Scanning Electron Microscopy Can Form Images of Patterns in Self-Assembled Monolayers[1]

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Scanning electron microscopy is able to form images of patterns of self-assembled monolayers (SAMs) of alkanethiolates adsorbed on gold. The contrast in these images is unexpectedly sensitive to the structures of the components of the SAMs. Several factors contribute to the contrast: the compositions of the SAMs; the compositions and quantities of adsorbates (both adventitious and intentional) on the SAMs; electron-beam-induced processes involving the SAMs and these adsorbates.

Introduction

Scanning electron microscopy (SEM) is capable of generating images of two-dimensional patterns of self-assembled monolayers (SAMs), obtained by the adsorption of two or more alkanethiols ($HS(CH_2)_nR$) onto the surface of gold films.[3] These images are remarkable for the large differences in brightness that accompany small differences in the molecular structure of the constituents of the SAMs. Several factors contribute to the contrast: the structures of the alkanethiolates in the SAMs; the compositions and quantities of adsorbates (both adventitious and intentional) on the SAMs; electron-beam-induced processes involving the SAMs and these adsorbates. The high sensitivity of electron microscopy to details of the structure of SAMs will be useful both in characterizing these increasingly important interfacial systems and in understanding the mechanisms of image formation in electron microscopic investigations of organic and biological samples.

Both molecular and macroscopic structure of SAMs can be controlled with great flexibility,[4] and SAMs can be used to generate test patterns to explore the origins of contrast. We surveyed three characteristics of the SAMs: (1) the character of the ω-functional group, R; (2) the length, n, of the alkyl chain and the thickness of the SAM; (3) the free energy of the surface of the SAM (and thus its potential to adsorb contaminants). All three characteristics influenced the brightness of the image obtained in SEM. Damage of the SAM by the electron beam, and the adsorption of volatile materials onto the SAMs during SEM, were also important in determining brightness.

Brightness and contrast are related to the yield of secondary electrons emitted from surfaces of insulating overlayers when they are exposed to a beam of electrons in the electron microscope.[5-7] In SAMs of alkanethiolates on gold, we expect most of the secondary electrons emitted by the sample (and contributing to image formation) to originate in the gold. Images due to the SAMs may arise by scattering of these electrons by components of the SAM[8,9] or by modulation of the surface potential by the SAM.[6,8] The escape depth of secondary electrons can be related to material properties such as density and to elemental properties such as atomic number (Z) and first ionization energy.[9]

Results and Discussion

We used samples comprising three SAMs: a central line[10] of $HS(CH_2)_{15}CH_3$ (used as an internal standard for brightness and abbreviated as $C_{15}CH_3$) flanked by two SAMs that differed in composition. Figure 1 illustrates the influence of the composition and structure of the SAM on the brightness of the image. We first examined the hypothesis that the brightness of an image would be related to the electron density of functional groups in the SAM. We found that, in general, increasing the average Z of heteroatoms in the functional groups within the SAM (e.g., from $C_{11}CH_3$ to $C_2(CF_2)_9CF_3$, from $C_{15}CH_2OH$ to $C_{15}COOH$, and from $C_{11}NHCOCH_3$ to $C_{11}NHCOCF_3$) resulted in a decrease in the brightness. We believe that increasing the concentration of high Z heteroatoms results in an increase in the electron density in the SAM and, as a result, in the increased scattering of secondary electrons. Differential attenuation of secondary electrons leaving the surface by scattering events, or by the occurrence of other phenomena related to properties (e.g., ionization potential or electron capture potential) influencing the interaction of secondary electrons with constituents of the SAM may result in the generation of contrast between adjacent alkanethiolate regions.

We examined the influence of the thickness of homologous SAMs on the brightness of the SEM image by comparing C_7CH_3, $C_{15}CH_3$, and $C_{21}CH_3$. Scattering of secondary electrons generated in the underlying gold would be expected to increase (and image brightness decrease) with increasing thickness of the monolayer.[8] In fact, the opposite result is observed: $C_{21}CH_3$ provides the brightest image (see Figure 1). Other phenomena associated with increasing the length of alkyl chains may account for the unexpected trend in image brightness. The packing of alkane chains in SAMs of alkanethiolates on gold is known

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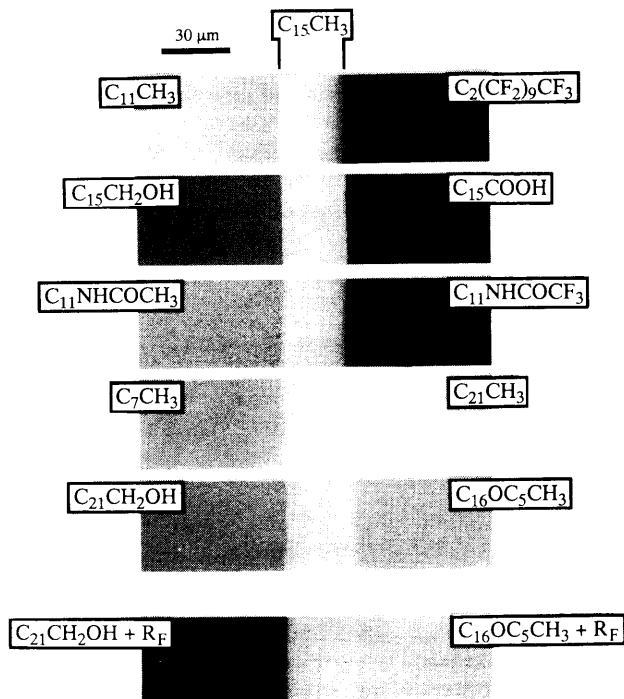
Figure 1. SEM micrographs of patterned SAMs on gold. The central region in each micrograph is $C_{15}CH_3$ and is used as an internal standard to facilitate comparison of intensities. This region is ca. 30 μm wide. Alkanethiols of the general formula $HS(CH_2)_nR$ were used to form the adjacent monolayers. The first subscript in the abbreviations used in the figure refers to n, the number of methylene groups in the alkanethiol used to form the monolayer (e.g., $C_{15}R$ refers to a monolayer formed from $HS(CH_2)_{15}R$). The bottom panel shows a patterned SAM ($C_{21}CH_2OH$, $C_{15}CH_3$, and $C_{16}OC_5CH_3$) that had previously been dipped in an oil of perfluorinated polyether (Fomblin, indicated by R_F) and then rinsed with ethanol, heptane, and distilled water.

to be increasingly ordered as the chain length increases.[11,12] The increase in order for longer chains correlates with a decrease in the interfacial free energy of the surface of the SAM.[13] Hence, the surface of C_7CH_3, which has the highest free energy of the three,[13] might be dark because of the presence of contaminants adsorbed preferentially on it.

To test the hypothesis that contaminants adsorbed on regions of different interfacial free energy influenced image brightness, we compared SAMs of two alkanethiolates of identical elemental composition but different interfacial energy. Initially, $C_{21}CH_2OH$ is darker than $C_{16}OC_5CH_3$ (the former has the higher solid–vapor interfacial free energy). This difference in brightness disappeared after approximately 1 min of exposure to the primary electron beam in the SEM. After the sample was removed from the microscope and exposed to laboratory air for a few minutes, $C_{21}CH_2OH$ again became darker than $C_{16}OC_5$-CH_3. These observations suggest that electron-impact-induced desorption of adventitious adsorbates from the higher-energy CH_2OH surface occurs and increases its brightness. They thus support the hypothesis of a significant role for adsorbates in determining brightness.

The ability of nonvolatile species to adsorb preferentially on alkanethiolates of higher interfacial energy and to influence contrast can be put to use to increase contrast. Comparison of the last two images in Figure 1 provides an example. A patterned SAM of $C_{21}CH_2OH$, $C_{15}CH_3$, and
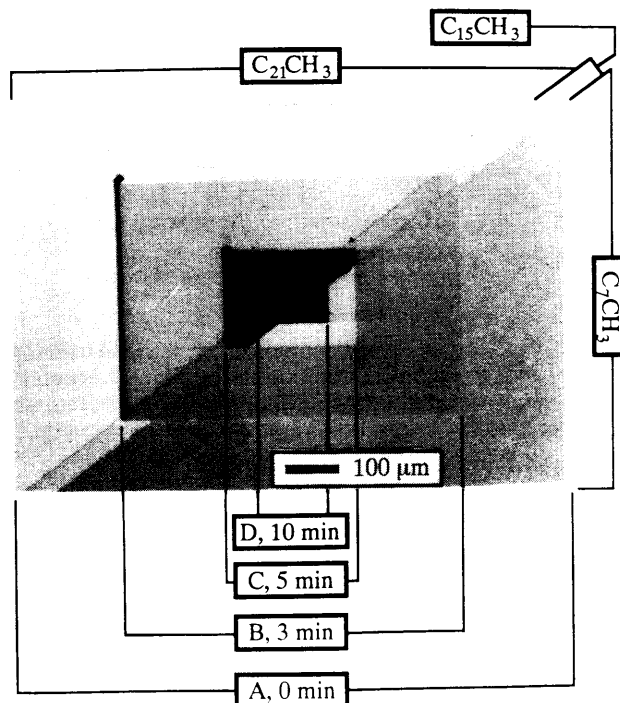
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Figure 2. An SEM micrograph of a patterned SAM on gold consisting of two regions ($C_{21}CH_3$ and C_7CH_3) separated by a strip of $C_{15}CH_3$. This pattern was divided into four regions (A, B, C, D) and each was exposed to the 35-kV (4 nA) primary electron beam for a different time before the electron micrograph was taken. The estimated, integrated flux of primary electrons to each of the regions before the micrograph was taken was as follows: A, 0 C/m^2; B, 3/m^2; C, 31 C/m^2; D, 243 C/m^2.

$C_{16}OC_5CH_3$ was immersed in a perfluorinated oil (Fomblin, Montefluos, Milano, Italy) before imaging. We anticipated that this fluorocarbon would adsorb more strongly to the surface with the higher free energy ($C_{21}CH_2OH$). Figure 1 shows that the $C_{21}CH_2OH$ became substantially darker on exposure to the Fomblin oil; the brightness of the C_{15}-CH_3 and $C_{16}OC_5CH_3$ remained approximately constant. This result is that expected if the interfacial free energy determines the extent of adsorption of Fomblin. (At lower magnification, variations in the brightness of the region of $C_{21}CH_2OH$ indicated that the coverage of the oil was nonuniform.)

Figure 2 illustrates the complex changes in brightness that can occur during the imaging of patterned SAMs. In the region that had not been exposed to the electron beam before the micrograph was taken (A, the outer region), $C_{21}CH_3$ and $C_{15}CH_3$ appear brighter than C_7CH_3. In region B, which was exposed to the electron beam for 3 min, all three areas ($C_{21}CH_3$, $C_{15}CH_3$, and C_7CH_3) darken relative to their respective brightnesses in region A. In region C, which was exposed to the electron beam for 5 min, the relative brightness of the three areas of alkanethiolate has changed: C_7CH_3 appears brighter than $C_{15}CH_3$ and C_{21}-CH_3. Finally, in region D, which was exposed to the beam for 10 min, all three areas of alkanethiolate appear dark, with little contrast between them. After the sample was removed from the vacuum chamber and exposed to the ambient in the laboratory for a few minutes, a decrease in the brightness of the C_7CH_3 in region C to a level similar to that in region A was observed.

The darkening of surfaces in SEM under prolonged exposure to an electron beam is well-known and has been attributed to the formation of a layer of carbonaceous material under the influence of electron bombardment.[8,14] We confirmed the formation of a layer of nonvolatile, carbonaceous material (of greater thickness than that of

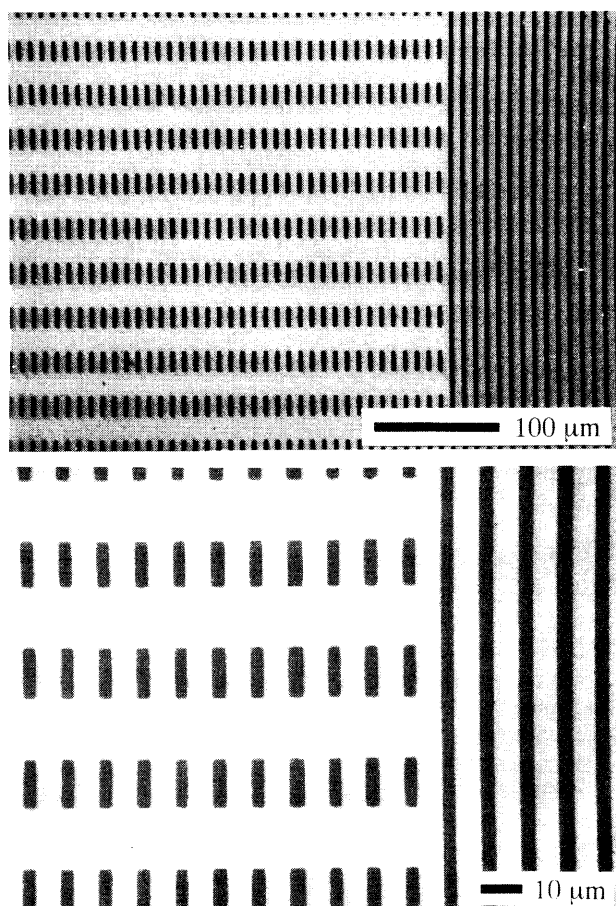**Figure 3.** SEM micrographs (low and high resolution) of a patterned SAM on gold consisting of two types of monolayers formed from $(CH_2)_{15}CH_3$ (lighter areas) and $HS(CH_2)_2(CF_2)_9$-CF_3 (darker areas).

imaging of gold surfaces that has been covered with SAMs in a complex pattern. A patterned SAM was formed from $HS(CH_2)_{15}CH_3$ using an elastomeric stamp, as described elsewhere.[17] The remaining, unreacted gold surface was derivatized with $HS(CH_2)_2(CF_2)_9CF_3$ to complete the patterned SAM shown in Figure 3. No pattern on the surface or topological alteration of the gold surface was apparent by optical microscopy.

Conclusions

This work demonstrates that SEM is useful in imaging SAMs that are patterned in composition. A number of processes—scattering of secondary electrons by high-Z components of the SAM, adsorption of adventitious impurities on the surface of the SAM, desorption of these impurities by the electron beam, damage to the SAM by the primary or secondary electrons—appear to contribute to the formation of the image, and interpretation of the image in terms of a single, simple model of the SAM and its interaction with the electron beam is not presently possible. The complexity of the processes contributing to the image does not substantially decrease the utility of this method of characterizing SAMs; this complexity may, with further definition, provide new procedures for doing so. The ability to control the structure and composition of SAMs makes these systems ideal for studying the mechanisms of image formation.

Experimental Section

Materials. Isooctane (2,2,4-trimethylpentane, Aldrich, 99+%) was percolated twice through activated, neutral alumina (EM Science). Absolute ethanol (Quantum Chemical Corp.) and isooctane were deoxygenated with dry N_2 prior to use. Perfluorinated polyether (Fomblin, Montefluos, Milan) was used as received. All thiols were available from previous studies.

Substrate Preparation. Gold films ($\sim$2000 Å thick) were prepared by electron-beam evaporation of gold (Materials Research Corp., Orangeburg, NY; 99.999%) onto single-crystal silicon (100) test wafers (Silicon Sense, Nashua, NH; 100 mm diameter, $\sim$500 μm thick) that had been precoated a film of titanium (Johnson Mathey, 99.99%; $\sim$50 Å thick) that acted as an adhesion promotor between the silicon oxide and the gold.

Monolayer Formation. The silicon wafers coated with gold were fractured into rectangular slides ($\sim$2 cm $\times$ 5 cm). A slide was placed flat on a stage movable by rotation of micrometers. A pen tip (Staedler, 757 030) was filled with $HS(CH_2)_{15}CH_3$ and suspended above one of the thin ends of the gold slide. The slide was raised and a meniscus was allowed to form between the pen tip and the surface of the gold.[10] Translation of the slide relative to the pen using the micrometer controls then resulted in the formation of a line of a SAM ($\sim$30 μm in width) down the long axis of the gold surface of the rectangular slide. The thickness of the line was controlled by maintaining a meniscus (viewed through a microscope) of approximately constant volume as the line was formed. After formation of this line of SAM from HS-$(CH_2)_{15}CH_3$, the slide was rinsed flat with heptane and then with ethanol. The slide was then dryed under dry N_2.

The slide was cut into several pieces ($\sim$0.5 cm $\times$ 2 cm) perpendicular to the line of $C_{15}CH_3$; these pieces were used to form the patterned SAMs shown in Figures 1 and 2. To form the SAMs on either side of the $C_{15}CH_3$, regions adjacent to the line were formed by the adsorption of alkanethiols from 1 mM ethanolic solution: $HS(CH_2)_{11}CH_3$, $HS(CH_2)_{15}CH_2COH$, HS-$(CH_2)_{15}COOH$, $HS(CH_2)_{11}NHCOCH_3$, $HS(CH_2)_{11}NHCOCF_3$, $HS(CH_2)_7CH_3$, $HS(CH_2)_{21}CH_3$, $HS(CH_2)_{21}CH_2OH$, and HS-$(CH_2)_{16}O(CH_2)_5CH_3$. $HS(CH_2)_2(CH_2)_9CF_3$ was adsorbed from a concentration of 10 mM in isooctane. Each solution was added dropwise from a Pasteur pipet on one side of the line of $C_{15}CH_3$. Because of the lyophobicity of the $C_{15}CH_3$, the solutions of

the SAM) under prolonged exposure to the primary electron beam by conducting both energy dispersive spectroscopy of X-rays generated during the electron microscopy and X-ray photoelectron spectroscopy (XPS) of samples after electron beam exposure. Figure 2 demonstrates that, in addition to such darkening of surfaces, an increase in the brightness of the image can occur during exposure to the electron beam. Figure 2 also shows that, for SAMs, the evolution of brightness with increasing exposure to the electron beam depends on the nature of the SAM. The competing processes of contamination,[8,14] electron-stimulated desorption[8] of adventitious adsorbates present on the SAM, and reaction of or damage to components of the SAM due to electrons[15,16] may all affect the contrast between patterned regions in SEM. We have, at present, no general method for distinguishing the relative contributions of these processes. The understanding of these processes will be important both in the interpretation of images and in assessing the ultimate limit of spatial resolution of SEM in the imaging of organics patterned on surfaces. For patterned SAMs that are compatible with high-resolution imaging (i.e., SAMs that damage slowly and have high initial contrast), our experiments suggest that imaging of submicrometer features will be possible.

Figure 3 gives an example of the use of SEM in the

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alkanethiols did not cross the line of $C_{15}CH_3$. For each type of SAM, except those which formed lyophobic surfaces, the solution was allowed to react with the gold surface for at least 5 min before rinsing the slide with heptane and ethanol as described above. This procedure resulted in the patterned SAMs shown in Figures 1 and 2. XPS suggested that SAMs formed in this manner have similar compositions to those formed as described previously.[4]

The patterned SAM shown in Figure 3 was prepared by first patterning the adsorption of $HS(CH_2)_{15}CH_3$ onto gold using a rubber stamp made out of poly(dimethylsiloxane) as described elsewhere.[17] The remaining gold surface was derivatized with $HS(CH_2)_2(CF_2)_9CF_3$ by placing the slide in a solution of the thiol (1 mM in isooctane) for 1 min. The sample was then rinsed as described above and imaged.

Instrumentation. Images were acquired in the secondary electron detection made of a JEOL JSM-6400 scanning microscope (chamber pressure $\sim 5 \times 10^{-6}$ Torr) using a 35-kV primary electron beam with a current was 2–4 nA. The electron detector was operated with a collection voltage of +300 V. For acquisition of the micrograph, the electron beam was slowly scanned over the image area for a total exposure time of 80 s. XPS was carried out using an SSX-100 spectrometer (Surface Science Instruments) using monochromatic Al Kα X-rays.

Note Added in Proof: The decrease in the brightness of images of SAMs as the chain length of alkanethiolates in the SAM decreases (e.g., from $C_{21}CH_3$ to C_7CH_3) may be influenced by the presence of low levels of oxidized sulfur species (e.g., RSO_3^-) in the thinner monolayers. We have recently measured, by secondary ion mass spectrometry, the presence of such species in areas of $C_{15}CH_3$ that appeared dark in SEM (López, G. P.; Biebuyck, H. A.; Frisbie, C. D.; Whitesides, G. M. Unpublished data) and others have also observed these species (Li, Y.; Huang, J.; McIver, R. T.; Hemminger, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 2428–2432. Tarlov, M. J.; Newman, J. G. *Langmuir* **1992**, *8*, 1398–1405). These species probably form by the reaction of alkanethiolates with oxygen in air. The rate of reaction of thiolates in SAMs on copper or silver exposed to air increases as the length of alkyl chains forming the SAM decrease. (Laibinis, P. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1992**, *114*, 9022–9028.)