

# Simple Methods for the Direct Assembly, Functionalization, and Patterning of Acid-Terminated Monolayers on Si(111)

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This article describes mild methods to directly assemble, functionalize, and pattern monolayers of undecylenic acid on hydrogen-terminated Si(111). These monolayers were assembled under very mild conditions from a neat solution of undecylenic acid containing 0.1 mol % 4-(decanoate)-2,2,6,6-tetramethylpiperidinoxy at room temperature without the need for UV light. Because of these mild conditions, monolayers exposing carboxylic acids could be assembled in one step without the need to protect the acid prior to its assembly. The monolayers were extensively characterized by horizontal attenuated total reflection infrared spectroscopy, X-ray photoelectron spectroscopy (XPS), and contact angle goniometry. The monolayers bonded to the silicon surface preferentially through the olefin with no detectable bonds between the carboxylic acids and silicon. The crystallinity of the monolayer was studied by infrared spectroscopy through the antisymmetric- $\nu_a(\text{CH}_2)$ - and symmetric- $\nu_s(\text{CH}_2)$ -stretches for methylene. Because it is important for future applications to assemble functional surfaces, methods to react the acid-terminated monolayers with trifluoroacetic anhydride and triethylamine to yield a symmetric anhydride on the monolayer were studied. These anhydrides were reacted with a variety of milligram-quantity amines to yield amide-terminated surfaces. This method was general, and a variety of amines could be bonded to the monolayer. The stabilities of these monolayers upon exposure to ambient conditions and under a variety of solvents were described. Because patterned monolayers have found wide applications, we have developed methods to pattern 1-octadecylamine and poly(ethylenimine) on the micrometer scale using soft lithography. In addition, polymer brushes of polynorbornene with thicknesses from 32 to 150 nm were grown from monolayers patterned with the Grubbs' catalyst. The patterned surfaces were imaged by scanning electron microscopy, scanning probe microscopy, and ellipsometry to determine the thicknesses of the patterns and the fidelity of the method.

## Introduction

Self-assembled monolayers (SAMs) on silicon is an area of intense study because of their applications in the development of new biomolecular and molecular electronic devices.<sup>1–13</sup> SAMs are directly assembled onto silicon without an intervening layer of silicon dioxide such that the electrical properties of silicon can be addressed through the SAMs. These surfaces are exciting because the display of important functional groups, such as single stranded DNA, carbohydrates, or proteins, can be detected using electrochemistry.<sup>8,10,14–16</sup> Recently, new biosensors based on SAMs on silicon and fundamental studies of electron tunneling through SAMs on silicon have been reported.<sup>7,10,12,14–18</sup>

Interest in this area is driven by opportunities to combine the selectivity of organic chemistry to display well-defined functional groups on SAMs with the terrific

electronic properties of silicon. Silicon is the most important electronic material in the electronics industry, yet its applications in biotechnology and nanotechnology are lacking because of limited methods of assembling, functionalizing, and patterning SAMs directly on silicon.

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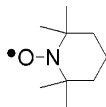
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## Scheme 1. Structure of TEMPO



Mild methods to assemble and pattern functional SAMs on silicon are needed to advance these fields such that a wide variety of small molecules and nanomaterials can be both readily displayed and patterned on a silicon wafer.

New methods to assemble SAMs on hydrogen-terminated Si(111) from olefins, aldehydes, alcohols, or Grignard reagents were recently reported.<sup>1–5,9,11,13–15,17,19–26</sup> Methods to assemble monolayers on Si(111) use heat, acyl peroxides, UV light, chlorination of the surface followed by reaction with Grignard reagents or alcohols, iodination of the surface followed by exposure to olefins and light, or scribing. Many of these methods are harsh and limit the range of functional groups that can be assembled on the surface. Mild methods to assemble well-ordered SAMs on silicon are still needed.<sup>5,9</sup>

The results reported in this article build on our previous work of assembling well-ordered monolayers on hydrogen-terminated Si(111) from olefins and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, Scheme 1).<sup>5</sup> Previously, we discovered that 1-octadecene in the presence of trace amounts of TEMPO formed crystalline monolayers when assembled at room temperature without the need for UV light. This very mild method of assembly prompted us to question whether SAMs terminated with interesting functional groups such as carboxylic acids could be assembled directly onto silicon.

Previous work to assemble SAMs on Si(111) that display reactive functional groups on the surface yielded promising results. SAMs terminated with alcohols, esters, olefins, and ethers have been assembled, but more reactive groups such as carboxylic acids are challenging because they can oxidize hydrogen-terminated Si(111) prior to the assembly of the monolayer.<sup>1–3,5,9,11,13,19–21,27</sup> Only one paper reports the direct assembly of an acid-terminated SAM onto Si(111) using UV light, but the SAM was not fully characterized.<sup>13,16,28</sup> Acid-terminated monolayers are important because they are readily activated and reacted with amines or alcohols to yield amides or esters. Interest in assembling

acid-terminated surfaces is shown by the numerous examples of these SAMs on other surfaces being activated to yield more functional surfaces.<sup>11–17,21,28,29</sup>

In this article, we report extremely mild methods to assemble, functionalize, and pattern SAMs terminated with carboxylic acids onto Si(111). Our methods do not require heat or exposure to UV light, thus enabling the assembly of a wide variety of monolayers. SAMs are assembled in the presence of undecylenic acid and a derivative of TEMPO. These SAMs are further functionalized by activation with trifluoroacetic anhydride and reaction with a variety of amines to expose amide-terminated SAMs. We will demonstrate that these SAMs are stable in apolar solvents and can be patterned on the micrometer scale using microfluidic channels formed through soft lithography.

## Experimental Section

**Materials and Methods.** Distilled water, 1-octadecene (90%), hexane, 10-undecenoic acid, trifluoroacetic anhydride, polyethylenimine (water-free), 1-dodecylamine (98%), 1-butylamine (99.5%), 1-octylamine (99+%), 1-hexadecylamine (90%), 1-octadecylamine (90%), and 48% hydrofluoric acid were purchased from Acros or Aldrich and used as received.  $\text{NH}_4\text{F}$  (40%) was purchased from J. T. Baker and used as received. All solvents were purchased from Acros and used as received. Single-side polished Si(111) wafers (n-type) were purchased from Silicon Inc, Boise, Idaho.

The synthesis of TEMPO-C<sub>10</sub> was described in a previous paper. It was stored in a  $-30\text{ }^\circ\text{C}$  freezer in a glovebox under  $\text{N}_2$ .<sup>5</sup> 10-Undecenoic acid was distilled with a Vigreux column under reduced pressure. Typically, 500 mL was distilled at one time. The first 100 mL of distilled 10-undecenoic acid was discarded. We collected the next 300 mL and transferred it to a Kontes flask. The Kontes flask was evacuated under reduced pressure for 48 h and back filled with  $\text{N}_2$ ; this process was repeated three times. The Kontes flask was stored in the glovebox. The same process was followed for the purification of 1-octadecene.

**Assembly of Monolayers of Undecylenic Acid.** Shards of Si(111) wafers were washed with hexanes, acetone, and methanol and then sonicated in acetone for 5 min. The shards were rinsed with water and treated with 5:1 (v/v) 40%  $\text{NH}_4\text{F}$ (aq)/48% HF(aq) for 30 s to remove the native silicon dioxide layer. The samples were then placed in 3:1 (v/v) concentrated  $\text{H}_2\text{SO}_4$ /30%  $\text{H}_2\text{O}_2$ (aq) (Piranha solution) for 1 h at  $90\text{ }^\circ\text{C}$  to clean the surfaces and oxidize the surface of the silicon shards. *Warning: Piranha*

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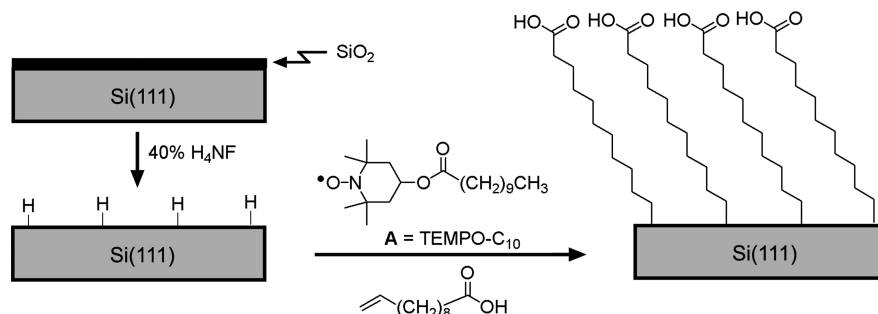
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**Figure 1.** Our method to assemble monolayers of undecylenic acid. Silicon wafers with a native silicon dioxide layer were immersed in 40% NH<sub>4</sub>F for 20 min under an argon purge. The silicon dioxide was etched to yield hydrogen-terminated Si(111). The wafer was immersed in a solution of undecylenic acid with 0.1 mol % TEMPO-C<sub>10</sub> (A) for 24 h.

solution is exceedingly dangerous and should be kept from organic materials and treated with care. The wafers were removed from the Piranha solution and washed with copious amounts of water. The wafers were hydrophilic after this treatment.

To form hydrogen-terminated Si(111), 40% NH<sub>4</sub>F was placed in a cup within a larger cup covered with a cap. The NH<sub>4</sub>F was purged with argon for 30 min to remove O<sub>2</sub> before the Si(111) shards were immersed. The larger cup was continuously purged with Ar while the Si(111) shards were immersed in NH<sub>4</sub>F for 20 min. The shards were removed, and the NH<sub>4</sub>F spontaneously dewetted from the surface. The shards were dried under a stream of N<sub>2</sub>.

The shards were immediately taken into the glovebox as is and immersed in a neat solution of undecylenic acid with 0.1 mol % TEMPO-C<sub>10</sub>. Transferring the silicon shards into a glovebox immediately after forming the hydrogen-terminated surface is important because the surface rapidly oxidizes to silicon dioxide under ambient conditions. The monolayers were assembled at room temperature in a sealed Schlenk flask under N<sub>2</sub> for 24 h. After 24 h, the shards were removed and washed with copious amounts of hexane, acetone, and methanol. Finally, the shards were sonicated twice for 3 min in CH<sub>2</sub>Cl<sub>2</sub>. New CH<sub>2</sub>Cl<sub>2</sub> was used for each sonication.

**Activation of Carboxylic Acids with Trifluoroacetic Anhydride and Reaction with Amines.** SAMs terminated with carboxylic acids were immersed in 0.1 M acetic anhydride and 0.2 M triethylamine in DMF. After 15 min, the wafers were removed and immediately immersed in a 0.01 M solution of an amine in methylene chloride or THF for 30 min. The wafers were removed and rinsed with acetone, methanol, and water.

**X-ray Photoelectron Spectroscopy (XPS).** The samples were studied by XPS at the University of Illinois at the Center for Microanalysis of Materials (CMM) with the help of Rick Haasch. The instrument was a Kratos axis ultra X-ray photoelectron spectrometer. The dimensions of the image area were 300 × 700 μm<sup>2</sup>, and the takeoff angle was 45°. The pass energy on the survey scan (0 to 1100 eV) was 160 eV. High-resolution scans of Si(2p) (92 to 108 eV binding energy), C(1s) (274 to 300 eV binding energy), O(1s) (523 to 539 eV binding energy), and F(1s) (680 to 696 eV binding energy) were performed. The atomic compositions were corrected for the atomic sensitivities and measured from the high-resolution scans. The atomic sensitivities were 1.000 for F(1s), 0.780 for O(1s), 0.278 for C(1s), and 0.328 for Si(2p).

**Contact Angle Goniometry.** Contact angles were measured on a Ramé-Hart model 100 goniometer at room temperature and ambient humidity. An Eppendorf EDOS 5222 was used to dispense distilled water. Small drops of water (5 μL) were dispensed, and the contact angles were measured immediately. A minimum of 15 measurements at two different spots on the surface were collected for each sample. The error in the measurements of advancing contact angles was typically small; for contact angles of greater than 100°, most of the measurements came within ±1° of the reported value. Contact angles of less than 100° had errors of ±2°.

**Infrared Spectroscopy.** All measurements were made with a Bruker Tensor 27 spectrometer with a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector. Monolayers were assembled on silicon ATR crystals with dimensions of 80 × 10

× 5 mm<sup>3</sup>. The crystals were fabricated such that the Si(111) face was exposed along the long face. The spectrometer and sample chamber were continuously purged with water and carbon dioxide-depleted air.

The backgrounds for the samples were freshly prepared silicon dioxide surfaces on the ATR crystals. The ATR crystals were first cleaned with organic solvents and then immersed in Piranha solution for 60 min to remove residual organics on the surface. These ATR crystals were immediately used to measure the background scans. Spectra of SAMs were collected at a resolution of 4 cm<sup>-1</sup>, and spectra for hydrogen-terminated Si(111) were collected at a resolution of 2 cm<sup>-1</sup>.

**Scanning Probe Microscopy.** We used the MFP-3D scanning probe microscope from Asylum Research. The instrument was operated in AC mode with a frequency of 55.58 kHz, and the spring constant of the tips was 1 N m<sup>-1</sup>.

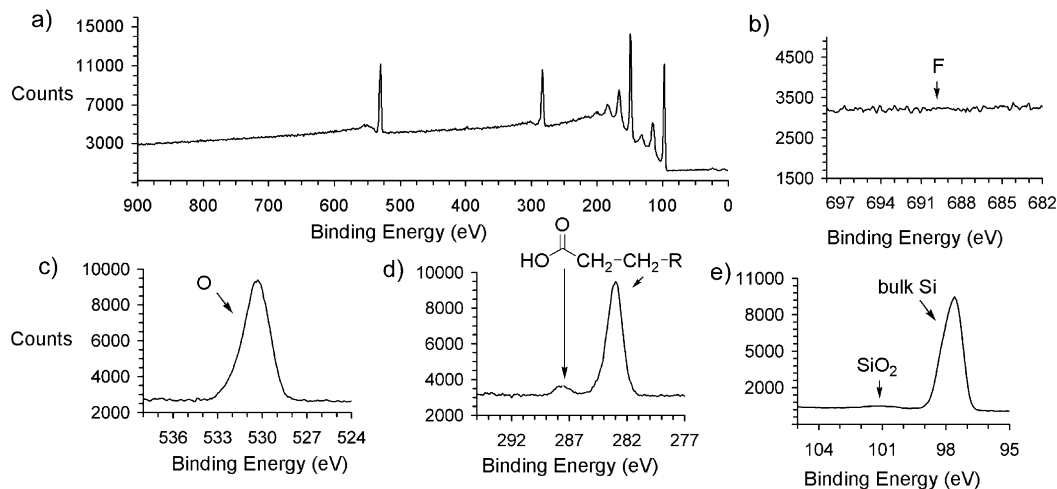
## Results and Discussion

**Assembly of SAMs from Undecylenic Acid.** The monolayers were assembled using 0.1 mol % of a derivative of TEMPO in neat undecylenic acid as described in detail in the Experimental Section (Figure 1). This method is based on our previous results for the assembly of well-ordered monolayers of 1-octadecene in the presence of TEMPO or derivatives of TEMPO.<sup>5</sup> SAMs of 1-octadecene were characterized by contact angle goniometry, ellipsometry, and XPS. These measurements showed that our method of assembly resulted in crystalline monolayers of 1-octadecene with a small concentration of TEMPO on the surface. Although the role of TEMPO in the assembly of monolayers was not determined, its presence was necessary for the assembly of well-ordered SAMs. This article extends our prior work to describe the assembly, functionalization, and patterning of monolayers terminated with carboxylic acids.

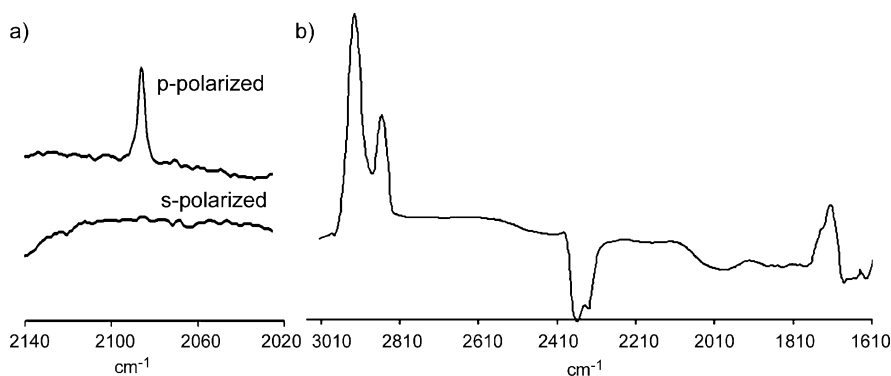
To characterize a SAM unambiguously, multiple methods must be used. Here, we characterized SAMs of undecylenic acid by X-ray photoelectron spectroscopy (XPS) and horizontal attenuated total reflection infrared (HATR-IR) spectroscopy. XPS was chosen because it describes the chemical composition of the surface and can detect the presence of oxidized silicon. HATR-IR spectroscopy was chosen because C–H and C=O regions describe the degree of crystallinity of SAMs and the presence of acids and amides.

The XPS spectrum of a monolayer of undecylenic acid is shown in Figure 2. In Figure 2a, we show a survey scan of the surface that clearly describes the presence of only O, Si, and C. High-resolution scans of the surface were done to further quantify the surface composition as 21% O, 36% Si, 0% F, and 42% C. The high-resolution scan for fluorine confirmed that Si–F and C–F bonds were not present. The high-resolution scan for carbon shows a peak for the methylene carbons at 283 eV and the carbonyl





**Figure 2.** (a) XPS survey scan of a SAM of undecylenic acid is shown. High-resolution scans for (b) fluorine, (c) oxygen, (d) carbon, and (e) silicon. We assign peaks for carbon and silicon based on literature references.



**Figure 3.** (a) HATR spectra of the Si(111)-H peak with p- and s-polarized light. (b) HATR spectrum of a SAM of undecylenic acid.

carbon at 288 eV. This result is expected because the carbonyl peak is seen at higher binding energies on acid-terminated SAMs.<sup>15</sup>

The high-resolution scans of Si and O reveal important information about the surface. The XPS spectrum of Si shows one peak for bulk Si and only trace amounts of SiO<sub>x</sub> at 102 eV. This result proves that the silicon surface underwent minimal oxidation during the assembly of the monolayer. The amount of SiO<sub>x</sub> was much less than 1% of the surface composition for many different samples.

The peak for oxygen in the XPS spectrum is broadly centered at approximately 531 eV. Possible sources of oxygen include carboxylic acids from undecylenic acid, TEMPO-C<sub>10</sub> (A in Figure 1), and SiO<sub>x</sub> on the surface. In our previous work on the assembly of SAMs from 1-octadecene and derivatives of TEMPO, we know that trace amounts of TEMPO-C<sub>10</sub> assemble onto silicon and account for some of the oxygen observed by XPS.<sup>5</sup> The lack of a peak in the silicon region for SiO<sub>x</sub> indicates that little of the observed oxygen is due to oxidized silicon. Thus, we attribute the observed oxygen peak to the presence of TEMPO-C<sub>10</sub> on the surface and the terminal carboxylic acids on the end of the SAMs. Because of the multiple sources of oxygen, we cannot make further assignments to this peak.

The HATR-IR spectra of hydrogen-terminated Si(111) and a SAM of undecylenic acid are shown in Figure 3. The assembly of our monolayer begins with the formation of a surface of hydrogen-terminated Si(111). Higashi et al. reported that etching the native oxide layer from a Si(111) wafer in argon-purged 40% NH<sub>4</sub>F results in a hydrogen-terminated Si(111) surface with a defect density

of 0.5%.<sup>24</sup> The Si(111)-H bonds are perpendicular to the exposed plane of the silicon wafer, thus these bonds are IR-active only with p-polarized light. The literature reference for the shift of the Si(111)-H peak is 2083.7 cm<sup>-1</sup> with a fwhm of 0.95 cm<sup>-1</sup>.<sup>24</sup> Dihydrogen and trihydrogen defects appear as peaks at 2111, 2120, and 2139 cm<sup>-1</sup> under both s- and p-polarized light.<sup>26,30</sup>

In the HATR-IR spectra of Si(111)-H surfaces with s- and p-polarized light (Figure 3a) we see only one peak at 2084 cm<sup>-1</sup> with a fwhm of 3.8 cm<sup>-1</sup> with p-polarized light. The HATR-IR spectrum of Si(111)-H with s-polarized light showed an absence of peaks. These results demonstrate that we formed well-ordered Si(111)-H surfaces.

The HATR-IR spectrum of undecylenic acid SAMs shows three important peaks. The peaks corresponding to the antisymmetric  $\nu_a(\text{CH}_2)$ - and symmetric  $\nu_s(\text{CH}_2)$ -stretches for methylene appear at 2923 and 2853 cm<sup>-1</sup> (Table 1). These results are significant because the  $\nu_a(\text{CH}_2)$  peak for crystalline SAMs ranges from 2918 to 2920 cm<sup>-1</sup> but for disordered SAMs it ranges from 2925 to 2928 cm<sup>-1</sup>.<sup>1,31</sup> Similarly, the  $\nu_s(\text{CH}_2)$  peak for crystalline SAMs appears at 2850 cm<sup>-1</sup>, but for disordered SAMs it appears at 2858 cm<sup>-1</sup>.<sup>1,31</sup> The location of  $\nu_a(\text{CH}_2)$  and  $\nu_s(\text{CH}_2)$  peaks within these ranges describes the crystallinity of SAMs. Our results show that we assembled monolayers with some

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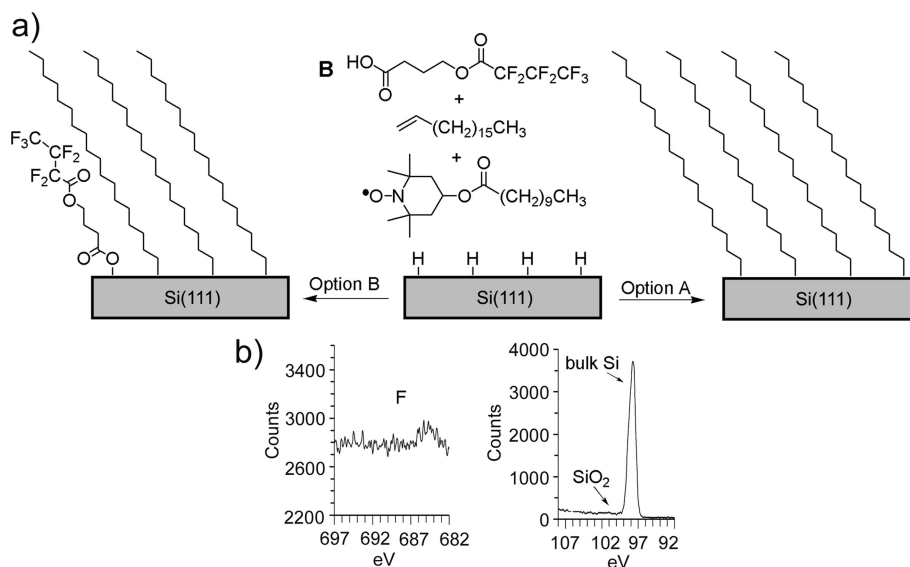
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**Table 1. Select Peaks from the HATR-IR Spectra of Monolayers of Thiols on Gold (Entries 1 and 2) and Olefins on Silicon (Entries t3–5)**

entry	monolayer	$\nu_a(\text{CH}_2)$ ( $\text{cm}^{-1}$ )	$\nu_s(\text{CH}_2)$ ( $\text{cm}^{-1}$ )	C=O ( $\text{cm}^{-1}$ )
1	Au-(CH <sub>2</sub> ) <sub>9</sub> -CH <sub>3</sub>	2920.5 <sup>a</sup>	2850.5 <sup>a</sup>	
2	Au-(CH <sub>2</sub> ) <sub>10</sub> -CO <sub>2</sub> H	2925 <sup>a</sup>	2853 <sup>a</sup>	1744 <sup>b</sup> , 1720 <sup>b</sup>
3	Si-(CH <sub>2</sub> ) <sub>10</sub> -CO <sub>2</sub> H	2923	2853	1710
4	Si-(CH <sub>2</sub> ) <sub>10</sub> -C(O)OC(O)-(CH <sub>2</sub> ) <sub>10</sub> -Si	2927	2856	1742, 1633
5	Si-(CH <sub>2</sub> ) <sub>10</sub> -CONH-(CH <sub>2</sub> ) <sub>x</sub> -CH <sub>3</sub>	2925	2856	1722, 1593
	Si-(CH <sub>2</sub> ) <sub>10</sub> -CO <sub>2</sub> H			

<sup>a</sup> From ref 31b. <sup>b</sup> From ref 34. These peaks were measured on SAMs of 16-mercaptohexadecanoic acid.



**Figure 4.** (a) We assembled monolayers from **B**, 1-octadecene, and TEMPO-C<sub>10</sub> in diglyme to study whether acids bonded to the surface at rates competitive with olefins. In option A, only olefins bonded to the surfaces, and the monolayer is composed of 1-octadecene. In option B, both the acids and olefins bond to Si(111)-H at competitive rates. (b) High-resolution XPS spectra of the fluorine and silicon regions for these monolayers showed no fluorine or SiO<sub>x</sub>. These results were consistent with option A.

degree of order, but the monolayers were not quite crystalline. This result was not unexpected as Chidsey et al. reported that SAMs of 11-mercaptoundecanoic acid on Au had values of 2925  $\text{cm}^{-1}$  for  $\nu_a(\text{CH}_2)$  and 2853  $\text{cm}^{-1}$  for  $\nu_s(\text{CH}_2)$  but that SAMs of 1-decanethiol had values of 2920.5  $\text{cm}^{-1}$  for  $\nu_a(\text{CH}_2)$  and 2850.5  $\text{cm}^{-1}$  for  $\nu_s(\text{CH}_2)$ .<sup>32</sup> On the basis of these data, the presence of carboxylic acids on the thiols prevented 11-mercaptoundecanoic acid from assembling into crystalline monolayers.

Silicon hydrides on Si(111) are 3.84 Å from each other, and the diameter of an alkyl chain is approximately 4.2 Å.<sup>2</sup> Thus, simple geometric arguments about the spacing of hydrides on silicon and the cross-sectional area of an alkane chain in a monolayer yield the result that approximately half of the silicon hydrides react when a monolayer is assembled.<sup>2,3,20,33</sup> Despite the expected presence of Si(111)-H peaks in the HATR-IR spectra of alkyl SAMs, this peak has not been observed by us or others.

**Mode of Bonding of Undecylenic Acid.** Undecylenic acid can bond to hydrogen-terminated Si(111) through the acid or olefin. In our previous work, we demonstrated that 1-octadecene assembled into SAMs on Si(111)-H through its olefin. Thus, 1-alkenes terminated with methyl groups assemble into ordered monolayers through their olefins, but the carboxylic acid of undecylenic acid provides another mode of bonding to Si(111)-H. We wished to study which functional group—the olefin or acid—bonded to the surface.

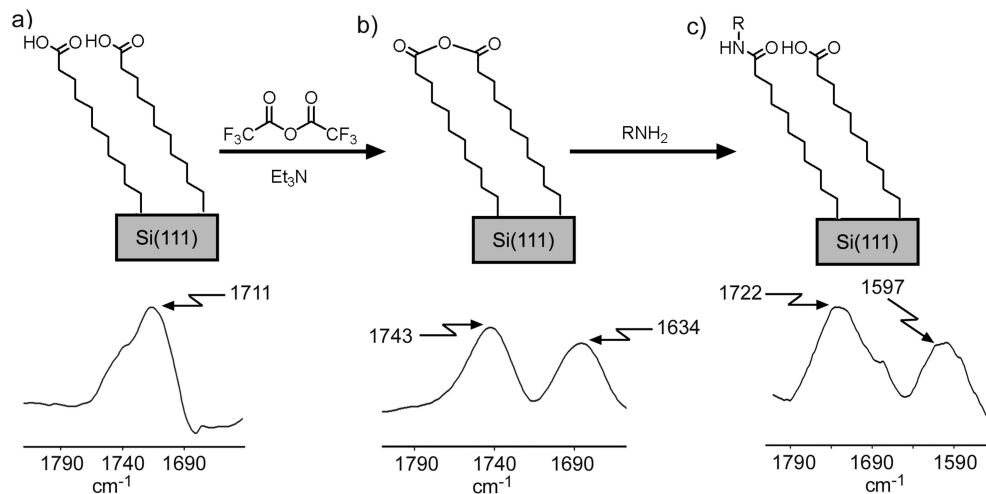
The advancing contact angle of water was 65° for SAMs of undecylenic acid. This value is consistent with a monolayer terminated with acids rather than olefins as they would be expected to exhibit a contact angle close to 100°. Our value for an advancing contact angle of water does not eliminate the possibility that a significant fraction of the undecylenic acid is bonded to the silicon surface through the acid group, but it provides evidence that acids are displayed on the surface.

A second piece of evidence for the assembly of monolayers through olefins rather than acids is outlined in Figure 4. We studied the assembly of monolayers from 1 mol % of TEMPO-C<sub>10</sub>, 2.37 g (3.0 mL, 9.4 mmol) of 1-octadecene, and 1.00 g (3.3 mmol) of **B** in 3 mL of diglyme. The diglyme was needed to dissolve the reagents because **B** had poor solubility in 1-octadecene. **B** was added to the assembly to provide a unique handle in the XPS to determine whether acids bond to the surface. We synthesized **B** because it has a pK<sub>a</sub> and nucleophilicity similar to those of undecylenic acid, but it can bond to the surface only through its acid. Thus, if acids bond to Si(111)-H, we will see fluorine in the XPS spectrum. If carboxylic acids do not bond to Si(111)-H, then we will not see a peak due to fluorine in the XPS spectrum.

The advancing and receding contact angles of water on these SAMs were 111° and 107°, respectively. These values were the same as we observed for SAMs assembled from 1-octadecene and TEMPO-C<sub>10</sub> in the absence of **B**. The compositions of these surfaces measured by XPS were 66% C, 10% O, 24% Si, and 0% F. In Figure 4b, we show

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**Figure 5.** Functionalization of acid-terminated SAMs. (Top) schematic of SAMs at several steps in the process. (Bottom) HATR-IR spectrum of each carbonyl region. (a) Acids were activated with trifluoroacetic anhydride to yield a (b) anhydride surface. (c) This surface was reacted with amines to yield a mixed monolayer of amides and acids.

the high-resolution scans of the fluorine and silicon regions to show the lack of fluorine and  $\text{SiO}_x$  on these surfaces.

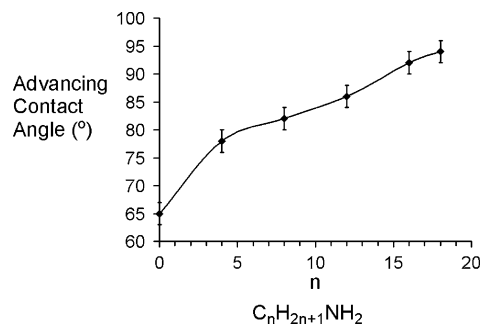
The absence of F and  $\text{SiO}_x$  in the XPS combined with the contact angles of water demonstrate that olefins selectively bonded to  $\text{Si}(111)\text{-H}$  in the presence of acids. The bonding of acids to a  $\text{Si}(111)\text{-H}$  surface was not detectable when an olefin was present in solution. Thus, SAMs assembled from undecylenic acid bond to the surface through olefins and exposed acids on the surface of the SAMs.

**Functionalization of Acids on the Surface with Amines.** We wished to develop a mild method to functionalize carboxylic acid-terminated monolayers on silicon. Our method to assemble SAMs uses approximately 5 g of olefin to functionalize a shard of silicon. This method would be prohibitively expensive for some olefins terminated with other functional groups. Here, we report a method to functionalize SAMs that uses commercially available undecylenic acid and milligram quantities of amines.

Our method is outlined in Figure 5 and is based on work by others to activate acids to bond amines to the surface.<sup>16,34</sup> We activated acid-terminated surfaces with trifluoroacetic anhydride to yield an anhydride-terminated SAM. This SAM was then reacted with amines to assemble amide-terminated SAMs. We tried a variety of different solvents for each step, and DMF and  $\text{CHCl}_3$  gave the best results.

We characterized these results by XPS and HATR-IR spectroscopy. The XPS of anhydride surfaces did not show the presence of fluorine. Activation of surface carboxylic acids could yield symmetric anhydrides as shown in Figure 5 or mixed anhydrides with the following structure:  $\text{CF}_3\text{C}(\text{O})\text{OC}(\text{O})(\text{CH}_2)_{10}\text{-Si}$ . The absence of fluorine in the XPS of anhydride monolayers suggests that the surface is composed of symmetric anhydrides. The HATR-IR spectra show the progression of acid to anhydride to amide (Table 1 and Figure 5). These spectra are consistent with previous results for these surfaces on Au and demonstrate that the SAMs were functionalized.<sup>34</sup>

To test this method we assembled amide-terminated surfaces with alkylamines of increasing lengths. We reacted the amide surfaces with amines of the general formula  $\text{H}_2\text{NC}_n\text{H}_{2n+1}$  where  $n$  equals 4, 8, 12, 16, and 18. A plot of advancing contact angles of water on these



**Figure 6.** Advancing contact angles of water on amide-terminated SAMs as a function of the number of carbons in the amines. Anhydride surfaces were reacted with amines as in Figure 5. The line is drawn as a guide to view the data.

surfaces versus the number of carbons in the amine is shown in Figure 6. Longer amines result in more hydrophobic surfaces as expected. The most hydrophobic surface was synthesized from 1-octadecylamine and yielded an advancing contact angle of water of  $94^\circ$ .

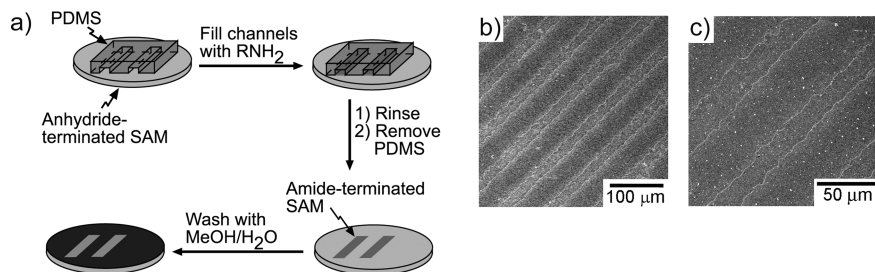
**Stabilities of SAMs Assembled from Undecylenic Acid.** We wished to measure the stabilities of undecylenic acid monolayers functionalized with 1-octadecylamine as in Figure 5. These monolayers are representative of surfaces that we and others may wish to use in further studies, thus knowledge of their stabilities over time is important. Their stabilities in water are particularly important for potential biological applications in DNA sensing, biosensors, or as surfaces on which to grow cells.

One method that we found particularly useful to study the stability of SAMs is contact angle goniometry. Contact angles can be measured quickly and provide information about which functional groups are exposed on a surface.<sup>3,18,29,35</sup> We began with a hydrophobic SAM with a large contact angle of  $94^\circ$  and expect that as the silicon is slowly oxidized to yield a glassy, hydrophilic layer on the surface the contact angle will decrease. Silicon wafers readily oxidize to yield a thin layer of silicon dioxide on the surface, but well-ordered alkyl monolayers greatly

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**Figure 7.** (a) PDMS slab patterned in bas-relief placed on an anhydride-terminated SAM. The channels were filled with amines dissolved in DMF. After 15 min, the channels were rinsed, and the PDMS was removed to expose an amide-terminated surface. The surface was washed with methanol and then water to quench the remaining anhydrides. (b) SEM micrographs of 30- $\mu\text{m}$ -wide lines of amide-terminated SAMs synthesized using 1-octadecylamine. The thin, bright lines are amide-terminated SAMs, and the wide, dark lines are acid/ester-terminated SAMs.

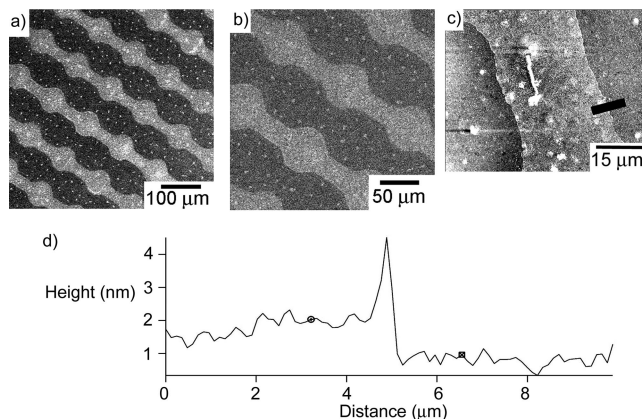
**Table 2. Changes in Advancing Contact Angles of Water on Amide-Terminated SAMs Assembled with 1-Octadecylamine after Immersion in Solvents for 12 or 72 h**

solvent	dielectric constant	duration (h)	decrease in contact angle (deg)
none	1.0	12	0
		72	0
hexanes	1.9	12	3
		72	4
$\text{CHCl}_3$	4.8	12	1
		72	7
THF	7.5	12	9
		72	16
$\text{H}_2\text{O}$	79	12	12
		72	21

inhibit the rate of this oxidation.<sup>2,3,22</sup> Thus, by measuring the decrease of advancing contact angles as a function of time, we will learn how well our SAMs protect silicon from oxidation.

We exposed amide-terminated SAMs to air and immersed them in various solvents taken directly from the manufacturer's bottle for 12 and 72 h. Silicon shards exposed to air for two months exhibited no change in their contact angles; these wafers are stable in air for long periods of time. Silicon shards immersed in hexanes or chloroform had small changes in their contact angles, but those immersed in tetrahydrofuran or water were quickly degraded after 12 h. The measurement of advancing contact angles provides a simple method to address the stability of these monolayers. Because we know that water can readily oxidize a silicon surface to  $\text{SiO}_2$ , we tried to correlate our results to the dielectric constant of the solvents. Our results indicate that the monolayers are stable in solvents with low dielectric constants, but they are unstable in solvents with high dielectric constants. These results are meant as a guide for future work with these monolayers, and effects such as the presence of  $\text{O}_2$ , trace water in the solvents, trace peroxides in THF, or HCl in chloroform must be examined. In future work, we will analyze the stabilities of our monolayers over time using XPS and HATR-IR spectroscopy.

**Patterning on the Micrometer Scale Using Soft Lithography.** We developed mild methods to assemble and functionalize monolayers of undecylenic acid, and in this section we describe a mild method to pattern these monolayers. We choose to use "soft lithography" for our patterning. Soft lithography is a series of techniques based on poly(dimethylsiloxane) (PDMS) and developed by Whitesides et al. that can be used to pattern features from nanometer to micrometer sizes.<sup>36</sup>



**Figure 8.** (a) and (b) SEM micrographs of patterned polyethylenimine on a silicon wafer. The light areas are polyethylenimine bonded to anhydrides on the surface. The small bright spots in the dark, unpatterned regions are due to polyethylenimine that was not washed from the channels prior to the removal of PDMS. (c) SPM micrograph of a patterned surface. The center region is the polyethylenimine-coated SAM, and the left and right regions are uncoated SAMs. The bright spots were dust particles on the surface. The dark line indicates the area that was integrated to give the thickness plot in d. The average thickness of the polymer layer was 1.0 nm.

In our method, we take advantage of the microfluidic channels formed by PDMS patterned in bas-relief in contact with a silicon wafer (Figure 7). Because PDMS is soft and compliant, it makes conformal contact with a flat surface. We begin by functionalizing acid-terminated SAMs to anhydrides using trifluoroacetic anhydride. Next, we place a PDMS mold in contact with the surface to form microchannels. Then, we use capillarity to flow a solution of an amine through the microfluidic channels. The amine contacts only anhydrides in the microfluidic channels, whereas anhydrides covered by PDMS were protected from reaction. After 15 min, the amines were washed from the microchannels, and the PDMS mold was removed.

**Pattern with 1-Octadecylamine.** A solution of 1-octadecylamine in DMF was used to pattern a silicon wafer with micrometer-sized lines (Figure 7b). The roughness of the patterned SAM is due to the roughness of the sides

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of the PDMS microchannels. These microchannels were fabricated using rapid prototyping, which involves the use of transparency masks with an edge resolution of about 5 micrometers. This roughness was transferred into the PDMS molds and the resulting patterns on Si(111).

**Pattern with Polyethylenimine.** A solution of polyethylenimine ( $M_n = 10\,000\text{ g mol}^{-1}$ ) in DMF was used to pattern SAMs (Figure 8). We choose this polymer because it has many amines along the backbone to bond to the surface, and it demonstrates that polymers can also be patterned with this technique. SEM images of patterned SAMs showed bright lines for the polyethylenimine-patterned regions separated by dark lines of unpatterned SAMs.

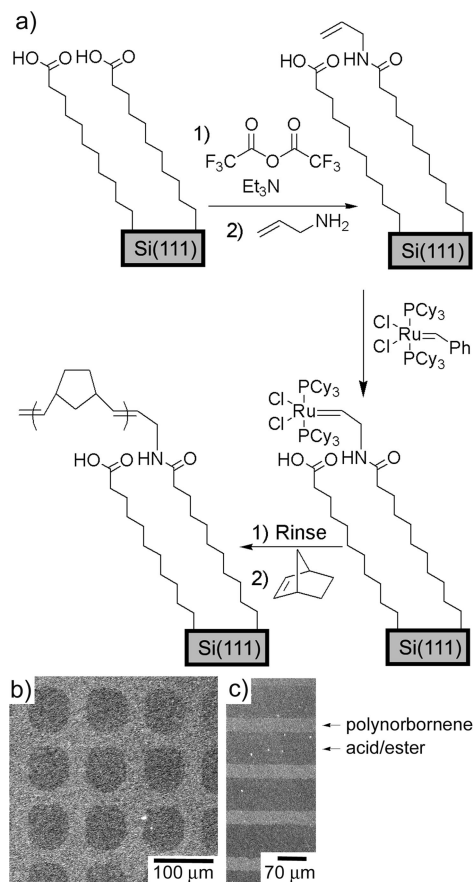
To further characterize the patterns, we used scanning probe microscopy (Figure 8c, d). The SPM micrograph of the surface showed that the polymer was approximately 1.0 nm thick and uniformly coated along the patterned region.

**Pattern with Poly(norbornene).** We grew polynorbornene from SAMs using the Grubbs' first generation catalyst by patterning a 2D grid of allylamine on the SAMs using the method described in Figure 7a. The olefin-terminated SAM was immersed in a solution of the Grubbs' catalyst in xylenes for 30 min in a glovebox (Figure 9a). The wafer was removed, rinsed thoroughly with xylenes, and placed in a 0.1 g mL<sup>-1</sup> solution of norbornene in xylenes. After 1 or 15 hours, the wafer was removed from the glovebox, washed thoroughly to remove excess norbornene, and imaged under an SEM (Figure 9b, c). Control experiments where the monolayer was not reacted with the Grubbs' catalyst did not show any polymer on the surface by ellipsometry or SEM. The thickness of polynorbornene was measured with an ellipsometer on large, unpatterned sections of silicon wafers. The thicknesses were 32 nm after 1 h and 150 nm after 15 h.

### Conclusions

This article describes three general methods to assemble SAMs with reactive end groups on silicon. We described mild methods to assemble undecylenic acid on a Si(111)-H surface, to functionalize an acid-terminated monolayer on silicon, and to pattern these monolayers on the micrometer scale. SAMs of undecylenic acid were characterized by contact angle goniometry, HATR-IR spectroscopy, and XPS. No detectable reaction between the carboxylic acid and Si(111)-H surface was measured.

The direct assembly of acid-terminated monolayers on silicon is important because acids are readily functionalized to expose other chemical groups. In our method, commercially available undecylenic acid is assembled directly on silicon without an intervening layer of silicon dioxide. The further functionalization and patterning of these SAMs are important because these methods extend the potential range of applications of SAMs on silicon. We demonstrated how these monolayers could be patterned by assembling an amide-terminated surface with a small



**Figure 9.** (a) We functionalized anhydride-terminated SAMs with allylamine to yield an olefin-terminated SAM. This SAM was immersed in a solution of the Grubbs' first generation catalyst for 30 min in a glovebox. The wafer was removed, rinsed, and immersed in norbornene to yield a polynorbornene surface. SEM micrographs of (b) a 2D grid and (c) parallel lines of SAMs exposing polynorbornene are shown.

molecule, a polymer, and a catalyst that was used to grow a polymer from the surface. These methods are generally applicable and will allow other, more functional surfaces to be assembled and patterned on silicon for applications in the areas of electronics, (bio)chemical sensors, microchemical systems, nanoscience, and beyond.

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