

Stability Study of Self-Assembled Monolayers on Silicon(111)

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Abstract

Monolayers on H-Si(111) were formed thermally using decene and 10-bromodecene. Samples were subjected to 100 percent humidity in order to induce oxidation for upwards of three weeks. The ability of bromine to bind to the Si(111) and inhibit oxidation through steric hindrance was intended to be analyzed. Atomic force microscopy (AFM), x-ray reflectivity (XRR), and x-ray photoelectron spectroscopy (XPS) were used to help characterize the monolayers and to compare the amounts of oxidation. AFM showed the step formation that is characteristic of H-Si(111), and oxidation could also be seen. When XRR was used to determine the physical characteristics of the monolayer, including the height, surface roughness, monolayer and silicon interface roughness, and chain packing density, it showed that the decene monolayer formed, but the 10-bromodecene monolayer did not. Measurements taken using XPS showed that the relative amounts of carbon absorbed to the surface increased over a period of 19 days, with a thin physisorbed monolayer forming from adventitious hydrocarbons present in the air. Lastly, it was seen that the decene monolayer on Si(111) inhibited oxidation.

Introduction

Nanoscale fabrication promises to set the stage for our future, yet more work must be done before this future is fully realized. Of particular importance to many fields, including molecular electronics, is the addition of organic monolayers to a silicon surface.^{1,2} The most common application of these monolayers is in the field of biosensors,^{1,3} but other possibilities exist. Uniting silicon, a common component of electronics and computers, with organic materials and biology will create a transition from the electronic world to the biological world at the most basic levels. This will allow us to develop novel detection devices and revolutionize many fields.

Monolayers grown on hydrogen-terminated Si(111) present a unique area of interest because of their potential properties, which include being atomically flat. A hurdle for the technology entering the mainstream is the long- and short-term stability of the surfaces. H-Si(111) readily oxidizes in air,⁴ changing the surface of the H-Si(111) to SiO_x. Silicon oxides form an insulating barrier between the organic layer and the silicon, hindering future devices.³ Adding

other molecules that protect the Si(111) by capping off the potential oxidation sites is a simple way to avoid the problem of oxidation.⁴ Using bromine molecules to bind to the Si(111) may be an efficient way to delay oxidation.

Background

Over the past decade manifold ways to create organic monolayers on hydrogen-terminated silicon have been developed, ranging from thermal addition,^{5,6,7,8} using UV light,^{9,10,11} peroxides,⁵ Grignard and alkyllithium reactions,³ electrochemical reactions,⁴ and scribing.¹² A commonality of many of these methods is the use of a free radical mechanism.^{5,6,7,9,10,11} One technique is to form a monolayer through an olefin addition. The initiator causes a hydrogen atom to break away from the Si(111), leaving a radical that then attacks the olefin. The double bond breaks as it takes a hydrogen atom from a neighboring silicon molecule, and this chain reaction continues along the length of the silicon.¹³ Using heat or UV light as an initiator can be a safer and more versatile method than harmful peroxides.⁷

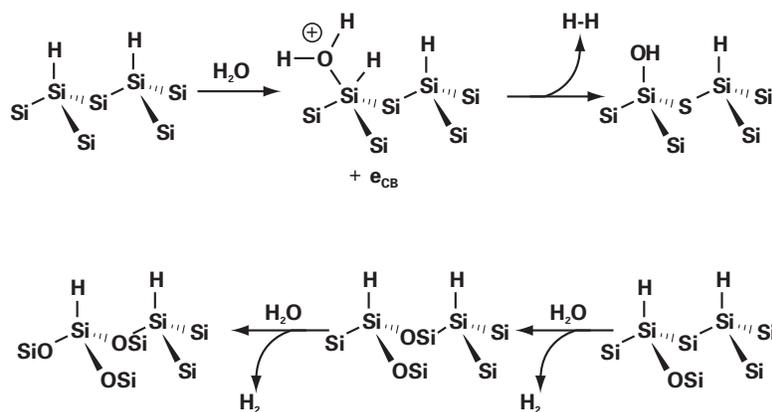


Figure 1: Mechanism of oxidation from water present in the humidity in the air.³

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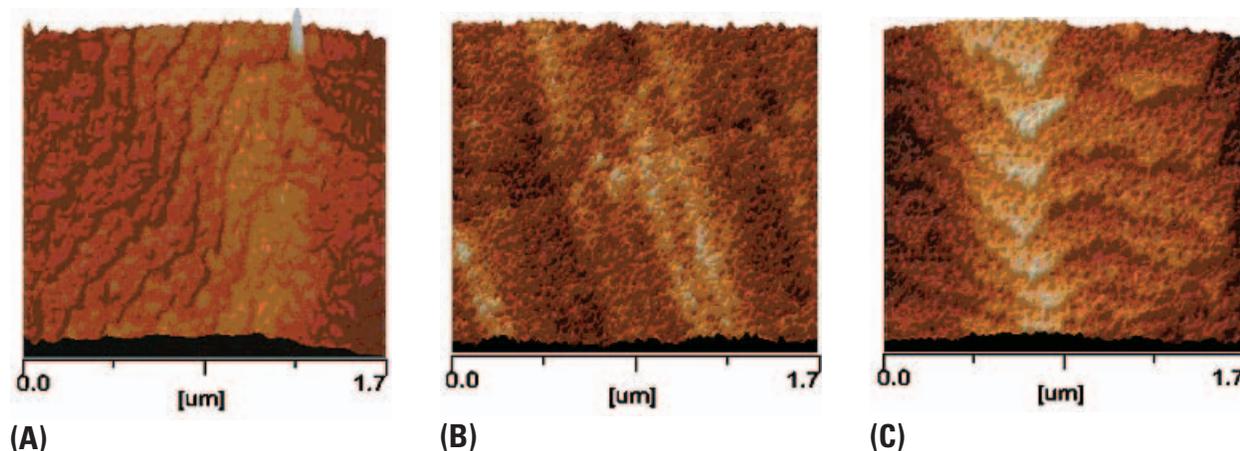


Figure 2: 1.6 μm x 1.6 μm AFM images of (a) H-Si(111), (b) decene monolayer on Si(111), and (c) 10-bromodecene monolayer on Si(111). Each shows the step morphology that is characteristic of H-Si(111) and ensuing monolayers.

Though hydrogen-terminated Si(111) readily oxidizes in open air, a monolayer can make the sample more resistant, even though oxidation will still take place.^{4,5,14} To prevent oxidation, the sample would have to be in an oxygen-free environment or not have any oxidation sites. One potential way to reduce the number of oxidation sites is through a halogenation of the silicon. It was recently shown that when bromine is present on the alkene chain, the bromine can detach and covalently bond to the silicon during UV treatment.⁹ The monolayer and the halogens minimize oxidation by blocking potential oxidation sites.^{3,15} Both are sufficient in size to sterically block molecules and make it more difficult for oxidation to take place.

Oxidation can take place through an oxidizing agent^{4,16} as well as through exposure to water vapor in the air.^{3,17} Figure 1

shows the oxidation mechanism. To induce as much oxidation as possible without using an oxidizing agent, the samples were placed in a chamber with 100 percent humidity. The amount of oxidation increases with the amount of water in the air, so the samples underwent more oxidation than they would in the same amount of time in ambient air.¹⁷

Approach

In order to fully characterize the monolayers and their oxidation, XRR, XPS, and AFM were used. Each technique provides certain advantages to view the results; their combined use gives qualitative and quantitative results.

Sample Preparation

The Si(111) samples were etched and passivated to leave only terminal hydrogens.¹⁸ During this process the samples were

placed at sharp angles within the solutions to minimize bubble formation. Bubbles on the surface can cause etch pits that make the surface no longer atomically flat, hindering uniform monolayer formation.¹⁹

Monolayer Formation

Past research has shown that a diluted solution can be used to form a dense monolayer.²⁰ An 8 percent mixture of 10-bromodecene and mesitylene was used, while the decene was neat. All solutions and samples were kept in a nitrogen environment until their exposure to humidity to prevent any extraneous oxidation. Heat was chosen to induce the free radical formation due to the high volatility of decene and 10-bromodecene. A unique cleaning procedure was used to remove physisorbed materials from the surface.

Humidity Exposure

After formation, the monolayers were placed in a sealed container with 100 percent relative humidity. The humidity was created when nitrogen was bubbled through water into the container. Samples were kept for up to three weeks inside the chamber to allow for as much oxidation as possible.

Analysis

AFM produces a localized true topographical image of the surface. Although it gives no chemical information on the sample, it does produce sub-1 Å resolution on the z-axis and 20 nm lateral resolution of the surface. AFM gives the morphology of the monolayer over a small location.

XRR gives a quantitative image of the entire uniform surface through information obtained from the reflected x-rays and Fresnel's equations.²¹ It yields the monolayer's height, surface roughness, monolayer and silicon interface roughness, and chain packing density. XRR analyzes the entire surface of the sample, while AFM and XPS only look at a small location. XRR is not readily able to measure the amount of oxidation that takes place, so another method was used to achieve that measurement.

XPS uses monochromatic x-rays to release electrons through the photoelectric effect to determine the relative ratio of the molecules within the sample. Though the exact number can be determined, it is very difficult and thus was not attempted. The oxidation level is measured by comparing the ratios of the silicon oxide and silicon between samples.

Results and Discussion

AFM images are shown in Figure 2. All three images demonstrate the expected step morphology. Because the step formation is seen throughout both monolayers, it is assumed that if a monolayer is present, it is conforming to the H-Si(111) morphology. Images were also taken after oxidation, with one shown in Figure 3. The white bumps seen across the surface are oxidation sites.

Figure 4 shows the reflectivity results for the fresh decene monolayer (a), the fresh 10-bromodecene monolayer (b), the fresh H-Si(111) sample (c), and the H-Si(111) sample exposed for 21 days (d), respectively. The peak seen for the fresh decene sample is indicative of a monolayer of uniform thickness, but this peak is not seen for the fresh 10-bromodecene sample. This means that a uniform 10-bromodecene monolayer did not form and the main purpose of this study cannot be accomplished, but secondary conclusions are drawn. As expected, no monolayer is present on fresh H-Si(111), but after 21 days of 100 percent humidity, a peak is seen, implying the presence of some kind of layer. Because the same sample was tested each time, the only variable is the amount of exposure time. XPS leads to similar conclusions about the consistency of the monolayer.

Table 1 shows the XRR analysis for decene monolayer and the H-Si(111) before and after oxidation. As expected, the decene sample showed no significant increases in the surface roughness. In contrast, the H-Si(111) sample changed drastically, showing that more oxidation took place on the sample without a monolayer. This means that the monolayer inhibited oxidation, lending support to the assumption that filling empty locations on the surface with bromine will inhibit oxidation even more.

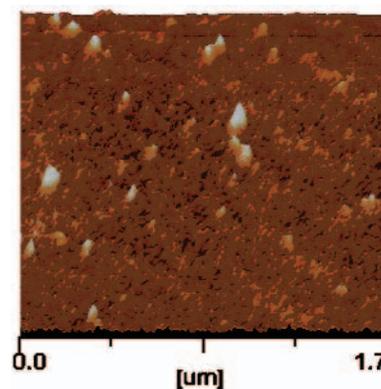
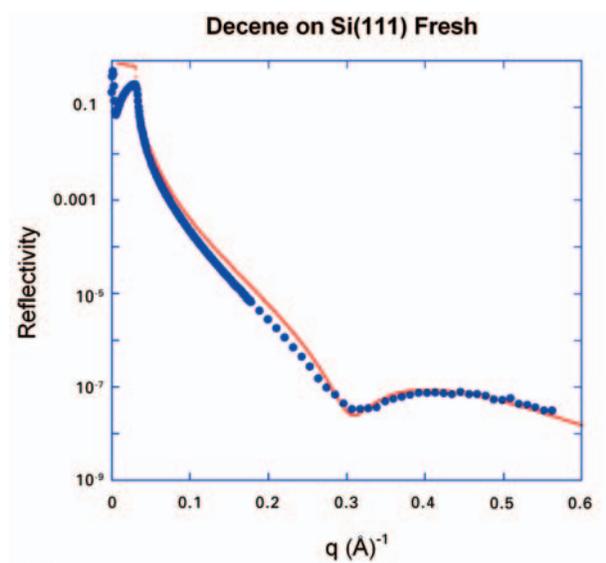
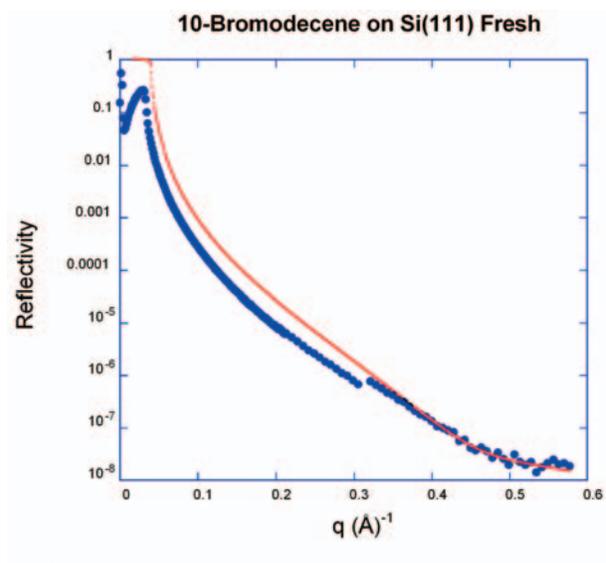


Figure 3: The morphology of a decene monolayer on Si(111) that has undergone oxidation. The light spots are sites of oxidation. The step formation can also be seen.

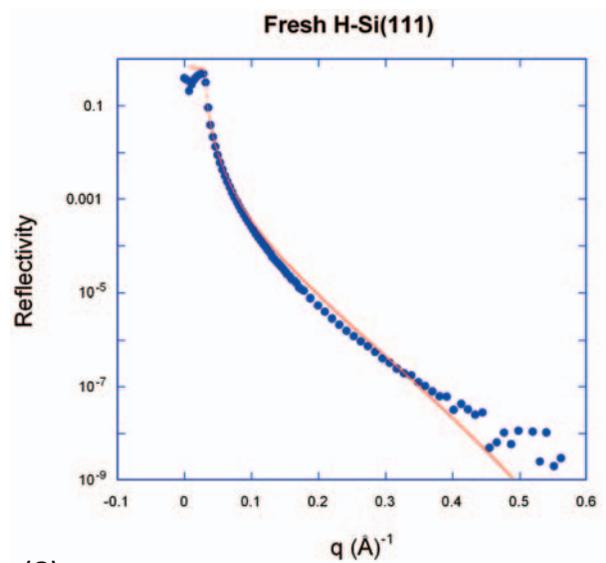
Stability Study of Self-Assembled Monolayers on Silicon(111) (*continued*)



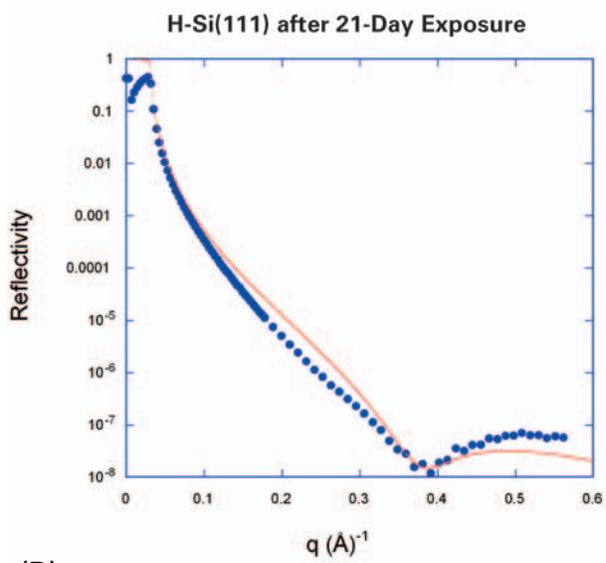
(A)



(B)



(C)



(D)

Figure 4: XRR results. Circles are actual data and lines are theoretical fits.

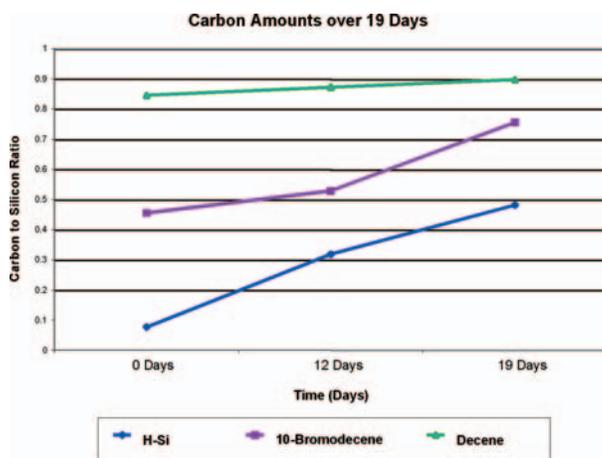


Figure 5: XPS results showing increases in the relative amounts of carbon on each sample's surface.

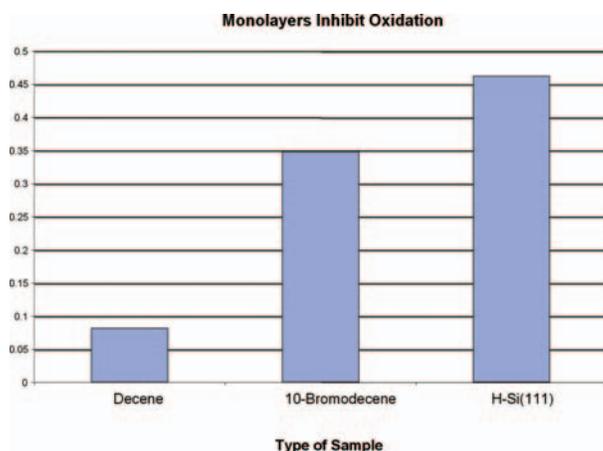


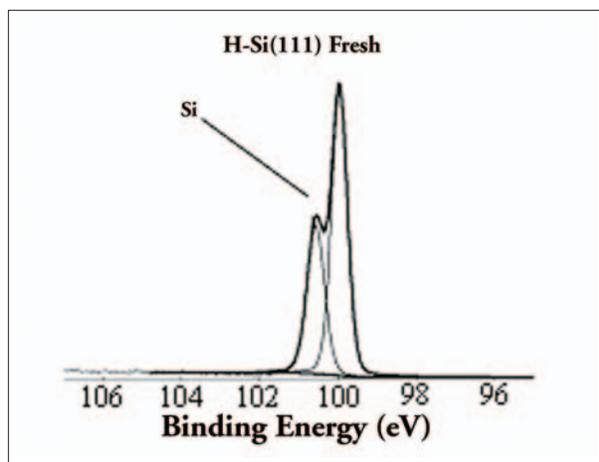
Figure 6: The amount of oxidation at 19 days for each sample.

Through XPS, it was seen that on the 10-bromodecene samples that underwent humidity testing, no bromine was present, but it was present on the fresh sample. This, combined with the fact that no monolayer was seen, means there are problems with the monolayer preparation. Potential problems could involve the bromine reacting with excess olefins instead of the Si(111) surface, or the solutions being too dilute. To resolve this issue, the preparation solution should be passed through a column and undergo NMR testing to determine its composition. Also, both monolayers should be prepared from neat solutions to remove any extraneous variables. X-ray fluorescence should also be used to further analyze the samples' consistency.

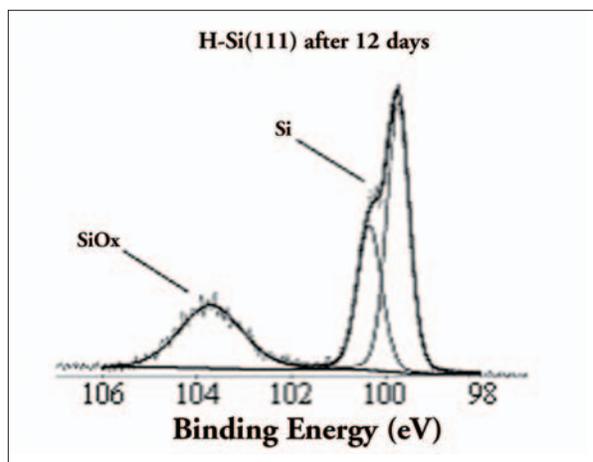
Figure 5 shows that relative amounts of carbon on the surface increased on all samples. It is believed that these are from adventitious hydrocarbons that physisorbed to the surface from the air. This may explain why a monolayer was seen on the H-Si(111) surface after 21 days of exposure. Figure 6 shows the amount of oxidation that took place after 19 days. Decene underwent the least amount of oxidation, as expected. The monolayer that was seen inhibits the oxidation process (Figure 1). Compared with the partially blocked 10-bromodecene and the fully open H-Si(111) surfaces, the oxygen molecules cannot readily reach the surface.

Lastly, in Figure 7 actual XPS peaks are shown for the H-Si(111) fresh (a), at 12 days (b), and at 19 days (c). The area of the SiO_x peak compared with that area of the Si peak gives the relative amount of oxidation. As expected, the SiO_x peak increases over time, showing that rampant oxidation occurs without the presence of a monolayer.

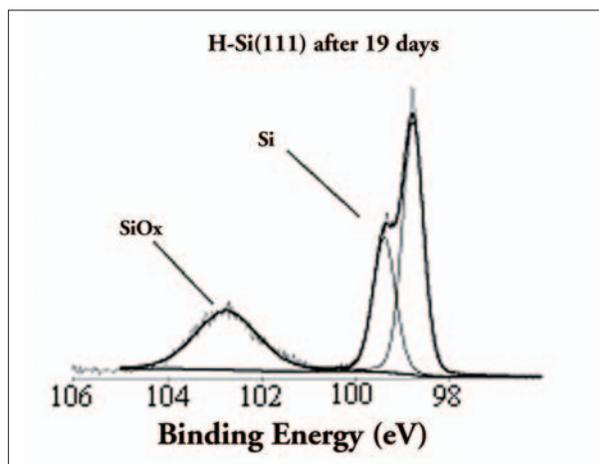
Stability Study of Self-Assembled Monolayers on Silicon(111) (*continued*)



(A)



(B)



(C)

Figure 7: Actual Si2P XPS peaks showing the progress of oxidation over time.

Table 1: XRR data analysis showing the determined film electron density (ρ_f), film thickness (t), Si-film interface roughness (σ_s), and film-air interface roughness (σ_i) and the calculated molecular tilt angle (α) and monolayer coverage (Θ).

Sample	ρ_f ($e/\text{\AA}^3$)	t (\AA)	σ_s (\AA)	σ_i (\AA)	α ($^\circ$)	Coverage Θ (ML)
Decene	0.26	10	4.5	2	40.7	.41
Fresh H-Si(111)	-	-	5	-	-	-
21-day H-Si(111)	0.25	7.7	4.5	1	-	-
21-day decene	0.25	10	5	2.3	-	-
21-day 10-bromodecene	0.17	9.9	5	2.3	-	-

Conclusions

Although the main goal of the study was not achieved because the 10-bromodecene monolayer was not properly formed, other things of interest were seen. A secondary conclusion, which agrees with current literature,^{4,5,14} is that a monolayer inhibits oxidation through steric hindrance. Also, adventitious hydrocarbons from the air attach to the surface over time, which can change the surface significantly. More work is needed to determine the oxidation-inhibiting effects of monolayers formed with halogens present. The monolayer preparation has to be perfected and further testing must be done to discover exactly what is taking place.

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