# Formation and Structure of Self-Assembled Monolayers of Alkanethiolates on Palladium

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***Abstract:*** The adsorption of *n*-alkanethiols onto polycrystalline thin films of palladium containing a strong (111) texture produces well-organized, self-assembled monolayers. The organization of the alkane chains in the monolayer and the nature of the bonding between the palladium and the thiol were studied by contact angle measurements, optical ellipsometry, reflection absorption infrared spectroscopy (RAIRS), and X-ray photoelectron spectroscopy (XPS). The XPS data reveals that a compound palladium-sulfide interphase is present at the surface of the palladium film. The RAIR spectra, ellipsometry data, and wetting properties show that the palladium-sulfide phase is terminated with an organized, methyl-terminated monolayer of alkanethiolates. The local molecular environment of the alkane chains transitions from a conformationally disordered, liquidlike state to a mostly all-trans, crystalline-like structure with increasing chain length ($n = 8-26$). The intensities and dichroism of the methylene and methyl stretching modes support a model for the average orientation of an ensemble of all-trans-conformer chains with a tilt angle of $\sim14-18°$ with respect to the surface normal and a twist angle of the CCC plane relative to the tilt plane of $\sim45°$. The SAMs are stable in air, although the sulfur present at the surface oxidizes in air over a period of $2-5$ days at room temperature. The differences in chain organization between SAMs formed by microcontact printing and by solution deposition are also examined by RAIRS and XPS.

## Introduction

This paper describes the preparation and characterization of self-assembled monolayers (SAMs) of *n*-alkanethiolates formed by the adsorption of *n*-alkanethiols on thin films of palladium. Our recent work[1,2] and work by Delamarche and co-workers at IBM-Zurich[3] have shown that these SAMs are good resists for thin-film patterning based on microcontact printing (μCP).[4-6] Initial experiments indicated that the Pd–S interface is a critical

contributor to the mechanism of the etch resistance of these SAMs and central to their utility for forming micropatterns of palladium by μCP.[2] This observation implies a different structural contributor to the mechanism of etch resistance exists in this case in comparison to that for SAMs of alkanethiolates on gold. A well-ordered, hydrophobic SAM is required on gold to prevent the transport of oxidizing ions to the surface.[6] The quality of the structures etched into palladium is improved by a hydrophobic SAM, but it is not essential to achieve good etch resistance.

SAMs of alkanethiolates on palladium have three characteristics that make them superior to SAMs on gold and silver as etch resists: (i) they generate etched structures with smaller edge roughness than on gold due in part to the differences in the grain sizes that develop in thin films of the metals deposited by electron-beam evaporation onto silicon substrates held at or near 300 K ($15-25$ nm for palladium vs $45-60$ nm for gold); (ii) they demonstrate greater selectivity against wet chemical etchants than those on gold, and yield fewer surface defects;[1] (iii) they are, in principle, compatible with CMOS devices and the processes used to produce them. The ability to pattern palladium by soft lithography has the potential to be useful in a number of areas of electronics, sensors, and catalysis. Palladium and its alloys are used in electronic devices as components in resistors, capacitors, and electrodes in integrated

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(1) Wolfe, D. B.; Love, J. C.; Paul, K. E.; Chabinyc, M. L.; Whitesides, G. M. *Appl. Phys. Lett.* **2002**, *80*, 2222–2224.

(2) Love, J. C.; Wolfe, D. B.; Chabinyc, M. L.; Paul, K. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **2002**, *124*, 1576–1577.

(3) Carvalho, A.; Geissler, M.; Schmid, H.; Micel, B.; Delamarche, E. *Langmuir* **2002**, *18*, 2406–2412.

(4) Xia, Y.; Whitesides, G. M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 550–575; Xia, Y.; Zhao, X.-M.; Whitesides, G. M. *Microelectron. Eng.* **1996**, *32*, 255–268.

(5) Xia, Y.; Whitesides, G. M. *Annu. Rev. Mater. Sci.* **1998**, *28*, 153–184. Xia, Y.; Zhao, X.-M.; Kim, E.; Whitesides, G. M. *Chem. Mater.* **1995**, *7*, 2332–2337. Xia, Y.; Rogers, J. A.; Paul, K. E.; Whitesides, G. M. *Chem. Rev.* **1999**, *99*, 1823–1848. Rogers, J. A.; Bao, Z.; Baldwin, K.; Dodabalapur, A.; Crone, B.; Raju, V. R.; Kuck, V.; Katz, H.; Amundson, K.; Ewing, J.; Drzaic, P. *Proc. Natl. Acad. Sci. U.S.A.* **2001**, *98*, 4835–4840. Michel, B.; Bernard, A.; Bietsch, A.; Delamarche, E.; Geissler, M.; Juncker, D.; Kind, H.; Renault, J. P.; Rothuizen, H.; Schmid, H.; Schmidt-Winkel, P.; Stutz, R.; Wolf, H. *IBM J. Res. Dev.* **2001**, *45*, 697–719. There is also a number of patents describing SAMs of alkanethiolates on palladium; these patents are listed in the Supporting Information.

(6) Kumar, A.; Abbott, N. A.; Kim, E.; Biebuyck, H. A.; Whitesides, G. M. *Acc. Chem. Res.* **1995**, *28*, 219–226.

circuits, and as finishes for contacts on surface-mount components and integrated circuits.[7] Palladium serves as a central component in sensors for hydrogen gas because it readily dissociates and absorbs up to 900 times its volume in hydrogen.[8] Palladium also is an active catalyst for hydrogenation[9] and hydrodesulfurization[10] reactions, as well as for the electroless deposition of metals (e.g., copper and nickel).[11]

The objective of this study was to define the nature of the interface formed between the palladium film and the thiolate adsorbates of a SAM overlayer, and to determine the structural organization of the alkane chains in the monolayers. We characterized these SAMs by optical ellipsometry, X-ray photoelectron spectroscopy (XPS), reflection absorption infrared spectroscopy (RAIRS), and contact angle goniometry. We also examined the organizational structure of the alkane chains and palladium−sulfur bonding formed in SAMs generated by $\mu$CP rather than deposition from solution. Significant differences do exist in the chain organizations adopted in each case, but these do not appear to have a significant consequence for the ability of those SAMs to resist etching.

## Experimental Section

**Materials.** 1-Octanethiol, 1-decanethiol, and 1-dodecanethiol were obtained from Aldrich. 1-Undecanethiol, 1-tetradecanethiol, 1-pentadecanethiol, 1-hexadecanethiol, and 1-octadecanethiol were obtained from TCI America. Dihexadecane disulfide, 1-heptadecanethiol, 1-eicosanethiol, 1-docosanethiol, 1-hexacosanethiol, and perdeuterated 1-hexadecanethiol-$d_{33}$ were available from previous studies.[12,13] Ethanol (100%) was obtained from Pharmco (Brookfield, CT). The palladium used to prepare the evaporated films was >99.99% pure (ESPI metals, Ashland, OR). Silicon (100) wafers were obtained from Silicon Sense (Nashua, NH) and were used as received. The *n*-alkanethiols with fewer than 17 carbons were percolated through a plug of activated, neutral alumina prior to use to remove any oxidized, polar sulfur compounds.

**Preparation of Thin Films of Palladium.** Films were obtained by depositing titanium (10 Å) onto the silicon wafer substrates to promote adhesion of the film, followed by 300−2000 Å of palladium. The evaporation was conducted in a dual-source, cryogenically pumped electron beam thin-film deposition system (base pressure ≈ 1 × 10$^{-7}$ Torr) using a graphite crucible liner for the palladium. The typical rate of evaporation was 8 Å/s for palladium at an operating pressure of (2−5) × 10$^{-7}$ Torr. The substrates were transported in either polystyrene Petri dishes or wafer carriers. The substrates for the measurements undertaken here were immersed in the appropriate solutions of thiol within 1 h (typically 20 min) after they were removed from the vacuum system. For soft lithography applications, we have found that the wafers

can be stored in an empty desiccator under vacuum for up to a week with reproducible results.

The grain size and roughness of the films was determined by contact-mode AFM (Dimension 3100), and was analyzed using the Nanoscope IV v5.12b18 software package (Digital Instruments, Santa Barbara, CA). The typical scan size was 1 $\mu$m × 1 $\mu$m. The crystallographic texture of the films was determined by conventional X-ray diffraction $2\theta$ and rocking angle measurements (with the latter carried out on the (111) reflection for Pd). The XRD measurements were made using a D-Max X-ray Diffractometer (Rigaku International Corporation, Tokyo, JN) with a fixed anode Cu source and monochromatic Cu K$\alpha$ radiation.

**Formation of Self-Assembled Monolayers of Alkanethiolates.** The SAMs were formed on freshly evaporated palladium films by immersing the samples in 1−10 mM solutions of the thiols in ethanol or 2-propanol for ~12−48 h. The solvents were degassed under argon for at least 30 min prior to use. The solutions were stored under argon in scintillation vials (20 mL) during the formation of the SAM. For thiols with $n >$ 16, and for dihexadecane disulfide, 1 mM solutions in solvent were used because of the low solubilities of those materials in ethanol. The samples were then rinsed thoroughly with ethanol and blown dry with a stream of nitrogen gas. Palladium films also were reacted with aqueous solutions of sodium sulfide (10 mM) in a similar manner. (CAUTION: Dissolution of sodium sulfide in water generates small amounts of H$_2$S gas, which is highly toxic. These experiments should be conducted in a fume hood. The solutions were quenched with bleach after the experiments.)

**Ellipsometry.** Ellipsometric measurements were made using an AutoEL-II Ellipsometer (Rudolph Research, Flanders, NJ) using a HeNe laser operating at a wavelength of 6328 Å and an incident angle of 70°. Prior to the formation of the SAMs on the samples, the pseudo-optical constants of the palladium substrate (2000 Å) were measured. The samples were rinsed in ethanol and blown dry with a stream of N$_2$ before the measurements were taken. The measurements of the SAM on a given sample were taken in four different locations, and the readings averaged. These data are presented in the form of an apparent mass coverage—i.e., values that reflect an equivalent thickness of the adsorbate layer deduced using the assumptions of the parallel layer model. The values were calculated using the double-layer absorbing film calculation program (v. 2.1, Rudolph Research) and fixed values for the optical constants ($n = 1.45$, $k = 0$) of the adsorbates.

**X-ray Photoelectron Spectroscopy.** Spectra were obtained using a Kratos Axis Ultra photoelectron spectrometer using Al K$\alpha$ radiation (15 kV, 225 W, base pressure ≈ 5 × 10$^{-10}$ Torr). Survey spectra were collected at a constant pass energy of 160 eV from a 0.37 × 1.0 mm$^2$ area of the sample. High-resolution spectra of the C(1s), S(2p), and Pd(3d) core levels were collected at a pass energy of 20 eV with the same spot size. The binding energies were corrected by referencing the C(1s) binding energy to 285 eV. Curve fitting of the S(2p) core levels was performed using Gaussian−Lorentzian (70%:30%) line shapes. The spin−orbit doublet separation was held constant at 1.18 eV and with a fixed 2:1 area ratio.[14] The curve fitting was carried out by starting at the low binding energy side of the S(2p) envelope and systematically adding component core levels toward higher binding energies as required.

**Infrared Spectroscopy.** RAIR spectra of the monolayers of alkanethiolates were obtained using a Nexus 670 FT-IR (Nicolet, Madison, WI) equipped with a surface grazing angle attachment (SAGA, Thermo Spectra-Tech, Shelton, CT) and a liquid nitrogen cooled MCT detector. The incident reflection angle was set at 80°. Spectra of SAMs were measured on silicon substrates bearing 2000 Å films of palladium. The background spectra were collected from a palladium reference taken from the same set of substrates as the samples and modified with a SAM formed from perdeuterated hexadecanethiol.

(7) Moniz, B. J. *Metallurgy*, 2nd ed.; American Technical Publishers: Homewood, 1994.

(8) Barton, J. C.; Lewis, F. A.; Woodward, I. *Trans. Faraday Soc.* **1963**, *59*, 1201−1208.

(9) Lewis, F. A. *The Palladium Hydrogen System*; Academic Press: New York, 1967.

(10) Walsh, D. E. Two-step upgrading of olefinic sulfur-rich cracked naphtha by hydrodesulfurization and treatment over metal-containing MCM-22 zeolites, PCT Int. Appl. 0208360, 2002; Qian, W.; Yoda, Y.; Hirai, Y.; Ishihara, A.; Kabe, T. *Applied Catalysis, A: General* **1999**, *184*, 81−88. Shirai, M.; Pu, Y.; Arai, M.; Nishiyama, Y. *Appl. Surf. Sci.* **1998**, *126*, 99−106. Sugioka, M.; Sado, F.; Matsumoto, Y.; Maesaki, N. *Catal. Today* **1996**, *29*, 255−259.

(11) Kind, H.; Gieissler, M.; Schmid, H.; Michel, B.; Kern, K.; Delamarche, E. *Langmuir* **2000**, *16*, 6367−6373. Brandow, S. L.; Chen, M.; Wang, T.; Dulcey, C. S.; Calver, J. M.; Bohland, J. F.; Calabrese, G. S.; Dressick, W. J. *J. Electrochem. Soc.* **1997**, *144*, 3425−3434.

(12) Bain, C. D.; Troughton, E. B.; Tao, Y. T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321−335.

(13) Bain, C. D.; Evall, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989**, *111*, 7155−7164. Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989**, *111*, 7164−7175. Haag, R.; Rampi, M. A.; Holmlin, R. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1999**, *121*, 7895−7906.

(14) Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. D. *Handbook of X-ray Photoelectron Spectroscopy*; Physical Electronics: Eden Prairie, MN, 1995.

The deuterated SAM minimizes the contributions from C−H stretching modes of adventitious organic materials adsorbed on the substrate; the C−D stretching modes appear in the range of 2250−2000 cm$^{-1}$. Reference substrates for SAMs on gold and silver were prepared in the same manner. Spectra were obtained using 1024 scans at 2 cm$^{-1}$ resolution and at a mirror modulation velocity of 1.9 cm/s. The samples were rinsed in ethanol and blown dry with a stream of nitrogen gas before the measurements were taken. The baselines of the spectra were corrected over the range of 3000−2800 cm$^{-1}$.

**Contact Angles.** Limiting values of the advancing and receding contact angles were measured on static drops of water or hexadecane using a Ramé−Hart goniometer with a Matrix Technologies Electrapipet to control the advancement and recession of the drop. Contact angles were measured on both sides of the drop for at least three advancements or recessions of the drop. The data were collected from a minimum of five independent drops over a minimum of three independent samples.

## Results

**Formation of SAMs on Palladium.** Polycrystalline films of palladium were prepared by evaporating 1.5 nm of titanium onto a silicon wafer followed by either 30 or 200 nm of palladium in an electron-beam thin film deposition chamber. The substrates were typically used within 1 h after they were removed from the deposition vacuum chamber. The XPS data showed that the palladium samples are not extensively oxidized under these conditions.[15] The topography of the palladium films was characterized by atomic force microscopy. These micrographs showed that the average grain size of the palladium films deposited in our e-beam thin-film evaporator was ∼15−20 nm with an average (rms) roughness of 0.8 nm (Figure 1a). X-ray diffraction measurements of the palladium films revealed that the (111) plane is the dominant surface texture with a mosaic spread (as judged by the fwhm of the (111) reflection) of ∼7°.

We prepared SAMs on these substrates by immersing them in dilute solutions (1−10 mM) of the alkanethiols in either ethanol or 2-propanol at room temperature (∼25 °C). The solvents were degassed with argon for at least 30 min prior to use. This procedure minimized the oxidation of the thiols during the formation of the SAM (see discussion on the PdS interface below). The typical time allowed for the formation of the SAM was 12−24 h for characterization by optical ellipsometry, XPS, RAIRS, and contact angle goniometry. The solutions were stored under an atmosphere of argon in sealed scintillation vials during the incubation. Exposure of the substrates to solutions of thiol for periods greater than 12 h did not change the quality of the organizational structure of the alkane chains of the SAM as judged by the data obtained from wetting and RAIRS studies (discussed below).

**Surface Wetting Properties.** The contact angle formed by a liquid at an interface is sensitive to the molecular structure of the surface and provides a measure for the quality of a SAM.[12,16] Figure 2 shows the static advancing ($\theta_a$) and receding ($\theta_r$) contact angles of water and hexadecane (HD) measured on the SAMs formed by *n*-alkanethiols of various chain lengths (HS(CH$_2$)$_{n-1}$CH$_3$, *n* = 8,10,11,12,14,15,16,17,18) on palladium films (30 nm-thick). The wetting behaviors of the SAMs on palladium are similar to those observed for analogous SAMs

(15) While the surface will chemisorb oxygen readily, palladium resists oxidation in bulk up to 400 °C. See ref 9.
(16) Adamson, A. W.; Gast, A. P. *Physical Chemistry of Surfaces*, 6th ed.; John Wiley & Sons: New York, 1997. Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 3665−3666.
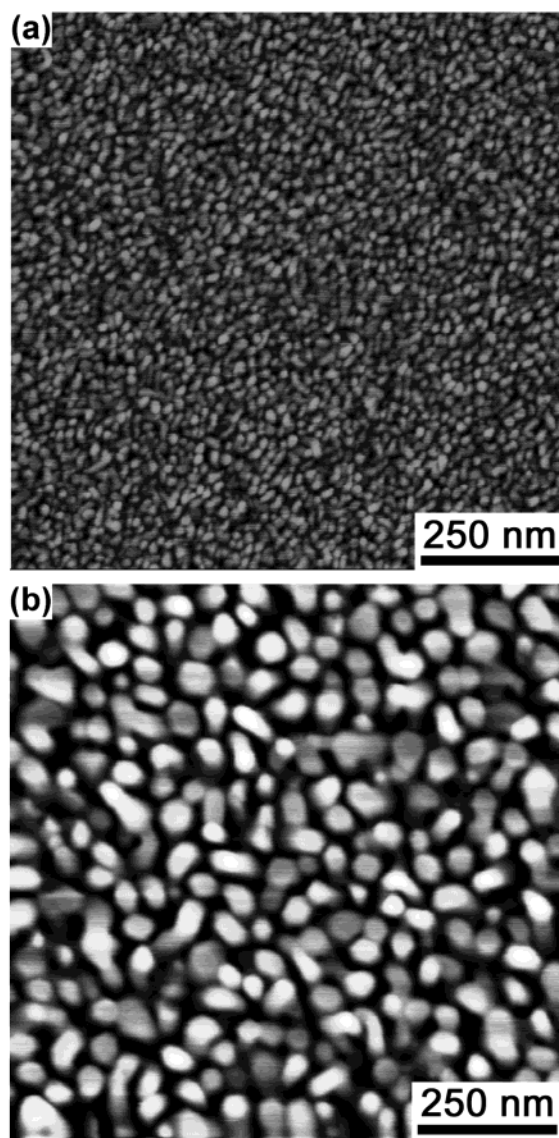
**Figure 1.** Atomic force micrographs recorded in contact mode of (a) a 200 nm-thick palladium film (vertical scale = 10 nm) and (b) a 200 nm-thick gold film (vertical scale − 25 nm). The substrates were prepared under identical deposition conditions.

on gold, silver, and copper.[17] The advancing contact angles increase slightly with increasing chain lengths: $\theta_a$(water) = 112° − 120° and $\theta_a$(HD) = 35° − 51°. We attribute this trend to a progressive ordering of the molecular environments of the alkane chains (i.e., fewer conformational defects and perhaps higher coverages) as the number of carbon atoms increases. The measured receding contact angles for water ($\theta_r$ = 99° − 101°) are similar for all chain lengths. This behavior is also comparable to that seen for the SAMs formed by *n*-alkanethiols on the coinage metals.[17] When taken together, these observations suggest that the chains of the SAMs on palladium are highly oriented and that the structure of the outermost surface is a low-energy, methyl-terminated interface.[12,17]

Table 1 compares the measured contact angles of water and HD on a SAM of octadecanethiolate on palladium to those reported in the literature for SAMs on gold, silver, and copper.

(17) Laibinis, P. E.; Whitesides, G. M.; Allara, D. L.; Tao, Y. T.; Parikh, A. N.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 7152−7167.
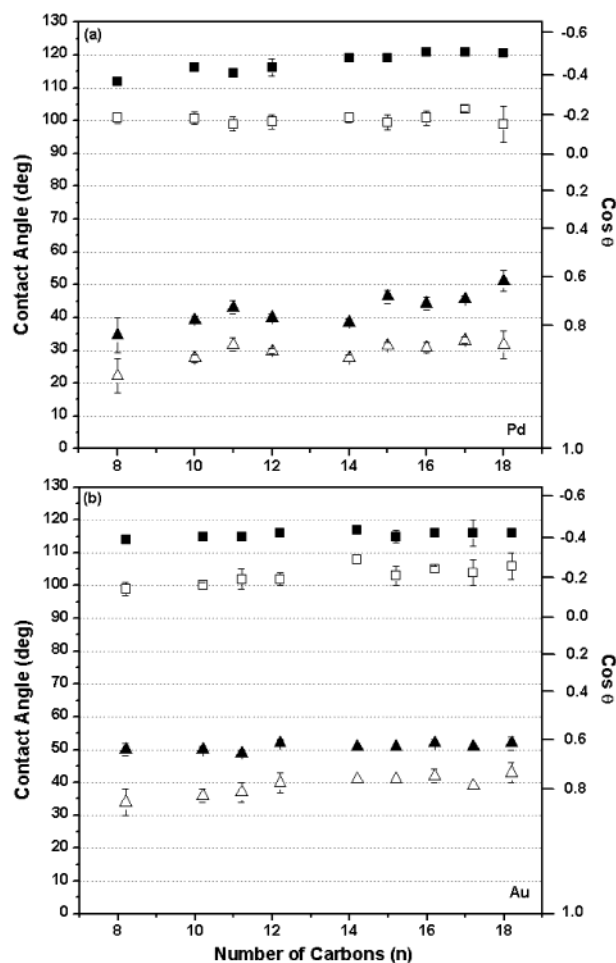
**Figure 2.** Wetting of monolayers of *n*-alkanethiolates on (a) palladium and (b) gold by water (squares, filled (■, $\theta_a$) and open (□, $\theta_r$)) and hexadecane (triangles, filled (▲, $\theta_a$) and open (△, $\theta_r$)). The contact angle data for gold were taken from ref 17. Comparable values (within the error reported previously for these systems) were obtained as part of this study.

**Table 1.** Wetting Properties of Water and Hexadecane in Air on SAMs of Octadecanethiol (*n*-$C_{18}H_{37}$SH) Adsorbed on Palladium, Gold, Silver, and Copper

| | wetting ($\theta_a$, $\theta_r$, and $\Delta\theta$)[a] | | | | | |
|---|---|---|---|---|---|---|
| | $H_2O$ | | | HD | | |
| Pd/SC$_{18}$H$_{37}$ | 121 ± 1 | 99 ± 5 | 22 | 51 ± 3 | 32 ± 4 | 19 |
| Au/SC$_{18}$H$_{37}$ | 115 | 105 | 10 | 48 | 36 | 12 |
| Ag/SC$_{18}$H$_{37}$ | 116 | 103 | 13 | 50 | 40 | 10 |
| Cu/SC$_{18}$H$_{37}$ | 120 | 103 | 17 | 48 | 32 | 16 |

[a] Contact angle data for Au, Ag, and Cu were taken from ref 17 and were reported with deviations of ≥ 2°. Comparable values (within the error reported previously for these systems) were obtained as part of this study.

The hysteresis ($\Delta\theta = \theta_a - \theta_r$), a qualitative measure of the heterogeneity, roughness, or conformational disorder, is larger than that for SAMs on gold and silver. The AFM data (Figure 1) show that the roughness of the palladium films is comparable to that of the gold films. The difference in grain sizes between the palladium and gold films likely contributes in some degree to the contact angle hysteresis. We believe it is more likely, though, that the majority of the increased hysteresis arises as a result of the disorder (i.e., conformational defects) present in the SAM. We should note, however, that the data discussed below suggest that the densities of these conformational defects still must be quite low.
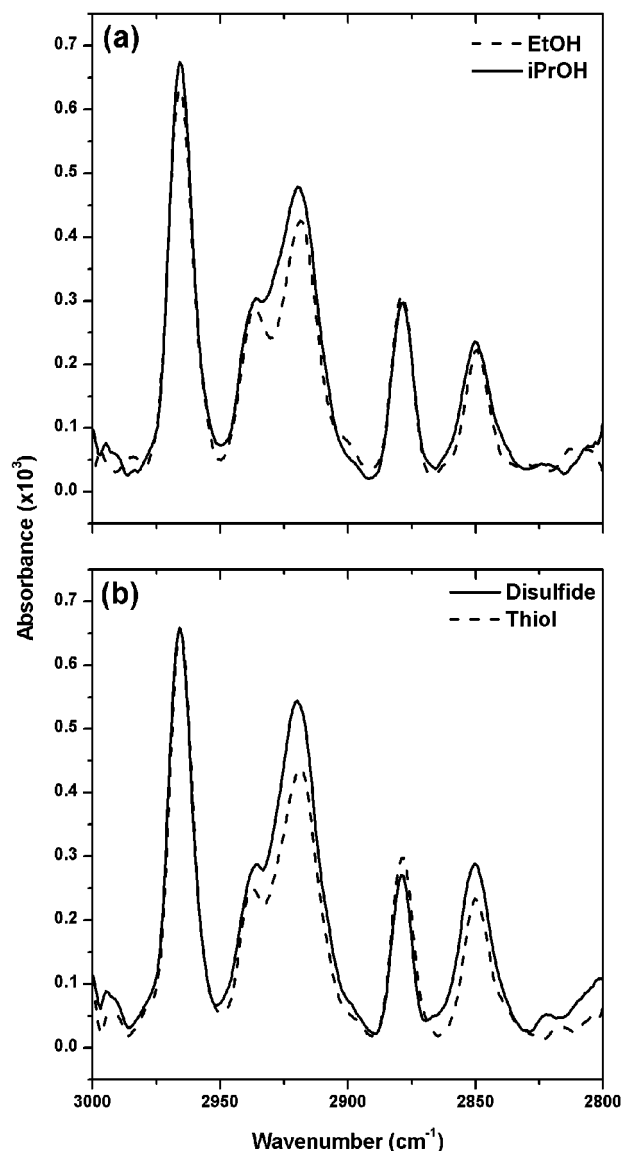
**Figure 3.** (a) RAIR spectra of the SAMs formed from 1 mM solutions of hexadecanethiol in degassed ethanol (dashed line) and 2-propanol (solid line). (b) RAIR spectra of the SAMs formed from 1 mM ethanolic solutions of hexadecanethiol (dashed line) and dihexadecane disulfide (solid line).

**Effect of Solvent on the Structure of the SAM.** SAMs formed from solutions of hexadecanethiol in ethanol and 2-propanol (10 mM) at 25 °C did not demonstrate any qualitative differences in wettability, and the RAIR spectra were essentially indistinguishable. Representative RAIR spectra measured in the C−H stretching region of SAMs formed from those solutions are shown in Figure 3a. These data suggest that the formation of the SAM at room temperature is not hindered by reactions occurring with the solvent (e.g., dehydrogenation of the ethanol on the palladium surface).

**Effect of Disulfide Contamination on the Structure of the SAM.** Significant differences in the SAMs formed on palladium by either hexadecanethiol or dihexadecane disulfide were evident in the corresponding RAIR spectra measured in the C−H stretching region (Figure 3b) and contact angle data. First, the intensities of the methylene stretches for the SAM prepared from the disulfide are somewhat more intense than those found for the SAM formed from the thiol. Second, although the advancing contact angle values of water on the SAMs formed by the

disulfide and thiol were nearly identical ($\Delta \approx 2-3°$), the hysteresis for the disulfide SAM was ~10° larger than that for the monolayer formed from the thiol-based monolayer. The contact angles of hexadecane on the SAMs from the disulfide were 5−8° lower than those from the thiol. These data suggest that the disulfide SAM is more "defective" in some way. It is likely, however, that factors other than the chain organization present in the SAM contribute to these differences.

We believe that the structure of the SAM formed from the disulfide is essentially the same as that formed from the thiol, but that there is a greater degree of contamination on the surface of the SAM by multilayers of physisorbed disulfide. The $C_{16}$ disulfide is sparingly soluble in ethanol and palladium films immersed in this solution emerge with a slighty hazy appearance. This dull luster remains even after rinsing repeatedly with ethanol and 2-propanol. Sonication of the samples in 2-propanol for 3−5 min restores the luster of the metal surface, but it is likely some amount of the disulfide remains. We believe that it is the presence of such physisorbed disulfide that accounts for both the intensity differences seen in the RAIR spectra as well as the variations in the contact angle data.

Trace contaminants of disulfide in thiol solutions do not appear to hinder the adsorption of the kinetically favored thiol onto gold and no gross structural difference between SAMs formed from thiols and disulfides has been observed.[18] Electrochemical data show, however, that the SAMs formed from disulfides do, in fact, contain a larger number of pinhole defects than SAMs from thiols, but these remain a subtle perturbation to the broader aspects of the chain organization.[19] Our qualitative results for SAMs formed on palladium from disulfides and thiols do not establish whether similar defects are present in this system as well. The data do suggest that trace (<5%) disulfide impurities in a thiol solution will not affect the structure of the SAM, but physisorption of disulfides (particularly for $n > 16$) may result if their solubility limits are exceeded. To minimize the effect of this contamination of the surface by physisorbed disulfides in our experiments, we employed freshly prepared solutions of the thiols and degassed the solvents prior to use to reduce the rate and extent of the oxidation of the thiols in solution to the disulfide.

**Effect of Temperature on SAM Formation.** Figure 4 shows the RAIR spectra measured in the C−H stretching region for the SAMs formed from hexadecanethiol and decanethiol after 18 h using adsorbate solutions held at either 25 °C or 45 °C. Both spectra show significant dichroism and frequencies for the $\nu_a(CH_2)$ and $\nu_s(CH_2)$ stretching modes (~2919 and 2850 cm$^{-1}$ for $C_{16}$) that are consistent with a largely all-trans organization of the chains (see below). The intensities further support a model for the chain organization that involves a cant angle of the chain axis that is less than is the case for SAMs on Au (see below).[17] The spectra for the SAMs formed from hexadecanethiol at 25 °C and at 45 °C are indistinguishable. The structure of the SAMs formed from decanethiol are, however, sensitive to the temperature at which the SAMs are incubated. The SAMs prepared at 45 °C, for example, show a decrease in the intensities of the C−H methylene stretching modes (appearing at ~2922 and
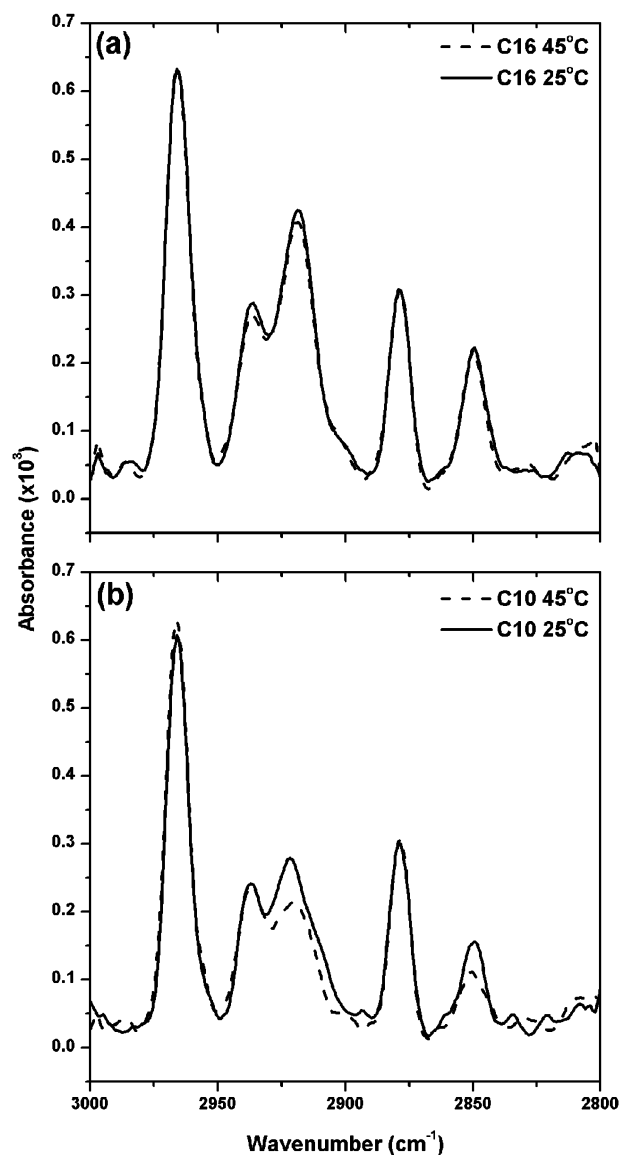


**Figure 4.** RAIR spectra of the SAMs formed from 1 mM ethanolic solutions of (a) hexadecanethiol and (b) decanethiol at 25 °C (solid line) and at 45 °C (dashed line).

2850 cm$^{-1}$). In addition, there is a small shift of the antisymmetric methylene stretch from 2922 to 2921 cm$^{-1}$. These data suggest that the organization of the SAM formed from decanethiol at 45 °C is somewhat more ordered than that formed at 25 °C. The increased order may result both from the effect of annealing on the lateral organization and from coverage differences that reduce the number of kinks and gauche defects. Previous studies of the annealing of SAMs on gold and silver at elevated temperatures showed improved ordering of the lateral organization results for these related SAMs of alkanethiolates as measured by STM experiments.[20] Other experimental evidence suggests that the organizational structure of the alkane chains of the SAMs formed from long-chain thiols ($n \geq 16$) on gold (as deduced from the IR spectra) does not improve in a marked way with annealing.[21]

(18) Biebuyck, H. A.; Bain, C. D.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1825−1831; Bain, C. D.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1989**, *5*, 723−727.
(19) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. *J. Am. Chem. Soc.* **1987**, *109*, 3559−3568.
(20) Bucher, J. P.; Santesson, L.; Kern, K. *Langmuir* **1994**, *10*, 979−983. McCarley, R. L.; Dunaway, D. J.; Willicut, R. J. *Langmuir* **1993**, *9*, 2775−2777. Yamada, R.; Wano, H.; Uosaki, K. *Langmuir* **2000**, *16*, 5523−5525.
(21) Bensebaa, F.; Ellis, T. H.; Badia, A.; Lennox, R. B. *Langmuir* **1998**, *14*, 2361−2367.

**Nature of the Palladium−Sulfur Interface.** Our studies of the etch resistance of SAMs on palladium suggested that the interface formed between the surface of the palladium and alkanethiol plays a major role in the mechanism by which these materials serve as resists to chemical etchants.[2] Most notably, we found that a number of thiols that differed in hydrophilicity and chain length were good etch resists on palladium. Previous studies of SAMs on gold have postulated that the mechanism for the etch resistance of that system requires a well-ordered, hydrophobic monolayer to prevent the transport of oxidizing ions to the surface.[6] We hypothesized that a thin interphase of PdS formed between the oriented monolayer of alkanethiolates and the bulk palladium film could account for the differences in the apparent mechanisms of etch resistance. The formation of such an interphase would require that, during the assembly, the C−S bond of some of the alkanethiols from solution are cleaved on the palladium surface to liberate the sulfur atoms needed to grow this metal sulfide layer. The data reported below support this complex model of the assembly process.

**Photoelectron Spectroscopy.** Figure 5 shows core-level survey spectra of the SAMs formed on palladium from dodecanethiol and hexadecanethiol. The spectrum of an untreated palladium substrate is also included as a reference. These spectra show that, in addition to an increase in the amount of carbon present relative to the amount of adventitious contaminants found on the nascent substrate, sulfur is only present on the surfaces treated to form a SAM. The assembly process also displaces (or precludes the adsorption of) the oxygen-containing species found on the starting substrate, as judged by the absence of an O KLL Aüger line in the spectra of the treated samples; the O(1s) line is obscured by the Pd(3p$_{3/2}$) core level.

The line shapes of the high-resolution S(2p) core level spectra indicate that there are at least three types of sulfur-containing species present on the surface; a representative spectrum for a SAM of hexadecanethiolate is shown in Figure 6a. We were able to fit this complex line shape using three pairs of spin−orbit-split components (S(2p$_{3/2}$) and S(2p$_{1/2}$)), assuming a Gaussian:Lorentzian (70%:30%) line shape and a splitting energy fixed at 1.18 eV.[14] The binding energies and the relative concentrations of the three sulfur species are listed in Table 2. We assign the species with the S(2p$_{3/2}$) binding energy of 162.3 eV to that of sulfur present in a metal sulfide interphase. The sulfur species with a binding energy of 163.2 eV is assigned to that of an alkanethiolate species present in a SAM. The high-resolution C(1s) line shape is consistent with the presence of the aliphatic chain of such a moiety. These assignments also fit well with the precedents set by the literature for alkanethiolate monolayers on gold, silver, and copper[17] and model experiments performed on palladium using aqueous solutions of Na$_2$S to generate a metal sulfide interphase. In the latter experiments, the reactions showed that a dominant feature for the S(2p$_{3/2}$) core level appears at 162.8 eV, a value consistent with and confirming the assignments of the metal sulfide species seen in the reactions of the *n*-alkanethiols. These data clearly argue that the assembly process that leads to the binding of thiolate involves contributions from C−S bond scission processes. The nature of the minor component at 164.9 eV is not completely understood. Because of the low intensity and the complexity of the S(2p) line shape, significant uncertainty accompanies the assignment of this S(2p$_{3/2}$) core level. The apparent value falls
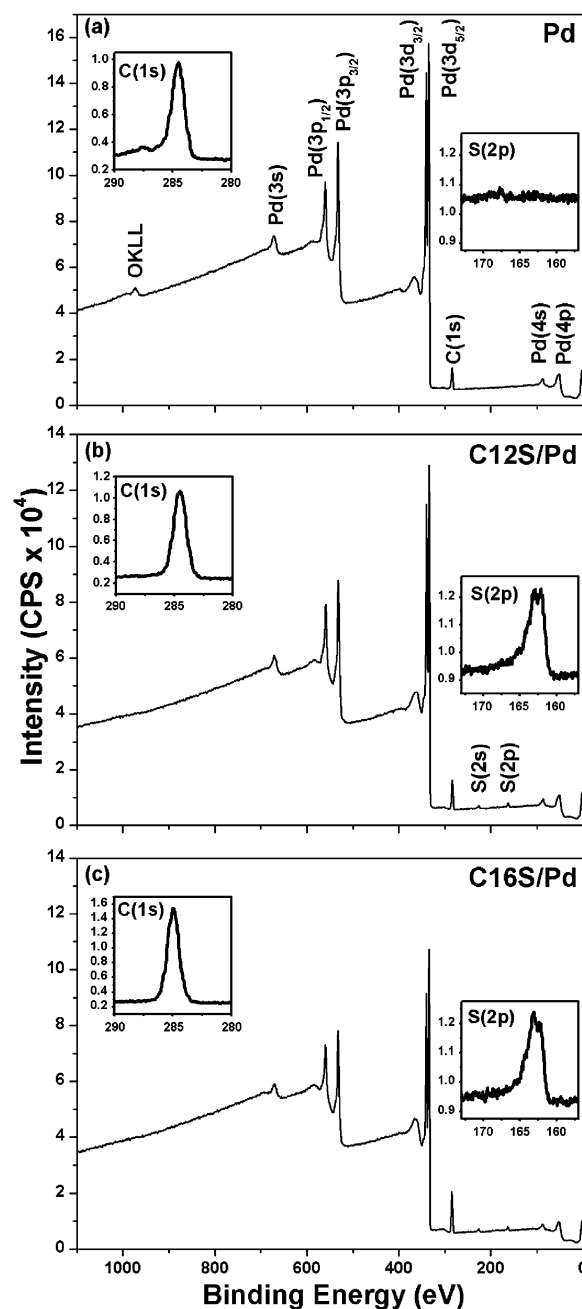


**Figure 5.** XP survey spectra of (a) an untreated palladium thin film, and a palladium substrate bearing either (b) a SAM of dodecanethiolate or (c) a SAM of hexadecanethiolate. The inserted spectra show the high-resolution spectra acquired for the C(1s) and S(2p) core level binding energies.

in a region where physisorbed disulfide molecules would appear. We cannot confirm whether disulfides or other low-coverage sulfur-containing species are, in fact, present in the adsorbed adlayer structure.

The metal sulfide species that are clearly revealed in the XPS data are not likely ones that can be related to a known bulk binary phase, such as the common tetragonal phase PdS. The sulfur coverages are simply too low to support the formation of appreciable quantities of this compound phase (at least not for the case of the SAMs formed via the reaction of palladium with *n*-alkanethiols). A high symmetry adlayer or substitutional structure would appear to be a more likely structural prospect for this sulfide phase, a point we consider in detail below.
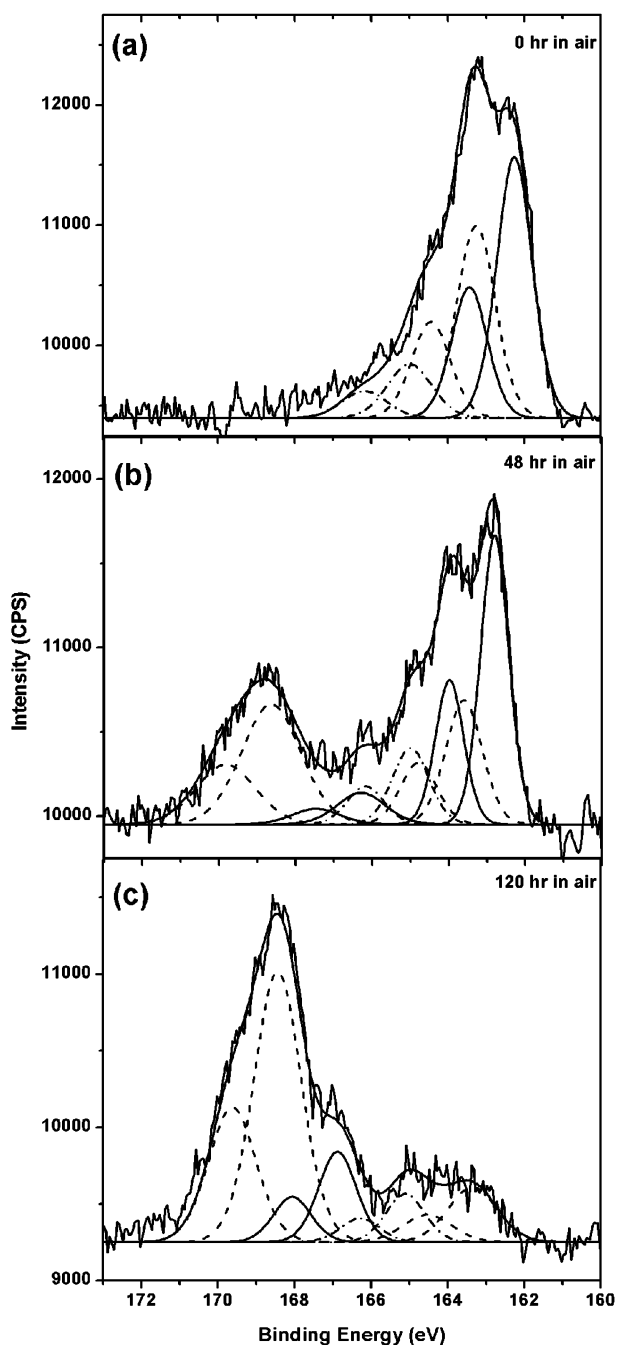
**Figure 6.** High-resolution XPS data for the S(2p) core levels of a SAM formed from hexadecanethiol (a) after exposure to a 1 mM degassed ethanolic solution stored under argon for 18 h, (b) after exposure to dry air for 48 h, and (c) after exposure to dry air for 120 h.

**Stability of the SAM in Air.** We found that the SAMs formed on palladium react over the course of days with atmospheric oxygen. For example, core levels for two new sulfur-containing species are observed at binding energies of 166.3 and 168.6 eV after storing the SAM for 48 h in a dry, ozone-depleted air atmosphere (Figure 6b). These changes are not seen when the SAM is stored either in UHV or an argon-purged environment. The intensity of these peaks (associated with an oxidation product) increase as the thiolate species are oxidized further after 120 h of exposure (Figure 6c). The inference that follows from these data is that the sulfur atoms of both the thiolate and sulfide species are oxidized to an alkyl

**Table 2.** S ($2p_{3/2}$) Core Level Binding Energies Determined by Curve Fitting for C16 SAM as a Function of Exposure in Air

| binding energy[a] (atomic %) | | | |
|---|---|---|---|
| 0 h in air | 48 h | 120 h | assignment |
| 162.3 (44.4%) | 162.8 (33.9%) | | Pd$-$S |
| 163.2 (40.2%) | 163.6 (18.8%) | 163.4 (13.1%) | CH$_3$(CH$_2$)$_n$S$^-$ |
| 164.9 (15.4%) | 165.0 (11.5%) | 165.1 (9.0%) | $-$S$-$S$-$, ? |
| | 166.3 (29.4%) | 166.9 (16.5%) | $-$SO$_2^-$ |
| | 168.6 (6.4%) | 168.5 (61.4%) | -SO$_3^-$ |

[a] eV.

sulfonate or sulfate anion by the air exposure. The species at 166.3 eV is likely only partially oxidized relative to the species at 168.6 eV. The oxidation of adsorbed thiolates in air has been reported for both silver and copper previously;[17] the oxidation process appears, however, to be more rapid in the case of palladium (days versus weeks).

**Thickness of the PdS Interlayer.** Depth profiling by scanning Aüger electron spectroscopy and ion sputtering revealed that the penetration of the sulfide phase into the bulk palladium is limited. Layers formed via the reaction of a thin film of palladium with a 10 mM aqueous solution of Na$_2$S for 24 h at 25 °C showed that the metal sulfide interphase was less than 10$-$20 Å thick. A comparison of the integrated S(2p) intensities of the Na$_2$S and *n*-alkanethiol-derived interphases suggest that the latter yields a metal-sulfide interphase that is no more than 1$-$2 monolayers in thickness (see below). The scanning Aüger measurements did not show any grain-boundary segregation of the sulfur at the surface within the limits of the resolution of this method. We do not fully understand the factors that limit the penetration depth of the sulfide phase except to note that barriers to interdiffusion appear to be reasonably large.

**Structure of the Alkane Chains in the Monolayer.** Several lines of experimental data speak to the character of the chain organizations present in the SAMs that form atop the complex metal-sulfur interface described above. We discuss each of these in turn in the sections that follow.

**Film Thickness.** Optical ellipsometry provides inferential insights into the quality of the SAM by establishing the mass coverage of the chains and their structure$-$property correlations.[12,19,22] Toward this end, we determined the average thickness of the films formed by the adsorption of alkanethiols with varying chain lengths ($n$ = 8, 10, 12, 16, 18, 22) on palladium (Figure 7). The average thicknesses measured for analogous SAMs on gold are shown as a reference for the benefit of the reader. We assumed a constant refractive index of $n$ = 1.45 for the films for the reduction of the data.[23] The limiting mass coverage reached for each alkanethiol on palladium is comparable to that formed on gold. This observation suggests that there are not multilayers of either thiol or disulfide adsorbates present in a significant way on the surface of the palladium substrate. The best fit to the palladium data (by the method of least squares) has a slope of 1.87 Å per methylene unit (CH$_2$) and a (nonphysical, see below) *y*-intercept of $-$0.77 Å. This slope is greater than that reported for SAMs formed on gold (1.50 Å per methylene).[12,19]

(22) Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 4481$-$4483.
(23) The refractive index selected is an average value of the refractive indices of hydrocarbons and thiols. The refractive indices for hexadecane (1.4345), decanethiol (1.4509), dodecanethiol (1.4589), and octadecanethiol (1.4645) are reported in the CRC Handbook of Chemistry and Physics, 75th ed.; 1994.
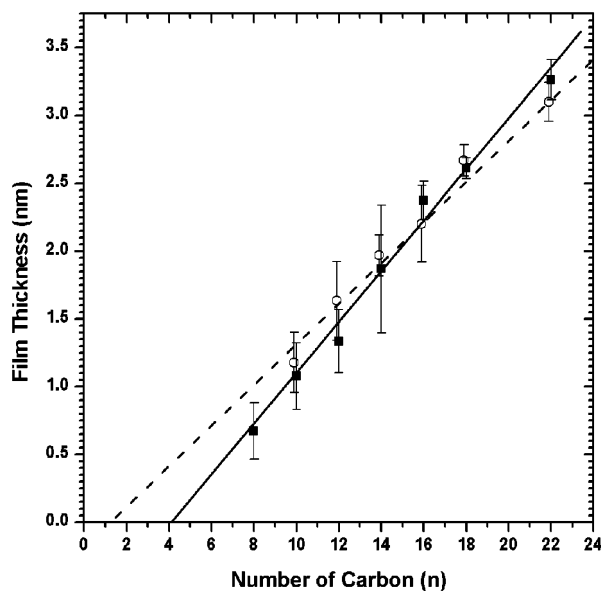
**Figure 7.** Thickness of the monolayer formed by an *n*-alkanethiol adsorbate solution on palladium (■) and on gold (○) as a function of the number of carbon atoms in the alkane chain, *n*. The solid line represents the best-fit linear regression for the palladium data. The dashed line shows a corresponding linear fit for the SAMs on gold.

The average measured thickness of the SAMs formed by long-chain thiols ($n \geq 16$) on palladium were consistently greater than those for gold. This observation agrees with the results reported by Delamarche et al. for hexadecanethiol and eicosanethiol.[3] The standard deviations of the measurements for SAMs on palladium and gold are ∼2−3 Å, and, thus, preclude a more quantitative analysis of the structure of the alkane chains in the monolayer based on these data alone. The nonphysical intercepts also illustrate that a systematic bias is present in the calculations; this bias probably results from the pseudo-substrate constants adopted in the modeling. The origin of this effect likely resides in the complex chemical state of the initial palladium film used to measure this parameter. Recall that the XPS data showed that the chemisorption of the thiols involves both a displacement of an adventitious adsorbate layer and the incorporation of sulfur into a metal sulfide interlayer. Both of these reactions should modify the optical properties of the palladium substrate. We have not accounted for these perturbations of the optical constants in a quantitative manner, but note that the data shown in Figure 7 demonstrate that they impact the chain-length dependent data in a systematic way.

**Film Structure Insights via Infrared Spectroscopy.** The vibrational modes appearing in the C−H stretching region of a SAM provide powerful insights into the local molecular environment and organizational structure of the alkane chains of the monolayer. These inferences, in the present case, follow from the application of a model based on the dipole selection rules. This boundary value dictates that it is only that component of a transition dipole moment that projects onto the surface normal direction that can result in measurable absorbances. The intensity of each mode observed in a RAIR spectrum can be related to both the magnitude and orientation of the transition dipole moments of each mode (for a given set of optical boundary values established by the details of the experimental geometry used in making the measurement). These issues have
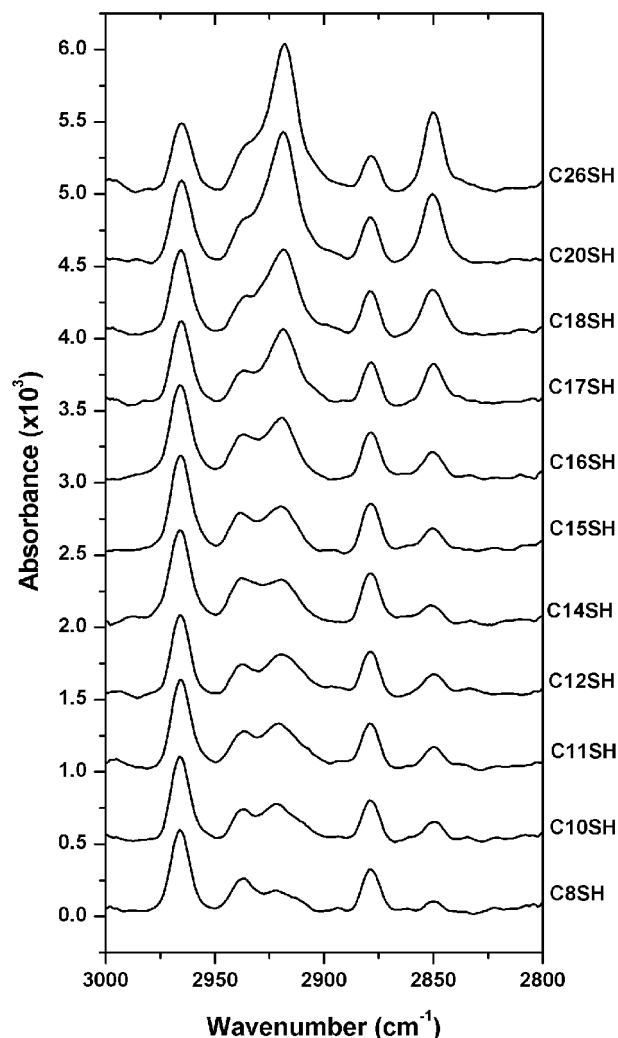


**Figure 8.** RAIR spectra in the C−H stretching region of SAMs formed from alkanethiols $HS(CH_2)_{n-1}CH_3$ ($n = 8, 10, 11, 12, 14, 15, 16, 17, 18, 20, 26$), on a thin film of palladium (200 nm). The data, plotted as absolute absorbances, have corrected baselines that are offset vertically for clarity.

been discussed in significant detail in the literature[17,24−26] and numerous applications made in structural studies of SAMs.[17,19,21,25,27−29] Previous numerical simulations and experimental evidence for alkanethiol-derived SAMs on gold and silver (ones especially relevant to the case of interest here) provide a relevant model to understand the chain organizations adopted in the SAMs on palladium. The chain-length-dependent RAIR spectra measured in the C−H stretching region for *n*-alkanethiolate SAMs on palladium (Figure 8) can be well understood in the context of a model all-trans-conformer chain; a schematic of which is depicted in Figure 9.

The data in Figure 8, whose mode assignments and frequencies are summarized in Table 3, illustrate that a simple set of structure−property correlations operate in SAMs on palladium.

(24) Allara, D. L.; Nuzzo, R. G. *Langmuir* **1985**, *1*, 52−66; Allara, D. L.; A., B.; C. A., P. *Macromolecules* **1978**, *11*, 1215−1220.
(25) Allara, D. L.; Nuzzo, R. G. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1984**, *25*, 185.
(26) Parikh, A. N.; Allara, D. L. *J. Chem. Phys.* **1992**, *96*, 927−945.
(27) Nuzzo, R. G.; Dubois, L. H.; Allara, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 558−569.
(28) Nuzzo, R. G.; Korenic, E. M.; Dubois, L. H. *J. Chem. Phys.* **1990**, *93*, 767−773.
(29) Walczak, M. M.; Chung, C.; Stole, S. M.; Widrig, C. A.; Porter, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 2370−2378.
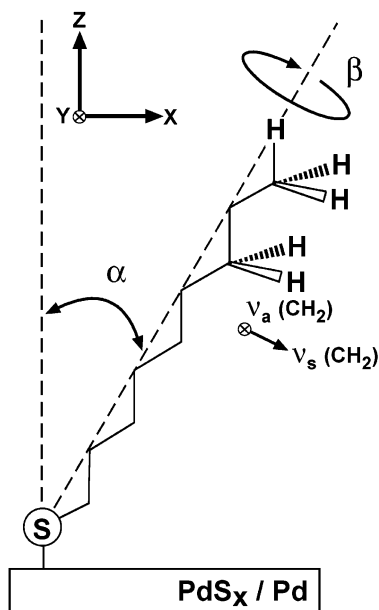
**Figure 9.** Schematic view of an all-trans conformer of a single, long-chain alkanethiol adsorbed on palladium. The tilt angle ($\alpha$) is defined with respect to the surface normal direction. The twist angle ($\beta$) describes the rotation of the CCC bond plane relative to the plane of the surface normal and the tilted chain.

First, the intensities of the methyl stretching modes show very little sensitivity to the chain-length of the alkanethiol used to form the SAM. This observation suggests that the organization of the methyl groups at the ambient surface is similar in each SAM (a point we consider in more detail below). Second, the organization of the chains, especially for $n \geq 16$, is well approximated by the all-trans conformer model described above. This inference is most powerfully supported by the observation that the frequencies of the methylene antisymmetric stretching mode for the long chain-length SAMs fall at values associated with crystalline habits of alkyl chains and well-ordered SAMs. For example, the peak positions and line shapes of the antisymmetric ($d^-$, 2918–2919 cm$^{-1}$) and symmetric ($d^+$, 2850 cm$^{-1}$) methylene stretches in the SAMs formed from long-chain alkanethiols ($n \geq 16$) are similar to those for crystalline docosanethiol (2918, 2851 cm$^{-1}$) and for SAMs on gold (2918, 2850 cm$^{-1}$).[19] This orientational ordering is chain-length dependent, as is most clearly illustrated by noting that the peak value for the $d^-$ mode shifts from 2919 to 2922 cm$^{-1}$ as the number of carbons decreases from $n = 16$ to $n = 8$. This progression suggests an increasing contribution from gauche conformers; the peak of the $d^-$ mode for liquid octanethiol is 2924 cm$^{-1}$.[19] Third, the chains appear to adopt an average chain cant that is greater than that of the related SAMs on silver, but less than that for the layers on gold.[17,19,30] As discussed in more detail below, this significant aspect of the chain organization follows explicitly from a quantitative consideration of the mode intensities and dichroism seen in the C–H stretching region. When taken together, these data are consistent with a structural model involving a close-packed, crystalline-like environment of extended trans conformers with relatively few gauche defects for the SAMs with alkane chains containing 16 or more carbons. The molecular environment of the alkyl chains relaxes from this state to one involving more disorder (i.e., liquidlike) as the

(30) Dubois, L. H.; Nuzzo, R. G. *Annu. Rev. Phys. Chem.* **1992**, *43*, 437–463.

number of carbons in the alkane chain ($n$) decreases. The trends seen in the contact angle measurements of the SAMs further supports this conclusion. We defer a more detailed discussion of these issues to later in the paper.

**Application of SAMs of *n*-Alkanethiolates on Pd as Etch Resists.** The utility of the SAMs formed on palladium as patterned etch resists stems from the properties of layers formed by printing the thiol rather than deposition from solution.[4,6] For this reason, we examined the structural properties of SAMs deposited by a printing protocol analogous to microcontact printing using RAIRS and XPS in order to understand how the structural organization and the interface composition differed from those of SAMs formed in solution.

**Structure of the SAM Prepared by Contact Printing.** In a typical printing procedure used to generate micro- and nanostructures, a dilute solution of thiol (0.2 – 5 mM) in ethanol is applied to a topographically patterned poly(dimethylsiloxane) (PDMS) stamp by spreading with a cotton swab or by spin-casting. The stamp is then placed in contact with a metal thin film for 5–30 s.[4] In the present work, we adopted a model protocol for the printing using an unpatterned PDMS pad to transfer the ink.[31] The RAIR spectrum of a hexadecanethiolate SAM formed by this contact printing protocol shows that the structure obtained after 1 h of contact time is identical to that of a SAM deposited from solution (5 mM) after 12 h of immersion (Figure 10). For printing times of less than 1 min, the SAMs obtained are more structurally disordered—e.g., the intensities of the methylene stretches increase and the frequency of the $d^-$ peak shifts markedly to wavenumber values higher than those found for the solution-deposited SAM. We attribute the character of this disorder to the gauche-conformer defects that result from a lower mass coverage of the thiolate chains than is present in a solution-deposited SAM.

The coverage reached in the printing follows mass action principles related to the ink concentrations as well. Figure 11 shows the RAIR spectra of the hexadecanethiolate SAMs formed by contact printing for a constant contact time as a function of ink-solution concentration. Concentrations of thiol less than 1 mM produced monolayers with apparently low mass coverage and disordered alkane chains. Concentrations greater than 10 mM improved the structural outcome, but not markedly for this printing time for this particular ink.

**Nature of the SAM–Palladium Interface Formed by $\mu$CP and Wet Etching.** XPS studies of the S(2p) core levels of SAMs prepared by $\mu$CP did not reveal any substantial differences between the sulfur species present after printing or solution deposition. There was evidence of a minor amount of oxidation of the sulfur transferred by printing; a weak but very broad peak was present at ~168 eV. The printing experiments were performed under ambient atmospheric conditions and this exposure would account for the small amount of oxidation observed.

We also exposed dodecanethiolate and hexadecanethiolate SAMs prepared by contact printing to an aqueous ferric chloride etchant for periods up to three times the typical time required to etch a 30 nm-thick film of palladium (90 s). The XPS data for the sulfur region of the exposed and unexposed samples were indistinguishable. This result suggests that the etchant does

(31) Jeon, N. L.; Finnie, K.; Branshaw, K.; Nuzzo, R. G. *Langmuir* **1997**, *13*, 3382–3391.

***Table 3.*** Peak Positions for C–H Stretching Modes of Alkanethiols in SAMs on Palladium

| | peak positions for HS(CH$_2$)$_{n-1}$CH$_3$ absorbed at palladium (cm$^{-1}$) | | | | | | | | | | |
| mode description[a] | n=8 | n=10 | n=11 | n=12 | n=14 | n=15 | n=16 | n=17 | n=18 | n=20 | n=26 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $\nu_s$(CH$_2$), d$^+$ | 2850 | 2851 | 2851 | 2850 | 2851 | 2850 | 2850 | 2850 | 2850 | 2850 | 2850 |
| $\nu_s$(CH$_3$), r$^+$ | 2879 | 2879 | 2879 | 2879 | 2879 | 2879 | 2879 | 2879 | 2879 | 2879 | 2878 |
| $\nu_a$(CH$_2$), d$^-$ | 2922 | 2922 | 2921 | 2920 | 2920 | 2920 | 2919 | 2919 | 2918 | 2919 | 2918 |
| $\nu_s$(CH$_3$), r$^+$ (FR) | 2937 | 2937 | 2936 | 2937 | 2938 | 2938 | 2937 | 2936 | 2935 | 2935 | 2935 |
| $\nu_a$(CH$_3$), r$_a^-$ (i.p.) | 2966 | 2966 | 2966 | 2966 | 2966 | 2966 | 2966 | 2965 | 2966 | 2965 | 2965 |

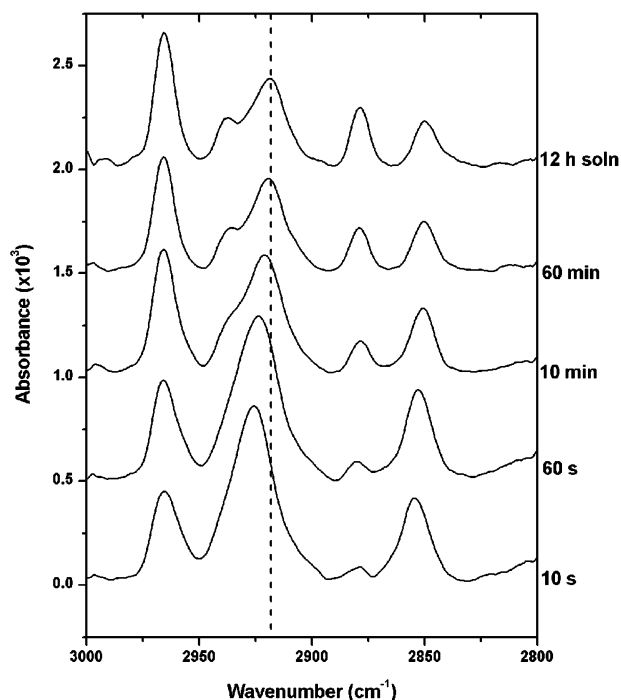[a] FR = Fermi resonance, i.p.= in plane (All values are reported ± 1 cm$^{-1}$).



***Figure 10.*** RAIR spectra of SAMs of hexadecanethiolate on palladium formed by contact printing (5 mM thiol solution) with different lengths of contact time using an unpatterned PDMS transfer pad. The spectra of a SAM formed for 12 h in 5 mM solution of thiol is shown as a reference. The dashed line indicates the peak position for the d$^-$ mode for a crystalline hydrocarbon (2918 cm$^{-1}$).



***Figure 11.*** RAIR spectra of SAMs of hexadecanethiolate on palladium formed by contact printing for 60 s using ink solutions with different concentrations of hexadecanethiol. The dashed line indicates the peak position for the d$^-$ mode for a crystalline hydrocarbon (2918 cm$^{-1}$).

not degrade the alkanethiolate or the sulfide interphase over the typical time required for pattern transfers by $\mu$CP and etching.[32]

## Discussion

The structural ordering of SAMs of alkanethiolates on gold and silver has been characterized in great depth both by experiment and by theory-based methods.[12,17,19,26,29,30,33–35] The structures formed on palladium are reminiscent of those found in these more extensively studied systems, and the data reported here can be interpreted by analogy. The trends and values of the mass coverages determined by ellipsometry and the wetting properties determined by contact angle measurements are comparable with the related data for similar SAMs formed on
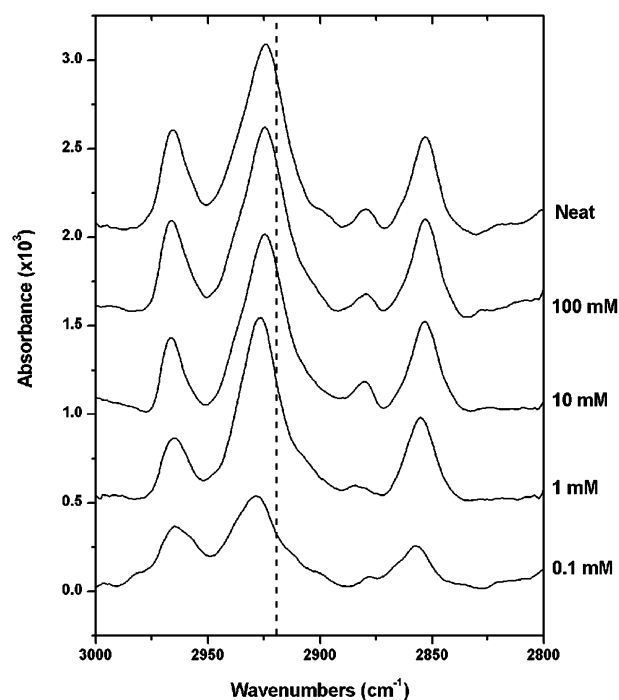
any of the coinage metals. For example, the film thicknesses and hydrophobicity increase with chain length (as was seen for the case of SAMs on gold[12]). The line shape and peak shifts of the RAIR spectra change smoothly with increasing chain length from a more disordered, liquidlike film for short chain lengths ($n < 14$) to a more crystalline-like environment for long chain lengths ($n > 14$). This trend also is consistent with that seen for SAMs on the coinage metals.[17,19] The absolute intensities also follow the trends seen in those SAMs. The narrow line widths and the limiting peak frequency (2919 cm$^{-1}$) of the d$^-$ mode for the long chain SAMs supports a fully extended, predominantly all-trans organization of the alkane chains with few gauche defects in these monolayers. The range of the chain-length-dependent shift of the d$^-$ mode is slightly greater than that for long chain SAMs on gold and silver; the smaller grain sizes and larger mosaic spread of the thin films of the palladium substrates used here are likely contributors to this structural sensitivity. These observations suggest that the alkane chains in the monolayer become densely packed and oriented away from the surface, and for this reason, the structure–property correlations of the SAMs should resemble those for SAMs on gold and silver.

The limiting organization of the chains present in a SAM of alkanethiolates on palladium can be described in the context of

(32) We note that, in pattern transfer experiments, the regions functionalized by $\mu$CP do dissolve in the etchant when exposed for times longer than the time required to etch the unpatterned regions. We have not determined whether this observation is a result of dissolution of the palladium–sulfide layer or is a result of etching at defect sites and subsequent dissolution of the underlying palladium.
(33) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533–1554.
(34) Nuzzo, R. G.; Zegarski, B. R.; Dubois, L. H. *J. Am. Chem. Soc.* **1987**, *109*, 733–740.
(35) Fenter, P.; Eisenberger, P.; Li, J.; Camillone, N.; Bernasek, S.; Scoles, G.; Ramanarayanan, T. A.; Liang, K. S. *Langmuir* **1991**, *7*, 2013–2016.

the structural model presented in Figure 9. The model describes the organization of the average chain in terms of two angles, $\alpha$ and $\beta$, that define the tilt of the long axis of the chain and rotation of the CCC plane around that axis relative to the plane of the tilt. For the SAMs formed on gold and silver, these values of $\alpha$ and $\beta$ were found to fall in the range of $\alpha = 25-30°$, $\beta = 50-55°$ and $\alpha = 10-15°$, $\beta \approx 45°$, respectively.[17,27,29,30,33,36] It is now known that the structures of the SAMs on gold actually involve a multichain unit cell[28,30,37] spaced with a sub-cell lattice periodicity of a simple $(\sqrt{3} \times \sqrt{3})R30°$ adlayer structure. The orientation indicated by the angles described in Figure 9 is one that averages such details to a single chain model, a feature significant to the discussion that follows.

We start by making a more detailed comparison between the RAIR spectra of the related, long-chain SAMs formed on gold, silver, or palladium from octadecanethiol (Figure 12a). As noted above, the frequencies of the $d^-$ modes for each are as expected for an assembly of essentially all-trans chains. The progression of intensities for the $d^-$ modes rises in the ascending order of silver, palladium, and gold. This observation suggests that the chain tilt ($\alpha$) of the SAM on palladium likely lies between that of gold and silver.

A closer inspection of the data, however, reveals that the palladium system appears to follow a closer analogy to the structure of the SAM on silver than it does to that of gold. This detail is most clearly illustrated by a consideration of the intensity trends and dichroism seen in both the methylene and methyl C—H stretching vibrations. The larger tilt of the SAM on gold is partially reflected in the generally larger intensities seen in all the C—H stretching modes, particularly the $d^-$ mode, compared to those of the silver and palladium-based systems. The twist of the chains ($\beta$) also contribute to the large intensities of the modes and, as noted above, the $\beta$ for SAMs on gold is larger than that for silver; it is this difference that is reflected not only in variations seen in specific band intensities but also in the differences in dichroism observed. As suggested by Figure 9, such differences in the values of $\beta$ could act in concert with the chain tilt to determine the magnitudes of the projections of the $d^-$ transition moment on the surface normal direction. The dichroism and intensities of the RAIR spectra of the SAMs on palladium can be directly related to aspects of the structures of either the silver or gold cases in the context of a simple model based on these assumptions.

We start by noting that the dichroism observed in the spectra shown in Figure 12a suggests that the twist angle, $\beta$, for the alkane chains in the monolayer on palladium is similar to that found for silver. This observation strongly implies that the value of $\beta$ is ~45°. The intensities of the methylene stretches also indicate the degree of the tilt of the chain relative to the surface normal direction. As the intensities measured for the $d^-$ and $d^+$ modes for SAMs of octadecanethiolate on palladium are between those measured for analogous SAMs on gold and silver (Figure 12a), the cant angle likely lies between these limits (~26-28° on gold and ~11-14° on silver).[17,29] We can quantitatively rationalize the tilt angle of the structure on palladium based on a simple calculation of the maximum intensities expected for the component of the dipole moment
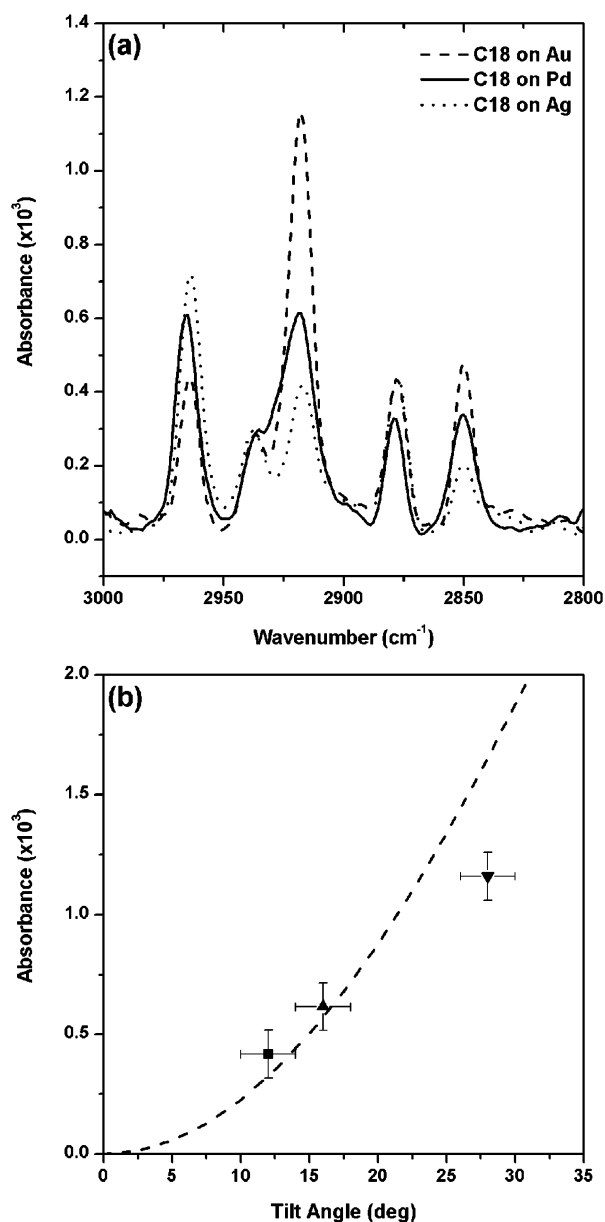
(36) Strong, L.; Whitesides, G. M. *Langmuir* **1988**, *4*, 546-558. Dubois, L. H.; Zegarski, B. R.; Nuzzo, R. G. *J. Chem. Phys.* **1993**, *98*, 678-688.
(37) Hahner, G.; Kinzler, M.; Thummler, C.; Woll, C.; Grunze, M. *J. Vac. Sci. Technol.* **1992**, *A10*, 2758.

***Figure 12.*** (a) RAIR spectra of a SAM of hexadecanethiolate on palladium (solid line), on gold (dashed line), and on silver (dotted line). (b) Intensity modula of the $d^-$ mode as a function of the tilt angle, $\alpha$. The data points represent measured values for the $d^-$ mode for SAMs of hexadecanethiolate on silver (■), palladium (▲), and gold (▼) located at their expected ranges of $\alpha$. The dashed line represents the expected modula for the $d^-$ mode as a function of $\alpha$ at a twist angle $\beta = 45°$. The modula were calculated using the relationship: $I \approx (\mu*E)^2$ where $\mu*E$ is the projection of the dipole moment of the stretching mode onto the vector of the electric field normal to the surface and the orientation of the dipole ($\mu$) is a function of $\alpha$ and $\beta$.

of the $d^-$ mode projected onto the electric field of the incident polarized light (parallel to the surface normal) at a tilt angle, $\alpha$ (Figure 12b). We assume in the model that the contributions of the optical constants of all three metals to an absorption measurement are identical and, for the purposes of comparison, that the twist angle is identical for all three SAMs ($\beta = 45°$). These model calculations show that, to within the experimental uncertainty, the structure of the SAM on palladium is more similar to that for silver than gold and that an estimated value of $\alpha$ ranges between 14 and 18°. It is important to note that the $d^-$ intensity of the SAM on gold can still be accounted for within

the constraints of this model. The deviation seen in Figure 12b, for example, is completely lifted when a fully convergent model is constructed that accounts for both α and β—i.e., the larger value of β on gold.[17,26]

The data of Figure 8 illustrate that the direct analogy between the structure present on silver and palladium is even more explicit than the simple model presented above may suggest. Note, for example, that the chain-length-dependent RAIR spectra of the SAMs on palladium show no experimentally significant sensitivities exist in the intensities of the C—H stretching modes of the methyl groups, even for those cases where an odd or even chain-length thiol is used to form the SAM. This result cannot be rationalized within the constraints of any structural model of a SAM organization defined by an average single chain tilt (α) and twist (β) where the value of α is conserved in an odd−even series. Indeed, it suggests that the value of α must switch from positive to negative values (and visa versa) as the chain length is incremented by one methylene group. This argument was discussed at length in an earlier paper on the structure of alkanethiolate SAMs on silver.[17]

In light of our current understanding of the structure of SAMs, we suspect that a subtle feature might be involved in this structure−property correlation; one related to the organization of the SAM into an ordered structure based on a multichain unit cell. Such structures are now well established for SAMs on gold, but are less well characterized in the other systems. The intriguing aspect of the multichain structure resides in the fact that it can completely rationalize the value of β. An orthorhombic sub-lattice,[28] for example, would commonly place the axis of the chains' CCC planes with a setting angle of 90°. The single chain average of β for any canted structure incorporating this sub-lattice would be 45°, the experimentally determined value. Both the corrugation of the ambient methyl surface projections as well as the bonding present at the metal-sulfur interface are preserved by tilting the chains into one of two equivalent nearest-neighbor configurations. The symmetry of the tilt direction in both configurations of such a multichain unit cell would eliminate any odd−even chain length sensitivities in the methyl mode intensities (as seen experimentally in the RAIRS data) and in the physical properties such as wetting (which is also seen experimentally). The structures on gold provide a unique counterpoint in this regard, showing significant odd−even effects in several experimental measures, particularly in the dichroism seen in RAIR spectra. These latter structures thus serve as an interesting point of comparison and suggest that significant opportunities exist for direct structural probes (e.g., diffraction methods) to clarify these issues.

The interpretation of the nature of the palladium−sulfur bonding is both complicated and made more intriguing by the noted incorporation of sulfur into the interface via the desulfurization of the thiols present in solution. Our XPS data show that the ratio of sulfur present as either a thiolate or sulfide species typically ranges from ∼1:1 to 1:2 (as determined from the atomic concentrations deduced via curve fitting and neglecting complications due to final state effects, or the differential attenuation due to metal atoms or the alkyl chains). Making the logical assumption that the thiolate species correspond to a single chain in the SAM, there are between one and two additional sulfur atoms present at the interface in the form of a palladium sulfide interphase.

Previous LEED and STM studies of sulfur adlayers formed on Pd(111) (the dominant texture of the films used here) document a number of ordered overlayer structures with reported sulfur atom coverages that range from 1/3 to either 2/7 or 3/7 for the most common ordered phases with other additional coverages less commonly found.[38] The most common structures correspond to the translational symmetries of $(\sqrt{7} \times \sqrt{7})R19.1°$ (2/7 and/or 3/7 coverage) and $(\sqrt{3} \times \sqrt{3})R30°$ (1/3) overlayers. The surface area of the $\sqrt{7}$-unit cell is 45.8 Å$^2$, whereas that of the $\sqrt{3}$ structure is 19.6 Å$^2$.[39] Inclusion of all of the sulfur measured by XPS (i.e., one thiolate and 1−2 sulfide species) in a two-dimensional overlayer (at the coverage factors suggested by prior studies for the $\sqrt{7}$ structure) yields a density of the chains in the monolayer of 45.8 Å$^2$/molecule. By way of reference, the density of the chains present in SAMs supported on Au(111) is 21.7 Å$^2$/molecule (or 4.99 Å between sulfur atoms)[30] and on silver most likely does not exceed 19.1 Å$^2$/molecule (or 4.7 Å between sulfur atoms), although distances shorter than that have been suggested.[17,33,35] As the distance between the sulfur atoms in both these systems is greater than the distance of closet approach of the alkane chains (4.24 Å or ∼18 Å$^2$/molecule),[30,40] the chains maximize their van der Waals interactions by tilting. The structural organization of the alkane chains on palladium inferred from the IR spectra, ellipsometry measurements and contact angle data do not correlate with the structure of chains expected for a packing density of 45.9 Å$^2$/molecule. The resulting overlayer would be a low coverage phase with a corresponding high degree of structural disorder in the alkane chains.

The surface area of the $\sqrt{3}$-unit cell is 19.6 Å$^2$. Assuming one chain per unit cell, the packing density is also 19.6 Å$^2$/molecule. This value falls between the packing densities for the chains in SAMs on gold and silver and, thus, is a consistent spacing with which to rationalize the data for the structural organization of the chains. This analysis does not account, however, for the additional sulfur measured by XPS. It seems most likely that all the sulfur present at the interface cannot be confined to a two-dimensional surface structure, but rather, must reflect a metastable, compound palladium-sulfide interphase. The bulk crystal phase for the most common sulfide (PdS) is tetragonal.[41] This compound cannot be a relevant structural model for an ordered interphase that projects a spacing consistent with a $\sqrt{3}$ adlayer structure as there is not an appropriate mapping possible of the crystal planes of the tetragonal phase onto the (111) texture of the palladium surface. This fact suggests that the interphase is a substitutional, and likely metastable, phase. This observation further suggests that some consideration may need to be given to the results of some LEED studies, which tend to ascribe the character of the $\sqrt{3}$ overlayer to that of a simple adlayer structure with a coverage of 1/3 θ.

The data collected for the SAMs formed by μCP suggest that the quality of the SAM formed from solutions of thiols at the concentrations typically reported in the literature (0.1 mM to

(38) Bomermann, J.; Huck, M.; Kuntze, J.; Rauch, T.; Speller, S.; Helland, W. *Surf. Sci.* **1996**, *358*, 849−854. Liu, W.; Mitchell, K. A. R.; Berndt, W. *Surf. Sci.* **1997**, *393*, L119-L125. Speller, S.; Rauch, T.; Bomermann, J.; Borrmann, P.; Heiland, W. *Surf. Sci.* **1999**, *441*, 107−116.
(39) The nearest-neighbor distance between palladium atoms in the (111) plane is 2.75 Å. Kittel, C. *Introduction to Solid State Physics*, 7th ed.; John Wiley & Sons: New York, 1996.
(40) Ulman, A.; Eilers, J. E.; Tillman, N. *Langmuir* **1989**, *5*, 1147−1152.
(41) Crystal Lattice Structures, CCMS Databases, Naval Research Laboratories, http://cst-www.nrl.navy.mil/lattice/.

10 mM) and printed for a typical time of 10 s have more defects and a lower mass coverage than the SAMs formed for long periods of time in solution. This observation does not support the empirical evidence that the SAMs on palladium are superior to those on gold as etch resists simply due to the properties of the chain organizations they present.[3] We believe that the improved etch constrast is due to a difference in the kinetic rates of etching bare palladium and the palladium-sulfide phase formed upon printing, as further mediated by the SAMs they present at the ambient interface with the etchant. Indeed, while more difficult to pattern in some ways than long chain alkanethiols, sulfur phases that lack the SAM terminus are effective resists in their own right,[2] and a compelling demonstration of the effectiveness of a compound interphase as a mediator of reactions occurring at the solid−liquid interface.

## Conclusion

The data presented here indicate that a metastable, palladium-sulfide interphase is generated during the formation of a SAM of alkanethiolates on the surface of palladium, and that the structure of the monolayer is most similar to that found on silver. We expect that the structure−property correlations of these SAMs will also resemble those for silver. One significant advantage of this system over silver is that the palladium substrates do not oxidize readily. This property makes palladium a more convenient substrate to handle and use for soft lithography than silver. A disadvantage of SAMs of alkanethiolates on palladium is that they are less stable in air than are SAMs on gold and silver. The sulfur species oxidize within 2−5 d. The utility of palladium as a substrate for microcontact printing offers a good alternative to the coinage metals for applications that require CMOS-compatible processing or catalytic surface activity. These results may also suggest a new strategy for preparing ultrathin, inorganic materials on surfaces by soft lithography wherein the reactive "ink" directly forms a new substitutional phase at the surface rather than an organic scaffold for subsequent chemical modification.

**Supporting Information Available:** Select list of US patents describing some applications of SAMs of alkanethiolates on palladium. This material is available free of charge via the Internet at http://pubs.acs.org.

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