

ARTICLES

Characterization of Self-Assembled Alkanethiol Monolayers on Silver and Gold Using Surface Plasmon Spectroscopy

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We report the surface plasmon study on a variety of self-assembled monolayers (SAMs) of *n*-alkanethiols, $\text{HS}(\text{CH}_2)_n\text{CH}_3$ ($n = 11, 13, 15, 17, 19$), absorbed to silver and gold surfaces, in terms of thicknesses, indices, and tilt-angles. We have found that the refractive indices for the alkanethiols attached to Ag increase gradually as alkyl chain length increases. Likewise, the refractive indices for Au increase gradually to an alkyl chain length of $n = 17$, at which point its refractive index decreases slightly. The indices vary from a low value of 1.33 to 1.44. This gradual increase in index is not unexpected since it suggests that differences in packing and consequent bulk polarizability, $\chi^{(1)}$, is affected by alkyl chain length. A molecular modeling minimized *n*-alkanethiol length and its corresponding experimental surface plasmon thickness were used to determine the tilt-angle for each of the various alkanethiols via a projection analysis. We found that the tilt-angles of the *n*-alkanethiols attached to Ag begin to increase from 0° starting with $n = 15$; however, the tilts on Au have an average of $\sim 41^\circ$, seemingly independent of carbon chain length.

Introduction

Since the work of G. Whitesides *et al.*,^{1–3} there has been an intense experimental and theoretical effort to verify the structure and optical properties of self-assembled monolayers (SAMs) of various length alkanethiols bonded to thin (111) layers of silver or gold. Much of this effort has been concentrated on gold films. Recent *ab-initio* and MM2 molecular modeling work by Sellers *et al.*⁴ conclude that the $\text{SC}_{16}\text{H}_{33}$ alkanethiol SAM has an absolute tilt to the Au(111) surface normal of $\sim 30^\circ$, regardless of whether the sulfur hybridization is sp^3 or sp , in agreement with experiment.^{3,5,6} X-ray diffraction studies by Fenter⁷ and co-workers indicate there is direct evidence that the monolayer tilt structure on Au(111) depends upon the hydrocarbon chain length. Their data show that the tilt-angle does not change continuously, but instead appears to have two distinct values, $\sim 31^\circ$ for chain lengths $\text{CH}_3(\text{CH}_2)_n\text{SH}$ of $n \geq 13$ and $\sim 34^\circ$ for lengths $n \leq 11$. From their low-angle X-ray scattering results Fenter and his co-workers conclude that there are also two distinct packing structures corresponding to these long and short chain length regimes. However, previous work by Fenter⁸ also indicates that self-assembly of *n*-alkanethiols as disulfides, in particular an in-depth study of the $\text{CH}_3(\text{CH}_2)_9\text{SH}$ monolayer on Au(111), results in an optimal tilt-angle of $\sim 37^\circ$. Fenter and his associates have also studied the intermolecular hydrocarbon and sulfur–Au morphology with low-angle X-ray scattering.^{8–12}

Theoretical work involving orientation of certain SAMs on Ag are limited,⁵ but experimental work with SAMs on Ag have indicated average tilt-angles of $\sim 12^\circ$,¹ $\sim 13^\circ$,¹³ and $\sim 15^\circ$,¹⁴ for a variety of *n*'s. Recent surface-enhanced Raman spectroscopic studies on the alcohol $\text{HO}(\text{CH}_2)_{21}\text{SH}$ bonded to a Ag(111) surface indicate a $5 \pm 5^\circ$ tilt-angle.¹⁵

To further clarify these structural morphology issues, we present our results based on short-range surface plasmon work

for a series of SAMs of alkanethiols, $\text{CH}_3(\text{CH}_2)_n\text{SH}$, with $n = 11, 13, 15, 17$, and 19 , bonded to $\sim 500 \text{ \AA}$ thermally evaporated films of Ag and Au on BK7 microscope slides. Traditionally, methods including ellipsometry, contact angle, and external reflection infrared spectroscopy (IRS) have been utilized to characterize SAMs bonded to Ag or Au. In this work, surface plasmon spectroscopy (SPS) is used as the primary technique for characterization of these alkanethiol monolayers. SPS allows the determination of not only the monolayer's thickness but its refractive index as well at a nonabsorbing wavelength. Of the methods listed above, ellipsometry has been the primary technique used to determine the monolayer thickness. In determining monolayer thickness by ellipsometry, previous authors have assumed the refractive index of the SAMs of various length alkanethiols to be a constant value of 1.45, independent of chain length and packing considerations.^{3,4} Our results show that the refractive index does in fact change with respect to alkanethiol chain length and associated polarizability differences governed by packing. We provide comparisons of the ellipsometric thicknesses, using experimental plasmon refractive indices, with the thickness measurements obtained through our plasmon work for both Ag and Au. These thicknesses prove to be identical within experimental error. We also report contact measurements for comparison of our results to other work. Reported tilt-angles of SAMs for the various alkylthiolate chain lengths are based on a projection analysis using chain lengths obtained from molecular mechanics calculations for an anti-configuration of the methylene groups and the SPS-determined thickness.

Experimental Section

Preparation of Glass Slides. Fischerbrand BK-7 microscope slides were used as the substrate for the vapor-deposited metals. The microscope slides came in the size of $25 \times 75 \times 1 \text{ mm}$ and were cut to a size of $25 \times 25 \times 1 \text{ mm}$ to better match the

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dimension of the prism face. Even though the slides were "precleaned", it was necessary to perform a rigorous cleaning procedure. This procedure has been previously discussed.¹⁶

Metal Film Preparation. A 500 Å sample of Ag or Au was thermally evaporated onto clean BK-7 glass substrates using an Edwards E306A coating system. Within the chamber the 25 × 25 × 1 mm BK-7 slides were placed on a specially prepared mask. The chamber was then evacuated to a pressure of $(4-6) \times 10^{-7}$ mbar, at which time the metal was deposited at a rate of 1–2 Å/s. The best metal plasmon curve, one having the deepest resonance minimum, was obtained by using 99.9999% Ag and 99.999% Au, purchased through Aldrich. A film thickness monitor located within the coating chamber monitored the rate and thickness of the metal film being deposited. Upon removal from the chamber, the metal-coated slides were subjected to no longer than 20 min in the atmosphere before being immersed in the thiol solutions. Control SPS experiments indicated that there were no differences in the plasmon spectra obtained for either freshly prepared Ag- or Au-coated slides that were immersed immediately in alkanethiol solutions upon removal from the deposition chamber and those subjected to 20 min in the laboratory atmosphere before immersion. This period of time was necessary to collect ellipsometric and/or plasmon data for determination of the optical constants of the pure metal films.

An experimental picture of Au films prepared in this fashion has emerged recently that is consistent with microcrystalline assemblies $\ll 6328$ Å, showing at least an 80% 111-face normal to the slide surface.¹⁷ Previous work¹ indicates that silver is also heavily 111 textured although less so than gold. In this approximation, such metal surfaces and the SAMs bonded to them can be treated as "flat" in our plasmon experiments and theory done at this HeNe wavelength. Unfortunately, experimental difficulties with plasmon interface requirements prohibit the use of single-crystal mica substrates, which would guarantee nearly a 100% 111-faced metal surface.¹⁸ We point out that the use of a thin ~ 50 Å Cr film preceding the deposition of the Au film, a protocol commonly used to prepare Au electrodes that adhere better to glass slides, broadens the plasmon resonance curve, so we have not used it.

Monolayer Preparation. Reagent grade *n*-alkanethiols ($n = 11, 15, 17$) were obtained through Aldrich. *n*-Alkanethiols ($n = 13, 19$) were synthesized and purified according to a procedure by Bain.³ Solutions of 1 mM were prepared in reagent grade heptane, obtained from Mallinckrodt. Control experiments indicated that the plasmon spectrum of the pure Ag- or Au-coated slide immersed in reagent grade heptane and dried caused no shift in the attenuated total reflectance (ATR) curve. This was shown over a time period of 72 h, much longer than the time the slides were immersed in the dilute thiol solutions. Previous experimentation had shown thiol solutions using absolute ethanol over a 2 h period would cause the thin Ag or Au film to lift off the BK-7 glass surface. Heptane did not cause this problem.

After the initial plasmon spectrum of the pure Ag or Au film was obtained, the index matching fluid was removed from the back of the slide by thoroughly rinsing with heptane. Next, the slide was immediately immersed in the thiol solution. The alkanethiol monolayers were allowed to spontaneously self-assemble on the thin metal films for 24 h. Longer time periods of 48 and 72 h were examined with no observable effect on monolayer formation and thickness. After the 24 h period, the slide was removed and rinsed with fresh heptane and dried with a light stream of dry N₂.

Ellipsometric Film Thickness Measurements. A Rudolph Research Auto EL^R-II instrument was used at 632.8 nm to obtain

the ellipsometric data at a constant reflectance angle of 140° by averaging measurements recorded from four separate spots on each slide. A computer program, written by Rudolph Research, was used to determine the index and monolayer thicknesses. In our protocol, the film thickness of the bare metal film was obtained first with SPS, followed by ellipsometric and SPS measurements of the combined metal–SAM films. We emphasize that the refractive indices used in calculation of the ellipsometric monolayer thicknesses were obtained from the surface plasmon measurements.

Contact Angle Measurements. A Rame'–Hart Model 100-00 115 goniometer was used for the contact angle measurements. These were obtained using Millipore water in air as the probe liquid. Both advancing (θ_a) and equilibrium (θ_e) contact angle measurements were recorded. The advancing measurements were taken according to the protocol discussed by Walczak,¹³ while the equilibrium contact angle was obtained after allowing sufficient time for the water droplet to come into equilibrium with the slide surface. In this work, contact angles are used as a qualitative measurement for comparison to previous values^{1,13} where monolayers were self-assembled from absolute ethanol.

Surface Plasmon Spectroscopy. Surface plasmon apparatus, measurement, and theory as we use it in this work have been discussed elsewhere.^{16,19,20} The ATR resonance curve due to plasmon generation is extremely sensitive to variations in the refractive index and thickness of the dielectric at the metal–dielectric interface. The unique shape and angular position of the minimum of the pure metal SPS resonance curve is determined by its thickness (d) and complex index (n and k). After self-assembly of the alkanethiols, the optical thickness and complex index or dielectric of the SAM film changes the refractivity of the combined films, thereby changing the shape and angular position of the ATR minimum. From this resonance curve shift and knowledge of the optical thickness and complex index of the metal, the thickness and refractive index of the monolayer film can be determined as explained previously using a nonlinear least-squares procedure.¹⁶ At 6328 Å, the SAM film presents no absorption or imaginary index component; therefore, a single-wavelength SPS curve can uniquely determine the thickness and real index of this monolayer from the reflectivity versus angular position of the SPS spectrum. However, the thickness and complex index of the pure metal film cannot be uniquely determined at a single wavelength. In our previous SPS work on Ag/Au bimetallic films at 6328 Å, this limitation has not precluded determinations of these three parameters that are consistent with known literature values.²¹ Our experimental benefit rests in a very accurate and precise nonlinear fitting of the SPS curves in what we have called "exact" fits with extremely small residuals that were never greater than $\pm 1\%$ in the worst case. In fact, nonlinear least-squares fits of the combined metal–SAM film with known metal parameters and unknown SAM parameters (d, n, k) result in a null contribution to the imaginary index. An estimate of the accuracy for plasmon-determined thicknesses found in Table 1, based on the residuals fit, is ± 1 Å for both Ag and Au.

Results and Discussion

Table 1 summarizes our experimental plasmon and ellipsometric results for $n = 11, 13, 15, 17$, and 19 alkanethiols, CH₃(CH₂)_{*n*}SH, bonded to ~ 500 Å films of either Ag or Au. Figures 1 and 2 contrast pure Ag and Au SP spectra with each other as well as with SAMs on these metals for $n = 11$ and $n = 19$ cases. Table 1 shows that the alkylthiolate refractive indices for Ag gradually increase as alkyl chain length increases. The indices vary from a low value of 1.33, similar to water, to 1.44, a value close to the index of 1.45, which earlier work^{3,5,13}

TABLE 1: Plasmon and Ellipsometric Monolayer Thicknesses and Indices^a

methylene chain length (<i>n</i>)	Ag			Au		
	index	plasmon	ellips	index	plasmon	ellips
11	1.33	19	19	1.33	14	13
13	1.34	22	22	1.38	16	14
15	1.35	24	23	1.41	18	16
17	1.41	25	25	1.45	20	17
19	1.44	27	28	1.41	21	20

^a All thickness values are in angstroms. Ellipsometric thicknesses are determined from SPS indices. An estimate of the accuracy for plasmon-determined thicknesses, based on the residuals fit, is ± 1 Å for both Ag and Au.

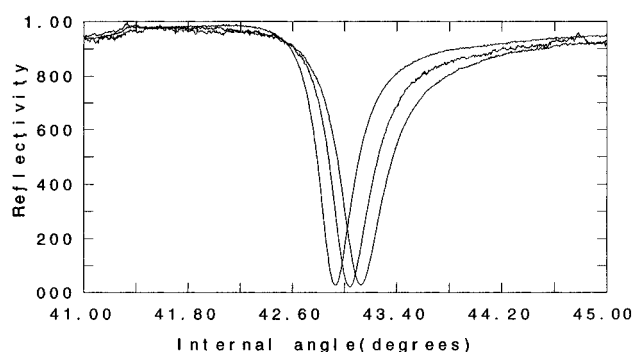


Figure 1. Experimental surface plasmon resonance curves of pure Ag with certain alkanethiol SAMs. The first resonance curve on the left is that of pure Ag. The next two curves with minima located at increased internal angles are those of Ag with an alkanethiol $n = 11$ and $n = 19$, respectively.

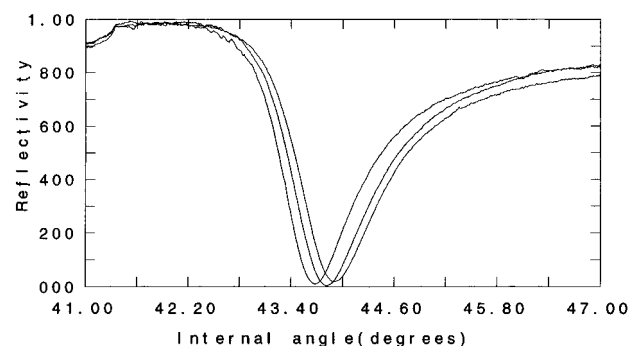


Figure 2. Experimental surface plasmon resonance curves of pure Au with certain alkanethiol SAMs. The first resonance curve on the left is that of pure Au. The next two curves with minima located at increased internal angles are those of Au with an alkanethiol $n = 11$ and $n = 19$, respectively. Note that the fwhm values of the gold curves are about 2.5 times greater than those of the silver counterparts.

has used for ellipsometric thickness determinations. This gradual increase in index is not unexpected since it suggests that differences in packing and consequent bulk polarizability, $\chi^{(1)}$, is affected by alkyl chain length. Likewise, the refractive indices for Au increase gradually to an alkyl chain length of 17, at which point its refractive index decreases slightly. We do not understand the reason for this decrease, although this is not an experimental artifact. Alkanethiolate thicknesses on Ag and Au obtained by plasmon and ellipsometric measurements are very close and within experimental error, ± 1 Å for Ag and ± 2 Å for Au, corresponding to a $\pm 5\%$ and $\pm 10\%$ thickness difference for Ag and Au, respectfully.

Our advancing contact angle measurements are listed in Table 2. They are nearly identical to the $n = 11$ –19 methylene-length measurements obtained previously for Au^{1,3} and for Ag.¹³ Table 2 compares the advancing and equilibrium contact angles. The wettability of a monolayer, indicated by a decreasing contact angle, is a function of its surface properties and not a function

TABLE 2: Contact Angle Measurements^a for Varying Methylen Chain Length Alkanethiols

methylene chain length (<i>n</i>)	Ag		Au	
	advancing	equilibrium	advancing	equilibrium
(pure metal)	100	96	98	94
11	112	108	115	111
13	113	108	116	114
15	112	109	116	112
17	113	108	117	112
19	112	108	117	113

^a Contact angle measurements are in degrees.

TABLE 3: Tilt-Angles^a of Alkanethiol Monolayers

methylene chain length (<i>n</i>)	tilt-angle projection analysis	
	Ag	Au
11	0	45
13	0	42
15	8	42
17	17	40
19	18	41

^a The average molecular tilt-angle is determined with respect to the plane defined by the surface of metal atoms. We estimate the error in the calculated tilt angle to be $\pm 3^\circ$ for Ag and $\pm 4^\circ$ for Au.

of the interior medium.²² The medium would be expected to indirectly affect surface properties by affecting the order, pack, and tilt of surface functional groups. Since the terminal methyl group will dictate the surface properties of the alkanethiol monolayers, the contact angles should be consistent for each metal surface study, independent of the carbon chain length, as Table 2 illustrates.

Previous studies have utilized ethanol as the supporting solvent for self-assembly of alkanethiol monolayers on Au and Ag. In this study we have used heptane, for reasons described previously. Results from our contact angle measurements indicate that heptane, and possibly other solvents, can be used successfully for self-assembly of monolayers from solution without changing the monolayer's structural characteristics to any appreciable amount.

The tilt-angles of the alkanethiolates on Au and Ag are shown in Table 3. These angles were calculated by determining the projection of an alkanethiol molecular length onto the metal surface using the experimental plasmon thickness. The alkanethiol molecular length was evaluated using the geometric optimization of one $\text{CH}_3(\text{CH}_2)_n\text{SH}$ ($n = 11, 13, 15, 17, 19$) molecule bonded to either a Au(111) or Ag(111) surface and minimized with a modified MMX force field using PCMODEL molecular modeling software (Serena Software, Bloomington, IN). The MMX force field used in PCMODEL is derived from the MM2 (QCPE-395, 1977) force field of N. L. Allinger,²³ with the π -VESCFC routines taken from MMP1 (QCPE-318), also by N. L. Allinger.²⁴ The force constant parameters utilized in all modeling calculations were obtained from previous work by Sellers⁴ and co-workers, for sp-hybridized sulfur. They calculated tilt-angles for both sp^3 - and sp -hybridized sulfur attached to Au, but only sp for Ag. Their results suggested modeling only a 16 carbon length alkanethiol, that there was no relative difference in the absolute tilt, $\sim 30^\circ$, for either sp^3 - or sp -hybridized sulfur on Au. Furthermore, their results for the 16 carbon length alkanethiol on Ag suggest an average tilt-angle of $0 \pm 5^\circ$.

We have modeled the alkanethiol SAMs on both Ag and Au using the sp -hybridized sulfur force field and constants as determined by Sellers and co-workers⁴ assuming an anti-configuration of the methylene groups in the alkane backbone.

The average length of an alkanethiol was calculated from the surface of the metal to the terminal methyl group by first

finding the energetically minimized length of a single alkanethiol modeled on either Au or Ag. For this purpose, the alkanethiol was bonded to a hollow site on the metal surface following a hexagonal surface coverage description,⁴ geometry specified in Scheme I of ref 4. In this description the Ag-surface to sulfur bond length is fixed at 2.4 Å. For Au this bond length is fixed at 1.9 Å. This is the MM-minimized alkanethiol length that we used to determine the tilt-angle via a projection analysis, values found in Table 3. We estimate the error in the calculated tilt angle to be $\pm 3^\circ$ for Ag and $\pm 4^\circ$ for Au. We also "attempted" to calculate the tilt-angle of an ensemble of six alkanethiols surrounding one, arranged in a hexagonal hollow-site pattern using PC Model. In this calculation the alkanethiol molecules, methylenes in an anti-configuration, were minimized as a group attached to the fixed metal substructure. Without refinement of these results with regard to a global energy minimization search, we found an average tilt-angle of 28° for Ag and 34° for Au. Clearly, these calculated angles are very crude, and without a great deal of further refinement they cannot be compared to either our projection-based tilt-angles or those calculated for the $n = 15$ alkanethiol by Sellers and co-workers.⁴

Our experimental projection-based tilt-angles on Ag are less than those of the corresponding monolayer on Au, as has been found in other work. It is not surprising that the increased tilt-angle of the alkylthiolates on Au over those of Ag are caused by factors related to energetic stabilization of the monolayer structure. Sellers concludes that this is primarily due to the greater spacing between the Au atoms on the Au(111) surface in comparison to Ag(111) structure and the decrease in the sulfur-metal bond distance in Au over that of Ag.⁴ Our tilt-angle projection results tend to follow this same trend, with tilts on Ag being much less than those of the corresponding monolayer on Au. However, our study indicates that the tilt-angles on Ag begin to increase from 0° starting with $n = 15$. Our tilt-angles obtained for the various alkanethiol SAMs on Ag are in disagreement with previous results^{1,13,14} which indicate an average tilt of $\sim 13^\circ$. On the other hand, Sellers,⁴ modeling only $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ on Ag(111) and Ag(100), indicates a tilt-angle of $\sim 0 \pm 5^\circ$, in basic agreement with our result for this molecule.

Interestingly, in our studies, we have found n -alkanethiols attached to Au where $n \geq 13$ to have a tilt-angle of $\sim 40^\circ$ to $\sim 42^\circ$, seemingly independent of carbon chain length, as Fenter⁷ and co-workers had seen previously. With $n = 11$, our studies indicate an average molecular tilt of $\sim 45^\circ$, 3° greater than the longer chain alkanethiols. Fenter's⁷ studies also showed an $\sim 3^\circ$ difference between the tilt-angles of alkanethiols where $n \geq 13$ ($\sim 31^\circ$) and $n \leq 11$ ($\sim 34^\circ$). Even though there is a consistency within the tilt-angles of both our and Fenter's experiments, the tilt-angles are still $\sim 10^\circ$ greater than in previous studies^{1,5,7} performed on Au(111). Perhaps, because our Au surfaces are not entirely 111, but somewhat polycrystalline,¹⁷ the surface structure including defects could affect the packing of the SAMs on our thermally deposited metal surfaces, resulting in an increase in the relative molecular tilt-angle. However, we cannot at this time suggest other explanation(s).

In this study we have found that refractive indices do in fact change and increase as the length of the alkanethiol carbon chain increases in SAMs on either Au or Ag. One of the most interesting results is the overall low value of the indices of the alkane thiol SAMs, which range from 1.33 to 1.44 for methylene chain lengths, $(\text{CH})_n$, ranging from 11 to 19, respectively. These values for SAMs are significantly lower than corresponding indices for bulk liquids, which range between 1.45 and 1.60 for organic material. In a nonabsorbing spectral region, SPS analysis allows an accurate determination of both the index and

thickness of films ≤ 100 Å, at a single wavelength, which is not the case for ellipsometric analysis. For films below ~ 100 Å, ellipsometric measurement cannot uniquely determine both the thickness and the real part of the index at a single wavelength. Typically, an index of 1.50 is used for organic monolayers²⁵ to facilitate a calculation of thickness. However, a range of indices of 1.3-1.5 produces ellipsometric thickness errors of no more than $\sim 15\%$. Depending on application, this may be very acceptable, particularly on rough surfaces. In this study, we were interested in accurately determining both the index and thickness of thin organic films to determine tilt-angle and to provide new index information regarding the polarizability of very thin films. Ellipsometry does furnish accurate values of film thickness and index, at a single wavelength and fixed compensator arm angle, for films ≥ 100 Å with an appropriate phase shift, Δ , versus ψ ($\tan\psi = r_p/r_s$) curve analysis.^{26,27} Thickness values obtained by SPS and ellipsometric techniques vary only slightly when using the experimental SPS refractive indices in the ellipsometric thickness calculations, lending support to the accuracy of the plasmon measurements. Tilt-angles for the alkanethiols on silver tend to be small and vary according to chain length. Tilt-angles of the alkylthiolates studied on Au tend to be greater than values seen previously, indicating that surface defects on the polycrystalline metal substrates have affected the two-dimensional ordering of the adsorbates.

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References and Notes

- Laibinis, P. E.; Whitesides, G. M.; Allara, D. L.; Tao, Y.-T.; Parikh, A. N.; Nuzzo, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 7152.
- Whitesides, G. M.; Laibinis, P. E. *Langmuir* **1990**, *6*, 87.
- Bain, C. D.; Troughton, B. E.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321.
- Sellers, H.; Ulman, A.; Shnidman, Y.; Eilers, J. E. *J. Am. Chem. Soc.* **1993**, *115*, 9389.
- Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559.
- Nuzzo, R. G.; Dubois, L. H.; Allara, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 558.
- Fenter, P.; Eisenberger, P.; Burrows, P.; Forrest, S. R.; Liang, K. *S. Physica B* **1996**, *1*.
- Fenter, P.; Eberhardt, A.; Eisenberger, P. *Science* **1994**, *266*, 1216.
- Fenter, P.; Eisenberger, P. *Phys. Rev. Lett.* **1993**, *70* (16), 2447.
- Camillone, N., III; Chidsey, C. E. D.; Eisenberger, P.; Fenter, P.; Li, J.; Liang, K. S.; Liu, G.-Y.; Scoles, G. *J. Chem. Phys.* **1993**, *99* (1), 744.
- Liu, G.-Y.; Fenter, P.; Chidsey, C. E. D.; Ogletree, D. F.; Eisenberger, P.; Salmeron, M. *J. Chem. Phys.* **1994**, *101* (5), 4301.
- Fenter, P.; Burrows, P. E.; Eisenberger, P.; Forrest, S. R. *J. Cryst. Growth* **1995**, *152*, 65.
- Walczak, M. M.; Chung, C.; Stole, S. M.; Widrig, C. A.; Porter, M. J. *J. Am. Chem. Soc.* **1991**, *113*, 2370.
- Bryant, M. A.; Pemberton, J. E. *J. Am. Chem. Soc.* **1991**, *113*, 3629, 8284.
- Nemetz, A.; Fischer, T.; Ulman, A.; Knoll, W. *J. Chem. Phys.* **1993**, *98* (7), 5912.
- Ehler, T. T.; Noe, L. J. *Langmuir* **1995**, *11*, 4177.
- Nuzzo, R. G.; Fusco, F. A.; Allara, D. L. *J. Am. Chem. Soc.* **1987**, *109*, 2358.
- Chidsey, C. E. D.; Loiacono, D. N.; Sleator, T.; Nakahara, S. *Surf. Sci.* **1988**, *200*, 45.
- Sprokel, G. J.; Santo, R.; Swalen, J. D. *J. Mol. Cryst. Liq. Cryst.* **1981**, *68*, 29.
- Sprokel, G. J. *J. Mol. Cryst. Liq. Cryst.* **1981**, *68*, 39.
- Johnson, P. B.; Christy, R. W. *Phys. Rev. B* **1972**, *6*, 4370.
- Sondag-Huethorst, J. A. M.; Fokkink, L. G. *J. Langmuir* **1995**, *11*, 2237.
- Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99* (25), 8127.
- Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1.

(25) Ulman, A. *An Introduction to Ultrathin Organic Films from Langmuir-Blodgett to Self-Assembly*; Academic Press: New York, 1991; Chapter 1.1.

(26) Muller, R. *Adv. Electrochem. Electrochem. Eng.* **1973**, 9, 167.

(27) Azzam, R. M. A.; Bashara, N. M. *Ellipsometry and Polarized Light*; North-Holland: Amsterdam, 1977.