Self-Assembled Monolayers Derived from Bidentate Organosulfur Adsorbates

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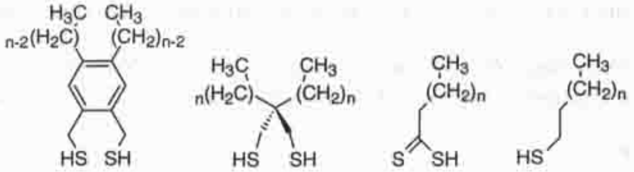
ABSTRACT

The adsorption of a series of 1,2-bis(mercaptomethyl)-4,5-dialkylbenzenes (**1**), spiroalkanedithiols (**2**), and aliphatic dithiocarboxylic acids (**3**) on gold yielded new types of self-assembled monolayers (SAMs). The new SAMs were characterized by optical ellipsometry, contact angle goniometry, and polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS). These results were compared to those obtained from SAMs derived from normal alkanethiols (**4**) of analogous chain length. Comparisons of ellipsometric thickness and contact angle wettability showed that the new SAMs were well packed and highly oriented. Comparisons of the PM-IRRAS data showed that the SAMs generated from **1** and **2** exhibited slightly less crystallinity than their alkanethiolate-based analogs, while the SAMs generated from **3** exhibited comparable crystallinity to their alkanethiolate-based analogs. Moreover, the SAMs derived from **1** and **2** showed no "odd-even" wettability or PM-IRRAS effects, while those derived from **3** showed remarkably large "odd-even" effects compared to those derived from normal alkanethiols.

INTRODUCTION

The spontaneous adsorption of organic compounds onto solid substrates can be used to generate chemically and structurally well-defined self-assembled monolayers (SAMs) that have found wide reaching applications in a variety of fields such as wetting [2], adhesion [3], corrosion resistance [4], and microelectronic materials [5]. Because of their ease of sample preparation, highly ordered structure, and rich end-group chemistry, SAMs derived from alkanethiols on gold are the most extensively studied self-assembled monolayer system [6,7]. Despite these attractive features, these SAMs exhibit at least two shortcomings. First, the long-term stability of alkanethiolate-based SAMs is less than satisfactory; they decompose in solution upon exposure to moderate heat (e.g., 70 °C in hexadecane) [7]. Moreover, displacement of the original molecular adsorbates of SAMs occurs when the films are immersed in a solution comprised of different thiols [7,8]. Second, it is difficult to generate well-defined multicomponent surfaces from a mixture of two or more alkanethiols [9,10]. Coadsorption of different alkanethiols often leads to inhomogeneous mixing and/or domain formation (known as "islanding") [11,12].

A major objective of our research is to synthesize and study new types of SAMs generated by the adsorption of bidentate compounds (e.g., **1**, **2**, and **3** in Figure 1) [13-15]. These bidentate adsorbates are specifically designed to provide enhanced stabilities *via* multiple interactions of sulfur with the surface of gold. Schlenoff and co-workers have suggested that multiple attachments of sulfur to the surface of gold might provide monolayers with enhanced stabilities [8]. In addition, we anticipated that studies of these monolayers should provide an opportunity to explore the structural features of SAMs on gold because it might be possible to influence the structure of the films by altering the nature of the binding between the adsorbate and the underlying surface of gold. Specifically targeted bidentate adsorbates such as spiroalkanedithiols (**2**) and aliphatic dithiocarboxylic acids (**3**), for example, in which the sulfur atoms are spatially restricted in their ability to bind to the three-fold hollow sites of Au(111), might generate SAMs with equilibrium structures that are different than those of SAMs generated from normal alkanethiols.



	1	2	3	4
n = 12		C15	C15	C15
n = 13		C16	C16	C16
n = 14	C17	C17	C17	C17
n = 15	C18	C18	C18	C18
n = 16	C19		C19	C19
n = 17	C20			C20

Figure 1. Structures of the 1,2-bis(mercaptomethyl)-4,5-dialkylbenzenes (**1**), spiroalkanedithiols (**2**), aliphatic dithiocarboxylic acids (**3**), and the corresponding normal alkanethiols (**4**) used for generating SAMs on gold. For all adsorbates shown here, the number of carbon atoms per chain is considered to be the same for a given value of n.

EXPERIMENT

Materials

Gold shot (99.99%) was purchased from Americana Precious Metals. Polished single-crystal silicon (100) wafers were purchased from Silicon Sense, Inc. Chromium rods (99.9%) were purchased from R. D. Mathis Company. The water (H_2O) and hexadecane (HD) used for the contact angle measurements were of the highest purity available from Aldrich Chemical Co. The normal alkanethiols used to prepare the SAMs were either commercially available or synthesized using established methods. The details of the synthesis and characterization of the 1,2-bis(mercaptomethyl)-4,5-dialkylbenzenes [13], the spiroalkanedithiols [14], and the aliphatic dithiocarboxylic acids [15] have been described elsewhere.

Preparation of SAMs

The methods used to evaporate thin films of gold onto the surfaces of silicon wafers have been described previously [13-15]. Solutions of thiols (ca. 1 mM) were prepared in weighing bottles that were pre-cleaned by soaking for 1 h in "piranha" solution (ca. 7/3 H_2SO_4/H_2O_2) (*caution: "piranha" solution reacts violently with organic materials and should be handled carefully*). The bottles were thoroughly rinsed with deionized water and absolute ethanol and dried before use. The gold-coated wafers were cut into slides (ca. 1 cm x 3 cm) using a diamond-tip stylus. The slides were washed with absolute ethanol and dried under a flow of ultrapure nitrogen. The slides were immersed in solutions of the respective thiols (**1** and **2** in isooctane; **3** and **4** in ethanol). The monolayers were allowed to equilibrate in solution for 24 h (**1**, **3**, and **4**) or 48 h (**2**). Before characterization, the resultant SAMs were thoroughly rinsed with both toluene and ethanol (**1** and **2**) or ethanol only (**3** and **4**) and blown dry with ultrapure nitrogen.

Ellipsometric Thickness Measurements

The thicknesses of the SAMs were measured with a Rudolf Research Auto EL III ellipsometer, which was equipped with a He-Ne laser operating at a wavelength of 632.8 nm and an angle of incidence of 70°. Immediately after evaporation, the optical constants for the bare gold were measured. To calculate the thicknesses of the SAMs, a refractive index of 1.45 was assumed for all films. The data were collected and averaged over three separate slides using three spots per slide for each type of SAM.

Contact Angle Measurements

Advancing and receding contact angles of H_2O and HD were measured at 293 K and ambient relative humidity using a ramé-hart model 100 contact angle goniometer. The contacting liquids were dispensed and withdrawn at the slowest possible speed (*ca.* 1 μL/s) using a Matrix Technologies micro-Electrapette 25. The measurements were performed while keeping the pipette tip in contact with the drop. The data were collected and averaged over three separate slides using three spots per slide for each type of SAM.

Infrared Spectroscopy

Polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) data were obtained using a Nicolet MAGNA-IR 860 Fourier transform spectrometer equipped with a liquid nitrogen-cooled mercury-cadmium-telluride (MCT) detector and a Hinds Instruments PEM-90 photoelastic modulator operating at 37 kHz. The polarized light was reflected from the sample at an angle of incidence of 80°.

RESULTS

As illustrated in Figure 1, we compared the SAMs generated from the bidentate adsorbates to those generated from normal alkanethiols by assuming that the SAMs derived from $[CH_3(CH_2)_{n-2}]_2C_6H_2[CH_2SH]_2$ (**1**), $[CH_3(CH_2)_n]_2C[CH_2SH]_2$ (**2**), and $CH_3(CH_2)_{n+1}CS_2H$ (**3**) should most readily correspond to those derived from $CH_3(CH_2)_{n+2}SH$ (**4**).

Ellipsometric thickness measurements can provide a rough measure of film quality [16]. We compared the thicknesses of the films generated from the bidentate compounds to those generated from normal alkanethiols (Table 1). The thicknesses of the films derived from the bidentate adsorbates are within ± 2 Å of the films derived from the corresponding normal alkanethiols, which is easily within the estimated experimental uncertainty of the ellipsometric measurement (± 2 Å). For all films, the thicknesses increase roughly linearly with the number of carbon atoms. These results are consistent with a model in which the long-chain bidentate compounds generate monolayer films with the alkyl chains densely packed and oriented away from the surface.

Table 1. Ellipsometric Thicknesses (Å) of SAMs on Au(111) Derived from Various Substrates.[a]

compound	C15	C16	C17	C18	C19	C20
1			20	21	23	26
2	17	18	19	20		
3	18	20	22	23	24	
4	18	20	21	22	23	25

[a] Average values of at least nine independent measurements are reported. Measured values were reproducible within ± 2 Å of the reported values.

Measurements of contact angles are recognized as useful tools for determining the structure and the quality of organic thin films [16]. The advancing contact angles of water ($\theta_a^{H_2O}$) were 114 ± 2° for the SAMs generated from both the bidentate adsorbates and the normal alkanethiols. These indistinguishable contact angles suggest that the monolayer surfaces are all similarly hydrophobic. We also measured the contact angles of hexadecane, since hexadecane exhibits remarkable sensitivity to the orientation and composition of low-energy hydrocarbon surfaces [17]. The data in Table 2 show that the SAMs generated from the 1,2-bis(mercaptomethyl)-4,5-dialkylbenzenes (**1**) and the spiroalkanedithiols (**2**) are invariant with chain length. In contrast, the wettabilities of the SAMs generated from the aliphatic dithiocarboxylic acids (**3**) and the normal alkanethiols (**4**) exhibit a parity (or "odd-even") effect as a function of chain length. The magnitude of the "odd-even" effect is, however, dramatically greater for the SAMs generated from **3**.

Table 2. Advancing Contact Angles (°) of Hexadecane of SAMs on Au(111) Derived from **1-4**.[a]

compound	C15	C16	C17	C18	C19	C20
1			48	49	50	49
2	47	48	49	49		
3	40	50	40	50	41	
4	47	50	47	50	48	51

[a] Average values of at least nine independent measurements are reported. Measured values were reproducible within ± 2° of the reported values.

The "odd-even" effect has been interpreted to reflect the increased exposure of more wettable methylene vs methyl groups at the interface [17]. A number of factors such as a disorder of the chain termini, unusual tilt angles, or conformational or electrical effects arising from the presence of the connecting groups in the dithiol compounds could contribute to the absence of "odd-even" effects for the SAMs generated from the 1,2-bis(mercaptomethyl)-4,5-dialkylbenzenes (**1**) and the spiroalkanedithiols (**2**). The enhanced "odd-even" effect observed from the SAMs generated from the aliphatic dithiocarboxylic acids (**3**) relative to that of the SAMs generated from the normal alkanethiols (**4**) might arise from a torsional stiffening of the alkyl chains due to chelation of the dithiocarboxylate head group to the surface of gold.

Surface infrared spectroscopy can be used to characterize the structures and conformations of organic thin films [18]. The frequency of the methylene asymmetric C-H stretch ($\upsilon_a^{CH_2}$) is particularly sensitive to the degree of order (or crystallinity) of the films [19]. SAMs generated from the 1,2-bis(mercaptomethyl)-4,5-dialkylbenzenes (**1**, Figure 2a) and the spiroalkanedithiols (**2**, Figure 2b) exhibit a $\upsilon_a^{CH_2}$ band at 2922 cm^{-1} and 2920 cm^{-1}, respectively. These values suggest that the alkyl chains of these SAMs are less crystalline than those of SAMs generated from normal alkanethiols (**4**), which exhibit a $\upsilon_a^{CH_2}$ band at 2919 cm^{-1} (Figure 2c). In contrast to the SAMS derived from **1** and **2**, the SAMs derived from the aliphatic dithiocarboxylic acids (**3**) exhibit a $\upsilon_a^{CH_2}$ band at 2919 cm^{-1} (Figure 2d), which is indistinguishable from that of the SAMs derived from **4**. We thus conclude that the SAMs derived from **3** have crystallinities that are similar to those of SAMs derived from normal alkanethiols.

CONCLUSIONS

Three unique classes of bidentate adsorbates were synthesized and used to generate new types of SAMs on gold. The new SAMs were characterized by optical ellipsometry, contact angle goniometry, and PM-IRRAS. The results support a model in which the SAMs derived from the bidentate adsorbates yield well-ordered, densely packed, and highly oriented films having qualities comparable to those derived from normal alkanethiols. The SAMs generated from the 1,2-bis(mercaptomethyl)-4,5-dialkylbenzenes and the spiroalkanedithiols exhibited slightly less crystallinity than their alkanethiolate-based analogs. In contrast, the SAMs derived from the aliphatic dithiocarboxylic acids were indistinguishably crystalline when compared to normal alkanethiolate-based SAMs. The "odd-even" effects varied greatly with the nature of the adsorbate: SAMs derived from the 1,2-bis(mercaptomethyl)-4,5-dialkylbenzenes and the spiroalkanedithiols showed no substantial "odd-even" effects, while the SAMs derived from the aliphatic dithiocarboxylic acids showed "odd-even" effects that were markedly greater than those found on SAMs derived from normal alkanethiols.

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