

Real-Time Measurements of the Gas-Phase Adsorption of *n*-Alkylthiol Mono- and Multilayers on Gold

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Results of surface acoustic wave, ellipsometric, and electrochemical experiments indicating that stable mono- or multilayer films result from the gas-phase chemisorption of *n*-alkylthiol molecules onto Au substrates are reported. Measurement of the mass and thickness of CH₃(CH₂)₆SH films indicates a single, stable monolayer, while CH₃(CH₂)₁₅SH deposition results in mono- or multilayers depending upon the experimental conditions. The first in situ kinetic measurements of the self-assembly of such layers are also discussed.

Introduction

We report the results of surface acoustic wave (SAW), ellipsometric, and electrochemical experiments indicating that stable mono- or multilayer films result from the gas-phase chemisorption of *n*-alkylthiol molecules onto Au substrates. Measurement of the mass and thickness of CH₃(CH₂)₆SH films indicates a single, stable monolayer, while CH₃(CH₂)₁₅SH deposition results in mono- or multilayers depending upon the experimental conditions. We also report the first in situ kinetic measurements of the self-assembly of such layers.

Self-assembled films, ranging in thickness from one to tens of monolayers, show considerable technological and scientific promise as platforms for electronic and optical devices, chemical sensors, lubricants, model biological membranes, electron transfer barriers, and catalysts.¹ Typically, self-assembled mono- and multilayer films are deposited from dilute solutions of amphiphilic molecules that exhibit a strong specific interaction with the substrate as well as intermolecular van der Waals interactions.

Solution-deposited, self-assembled films of S-terminated amphiphiles have been previously examined by ellipsometry, external reflectance Fourier transform infrared (FTIR) spectroscopy, electrochemistry, transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS).^{2,3} These studies revealed that films

consisting of *n*-alkylthiol molecules longer than about 15 Å are well-ordered monolayers. We are interested in manipulating this native structure to produce templates for the fabrication of quantum electronic components and selective coatings for chemical sensors. In some cases, it is convenient to prepare such structures in the vapor, rather than liquid, phase. The preliminary experiments reported here suggest that the properties of monolayer films prepared by either vapor or solution phase deposition are similar. This result is in accord with the only prior study of vapor-deposited alkylthiols; Nuzzo et al.^{3e} used ultra-high vacuum techniques to study the adsorption of CH₃-SH and (CH₃S)₂ to Au and found that both materials formed strongly bound films. The alkylthiol interaction did not involve cleavage of the S-H bond, but the disulfide interacted with the Au substrate by a thiolate interaction. Solution-deposited alkylthiol films are also thought to involve a thiolate-Au interaction.^{2e}

We have used SAW devices to study the real-time adsorption characteristics of *n*-alkylthiol molecules at atmospheric pressure. SAW devices are extremely sensitive to the presence of surface-confined adsorbates as a result of their high operating frequencies and confinement of the acoustic energy to within one wavelength of the surface.⁴ The velocity of the SAW, which is perturbed in direct proportion to the mass loading of the device, is measured as a change in frequency when the device is used as the feedback element of an oscillator circuit. Changes in the attenuation of the acoustic wave can be related to the viscoelastic properties of the surface-confined adsorbate as well.⁵

Results and Discussion

CH₃(CH₂)₆SH and CH₃(CH₂)₁₅SH were vapor-deposited onto Au-coated SAW devices by exposing them to an N₂ purge stream containing the appropriate vapor.⁶ The top of Figure 1 shows the change in SAW frequency as a function of time for the adsorption of CH₃(CH₂)₆SH. Dry N₂ is passed into the chamber containing the device; at *t* = 25 min, the pure N₂ stream is replaced by the thiol-

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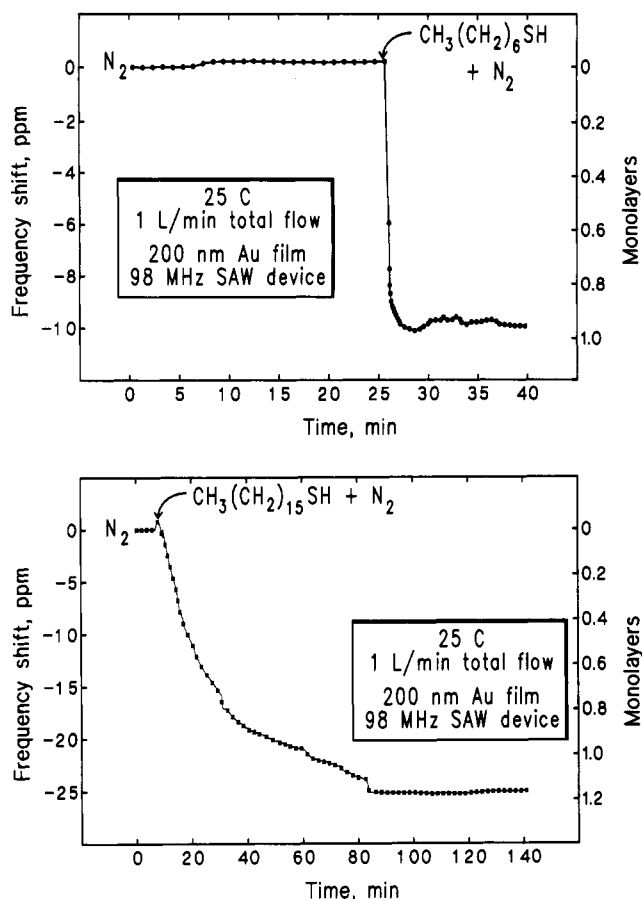


Figure 1. Frequency response measured for an Au-coated SAW device exposed to N_2 gas streams containing (top) $CH_3(CH_2)_6SH$ and (bottom) $CH_3(CH_2)_{15}SH$, both at approximately 25% of saturation. The flat part of each curve illustrates the stability of the SAW device. At the time denoted by the arrow the composition of the flow stream was changed from N_2 only to N_2 plus thiol. A mass corresponding to that of about a single, organized monolayer of the thiols forms on the Au surface.

containing (25% saturated) N_2 stream. An immediate decrease in the frequency is observed that corresponds to a mass increase of 115 ng/cm^2 .⁷ Based on the molecular weight of the adsorbate and an average area of $18.4 \text{ \AA}^2/\text{molecule}$,⁸ one monolayer of organized $CH_3(CH_2)_6SH$ has

(6) For ellipsometric and electrochemical experiments, Au was e-beam deposited onto Si wafers containing a few monolayers of the molecular "glue", (3-mercaptopropyl)trimethoxysilane (Goss, C. A.; Charych, D. H.; Majda, M. *Anal. Chem.* 1991, 63, 85). Prior to use, the Au surface was etched in a strong oxidant and then electrochemically reduced. SAW devices (98 MHz) on ST-quartz with Al transducers were designed at Sandia National Laboratories and fabricated by Crystal Technologies, Inc. (Palo Alto, CA). Au (2000 Å) was e-beam or thermally evaporated over a Ti or Cr adhesion layer in the active surface region between the transducers. For a complete description of the fabrication of the SAW devices used in these experiments, see ref 4a. The thiol vapor stream was produced by purging a Teflon jar containing 5–10 g of the organic material with N_2 . We estimate that this arrangement results in a 50% thiol-saturated stream; work is underway to quantify this estimate. In some cases the vapor was further diluted with pure N_2 prior to contact with the Au substrate. In all cases the total flow rate was 1.0 L/min. The SAW device and the thiol-containing gas stream were maintained at the same constant temperature ($25 \pm 0.03 \text{ }^\circ\text{C}$) by placing the device test case and a 3 m long stainless steel coil, through which the gas flowed, into an environmental chamber.

(7) The equation that relates the change in frequency (Δf) to mass per area (m) is $\Delta f/f_0 = -\kappa c_m f_0 m$. κ is the fraction of the center-to-center distance between the transducers covered by the Au film. In the present case its value ranges from 0.56 to 0.70. c_m is mass sensitivity ($1.33 \text{ cm}^2/\text{g}$ MHz for ST-quartz), and f_0 is the oscillator frequency (98 MHz).

(8) Vacuum deposition of Au onto quartz primarily results in formation of Au(111) crystallites. A projected coverage of $18.4 \text{ \AA}^2/\text{molecule}$ has been suggested for $CH_3(CH_2)_6SH$ on Au(111). See: Chidsey, C. E. D.; Loiacono, D. N. *Langmuir* 1990, 6, 682.

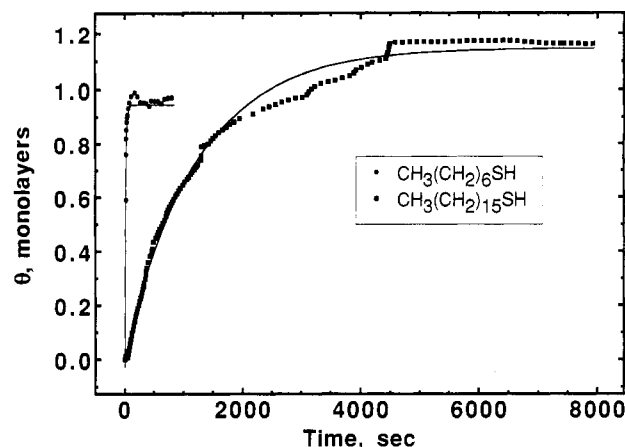


Figure 2. Kinetic analysis of the data shown in Figure 1. The points represent the frequency shift of the SAW device converted to surface coverage,^{7,8} and the line corresponds to a nonlinear least-squares fit of the data to eq 1. Best-fit values of $6.0 \times 10^{-2} \text{ s}^{-1}$ and $8.3 \times 10^{-4} \text{ s}^{-1}$ for the factor $kP_a S_0/N_0$ in eq 1 yield the lines shown for $CH_3(CH_2)_6SH$ (●) and $CH_3(CH_2)_{15}SH$ (■), respectively.

a calculated mass of about 120 ng/cm^2 . The final adsorbed mass is stable for a period of many hours under either a mixed thiol- N_2 or pure N_2 purge.

To confirm the results of SAW experiments and to show that films prepared by either vapor or solution phase deposition are similar, optical ellipsometry⁹ was performed on vapor-deposited films of the thiols. The data for four independently prepared and measured samples resulted in a calculated average thickness of 9 \AA ($\sigma = 3 \text{ \AA}$) for $CH_3(CH_2)_6SH$, in close agreement with measurements obtained from solution-deposited monolayers, 9–11 Å.^{2e,3d} Electrochemical analyses of several independently prepared monolayers formed by vapor-phase deposition of $CH_3(CH_2)_6SH$ were indistinguishable from films obtained by solution deposition onto identically prepared substrates.¹⁰ The results of SAW and electrochemical experiments employing $CH_3(CH_2)_8SH$ as the surface-derivatizing reagent are consistent with those for $CH_3(CH_2)_6SH$.

The bottom of Figure 1 shows the SAW responses for the vapor-phase adsorption of $CH_3(CH_2)_{15}SH$. The frequency change due to $CH_3(CH_2)_{15}SH$ adsorption corresponds to a mass loading of 272 ng/cm^2 ; the calculated loading for an "ideal" monolayer of this thiol is 234 ng/cm^2 .⁸ The difference between the theoretical and calculated value may result from the surface roughness of the Au substrate. The mass of the organic film is not altered significantly by prolonged exposure to either a thiol- N_2 or pure N_2 purge.

The adsorption kinetics of $CH_3(CH_2)_6SH$ and $CH_3(CH_2)_{15}SH$ fit a simple first-order Langmuir rate law, Figure 2, in which the rate of adsorption is proportional to the product of thiol partial pressure, P_a , and $(1 - \theta)$,

(9) Ellipsometric measurements were made by use of a Rudolf 43603-200E manual ellipsometer configured with a He-Ne laser at a 70° angle of incidence and a $45^\circ/135^\circ$ azimuth of the quarter-wave compensator. Film thicknesses were calculated by using a real refractive index of 1.45, the complex refractive index of a naked Au substrate measured prior to derivatization, and an algorithm developed at Sandia National Laboratories (Tardy, H. L. ELLIPSE User's Manual and Program Reference; Report No. 89-0008; Sandia National Laboratories: Albuquerque, NM, 1989).

(10) Electrochemical analysis involved observation of the cyclic voltammogram response of a thiol-modified electrode in an electrolyte containing a dilute concentration of $Ru(NH_3)_6^{3+}$. The shape of the voltammogram reflects the thickness and pinhole density of the organic adlayer. See ref 3d and (a) Amatore, C.; Savéant, J. M.; Tessier, D. J. *Electroanal. Chem. Interfacial Electrochem.* 1983, 147, 39. (b) Finklea, H. O.; Snider, D. A.; Fedyk, J. *Langmuir* 1990, 6, 371.

where θ is the fractional surface coverage

$$d\theta/dt = (kP_a S_0/N_0)(1 - \theta) \quad (1)$$

Here we assume that the total number of adsorption sites, N_0 , and the sticking coefficient, S_0 , are the same for both $\text{CH}_3(\text{CH}_2)_6\text{SH}$ and $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$. The curve fits of Figure 2 reveal that the product kP_a is about 100 times larger for $\text{CH}_3(\text{CH}_2)_6\text{SH}$ than for $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$. However, when the estimated relative partial pressures are taken into account, the rate constant, k , is comparable to the longer chain alkylthiol.¹¹ The fit of the kinetic data to Langmuir kinetics may seem surprising since self-assembly relies upon intermolecular van der Waals interactions; however, it simply reflects the much stronger interactions (45 kcal/mol^{3e}) between the thiols and the Au substrate.

Interestingly, we find that it is possible to form different kinds of $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ films by manipulating the deposition conditions. For example, when the partial pressure of $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ is increased above 50% of saturation, a monotonic increase in the mass loading of the SAW device is observed throughout the duration of its exposure. In one experiment, $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ vapor above 50% of saturation pressure passed over the SAW device for 3.3 h, which resulted in a coverage equivalent to 27 monolayers. However, after 6 h of N_2 purging, all of the thiol except for about two monolayers desorbed. This experiment suggests that high concentrations of $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ vapor result in primarily an amorphous coverage of material that is easily removed but that lower pressure deposition results in a stable, organized film that is insensitive to flowing N_2 or the laboratory ambient.

At an intermediate (25–50% of saturation) partial pressure of $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ vapor, the observed mass change is consistent with a four-level multilayer that is stable upon exposure to a continuous thiol- N_2 purge, a pure N_2 purge, or exposure to the laboratory ambient. The stability of multilayer films, compared to the easily removed films discussed above, suggests some degree of intermolecular organization.

In addition to mass changes, SAW experiments can reveal mechanical transformations in monolayer films; changes in the attenuation of the SAW can be related to changes in the viscoelastic properties of surface-confined adsorbates.⁵ During the formation of the four-layer $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ system, four discontinuities were observed in both the frequency and attenuation responses of the device. Interestingly, the spacing between discontinuities approximates a mass change of one monolayer, suggesting that each sequentially deposited monolayer transforms from an amorphous to ordered state with a concurrent change in viscoelasticity. Because only the long-chain thiols exhibit this behavior, we suspect that

stable multilayers are held together by interactions similar to those found in multilayer Langmuir–Blodgett films.¹²

Ellipsometric data for several $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ films prepared by vapor deposition are consistent with SAW experiments. The measured ellipsometric thicknesses range from 15 to 90 Å, corresponding to about 1–4 monolayers,^{2e} depending upon the deposition conditions. The results of electrochemical experiments¹⁰ are in qualitative agreement with the measured thicknesses obtained by ellipsometry.

Conclusion

We have used SAW devices to monitor real-time self-assembly of *n*-alkylthiol molecules onto Au. Short-chain thiols rapidly form a single monolayer, while long-chain thiols can more slowly form structures ranging from 1 to 4 monolayers in thickness. For $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$, a qualitative relationship exists between the partial pressure of the thiol vapor during deposition and the resulting film thickness; however, other factors, such as subtle differences in surface preparation or temperature, may also bear on this observation. When multilayer films of $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ form on SAW devices, there are discontinuities in the attenuation and frequency data corresponding roughly to one-monolayer mass equivalents. This result suggests that an amorphous precursor self-assembles, with an attendant change in viscoelasticity, prior to formation of the next monolayer. Organized films are found to be stable upon extended exposure to a variety of gas- and solution-phase ambients, while amorphous layers readily desorb when exposed to a flowing stream of N_2 . The results of ellipsometric and electrochemical experiments demonstrate that vapor- and solution-deposited monolayer films are of very similar stability.

We are presently investigating the conditions required for multilayer growth of *n*-alkylthiols from the vapor phase. Additional structure-specific experiments intended to elaborate the degree of organization of vapor-deposited thiol films, including variable take-off angle XPS and external reflection FTIR, are presently underway in our laboratories.

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