

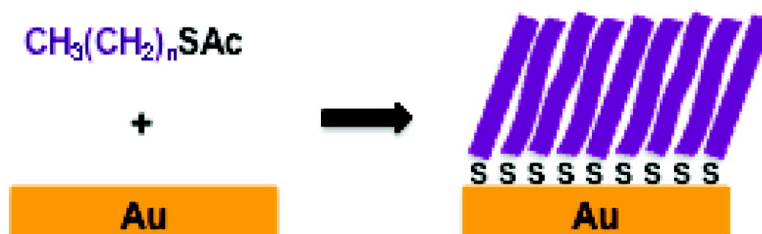
Letter

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Letters

SAMs on Gold Derived from the Direct Adsorption of Alkanethioacetates Are Inferior to Those Derived from the Direct Adsorption of Alkanethiols

Mathilde I. Béthencourt, La-ongnuan Srisombat, Pawilai Chinwangso, and T. Randall Lee*

Department of Chemistry, University of Houston, 4800 Calhoun Rd, Houston, Texas 77204-5003

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Self-assembled monolayers (SAMs) on gold derived from the direct adsorption of thioacetic acid *S*-decyl ester (C10SAc) and thioacetic acid *S*-octadecyl ester (C18SAc) were compared to the corresponding SAMs derived from the analogous adsorption *n*-decanethiol (C10SH) and *n*-octadecanethiol (C18SH). All SAMs were characterized using ellipsometry, contact angle goniometry, polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS), and X-ray photoelectron spectroscopy (XPS). The comparison revealed that the SAMs generated from the thioacetates are not as densely packed and well ordered as the SAMs generated from the thiols. Furthermore, studies of the kinetics of adsorption found that the thioacetates adsorb more slowly than the corresponding thiols.

Introduction

With advances in society comes a growing need for a reduction in the size and energy needs of devices, especially in the emerging fields of nanoelectronics and nanomedicine.¹ Thus, control over the nature of the surfaces of devices becomes an issue of prime importance in many technologies.^{2,3} What better strategy to follow than that of nature?¹ In vivo, molecules self-assemble to form diverse complex structures that exhibit important mechanical properties (e.g., collagen in skin and bone) or produce energy or matter (e.g., photosynthesis or DNA replication). As mimics of self-assembly in nature, self-assembled monolayers (SAMs) have been widely used over the past two decades⁴ to control surface properties in a variety of technologies ranging from cell

adhesion^{5,6} and molecular sensing^{7,8} to electronic devices^{9,10} and surface science.^{11,12} Because the technique of self-assembly involves the spontaneous organization of molecules into semicrystalline assemblies, the use of SAMs offers distinct advantages over the competing technique of Langmuir–Blodgett deposition,¹³ which typically requires problematic trial-and-error processes. Furthermore, because the formation of SAMs involves the adsorption of a surfactant-like molecule on a solid surface, different combinations of adsorbate/substrate (e.g., phosphines on platinum or palladium,^{14–16} silanes on silicon,^{17,18} siloxanes

* Corresponding author. E-mail: trlee@uh.edu.

(1) Park, H. H.; Jamison, A. C.; Lee, T. R. *Nanomedicine* **2007**, *2*, 425.
(2) Dayeh, S. A.; Soci, C.; Yu, P. K. L.; Yu, E.; Wang, D. *J. Vac. Sci. Technol., B* **2007**, *25*, 1432.
(3) Hansen, C.; Quake, S. R. *Curr. Opin. Struct. Biol.* **2003**, *13*, 538.
(4) Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 4481.
(5) Mrksich, M.; Chen, C. S.; Xia, Y.; Dike, L. E.; Ingber, D. E.; Whitesides, G. M. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 10775.

(6) Tidwell, C. D.; Ertel, S. I.; Ratner, B. D.; Tarasevich, B.; Atre, S.; Allara, D. L. *Langmuir* **1997**, *13*, 3404.
(7) Knoll, W.; Zizlsperger, M.; Liebermann, T.; Arnold, S.; Badia, A.; Liley, M.; Piscevic, D.; Schmitt, F. J.; Spinke, J. *Colloids Surf., A* **2000**, *161*, 115.
(8) Vergeese, T. M.; Berchmans, S. *Mater. Chem. Phys.* **2004**, *83*, 229.
(9) de Boer, B.; Meng, H.; Perepichka, D. F.; Zheng, J.; Frank, M. M.; Chabal, Y. J.; Bao, Z. *Langmuir* **2003**, *19*, 4272.
(10) Li, Q.; Zheng, J.; Liu, Z. *Langmuir* **2003**, *19*, 166.
(11) Schreiber, F. *Prog. Surf. Sci.* **2000**, *65*, 151.
(12) *Surface Science Research*; Norris, C. P., Ed.; Nova Science: New York, 2005.
(13) Gaines, G. L., Jr. *Insoluble Monolayers at Liquid-Gas Interfaces*; Interscience: New York, 1966.
(14) Ugo, R. *Coord. Chem. Rev.* **1968**, *3*, 319.

on glass,^{18,19} and thiols on gold, copper, or silver^{20–22}) can be used depending on the application of interest.

Of all known types of SAMs, the thiol/gold combination has experienced the greatest popularity, especially in academia. This preference has been driven by a number of factors. First, thiols have a strong, specific affinity toward gold.²³ Second, the inertness of gold²⁴ makes it a convenient substrate (unlike glass or silicon, where the quality of the SAMs is affected by the degree of humidity²⁵ and content of oxygen²⁶ in the air). Finally, the judicious use of organic synthetic transformations allows the fabrication of a wide range of surfaces by introducing selected functional groups along the molecular axis and/or at the ω terminus.^{27,28}

Nevertheless, as researchers explore the use of SAMs in systems that require increasingly complex functionality, the reactivity of the thiol group has become a growing concern in certain synthetic preparations. For example, when a neighboring functional group is thiol-sensitive, various unwanted side reactions can occur (e.g., intramolecular cyclization or intermolecular polymer formation). One strategy that circumvents these side reactions is the use of a protecting group for the thiol moiety. Free thiols can be protected as a thioether (*S*-benzyl derivative) or a thioester (*S*-acetyl or *S*-benzoyl derivative) or may be oxidized to a symmetrical disulfide.²⁹ Previous research has demonstrated that high-quality SAMs can be formed from disulfides;^{30,31} however, the assembly process is slower than that observed with thiols, and the properties of the resulting films can differ from those of thiol-derived SAMs. Alternative strategies include the in situ generation of free thiols in the assembly solution by the deprotection of functional groups (e.g., upon treatment with acid or base).^{32–34} This strategy, however, requires all other functional groups within the adsorbate molecule to withstand acidic or basic conditions. Interestingly, two reports have indicated that *S*-acetyl-protected species can be used directly (i.e., without deprotection) to generate SAMs on gold.^{32,35} Although the quality of the SAMs produced by this direct adsorption was not thoroughly investigated, both studies found that high adsorbate concentrations and long immersion

times were required to achieve monolayer coverages comparable to those obtained when using the corresponding thiols.

To provide a more comprehensive description of this relatively unexplored system, this letter provides a systematic investigation of SAMs generated by the direct adsorption of alkanethioacetates on gold. Specifically, we prepare SAMs from $\text{CH}_3(\text{CH}_2)_9\text{S}(\text{C}=\text{O})\text{CH}_3$ (**C10SAc**) and $\text{CH}_3(\text{CH}_2)_{17}\text{S}(\text{C}=\text{O})\text{CH}_3$ (**C18SAc**) and compare these SAMs to those prepared from the corresponding *n*-alkanethiols, $\text{CH}_3(\text{CH}_2)_9\text{SH}$ (**C10SH**) and $\text{CH}_3(\text{CH}_2)_{17}\text{SH}$ (**C18SH**). In these studies, we thoroughly characterize these short- and long-chain SAMs, respectively, by ellipsometry, contact angle goniometry, polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS), and X-ray photoelectron spectroscopy (XPS). Furthermore, we use ellipsometry to monitor and compare the kinetics of growth of all of the SAMs.

Experimental Section

Synthesis of Alkanethioacetates. The targeted *n*-alkanethioacetates (**C10SAc** and **C18SAc**) were synthesized in one step from the corresponding 1-bromoalkanes.³⁶ The final products were characterized by NMR spectroscopy in CDCl_3 using a QE-300 spectrometer (300 MHz ^1H). The starting materials (1-bromodecane and 1-bromooctadecane) as well as the corresponding *n*-alkanethiols (**C10SH** and **C18SH**) were purchased from Aldrich Chemical Co. and used without modification.

Thioacetic Acid *S*-Decyl Ester (C10SAc**).** Potassium thioacetate (3.1 g, 27 mmol) was dissolved in ethanol (30 mL), and the mixture was degassed by bubbling with argon for 30 min. An aliquot of 1-bromodecane (2.0 g, 9.0 mmol) was dissolved in 10 mL of ethanol and added to the mixture, which was then refluxed for 6 h. The ethanol was evaporated under vacuum, and the residue was dispersed in water (20 mL) and extracted with diethyl ether (3 \times 10 mL). The organic layer was then dried over anhydrous magnesium sulfate, filtered, and evaporated under vacuum. The resulting pale-yellow residue was purified by column chromatography on silica gel (1% diethyl ether in hexanes) to afford the pure C10 thioacetate in 71% yield (1.4 g, 6.4 mmol). ^1H NMR: δ 2.86 (t, $J = 7.5$ Hz, 2 H), 2.32 (s, 3 H), 1.56 (m, 2 H), 1.25 (br s, 14 H), 0.87 (t, $J = 6.6$ Hz, 3 H).

Thioacetic Acid *S*-Octadecyl Ester (C18SAc**).** This compound was prepared via the strategy used to prepare **C10SAc** but utilized 1-bromooctadecane (2.0 g, 6.0 mmol) as the starting material and a correspondingly adjusted proportion of potassium thioacetate (2.1 g, 18 mmol), which gave the pure C18 thioacetate in 77% yield (1.5 g, 4.6 mmol). ^1H NMR: δ 2.86 (t, $J = 6.9$ Hz, 2 H), 2.32 (s, 3 H), 1.55 (m, 4 H), 1.25 (br s, 32 H), 0.88 (t, $J = 6.6$ Hz, 3 H).

Because the presence of trace amounts of thiol impurities might compromise the conclusions of this study, we used ^1H NMR spectroscopy, thin-layer chromatography (TLC), and Ellman's reagent³⁷ to establish that there were no detectable thiol impurities in the alkanethioacetate samples. Perhaps even more convincing evidence that the thioacetate species rather than thiol impurities are the active species in SAM formation is provided by the XPS data (vide infra), where the SAMs derived from the thioacetates show a markedly greater content of oxygen than those derived from the thiols.

Preparation of SAMs. Ethanolic solutions of the thiols and thioacetates (both 1 mM) were prepared in vials previously cleaned with piranha solution (7:3 concentrated H_2SO_4 /30% H_2O_2). **Caution! Piranha solution reacts violently with organic materials and should be handled carefully.** The bottles were then rinsed successively with deionized water and absolute ethanol and then dried in an oven at 100 $^\circ\text{C}$. Gold surfaces were prepared by the thermal evaporation of chromium (ca. 100 \AA) onto ethanol-washed silicon wafers, followed by the evaporation of gold (ca. 1000 \AA). The resulting gold-coated wafers were cut into slides (ca. 1 \times 3 cm^2), washed with absolute

(15) Mallat, T.; Broennimann, C.; Baiker, A. *Appl. Catal.* **1997**, *149*, 103.
(16) Mitchell, G. E.; Henderson, M. A.; White, J. M. *J. Phys. Chem.* **1987**, *91*, 3808.

(17) Maoz, R.; Sagiv, J. *J. Colloid Interface Sci.* **1984**, *100*, 465.

(18) Wasserman, S. R.; Tao, Y.-T.; Whitesides, G. M. *Langmuir* **1989**, *5*, 1074.

(19) Gun, J.; Sagiv, J. *J. Colloid Interface Sci.* **1986**, *112*, 457.

(20) Laibinis, P. E.; Whitesides, G. M.; Allara, D. L.; Tao, Y.-T.; Parikh, A. N.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 7152.

(21) Laibinis, P. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1992**, *114*, 9022.

(22) Ihs, A.; Liedberg, B. *Langmuir* **1994**, *10*, 734.

(23) Dubois, L. H.; Nuzzo, R. G. *Annu. Rev. Phys. Chem.* **1992**, *43*, 437.

(24) Somorjai, G. A. *Chemistry in Two Dimensions: Surfaces*; Cornell University Press: Ithaca, NY, 1981.

(25) Khayankarn, O.; Pearson, R. A.; Verghese, N.; Shafi, A. *J. Adhes.* **2005**, *81*, 941.

(26) B ethencourt, M. I.; Barriet, D.; Frangi, N. M.; Lee, T. R. *J. Adhes.* **2005**, *81*, 1031.

(27) Colorado, R., Jr.; Lee, T. R. *Langmuir* **2003**, *19*, 3288.

(28) Zhang, X.; Chabal, Y. J.; Christman, S. B.; Chaban, E. E.; Garfunkel, E. *J. Vac. Sci. Technol., A* **2001**, *19*, 1725.

(29) Greene, T. W. *Protective Groups in Organic Synthesis*; Wiley: New York, 1999.

(30) Bain, C. D.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1989**, *5*, 723.

(31) Troughton, E. B.; Bain, C. D.; Whitesides, G. M.; Nuzzo, R. G.; Allara, D. L.; Porter, M. D. *Langmuir* **1988**, *4*, 365.

(32) Tour, J. M.; Jones, L. II; Pearson, D. L.; Lamba, J. J. S.; Burgin, T. P.; Whitesides, G. M.; Allara, D. L.; Parikh, A. N.; Atre, S. *J. Am. Chem. Soc.* **1995**, *117*, 9529.

(33) Cygan, M. T.; Dunbar, T. D.; Arnold, J. J.; Bumm, L. A.; Shedlock, N. F.; Burgin, T. P.; Jones, L. II; Allara, D. L.; Tour, J. M.; Weiss, P. S. *J. Am. Chem. Soc.* **1998**, *120*, 2721.

(34) Cai, L.; Bahr, J. L.; Yao, Y.; Tour, J. M. *Chem. Mater.* **2002**, *14*, 2905.

(35) Kang, Y.; Won, D.-J.; Kim, S. R.; Seo, K.; Choi, H.-S.; Lee, G.; Noh, Z.; Lee, T. S.; Lee, C. *Mater. Sci. Eng., C* **2004**, *C24*, 43.

(36) Evans, R. M.; Owen, L. N. *J. Chem. Soc.* **1949**, 244.

(37) Ellman, G. L. *Arch. Biochem. Biophys.* **1959**, *82*, 70.

Table 1. Ellipsometric Thicknesses ($\pm 2 \text{ \AA}$) of SAMs upon Equilibration with the Indicated Adsorbate for 48 h

adsorbate	thickness (\AA)
C10SH	13
C10SAc	11
C18SH	22
C18SAc	20

ethanol, and blown dry with nitrogen before being dipped into the respective adsorbate solutions. The nature/structure of the resultant monolayer was characterized after an immersion time of 48 h unless otherwise indicated (e.g., kinetics studies).

Measurements of Ellipsometric Thickness. The thicknesses of the monolayers were obtained with a Rudolf Research Auto EL III ellipsometer equipped with a He-Ne laser operating at 632.8 nm and oriented at a 70° angle of incidence. To determine the thicknesses, we assumed a refractive index of 1.45 for all of the films. For each type of film, data were collected and averaged from measurements on 10 distinct slides using 3 separate spots per slide. The thicknesses of the individual SAMs were reproducible to within $\pm 2 \text{ \AA}$ over all measurements.

Kinetics Study. We monitored the kinetics of adsorption of C10SH, C10SAc, C18SH, and C18SAc by measuring the ellipsometric thickness as a function of adsorption time. For a given set of data, the average values of the ellipsometric thickness for at least four measurements were within $\pm 2 \text{ \AA}$ of the values reported. Each slide was monitored sequentially (1) upon dipping for ~ 1 s, (2) at regular intervals over 2 h, (3) after 1 day, and (4) after 2 days.

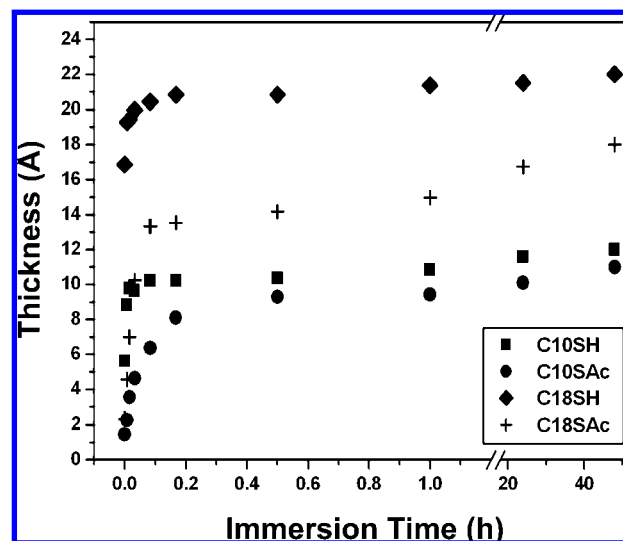
X-ray Photoelectron Spectroscopy (XPS). A PHI 5700 X-ray photoelectron spectrometer equipped with a monochromatic Al K α X-ray source ($h\nu = 1486.7$ eV) incident at 90° relative to the axis of a hemispherical energy analyzer was employed to obtain X-ray photoelectron spectra of the SAMs at a photoelectron takeoff angle of 45° from the surface and a pass energy of 23.5 eV. The binding energies were calibrated relative to the Au $4f_{7/2}$ peak at 84.0 eV. XPS spectra were curve fitted, and the intensities measured as peak areas were calculated using Phi Multipak V 5.0A from Physical Electronics.

Polarization Modulation Infrared Reflection Absorption Spectroscopy (PM-IRRAS). PM-IRRAS data were acquired using a Nicolet MAGNA-IR 860 Fourier transform spectrometer equipped with a liquid-nitrogen-cooled MCT detector and a Hinds Instruments PEM-90 photoelastic modulator (37 kHz). Infrared light was reflected from the sample at an angle of incidence of 80° . The final spectra were averaged from 64 scans at a spectral resolution of 4 cm^{-1} .

Contact Angle Measurements. Contact angles were measured with a Ramé-Hart model 100 contact angle goniometer. The contacting liquids, hexadecane (HD) and water (H_2O), were of the highest purity available commercially. They were dispensed and withdrawn using a Matrix Technologies micro-Electrapette 25. Contact angles were collected and averaged from measurements on four distinct slides using three separate drops per slide.

Results and Discussion

Ellipsometric Thicknesses. Ellipsometric measurements based on the value of the refractive index over a defined area are routinely employed to measure the nanoscale thickness of organic films.^{38–40} Whereas SAMs derived from C18SH are known to be densely packed and semicrystalline, those derived from C10SH are slightly disordered with gauche defects, particularly near the chain termini.²⁰ In initial studies, we prepared SAMs from a short-chain and a long-chain thioacetate (C10SAc and C18SAc, respectively) and compared their ellipsometric thicknesses to those of SAMs derived from the corresponding thiols (C10SH and C18SH, respectively). After two days of equilibration in the

**Figure 1.** Ellipsometric thicknesses of the SAMs formed from C10SH, C10SAc, C18SH, and C18SAc.

assembly solution (a sufficient duration for the thiol systems to reach equilibrium),⁴¹ we measured the ellipsometric thicknesses of the SAMs (Table 1).

The data in Table 1 demonstrate that the monolayers formed by thiols and thioacetates are indistinguishable within experimental error. We note, however, that the average thicknesses of the SAMs formed from the thioacetates were reproducibly smaller by $\sim 2 \text{ \AA}$ when compared to those of their thiol counterparts (i.e., the experimental precision is likely to be better than the estimated error of $\pm 2 \text{ \AA}$). Several hypotheses can be proposed to rationalize this apparent difference in the film thickness. For example, the presence of thioacetate moieties might affect the refractive index of the monolayers either intrinsically or by influencing the packing and/or tilt of the monolayers.⁴² It is also possible that the adsorption of the thioacetate moieties is less efficient or kinetically slower than that of the corresponding thiols. To gain insight into these issues, we first examined the kinetics of adsorption.

Kinetics of Adsorption. Figure 1 shows the adsorption profiles of C10SAc, C10SH, C18Ac, and C18SH as monitored by ellipsometry. Upon dipping in the adsorbate solution for ~ 1 s, both thioacetates show an initial thickness of $\sim 2 \text{ \AA}$, whereas the thickness of C10SH starts at $\sim 6 \text{ \AA}$ and that of C18SH starts at $\sim 17 \text{ \AA}$. After 1 min, the thicknesses of the SAMs formed from the thiols reach nearly asymptotic values, increasing only by $\sim 2 \text{ \AA}$ over the next 48 h. In contrast, the growth appears to be markedly slower for the thioacetates, particularly for the long-chain analog. These data are consistent with those in the two previous reports of thioacetate-based SAMs,^{32,35} which had indicated that thioacetates adsorb more slowly³⁵ and less efficiently³² than the corresponding thiols.

Studies of the kinetics of the growth of thiol-based SAMs on gold have employed a variety of techniques (e.g., ellipsometry, contact angle measurements, and XPS),^{41,43–45} which collectively indicate that the adsorption proceeds via two stages: (1) an initial regime during which the bulk of the monolayer adsorbs rapidly, followed by (2) a second regime during which the adsorbed

(41) Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321.

(42) Ulman, A.; Eilers, J. E.; Tillman, N. *Langmuir* **1989**, *5*, 1147.

(43) Buck, M.; Eisert, F.; Fischer, J.; Grunze, M.; Traeger, F. *Appl. Phys.* **1991**, *A53*, 552.

(44) Shon, Y.-S.; Lee, T. R. *J. Phys. Chem. B* **2000**, *104*, 8182.

(45) Garg, N.; Friedman, J. M.; Lee, T. R. *Langmuir* **2000**, *16*, 4266.

(38) Stenberg, M.; Sandstroem, T.; Stibler, L. *Mater. Sci. Eng.* **1980**, *42*, 65.

(39) Tomar, M. S. *J. Phys. Chem.* **1978**, *82*, 2726.

(40) Delamarche, E.; Michel, B. *Thin Solids Films* **1996**, *273*, 54.

molecules slowly reorganize and migrate to defect sites, maximizing their interchain van der Waals interactions. The data in Figure 1 support this two-regime model for the thiols; however, adsorption of the thioacetates appears to be more complicated. In particular, the presence of the acetate protecting group markedly slows the rates of adsorption in both regimes, which might be taken to indicate that chemisorption of the thioacetate moiety participates in (or is at least competitive with) the rate-determining step(s) in monolayer formation. Of relevance, we note that the analysis of the thioacetate-derived SAMs by XPS (vide infra) is consistent with a chemisorption process involving the predominant loss of the acetate groups.

However, the analysis of the film thicknesses near the end of the fast adsorption regime ($t \approx 10$ min) reveals that the SAM formed from **C18SAc** is considerably thinner than that formed from **C18SH** ($\Delta C18 \approx 7 \text{ \AA}$); in contrast, the SAM formed from **C10SAc** is only slightly thinner than that formed from **C10SH** ($\Delta C10 \approx 3 \text{ \AA}$). These observations indicate at least two things: (1) chain length plays a more important role in the kinetics of the adsorption of thioacetates than it does in the adsorption of thiols, which is reflected by there being an appreciable value (i.e., 4 \AA) for the difference [$\Delta C18 - \Delta C10$] and (2) for the adsorption of thioacetates, chain length plays a more important role in the slow regime than it does in the fast regime, which is reflected by greater values for $\Delta C18$ in the slow regime than in the fast regime. Collectively, these phenomena can be rationalized on the basis of a relatively polar transition state for the chemisorption of the thioacetate headgroup compared to that for the thiol headgroup. In this interpretation, the long alkyl chains of the C18 adsorbates create a low dielectric environment near the surface of gold, which raises the barrier to thioacetate chemisorption, reducing its rate relative to that for thiol chemisorption.

Analysis by XPS. X-ray photoelectron spectroscopy serves multiple purposes in the study of SAMs.²⁰ The observed binding energies depend on the electron density of a specific atom, varying primarily with the nature of the element considered and secondarily with the nature of the atoms directly attached to it (especially their electronegativity). Whereas XPS can be readily used as an elemental analysis tool, it is also possible in some cases to determine the connectivity between some atoms and/or the presence of certain functional groups.⁴⁶ With XPS, qualitative analyses of SAMs are routinely possible, but quantitative analyses are usually restricted to specific cases because of experimental uncertainties (e.g., in the cases of inhomogeneous SAMs, the matter-dependent attenuation length of photoelectrons is typically not known with certainty).⁴⁷

Figure 2 shows the XPS spectra of the carbon (C 1s), sulfur (S 2p), and oxygen (O 1s) regions for SAMs derived from **C10SH**, **C10SAc**, **C18SH**, and **C18SAc**. All spectra show the presence of carbon, sulfur, and oxygen in addition to the underlying gold substrate, thus demonstrating that the material detected by ellipsometry corresponds to the thiols/thioacetate rather than some adventitious material. To interpret more quantitatively the spectra obtained, we calculated the ratio of signal intensities separately for C 1s, S 2p, and O 1s versus that for Au 4f_{7/2} for each of the four adsorbates (Table 2). We assign the C 1s photoelectron peak centered at 284 eV to the carbon atoms in the alkyl chains.^{48,49} No evidence was found in the C 1s spectrum to

corroborate the presence of the thioacetate group at the surface: according to the literature,^{48,49} the carbonyl should give rise to a carbon signal in the range of 287–289 eV. Although no oxidized carbon species were observed in any of the C 1s spectra, we cannot fully rule out the presence of thioacetate because the carbonyl moiety would likely be positioned near the gold surface, which would lead to the attenuation of the signal by the overlying material.

We assign the photoelectron peaks with binding energies of 162 and 163 eV to the doublet S 2p_{3/2}–S 2p_{1/2}, respectively, for sulfur bonded to gold.^{48,50} An examination of the S 2p region of an XPS spectrum of SAMs on gold is particularly informative for two reasons. First, the presence of unbound sulfur associated with either the incomplete attachment of the adsorbates or the formation of a multilayer can be confirmed by the observation of a corresponding signal at 164 eV.^{48,50} Second, the potential oxidation of sulfur to sulfate or sulfonate species can also be evaluated.⁵¹ An analysis of the SAMs generated from both thiols and thioacetates indicates that all of the sulfur atoms are bound to the surface of gold and no oxidized sulfur species are present (Figure 2). Furthermore, the data in Table 2 show that measurements of the S 2p/Au 4f_{7/2} ratios for the SAMs derived from both of the thioacetates and both of the thiols gave 0.05 and 0.07, respectively, confirming that the packing density of the thiol-derived SAMs is greater than that for the thioacetate-derived SAMs (vide supra).

Importantly, the O 1s photoelectron peak with a binding energy of 532 eV is clearly present for both thioacetate-derived SAMs but barely noticeable for the thiol-derived SAMs. The O 1s/Au 4f_{7/2} ratios confirm this observation, showing an oxygen content that is 3 times greater in the monolayers derived from the thioacetates than in those derived from the thiols. Considering that these films were prepared and characterized using identical procedures (gold substrates, immersion times, air exposure times, and irradiation times), the presence of oxygen in the thioacetate spectra cannot be attributed to adventitious contaminants. Moreover, the presence of only trace amounts of oxygen in the thiol-derived spectra confirms the overall integrity of the system, including the high quality of the gold substrates. Therefore, the small but clearly detectable oxygen signal in the thioacetate-derived spectra can be attributed to the adsorbates. The true nature of the oxygen-containing functional groups, however, remains unknown (O 1s binding energies are not sufficiently sensitive to allow detailed interpretation), but we have ruled out the possibility of oxidized sulfur (vide supra).

Turning our attention back to the C 1s region, we note that the C 1s signal in Figure 2 is shifted to lower binding energy for both thioacetate adsorbates by 0.5 eV with respect to the binding energy of the corresponding thiol adsorbates. During X-ray irradiation, the positive charges generated by photoelectron emission cannot be easily dissipated through alkanethiolate SAMs because they are well-packed and therefore act as insulators.⁵² Loosely packed SAMs, however, are relatively poor insulators; consequently, the C 1s binding energy will shift to lower energies.^{53,54} Correspondingly, the shifts in binding energy in Figure 2 can thus be interpreted to indicate that the packing

(46) Ulman, A. *An Introduction to Ultrathin Film from Langmuir-Blodgett to Self-Assembly*; Academic: New York, 1991.

(47) Fadley, C. S.; Baird, R. J.; Siekhaus, W. J.; Novakov, T.; Bergstrom, S. A. *J. Electron Spectrosc. Relat. Phenom.* **1974**, *4*, 93.

(48) Gelius, U.; Heden, P. F.; Hedman, J.; Lindberg, B. J.; Bernt, J.; Manne, R.; Nordberg, R.; Nordling, C.; Siegbahn, K. *Phys. Scr.* **1970**, *2*, 70.

(49) Wenzler, L. A.; Moyes, G. L.; Raikar, G. N.; Hansen, R. L.; Harris, J. M.; Beebe, T. P., Jr.; Wood, L. L.; Saavedra, S. S. *Langmuir* **1997**, *13*, 3761.

(50) Lu, H. B.; Campbell, C. T.; Castner, D. G. *Langmuir* **2000**, *16*, 1711.

(51) Lee, T.-C.; Hounihan, D. J.; Colorado, R. J.; Park, J.-S.; Lee, T. R. *J. Phys. Chem. B* **2004**, *108*, 2648.

(52) Ishida, T.; Hara, M.; Kojima, I.; Tsuneda, S.; Nishida, N.; Sasabe, H.; Knoll, W. *Langmuir* **1998**, *14*, 2092.

(53) Park, J.-S.; Smith, A. C.; Lee, T. R. *Langmuir* **2004**, *20*, 5829.

(54) Biebuyck, H. A.; Bain, C. D.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1825.

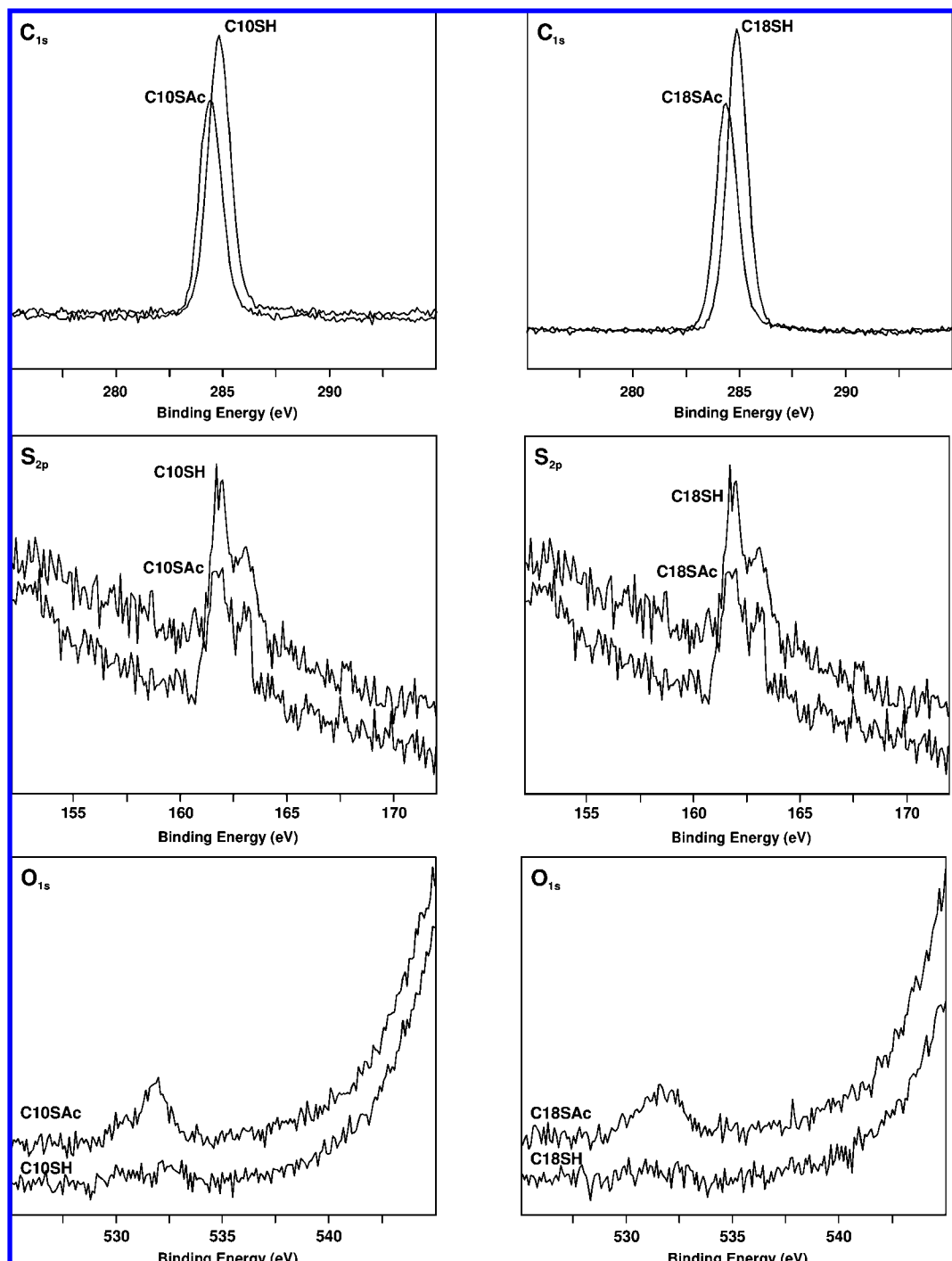


Figure 2. XPS spectra of C 1s, S 2p, and O 1s regions of SAMs generated from C10SH, C10SAc, C18SH, and C18SAc.

Table 2. Ratio of XPS Signal Intensities of C 1s, S 2p, and O 1s vs Au 4f_{7/2} for the Indicated Adsorbates

adsorbate	C 1s/Au 4f _{7/2}	S 2p/Au 4f _{7/2}	O 1s/Au 4f _{7/2}
C10SH	1.4	0.069	0.037
C10SAc	1.1	0.057	0.100
C18SH	3.1	0.065	0.033
C18SAc	2.1	0.045	0.110

densities of the SAMs generated from C10SAc and C18SAc are lower than those generated from C10SH and C18SH. Moreover, such a shift in C 1s binding energy can be used to provide information regarding the orientation of the alkyl chains in SAMs. Wöll and coworkers⁵⁵ reported a diminution of the C 1s binding energy (1 eV) for alkane monolayers oriented parallel to the

surface. Thus, the 0.5 eV shift to lower binding energy for C 1s peaks suggests loose packing and/or more highly tilted alkyl chains on average for the SAMs derived from thioacetates compared to those derived from normal alkanethiols.

The packing densities can also be evaluated by determining the ratio of C 1s intensity to Au 4f_{7/2} intensity.⁵⁶ In the case of thioacetates C10SAc and C18SAc (Table 2), we calculated the ratios of C 1s/Au 4f_{7/2} to be 1.1 and 2.1, respectively, which are smaller than those calculated for thiols C10SH and C18SH (1.4 and 3.1, respectively). This comparison suggests that the packing

(55) Himmel, H. J.; Wöll, C.; Gerlach, R.; Polanski, G.; Rubahn, H. G. *Langmuir* 1997, 13, 602.

(56) Liedberg, B.; Wirde, M.; Tao, Y.-T.; Tengvall, P.; Gelius, U. *Langmuir* 1997, 13, 5329.

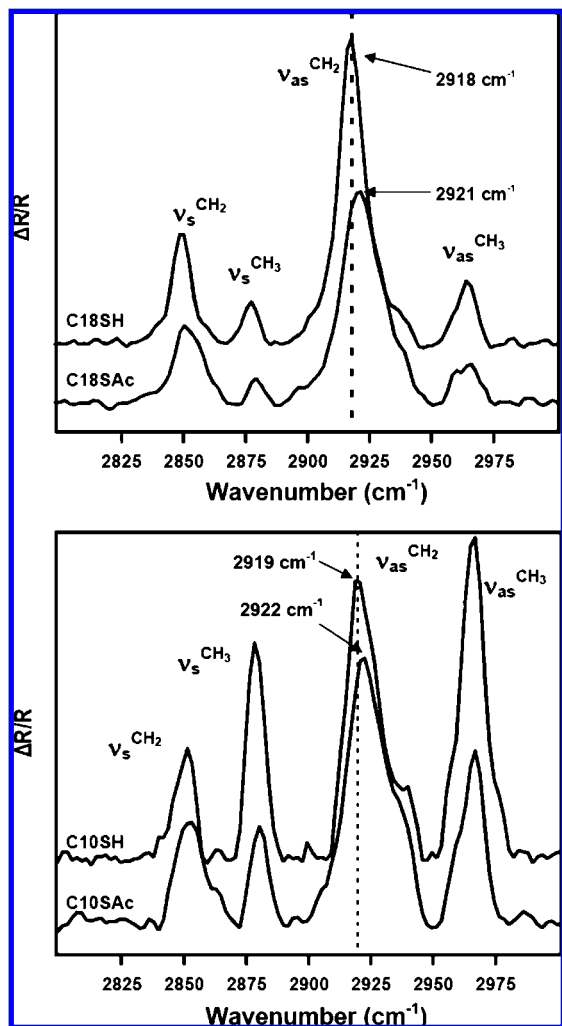


Figure 3. Surface infrared spectra (PM-IRRAS) of SAMs generated from **C10SH**, **C10SAc**, **C18SH**, and **C18SAc**.

densities are considerably lower for thioacetate-derived SAMs than for thiol-derived SAMs. In summary, the XPS data are consistent with the ellipsometry data, which together indicate that SAMs generated from thioacetates are less densely packed than those generated from thiols. This conclusion is further supported by the PM-IRRAS data, which are presented in the following section.

Analysis by PM-IRRAS. To evaluate the coverage and packing of SAMs generated from the thioacetates and the corresponding thiols, we collected their surface IR spectra. Figure 3 shows the C–H stretching regions of the PM-IRRAS spectra for the SAMs generated from **C10SH**, **C10SAc**, **C18SH**, and **C18SAc**. The C–H stretching region of hydrocarbon SAMs is strongly influenced by the conformation of the alkyl chains and their environment.^{57,58} Specifically, the frequency and width of the methylene antisymmetric ($\nu_{as}^{CH_2}$) and methylene symmetric ($\nu_s^{CH_2}$) bands are sensitive to the conformational order of the alkyl chains.⁵⁹ Correspondingly, Figure 3 shows that $\nu_{as}^{CH_2}$ and $\nu_s^{CH_2}$ appear at 2919 and 2948 cm^{-1} for **C10SH** and at 2918 and 2948 cm^{-1} for **C18SH**, which is consistent with both thiol-derived

Table 3. Advancing Contact Angles^a and Hysteresis^b for Hexadecane (HD) and Water on the Indicated SAMs

adsorbate	HD	water
C10SH	52 (6)	113 (5)
C10SAc	38 (8)	108 (8)
C18SH	52 (5)	114 (6)
C18SAc	34 (8)	110 (9)

^a Advancing contact angle, $\theta_a \pm 1^\circ$ ^b Hysteresis, $\Delta\theta = \theta_a - \theta_r$

SAMs having “crystalline” conformational order.^{60,61} These bands are broadened and shifted to higher wavenumber for both thioacetate-derived SAMs, appearing at 2922 and 2950 cm^{-1} for **C10SAc** and at 2921 and 2950 cm^{-1} for **C18SAc**. These observations indicate a more liquidlike conformational order for the latter SAMs.^{57–61}

The spectra in Figure 3 also show a substantial decrease in the intensity of the methyl bands in the thioacetate-derived SAMs compared to those in the thiol-derived SAMs. In surface infrared spectra, only the component of the dynamic dipole polarized in the direction normal to the surface plane is detected.⁶² For SAMs on gold with trans-extended alkyl chains containing an even number of carbon atoms, the methyl stretching mode is nearly perpendicular to the surface; consequently, its intensity is typically strong like those in the reflectance spectra of **C10SH** and **C18SH** in Figure 3. In contrast, the intensity of this band is diminished in the SAMs derived from the thioacetates. This reduction in intensity can be attributed to the diminished conformational order of thioacetate-based SAMs, which can plausibly lead to a reduction in the number of methyl groups oriented perpendicular to the surface. This difference is less noticeable for the C18 analogs than the C10 analogs as a result of the additional van der Waals interactions that stabilize the C18 SAMs, enhancing their crystallinity as a whole.⁴¹

Wettabilities of the SAMs. Contact angle goniometry is a sensitive tool for evaluating the composition, packing, and overall organization of organic thin films.²⁰ Contact angle measurements are used routinely to characterize the surface properties of a new coating or for quality purposes to ensure the reproducibility of a process.⁶³ Details such as the orientation of a terminal group can sometimes be inferred from the analysis of contact angle data.^{64–66} This high degree of sensitivity can, however, lead to drawbacks: for example, inconsistent contact angle data have appeared early in the literature, mirroring differences in the topography of the underlying gold rather than surface properties inherent to the organic layer.⁶⁷ Perhaps the most reliable way to interpret the quality of SAMs is to collect the contact angles using different types of contacting liquids and compare the data for each new system to those obtained using a well-characterized family of adsorbates. In our case, we compared SAMs generated from the alkanethioacetates to those generated from the corresponding normal alkanethiols. Table 3 shows that contact angles for both contacting liquids are lower for the alkanethioacetate-derived SAMs than for the alkanethiol-derived SAMs. Hexadecane (HD) is a nonpolar aprotic contacting liquid commonly

(60) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559.

(61) Nuzzo, R. G.; Dubois, L. H.; Allara, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 558.

(62) Bensebaa, F.; Ellis, T. H.; Badia, A.; Lennox, R. B. *Langmuir* **1998**, *14*, 2361.

(63) Whitesides, G. M.; Laibinis, P. E. *Langmuir* **1990**, *6*, 87.

(64) Graupe, M.; Takenaga, M.; Koini, T.; Colorado, R., Jr.; Lee, T. R. *J. Am. Chem. Soc.* **1999**, *121*, 3222.

(65) Colorado, R., Jr.; Villazana, R. J.; Lee, T. R. *Langmuir* **1998**, *14*, 6337.

(66) Tao, F.; Bernasek, S. L. *Chem. Rev.* **2007**, *107*, 1408.

(67) Abdelsalam, M. E.; Bartlett, P. N.; Kelf, T.; Baumberg, J. *Langmuir* **2005**, *21*, 1753.

(57) Snyder, R. G.; Hsu, S. L.; Krimm, S. *Spectrochim. Acta* **1978**, *34A*, 395.

(58) MacPhail, R. A.; Strauss, H. L.; Snyder, R. G.; Elliger, C. A. *J. Phys. Chem.* **1984**, *88*, 334.

(59) Snyder, R. G.; Strauss, H. L.; Elliger, C. A. *J. Phys. Chem.* **1982**, *86*, 5145.

used to probe purely dispersive interactions at organic interfaces.²⁰ For the SAMs derived from both alkanethiols, the contact angle of hexadecane was 52°; this value is common for SAMs presenting methyl groups at the interface, thus indicating good quality of the overall system.²⁰ For the SAMs derived from both alkanethioacetates, however, the contact angle of hexadecane was lower by about 15°. Because hexadecane is known to wet interfacial methylene groups more than it wets interfacial methyl groups,^{68,69} the data in Table 3 are consistent with the presence of methylene groups at the interface of alkanethioacetate-derived SAMs. Similar contact angle data have been observed for other loosely packed hydrocarbon SAMs on gold.^{49,53}

We also found that the contact angles of water are only slightly lower for the alkanethioacetate SAMs than for the alkanethiol SAMs. Indeed, water is less sensitive than hexadecane toward small structural differences at the interfaces of hydrocarbon films.^{61,69} Furthermore, the fact that we observed only a small difference in the contact of water suggests that no polar acetate groups are present at or close to the interface of SAMs derived from alkanethioacetates. As a whole, the wettability data are consistent with the other analytical tools, which indicate that SAMs on gold derived from alkanethioacetates are less ordered (less densely packed) than those derived from the corresponding alkanethiols.

Finally, we note that the hysteresis (defined by the difference between the advancing and receding contact angles) is slightly higher for the thioacetate-derived SAMs than for the thiol-derived

SAMs but still less than 10°. For the latter SAMs, values of hysteresis of $\leq 10^\circ$ are typically interpreted to indicate relatively smooth interfaces possessing a homogeneous distribution of functional groups. Whereas the same interpretation appears to hold true for the SAMs derived from alkanethioacetates, the slightly enhanced values of hysteresis might reflect a reduction in the smoothness/homogeneity when compared to SAMs derived from alkanethiols.

Conclusions

Our investigation of the direct adsorption of *n*-alkanethioacetates on gold has revealed that the SAMs generated by this approach are less densely packed and less ordered than SAMs generated likewise from analogous *n*-alkanethiols. Furthermore, the slightly elevated oxygen content in the thioacetate-derived SAMs suggests the entrapment of trace amounts of acetate moiety in these films. Like alkanethiols, alkanethioacetates attach to gold as surface thiolates, but the adsorption is markedly slower than that of alkanethiols. We attribute this relatively slow adsorption rate to an enhanced barrier to chemisorption of the thioacetate headgroup compared to that of the thiol headgroup, where the former reaction proceeds via a relatively polar transition state. As a whole, these studies confirm that alkanethioacetates can be used to generate SAMs on gold as long as rapid adsorption, dense packing, and crystalline order are not priorities.

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(68) Tao, Y.-T. *J. Am. Chem. Soc.* **1993**, *115*, 4350.

(69) Shon, Y.-S.; Lee, S.; Colorado, R., Jr.; Perry, S. S.; Lee, T. R. *J. Am. Chem. Soc.* **2000**, *122*, 7556.