region. Figure 9b shows that no oxygen was detected in the freshly prepared ADTCA SAM; in contrast, oxygen is present in the spectrum





**Figure 9.** XPS spectra of SAMs derived from  $\text{CH}_3(\text{CH}_2)_{14}\text{CS}_2\text{H}$  both freshly prepared and exposed to air and soft white light for 2 weeks. Spectral regions: (a) S 2p, (b) O 1s, (c) C 1s, and (d) Au 4f.

**TABLE 1: XPS-Determined Distribution of Atomic Species for SAMs on Au Derived from  $\text{CH}_3(\text{CH}_2)_{14}\text{CS}_2\text{H}$  and Exposed to Air and Soft White Light for 2 Weeks**

exposure time	% carbon	% bound sulfur	% unbound sulfur	% oxidized sulfur
$t = 0$	100	100	0	0
$t = 2$ weeks	56	40 <sup>a</sup>	6 <sup>a</sup>	10 <sup>a</sup>

<sup>a</sup> The peak intensities of the indicated species of sulfur are relative to that of bound sulfur in the freshly prepared SAM (i.e.,  $t = 0$ ).

of the partially desorbed SAM as indicated by the presence of the peak at 532 eV. To determine whether the oxygen is associated with any species other than sulfur, we also examined the spectral regions of carbon and gold (Figure 9, parts c and d, respectively). Although these spectra provide no evidence for the presence of oxidized carbon or gold, they confirm partial desorption of the SAM by exhibiting a relative decrease in the intensity of the carbon signal and a relative increase in the intensity of the gold signal. We note that the observed shift in the C 1s binding energy from 285 to 284 eV is likely due to decreased charging in the partially desorbed SAM, which should plausibly serve as a less effective insulator than the corresponding complete SAM.<sup>30</sup>

Table 2 shows the XPS-determined surface coverages of the four ADTCA SAMs and a SAM derived from *n*-hexadecanethiol after exposure to air and soft white light for 2 weeks. The coverages were determined by evaluating the percentage of carbon on the surface before and after exposure. For the ADTCA SAMs, the surface coverage was observed to decrease most rapidly for the SAMs having the shortest chain lengths, which

**TABLE 2: XPS-Determined Surface Coverage of SAMs Exposed to Air and Soft White Light for 2 Weeks<sup>a</sup>**

adsorbate	$(\text{C}_{1s}/\text{Au}_{4f})^i/(\text{C}_{1s}/\text{Au}_{4f})^j$
$\text{CH}_3(\text{CH}_2)_{10}\text{CS}_2\text{H}$	0.39
$\text{CH}_3(\text{CH}_2)_{12}\text{CS}_2\text{H}$	0.45
$\text{CH}_3(\text{CH}_2)_{14}\text{CS}_2\text{H}$	0.56
$\text{CH}_3(\text{CH}_2)_{16}\text{CS}_2\text{H}$	0.82
$\text{CH}_3(\text{CH}_2)_{15}\text{SH}$	0.99 <sup>b</sup>

<sup>a</sup> Key:  $t$  = exposed SAMs;  $i$  = freshly prepared SAMs. <sup>b</sup> Data for the *n*-alkanethiol SAM were collected separately for the purpose of comparison.

is consistent with the results above from the ellipsometry and wettability experiments. In contrast to the data for the ADTCA SAMs, we observed a substantially smaller decrease in coverage for the SAM derived from *n*-hexadecanethiol. We note further that analysis of the *n*-hexadecanethiol SAM by XPS revealed no oxidized sulfur species and no oxygen in the films (data not shown). Furthermore, for this SAM, there were no differences in the C 1s and Au 4f spectra before and after exposure.

Given the collective observations presented here and the previously proposed pathways for the oxidative desorption of *n*-alkanethiolate SAMs on gold,<sup>7,31,32</sup> we propose that the oxidation of ADTCA SAMs proceeds via diffusion of oxygen through the hydrocarbon layer to the bottom of the densely packed ADTCA SAMs.<sup>7,19,33</sup> In this model, the oxygen (either directly or through the intermediacy of ozone)<sup>7</sup> oxidizes the sulfur atoms to various oxidation states. This oxidation can directly lead to desorption from the surface due to a loss of donating ability by sulfur concomitant with oxidation.<sup>19,34</sup> It is

also possible that oxygen gives rise to C–S bond scission, particularly if ozone participates in the desorption process.<sup>7,33</sup> In any event, our data fail to distinguish whether the diffusion of oxygen is itself rate limiting or whether the desorption profiles simply correlate with the interchain van der Waals stabilization for the various chain lengths (i.e., the loss of oxidized molecules from the surface is more rapid for SAMs with shorter chain lengths because the intermolecular interactions are weaker than those with longer chain lengths).<sup>35</sup>

An enlightening observation is that the ADTCA SAMs appear to be less stable than corresponding *n*-alkanethiolate SAMs, despite the potential for the entropy-driven chelate effect to enhance the stability of ADTCA-based thin films.<sup>14</sup> The noted instability of ADTCA SAMs, however, is likely to arise from the fragile nature of the dithiocarboxylic acid functional group itself, which is known to undergo facile decomposition upon exposure to mild reagents and conditions.<sup>36–39</sup>

## Conclusions

We performed a series of experiments to evaluate the structure and stability of ADTCA SAMs on gold and to examine the effects arising from their exposure to various agents and laboratory conditions. These studies found that the desorption of the ADTCA SAMs is chain-length dependent, and the presence of oxygen enhances the rate of desorption. Specifically, ADTCA SAMs having shorter chain lengths were observed to desorb from the surface faster than those having longer chain lengths. Furthermore, with regard to exposure to various atmospheric conditions, the following trend in desorption rates was observed: oxygen > air > argon. In contrast, exposure to soft white light and water had little or no influence upon the rates of desorption. Analysis by XPS of partially desorbed SAMs revealed that oxidation of sulfur plays a critical role in the desorption process. Because ADTCA-based SAMs are relatively easy to remove, these materials should find use in applications where temporary nanoscale coatings are required (e.g., soft lithographic patterning).<sup>40</sup>

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