

Scanning Tunneling Microscope-Based Replacement Lithography on Self-Assembled Monolayers. Investigation of the Relationship between Monolayer Structure and Replacement Bias[†]

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Organothiolate self-assembled monolayers (SAMs) can be patterned using a scanning tunneling microscopy (STM) tip. Upon elevating the bias, the SAM is locally desorbed. By conducting this process in the presence of a second thiol component in a nonpolar solution (dodecane) above it, a different SAM component is locally introduced. Here, the influence of the chain length and headgroup of the initial SAM on this process is elucidated. SAMs composed of longer molecules require higher biases to effect this process, similar to the electrochemical desorption behavior of these molecules. When initial SAMs composed of headgroups other than methyl were studied, poor results were obtained: features were broad and replacement occurred more inconsistently. Several possible explanations for this behavior are discussed.

Introduction

As the study of nanometer-scale phenomena progresses, there is increasing interest in methods that offer the ability to pattern features at this length scale. Patterns of this type ideally must be chemically well-defined because the number, type, and orientation of chemical functional groups is a dominant attribute of the pattern. To this end, several methodologies have been developed for patterning self-assembled monolayers (SAMs) at the nanometer scale.¹ These methodologies are dominated by the use of scanning probes as they offer several mechanisms to pattern and to probe at the nanometer scale.

Among these approaches, we have recently reported a technique termed “replacement lithography” in which a SAM is locally disrupted, allowing a different component to replace it.² This technique, illustrated in Figure 1, uses scanning tunneling microscopy on an organothiolate self-assembled monolayer on an Au(111) facet and is capable of ca. 10 nm resolution.² We have recently employed it in the study of negative differential resistance behaviors in electroactive SAMs,³ the creation of surface-bound chemical gradients,⁴ and in the study of noncovalent binding into nanometer-scale patterns.⁵ In these investigations, the effects of several parameters, including scan rate and bias, on the efficiency of replacement have been illustrated.⁴

In this work, we seek to determine how the type of initial SAM on the surface influences the replacement lithography process. The overall scheme for this process is thought to involve localized desorption initially, followed by replacement by a second component in solution.² Given this scheme, the degree of replacement at a given bias likely correlates with the relative ease of the desorption step. Here we show that this is indeed the case: the bias of replacement correlates with the electrochemical, reductive desorption potential of the SAM.

Results and Discussion

Variation of the Chain Length of an Initial *n*-Alkanethiolate SAM. As the chain length of an *n*-alkane thiolate SAM

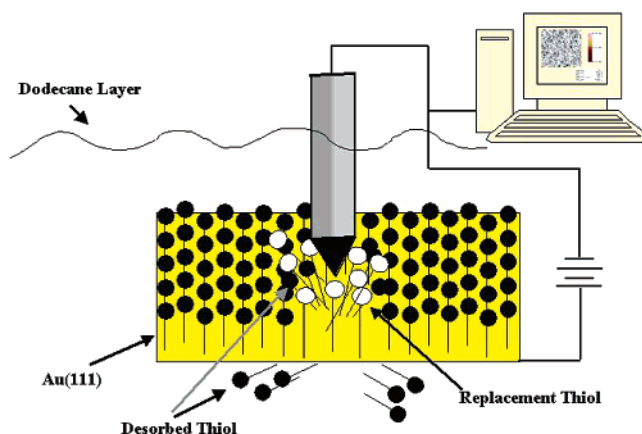


Figure 1. Schematic illustrating the process of replacement lithography.

increases, a higher bias is required to electrochemically desorb it from gold.^{6–18} Although it is not clear that replacement lithography operates via an electrochemical desorption mechanism, it seemed likely that this process would follow the same trend. To probe this, a series of *n*-alkanethiolate SAMs of various chain lengths were subjected to replacement lithography. Undecyl ferrocenyl-thioacetate (FcC₁₁Sac) was used as the replacing component, as it has been shown^{3–5} to have a large contrast by STM compared to an *n*-alkanethiolate SAM background. Upon a given SAM, the tip scanned a series of lines at incrementally higher applied biases. This process was repeated several times on different samples. Typical results are shown in Figure 2.

In Figure 2, the replaced regions appear brighter than the background C_{*n*}S–SAM regions (where *n* is the chain length of the thiol used initially to compose the SAM). This contrast has been observed and explained previously³ and, briefly, is due to the higher conductance of FcC₁₁S–SAM regions at the bias at which the pattern was visualized (1.25–1.5 V, tip negative). The relative difference in contrast between the panels in Figure 2 is negligible. The cause of this result is not entirely clear, but it is presumed that the conductance difference between regions within a given pattern is much larger than that between different

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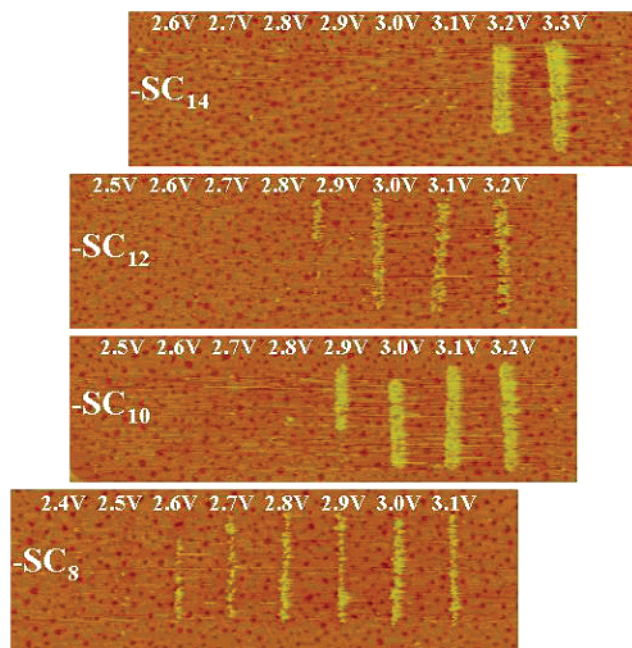


Figure 2. Series of STM images in which replacement lithography was attempted at incrementally higher biases. The designation $-\text{SC}_n$ denotes the chain length of the initial SAM. A series of lines of 100 nm length were written with the biases indicated above each. Imaging Conditions: z -scale = 3 nm; relative humidity = $55\% \pm 2\%$; imaging bias = 1.5 V; setpoint current = 10 pA; scan rate = 1.0 Hz; under dodecane.

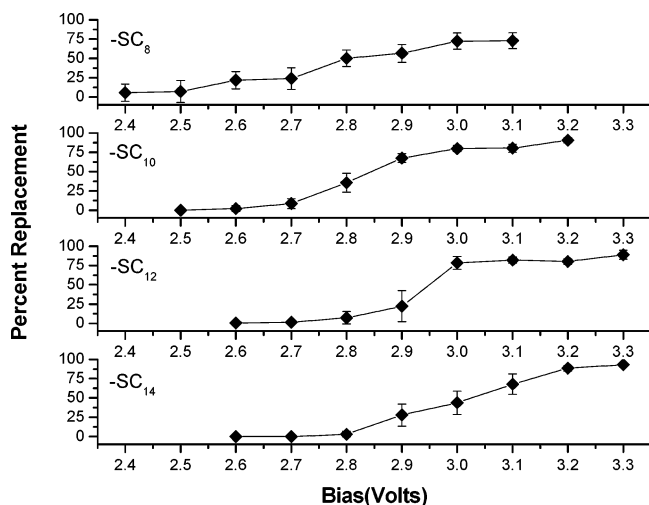


Figure 3. Graph indicating the percentage of replacement for different C_nS -SAMs (n is the number of carbons in the initial SAM). Lines are drawn through the points solely as a guide to the eye.

panels (e.g., different initial SAMs). The typical line width produced was similar for the different SAMs used (ca. 12 nm). However, the applied bias required to effect replacement increased with the chain length of the initial SAM. Thus, whereas some replacement was observed at a bias of 2.6 V upon a C_8S -SAM, the process did not commence until a bias of 3.0 V was used upon a C_{14}S -SAM (Figure 3). This behavior was consistent with desorption of the initial SAM as the rate-determining step for this process and the difficulty of desorption scaling with the chain length of the SAM.

The change in bias required for desorption (50–70 mV per methylene unit depending on whether one considers the onset or completion of the process) is larger than that observed for electrochemical desorption of a series of methyl-terminated SAMs (ca. 15 mV per methylene unit).^{10,17} This result is,

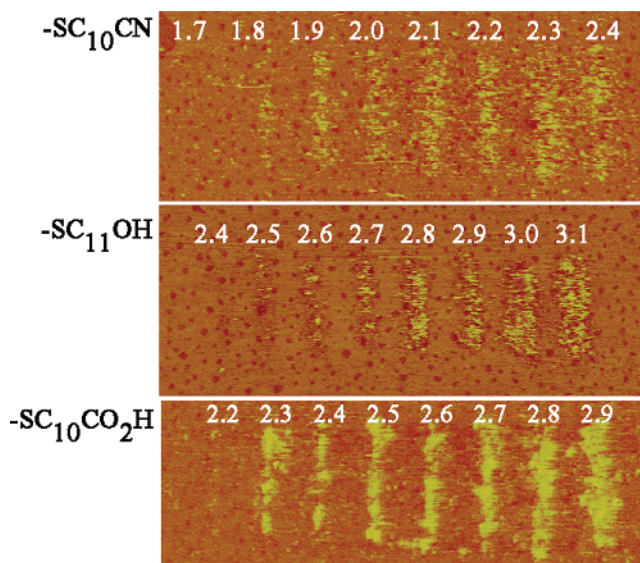


Figure 4. Series of STM images in which replacement lithography was attempted at incrementally higher biases on the SAMs indicated to the left of each image. The numbers above each line represent the applied bias used to effect replacement in that line region. Imaging conditions: z -scale = 3 nm; relative humidity = $55\% \pm 2\%$; imaging bias = 1.25 V for $-\text{SC}_{10}\text{CN}$ and $-\text{SC}_{10}\text{CO}_2\text{H}$ and 1.5 V for $-\text{SC}_{11}\text{OH}$; setpoint current = 10 pA; scan rate = 1.0 Hz; under dodecane.

however, not unexpected, particularly if the STM tip-induced desorption is electrochemical in nature. Desorption here is occurring in a much less polar environment (dodecane with some available water due to the controlled humidity) than found in the electrolyte solution in the electrochemical experiment. Indeed, Schneider and Buttry have shown that, even in electrochemical cells the difficulty of electrochemical desorption increases as the polarity of the solvent decreases.⁹

At intermediate biases, the process of replacement lithography is not an “all or nothing” process. Thus, the percentage of replacement versus applied bias was determined as described in the Experimental Section and graphed. These data are shown in Figure 3. The error bars indicate the 90% confidence intervals of the mean value. From both Figures 2 and 3, one can distinguish a steady increase in the applied bias required to initiate and to complete replacement. Interestingly, in the case of C_8S -SAM, although the minimum bias required for the onset of replacement was observed, full replacement (e.g., 100% on the graph) was not observed. There is a known decrease in the efficiency of packing of n -alkanethiolate SAMs of less than approximately 10 carbons.¹⁹ This lower efficiency could contribute to the incompleteness of replacement, although how this occurs is not clear at present. Similar behaviors are seen on other SAMs with nonmethyl headgroups (see below).

Variation in the Headgroup of the Initial SAM. The type of headgroup at the terminus of the SAM was also hypothesized to influence the desorption and subsequent replacement behavior. SAMs with carboxylic acid headgroups are, for example, known to desorb electrochemically at a lower bias than the analogous SAMs with methyl headgroups.^{10,12,13} The degree of order in the SAM and electrostatic repulsion between polar and/or charged headgroups are likely influencing factors in this process. To determine the bias dependence of replacement lithography on SAMs composed of differing headgroups, this process was studied on SAMs composed from mercapto-undecanol (HOC_{11}S -SAM), mercapto-undecanoic acid ($\text{HO}_2\text{CC}_{10}\text{S}$ -SAM) and cyanodecanethiol (NCC_{10}S -SAM). The results are shown in Figure 4. The process of replacement began

at a lower bias than that observed for the *n*-alkanethiolate SAM of similar chain length. However, the replaced lines are clearly much more diffuse. This result indicates that the extent of replacement was not as complete, and the line widths observed were wider. Moreover, higher concentrations of thiol in the dodecane solution were required for replacement (a ca. 70-fold greater concentration of Fc-C₁₁SAC was employed in these experiments compared to those on *n*-alkanethiolate SAMs). In addition, it was much more difficult to reproduce these data. The images shown in Figure 4 represent among the best of at least 60 trials. In contrast, replacement lithography on *n*-alkanethiolate SAMs was reproducible in the vast majority of trials.

We rationalize the results shown in Figure 4 based on three structural features of these SAMs. First, the degree of order in these SAMs is lower than that of *n*-alkanethiolate SAMs.¹⁹ Lower order would plausibly make it easier to initiate desorption but would also be less efficient at maintaining a "corral" to limit the spatial extent of replacement. The C₈S-SAM, however, also should have a somewhat lower order than the SAMs composed of longer *n*-alkanethiols. Although, replacement upon this SAM was incomplete, it did not appear diffuse. Second, it is possible that, upon desorption, thiols with polar headgroups aggregate in the nonpolar dodecane, and this aggregation could prevent them from efficiently vacating the local region around which they had been desorbed. Finally, given the polar nature of these headgroups, it is likely that the amount of water at the SAM/dodecane interface was higher than for an *n*-alkanethiolate SAM. The potential roles of water in STM imaging of SAMs with polar headgroups²⁰ and on the mechanism of replacement lithography² have been discussed in detail previously. In short, water is believed to facilitate the STM tip-induced desorption and this contention is consistent with the data observed here. Indeed, when the relative humidity was lowered to ca. 3% for several hours before conducting the replacement lithography experiment on several of these SAMs, although higher biases were required to initiate desorption, the results obtained were similar to those shown in Figure 4. On *n*-alkanethiolate SAMs, replacement lithography at this relative humidity does not occur. This observation is also consistent with the polar headgroups in these SAMs facilitating the availability of water at the SAM/dodecane interface more efficiently than for *n*-alkanethiolate SAMs.

Conclusions

From these data, it is concluded that the structure of a SAM strongly influences the process of replacement lithography. Specifically, longer, presumably more well ordered SAMs required a higher applied bias to undergo replacement. Conversely, shorter SAMs and SAMs with cyano, hydroxy, and carboxylic acid headgroups can undergo replacement at lower applied bias. However, this latter class of SAMs underwent replacement to a lesser degree of completion and with a poorer resolution. Thus, from the standpoint of high-resolution lithography, well-packed SAMs have a benefit even if they require a slightly higher bias to perform the operation.

Experimental Section

Octanethiol (C₈SH), decanethiol (C₁₀SH), dodecanethiol (C₁₂-SH), mercaptoundecanol (HOC₁₁SH), and mercaptoundecanoic acid (HO₂CC₁₀SH) were obtained from Aldrich and used

without further purification. Tetradecanethiol (C₁₄SH) was obtained from Fluka and used without further purification. The cyanodecanethiol (NCC₁₀SH) was available from previous studies and was used without further purification.²⁰ SAMs were prepared and replacement lithography was performed using previously described methods.² All replacement lithography was performed at relative humidity of 55% ± 2% as maintained by a hydrated dinitrogen flow. The concentration of the undecylferrocenyl thioacetate (FcC₁₁SAC) used to replace regions of various *n*-alkanethiolate SAMs was ca. 6 μM. The concentration of FcC₁₁SAC used to replace regions on SAMs with nonmethyl headgroups (e.g., CN, OH, and COOH) was ca. 430 μM. To determine the extent of replacement for a given bias, STM images were manipulated in imaging software (Scion Image Release Beta 4.0.2) as follows. A scale was determined for each image by converting the pixel count to nanometers. The images were then thresholded by selecting all pixels above a threshold value as replaced regions. The area of each of these regions was then determined by the following method: the widest point of any of the eight lines in a given image was determined. This widest point was multiplied by the length of the line drawn (100 nm, determined as the write speed of 20 nm/s multiplied by the write time of 5 s) to define the maximum replacement area. The area of each line was then individually divided by the theoretical maximum area to define the percentage of replacement for that trial (bias).

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