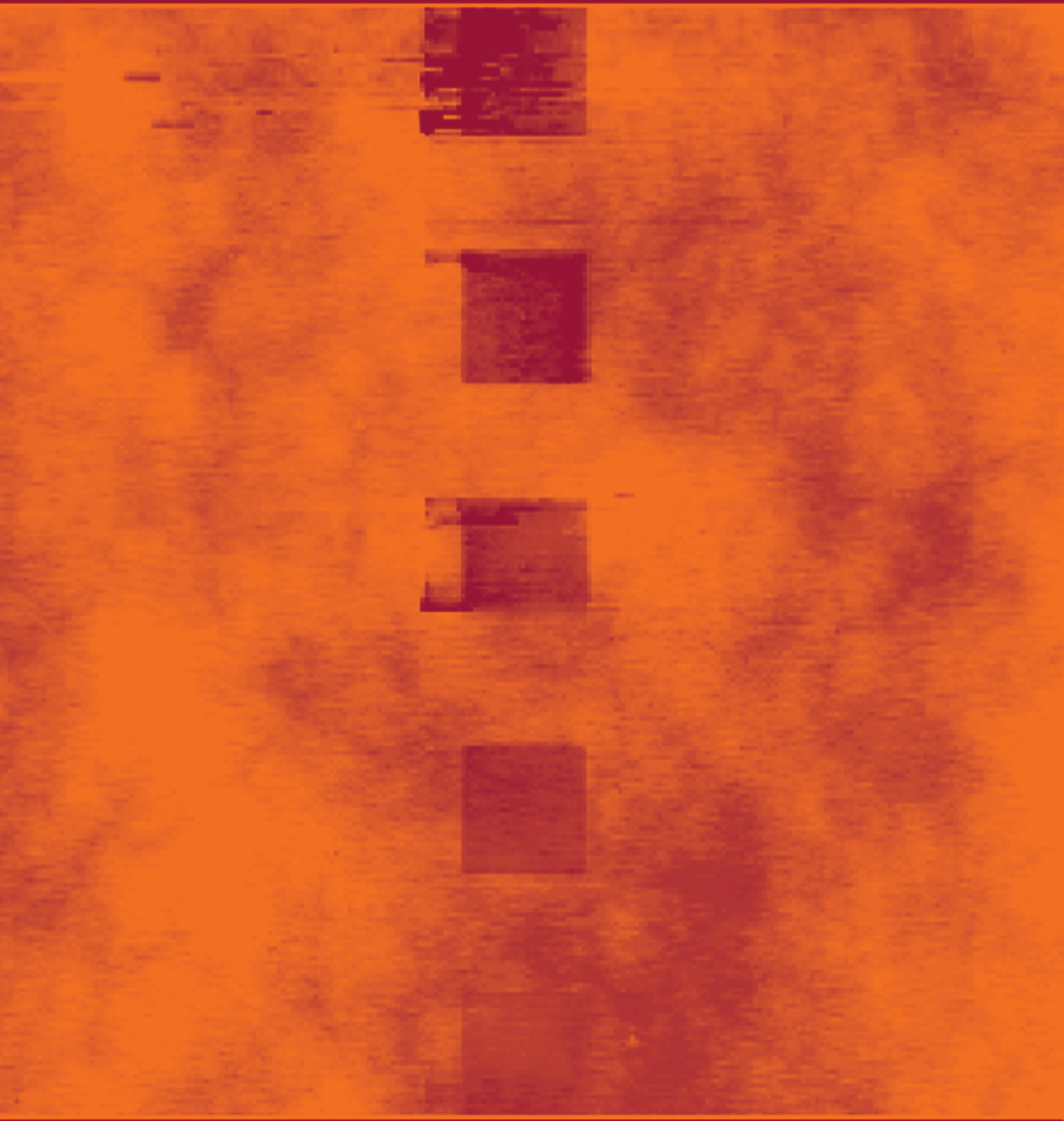
FIOs on Si-H topography



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Using Field-Induced Oxides as a Negative Resist in Bromostyrene and Octadecene Hydrosilylation Reactions

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Abstract

A self-assembled monolayer of an alkene or alkyne can be applied to a hydrogen-passivated silicon surface using UV hydrosilylation. This research shows that field-induced oxides can be used as a negative resist to selectively prevent bromostyrene attachment, providing a means of nanopatterning organic molecules on silicon. The negative resist effects were confirmed using AFM topography, lateral force microscopy, and secondary ion mass spectrometry. Evidence suggests that field-induced oxides also selectively replace bromostyrene on silicon. An attempt to apply a similar monolayer with octadecene was inconclusive.

Introduction

Nanopatterns on silicon surfaces have many potential applications in biological and chemical sensing, and also in nanoscale electronics. Field-induced oxide (FIO) patterns generated on a hydrogen-passivated silicon surface using an atomic force microscope (AFM) can be a powerful tool to selectively pattern self-assembled monolayers (SAMs). The chemical contrast offered by FIOs allows them to act as masks for SAMs that are generated via hydrosilylation reactions. This research shows that FIOs act as a barrier to bromostyrene and octadecene SAMs created by UV hydrosilylation onto Si(111). Barrier properties of the FIO pattern will be demonstrated by several surface-characterization techniques: topography images from an AFM, lateral force microscopy (LFM) images from an AFM, and secondary ion mass spectrometry (SIMS) composition maps and spectra. This research looks for differences between FIOs made before a bromostyrene SAM is applied and those made afterwards on the same sample, and it will attempt to create partial octadecene and bromostyrene monolayers on the same sample. The purpose of this research is to develop a multifunctional silicon surface that can be extended via chemical reactions to create a multifunctional biosensor.

Background

Higashi et al. developed a method for wet chemical hydrogen passivation of silicon, which etches away the native oxide and replaces it with a hydrogen monolayer.[1] It has been shown that the ammonium fluoride used as the final etch in this process must be deoxygenated in order to prevent the formation of oxygen etch pits.[2] An alkene or alkyne SAM can then attach to the Si-H using one of several methods, such as UV hydrosilylation. It has been suggested that UV hydrosilylation works by generating excitons in the silicon, weakening the Si-H bond and allowing a Si-C bond to form when immersed in an alkene or alkyne.[3] The molecule attaches to the surface and takes a hydrogen atom from a neighboring silicon atom, and a monolayer forms that propagates by a self-avoiding random walk on the Si(111) surface.[4] Other methods of attaching a monolayer include free radical initiation,[5] thermal initiation,[6] and mechanical scribing using an AFM while a sample is covered in a liquid compound.[7]

Dagata et al. discovered a way to use a scanning tunneling microscope (STM) to pattern oxides onto passivated silicon surfaces.[8] It was found that an AFM can achieve similar patterning by applying a positive voltage to the sample surface with respect to the AFM tip, which generates an oxidized region via an anodic reaction.[9] A water meniscus forms between the tip and the sample below it, and oxidizing agents are brought to the tip-sample junction when voltage is applied. The resulting FIO can be detected by AFM topography scans since it is higher than the surrounding Si-H due to volume expansion. FIOs can act as positive resists, allowing SAMs such as octadecyltrichlorosilane (OTS) to be applied selectively to them.[10] They can also resist alkaline etching, which lowers the surrounding Si-H and allows the creation of three-dimensional nanostructures.[11] However, no research was found that has utilized FIOs created before an SAM as a negative resist that prevents the SAM from forming on the FIO.

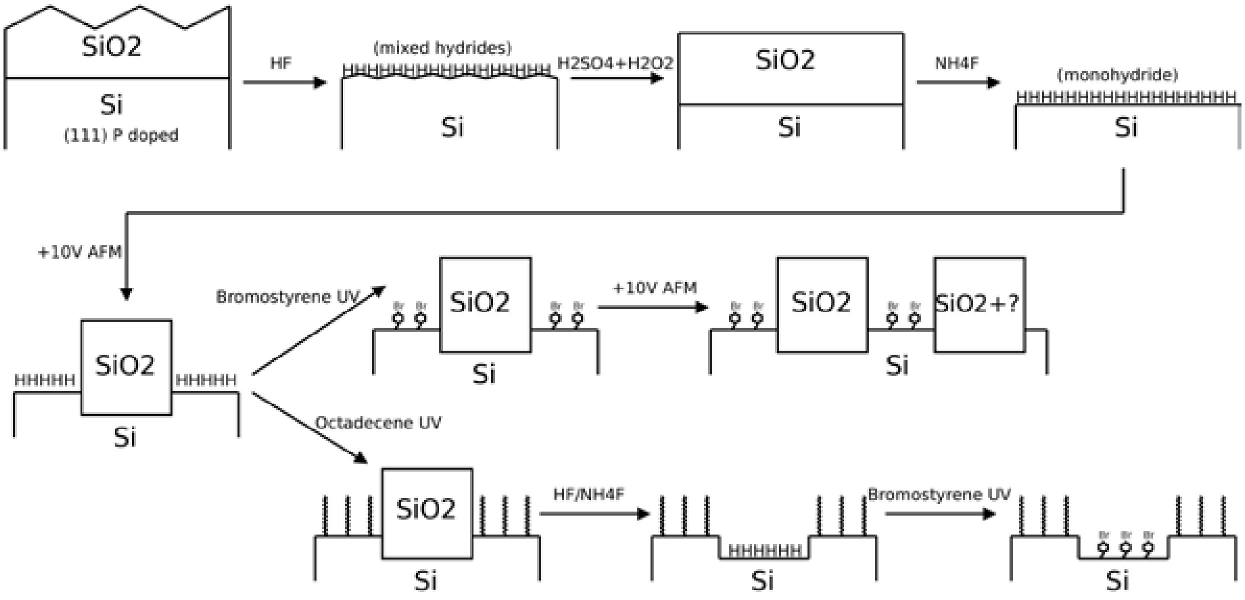


Figure 1: Flowchart of the procedure.

LFM can be used to detect FIOs because it can measure local chemistry changes.[12] LFM differentiates surfaces by showing the amount of friction a surface exerts on the cantilever tip. However, cross-talk between topography and LFM measurements can exist because of misalignments of the AFM cantilever tip, which also causes differences between trace and retrace images. Ensuring the tip is well aligned minimizes this cross-talk. Errors can be corrected by measuring the difference between forward and backward directions of the same scan for different misalignments and extrapolating to zero misalignment.[13]

FIOs can also be formed after a monolayer is applied. Ara et al. formed an FIO under a dodecene monolayer on Si. An OTS SAM was applied on top of the FIO while retaining Si-dodecene around it.[14] It was found that although the Si-H surface does not prevent oxidation indefinitely, and repeated scans with an AFM can lead to its degradation, the dodecene SAM provides better protection and is more durable. However, due to AFM height measurements, it was not clear if there was some dodecene remaining along with the OTS on the FIO. In the next step, bromine was used as a chemical tag that can be detected via SIMS to determine how much bromostyrene remains after an FIO is formed on it. This was compared with how well an FIO formed on Si-H resists the bromostyrene SAM.

On another sample, Ara et al. selectively etched away the FIOs to recreate an Si-H surface, and an octadecene SAM was attached to this surface.[14] This work applies bromostyrene on the etched FIOs and octadecene on the rest of the surface and uses SIMS to determine whether there is a clear separation between the bromostyrene and octadecene.

Basu et al. used an array of techniques to characterize the bromostyrene SAM made by UV hydrosilylation.[15] AFM topography has been used to show that steps on the Si-H surface were preserved after replacing hydrogen with bromostyrene. X-ray reflectivity was used to find an SAM thickness of 0.85 nm, and bromine atomic coverage was found to be 50%. No studies of bromostyrene SAMs using SIMS were found. The octadecene SAM made by UV hydrosilylation has also been characterized by ellipsometry, and its height was found to be 1.6 nm.[4] SIMS results of an octadecene SAM on Si(100) formed by thermal initiation indicate significant C_xH_y, SiC_xH_y, and

SiOH peaks.[16] AFM voltage has also been applied to the octadecene SAM on Si(100), resulting in silicon oxide growth under the SAM, which was characterized using SIMS.[17] Increases in the C_xH_yO and C_xH_yN peaks and decreases in the SiC_xH_y peaks were found on the modified regions. This project will attempt to obtain similar results to confirm that the octadecene and bromostyrene SAMs have formed on their respective surfaces.

Approach

A flowchart of the procedure is shown in Figure 1. Two samples were cut from a wafer of n-type P-doped Si(111) with miscut < 0.25° from Virginia Semiconductor. A diamond-tip microindenter was used to mark off a 50 µm x 50 µm region on each sample where the FIOs were placed in order to subsequently relocate the area with the AFM. For passivation, the samples were dipped in 0.5% HF for 60 sec to remove the rough native oxide, put in a 3:1 mixture of H_2SO_4 and H_2O_2 for 15 min to remove organic contaminants and create a flat oxide, put in argon-sparged 40% NH_4F for 10 min to remove the oxide and create an Si-H surface, and rinsed in argon-sparged nanopure water for 60 sec. The samples were rinsed in argon-sparged nanopure water for 5 sec between each step. The samples were put under a Thermomicroscopes CP Research AFM, and the silicon tip was connected to virtual ground through a 1MΩ resistor. By applying +10V to the sample relative to the tip, several FIO squares 2–10 µm in size were created inside the 50 µm square on each sample. The tip velocity was 2 µm/s, the force of the tip was set at 10 nN, and the relative humidity was

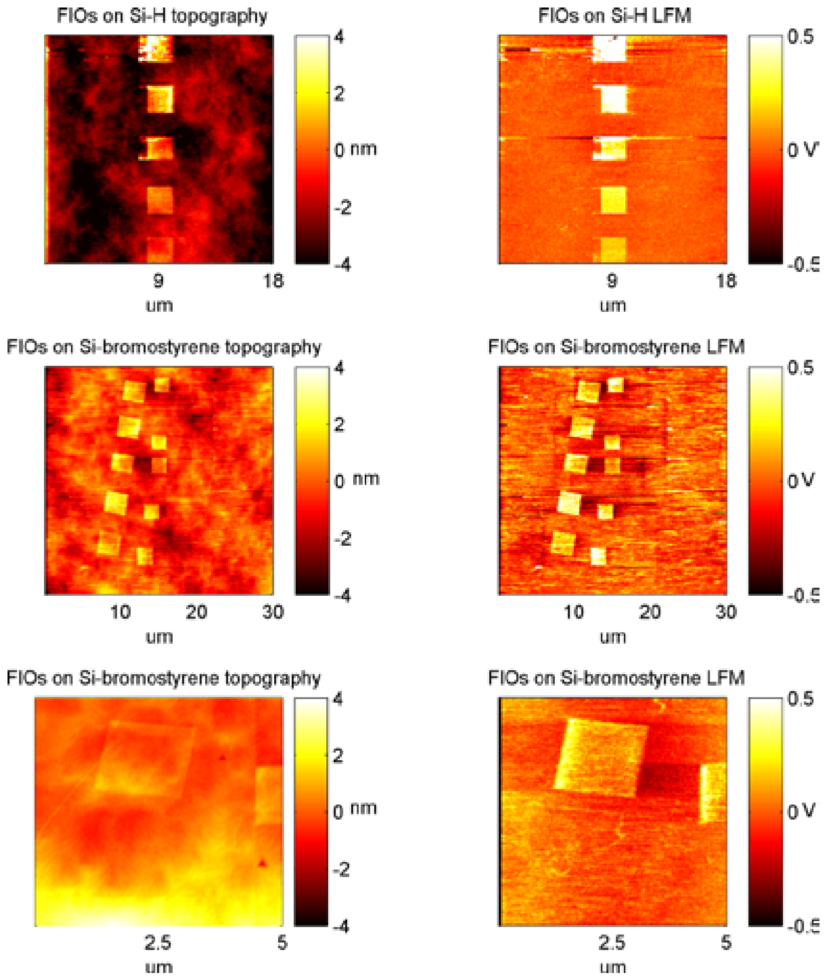


Figure 2: AFM images of 2 µm square FIOs. Top: FIOs on passivated Si. Middle: FIOs on the left were applied before UV hydrosilylation with bromostyrene, and FIOs on the right were applied after. Bottom: Close-up of middle images with high-resolution scanner so that steps can be seen in topography.

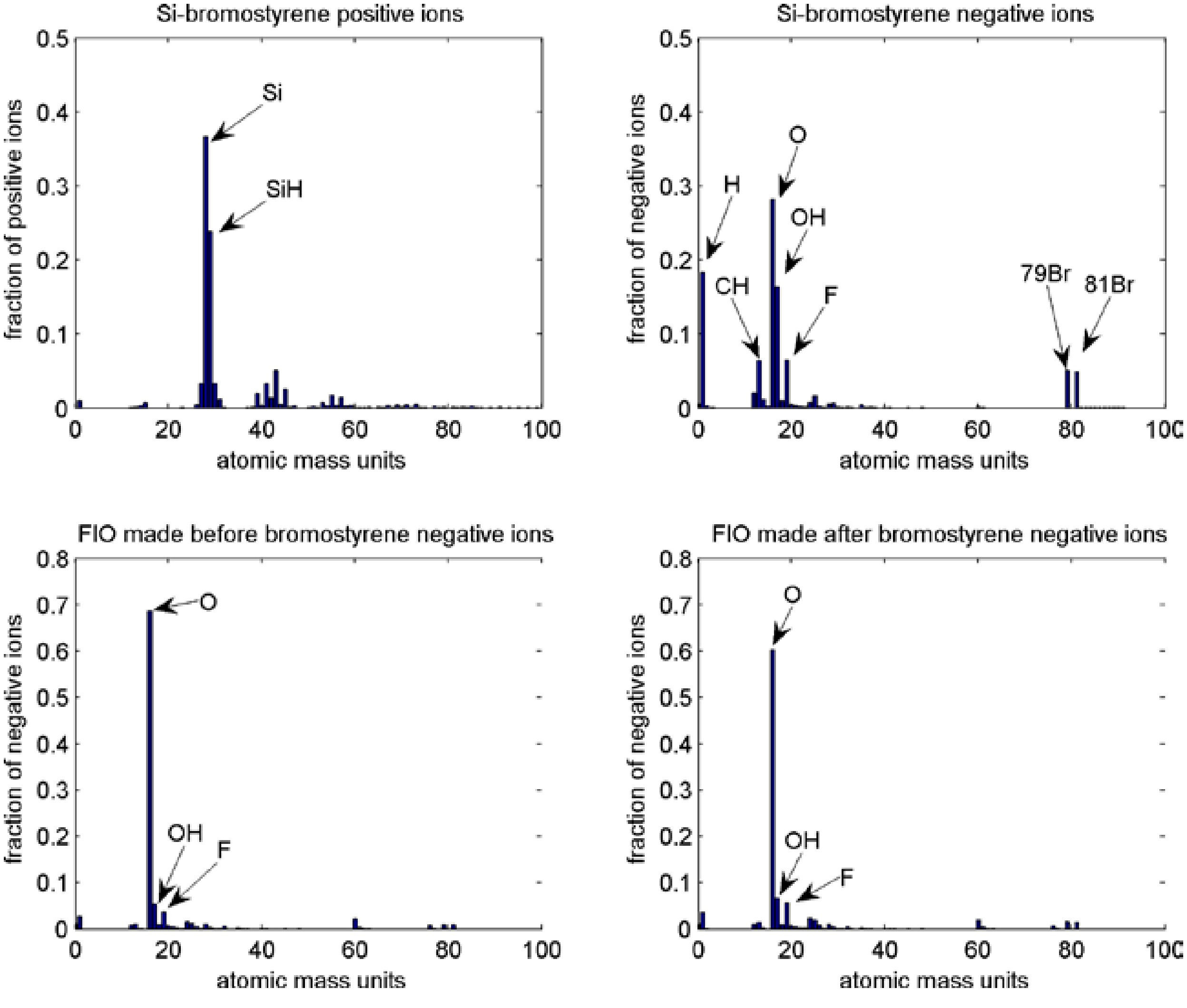


Figure 3: SIMS spectra showing positive and negative spectra of Si-bromostyrene, and negative spectra of an FIO applied before bromostyrene UV hydrosilylation and an FIO applied after bromostyrene.

kept between 35% and 40% by using a variable humidity nitrogen glove box that encases the AFM setup.

On the first sample a bromostyrene monolayer was applied by covering the sample with 4-bromostyrene in a Pyrex container and shining a UV pen lamp on it inside a glovebox for 24 hr. The lamp was placed 1–2 cm from the sample. To remove physisorbed bromostyrene, the sample was then sonicated twice for 7 min each time in chloroform, and twice for 7 min each time in toluene. This sonication procedure was used because SIMS results showed a significant amount of physisorbed bromostyrene on unpassivated silicon with an oxide layer after shorter sonications. New FIOs were then applied next to the previous ones using the AFM as described above. On the second sample an octadecene monolayer was applied by covering the sample with 1-octadecene and shining a UV pen lamp on it. The sample was sonicated in the same way as the first sample, then put in either argon-sparged 40% NH_4F for 5 min or 1% HF for 30 sec. It was then rinsed in argon-sparged nanopure water for 60 sec to remove the FIOs and replace them with a hydrogen monolayer. Then 4-bromostyrene was applied as above in order to apply bromostyrene exclusively to where the FIOs were, but exposure time to UV was shortened to 1.5 hr. The sample was then sonicated using the same procedure outlined earlier.

AFM topography and LFM images in contact mode, and topography images in tapping mode were taken of both samples after every step. Tapping mode is less likely to damage the surface but does not provide LFM. Both a 5-μm high-resolution scanner and a 100- μm large-area scanner were used, and scans

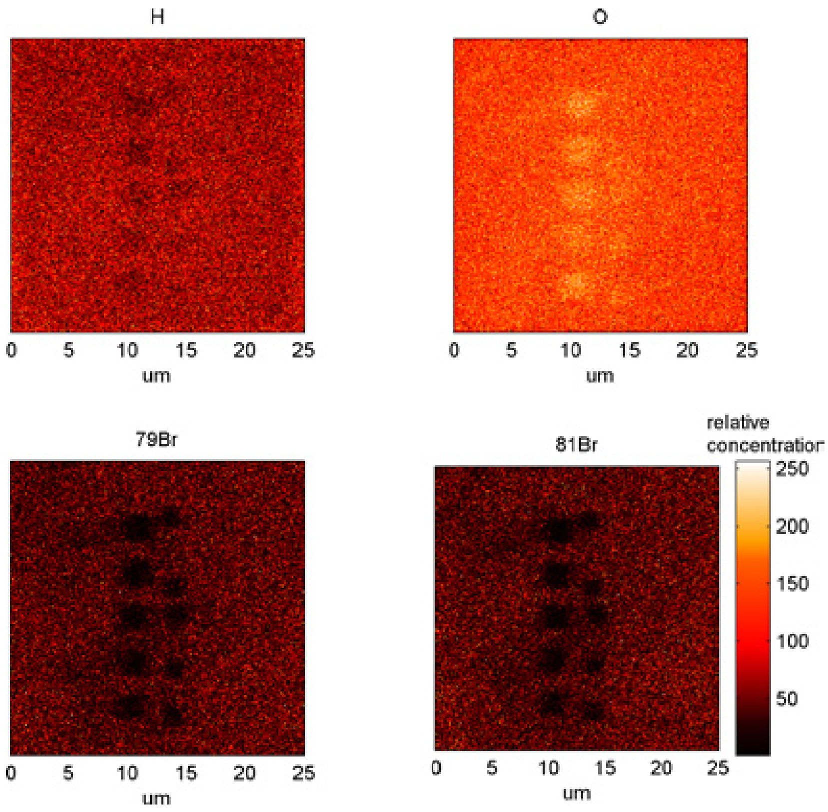


Figure 4: SIMS mapping of the amount of different elements in and around FIOs on Si-bromostyrene. FIOs on the left were applied before bromostyrene, and FIOs on the right were applied after.

Applied layer	Substrate	Applied layer – substrate difference	
		Topography (nm)	LFM friction (mV)
FIO (sample 1)	Si-H	2.70	585
FIO before bromostyrene	Si-bromostyrene	0.98	445
FIO after bromostyrene	Si-bromostyrene	0.99	502
FIO (sample 2)	Si-H	1.70	200
FIO	Si-octadecene	1.65	264
Si-H	Si-octadecene	-0.54	150
Si-bromostyrene	Si-octadecene	-0.51	46.3

Table 1. AFM topography and LFM measurements obtained in tapping mode averaged over five 2 μm squares.

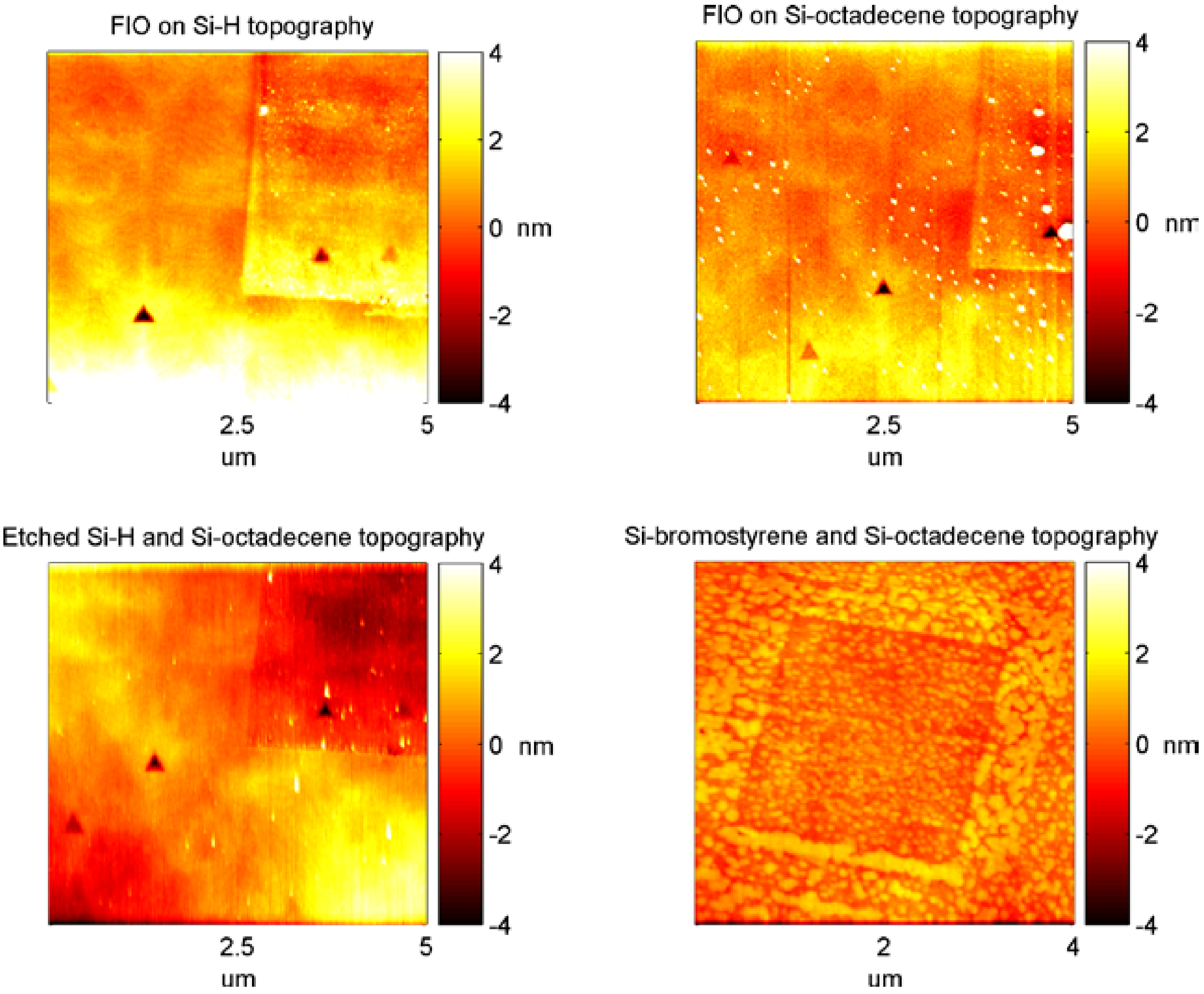
were taken using both x and y fast-scan directions. Attempting to align the tip perfectly perpendicular to the tip holder minimized cross-talk. Heights and LFM contrast were usually measured in tapping mode with the y fast-scan direction. Finally, a Physical Electronics PHI TRIFT III ToF-SIMS was used to compare spectra inside the FIOs and on the SAMs, and to obtain composition maps of relevant elements such as H, O, and Br in the area surrounding the FIOs. SIMS bombards a sample with ions, causing it to emit secondary ions, which are measured to determine surface composition.

Results and Discussion

AFM topography of the passivated silicon showed no etch pits and clear steps, confirming that passivation took place. Topography shows the FIOs to be higher than the Si-H substrate, and LFM contrast between them are clearly visible. FIOs were more visible for slow tip velocities and high relative humidities. It was observed that, as more FIOs were created using the same tip, it would become duller and the FIOs created would be less visible. Even when these factors were constant, the visibility of each FIO somewhat varied, between about 1 and 5 nm high.

The average height of the FIOs decreased by about 1.7 nm on the first sample after bromostyrene was applied to the sample (Table 1). This decrease is attributed to both the added height of the bromostyrene to the Si-H and to the partial surface and subsurface oxidation of the Si-H. However, the bromostyrene height of 0.85 nm obtained by X-ray reflectivity[15] cannot be directly compared with AFM height because of the different factors that influence each one. There was also an average LFM voltage contrast of 585 mV between the FIOs and the Si-H, indicating that the hydrophilic FIOs have greater friction than the hydrophobic Si-H. This contrast decreased only slightly to 445 mV after bromostyrene was applied, suggesting that bromostyrene did not attach to the FIOs. Steps could also be seen on the bromostyrene SAM, indicating that any bromostyrene existing on the surface was in a flat chemisorbed monolayer (Figure 2). After more FIOs were applied on the Si-bromostyrene, there were no significant differences observed in either topography or LFM between the old and the new FIOs.

The greatest amount of negative ions obtained by SIMS on the sample with a bromostyrene SAM, in decreasing order, were O, H, HO, F, CH, ^{79}Br, and ^{81}Br (Figure 3). When spectra are obtained by scanning FIO regions, a higher amount of O and a lower amount of Br and H were observed. Mapping on and around the FIOs also showed these results and allowed each FIO to be visible due to the contrast in these elements (Figure 4). This confirms that the FIOs were actually there and had replaced the hydrogen passivation, and that the FIOs were effective masks against the bromostyrene. There were few significant differences observed in either the mapping or the spectra of the FIOs made before and after the bromostyrene reaction, the only notable one being less oxygen on the FIOs created afterwards. This, combined with the lack of differences in topography and LFM, suggests that when voltage is applied by AFM onto Si-bromostyrene, FIOs do not form above or below the bromostyrene. Instead, FIOs replace the bromostyrene, producing FIOs similar to those made on Si-H. The greatest amounts of positive ions on the sample were Si, SiH, and various hydrocarbon chains. No contrast was seen on the FIOs when mapping with these positive ions. Also, ion count versus time plots showed that the amount of H decreased significantly and the amount of O increased as scanning time



FIO on Si-H topography

FIO on Si-octadecene topography

Etched Si-H and Si-octadecene topography

Si-bromostyrene and Si-octadecene topography

Figure 5. High-resolution AFM images of a sample undergoing octadecene and bromostyrene reactions. Top left: FIO applied on passivated Si. Top right: Same sample after undergoing UV hydrosilylation with octadecene. Bottom left: Same sample after then being etched by 1% HF. Bottom right: Different sample that underwent all the same steps, then UV hydrosilylation with bromostyrene.

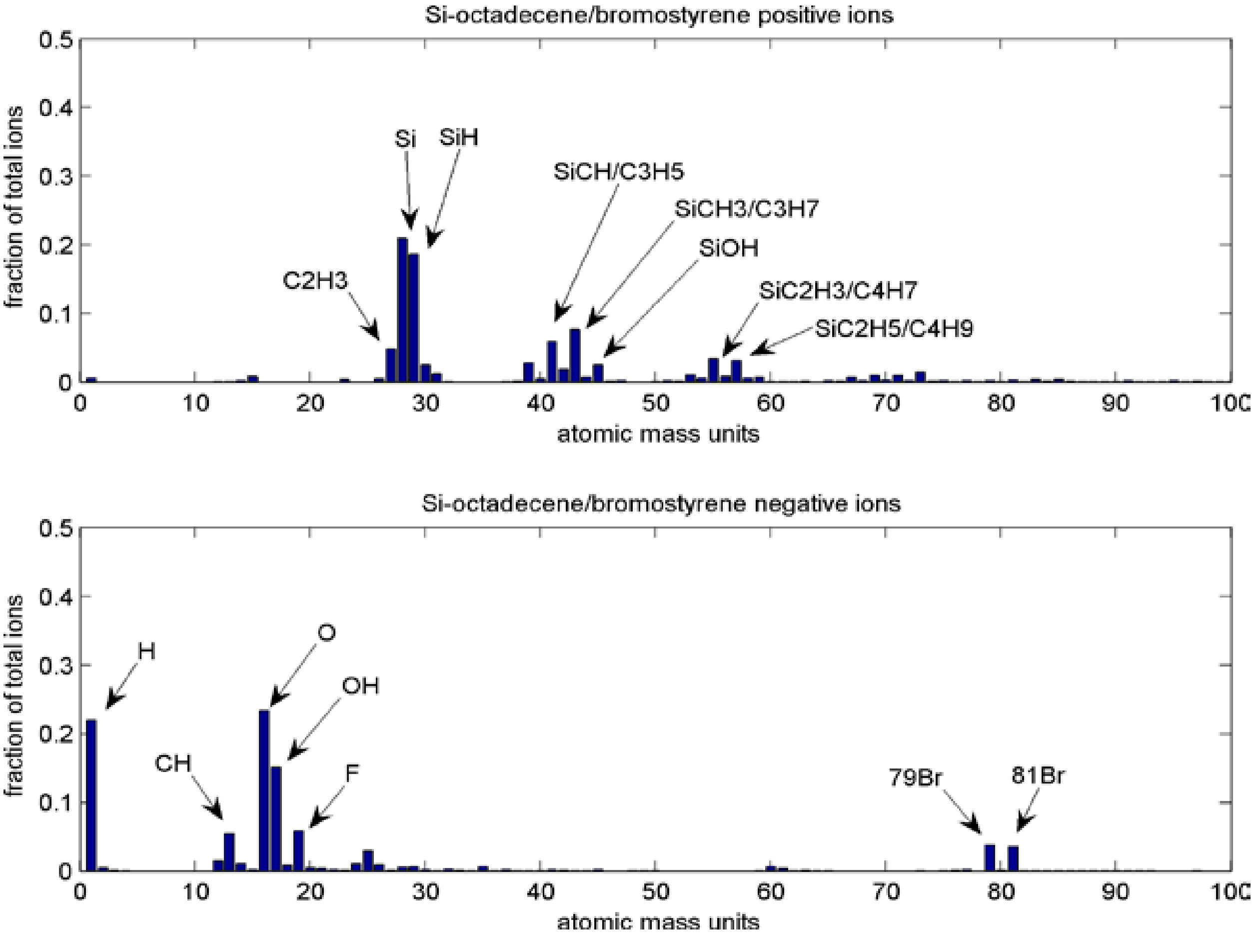


Figure 6. SIMS spectra of the substrate that underwent UV hydrosilylation with octadecene and then bromostyrene, showing mixture of octadecene and bromostyrene.

on an area increased. After 7 min of scanning a 25-µm area, the H signal had decreased about 50%. This suggests that some subsurface oxidation occurred on the sample.

On the second sample, steps could be seen on the octadecene SAM, indicating that either octadecene had been chemisorbed in a monolayer, or that octadecene had been mostly removed by sonication (Figure 5). FIO heights did not change after octadecene was applied. This could indicate that little octadecene attached to the Si-H, or that it attached evenly to both the Si-H and the FIOs. Upon etching with HF, the etched areas became lower than their surroundings, showing that only the FIOs had been etched. Steps could be seen in the etched areas, confirming that the passivation had worked. The height etched away is greater than that of the original FIO, showing that the applied AFM voltage in fact oxidized the silicon instead of just depositing a layer on top of it. After bromostyrene was applied to these squares, the height difference did not change noticeably. Afterwards, SIMS spectra of the substrate showed the presence of both the hydrocarbon chains from octadecene and the Br isotopes from bromostyrene (Figure 6). It is possible that both octadecene and bromostyrene are attached to the surface due to incomplete attachment of octadecene in the first hydrosilylation or replacement of some octadecene by bromostyrene.

Conclusion

FIOs created by positive AFM voltage were shown to be effective masks against a bromostyrene SAM applied by hydrosilylation on passivated Si(111). FIOs created on an existing bromostyrene SAM were found to have similar height, friction, and composition characteristics as FIOs created on passivated Si(111). While UV hydrosilylation was able to form a bromostyrene monolayer detected by height, friction, and composition, it was not able to form a clearly defined octadecene monolayer. A future direction for this work may be to use iodostyrene instead of octadecene, followed by bromostyrene, to form a multifunctional sample with two styrenes in different locations.

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