Selective Chemistry on Scanning Probe-Patterned Silicon Surfaces

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Abstract

This research project explores two different processes that can be used to pattern organic molecules on silicon. In the first process, hydrogen-terminated silicon surfaces were anodized in nanometer scale with a contact-mode atomic force microscope (AFM). Anodization was done by applying a positive bias voltage to the surface with respect to a conducting cantilever. Following anodization, patterned areas were selectively modified by allyltrichlorosilane. Ring Opening Metathesis Polymerization (ROMP) was then performed on the modified patterned areas in order to observe selective deposition of a norbornene polymer. Tapping mode AFM was used to image and quantify the selectively patterned substrate. In the second process, an organosilane monolayer was formed from a precursor vapor IPTMS onto the surface of silicon oxide. IPTMS has been shown to behave as an adequate linker between SiOx and proteins. X-ray photoelectron spectroscopy (XPS) was used to determine the relative extent of silanization of IPTMS on the SiOx substrate. Tapping mode AFM was used to image surface topography.

Introduction

Nanoscale patterning of organic and biological molecules is an active research area. Applications such as nanoscale polymer brush arrays, DNA nanoarrays, and protein nanoarrays all have potential use in nanoscale device fabrication and biological screening applications. For example, the gene chip is a device that enables the quick identification of DNA nucleotide sequences. The chip consists of multiple arrays of dots, each dot containing a unique DNA sequence, so every permutation of a particular chain length is represented. This assembly is referred to as the probe. A solution containing an unknown sequence is placed on the array, and hybridization occurs between the target and the probe with the complementary sequence.

DNA microarray hybridization can be used for many purposes, such as detecting gene expression and screening samples for single nucleotide polymorphism. Current gene chips suffer from complications due to a low practical limit on the oligonucleotide chain length. Each probe consumes an area of several microns on a side. For very long chains, the number of possible genetic permutations is too large to use microarray technology. If DNA probes could be patterned on a smaller scale, this would significantly increase the probe density of an array, allowing permutations of longer oligonucleotide sequences to be patterned in a smaller region. The ultimate goal of this research is to pattern DNA arrays, polymer bushes, and protein arrays on the nanometer scale.

Background

With the recent development of soft-lithography techniques, the miniaturization of microarray technologies has become a heavily studied field. This research focuses on the miniaturization of microarray technology down to the nanoscale.

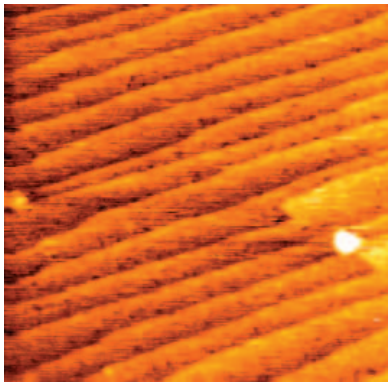


Figure 2: Atomically flat silicon(111) surface imaged by contact mode AFM.

A multidisciplinary approach is required to accomplish this miniaturization. The fabrication of a nanoarray has been broken into four steps: (1) substrate preparation, (2) nanopattern development by scanning probe lithography, (3) organic linker deposition on patterned surfaces, and (4) loading of biological molecules (if required). A practical method is needed to prepare a suitable substrate. Hydrogen-terminated silicon(111) was chosen as a substrate because it is compatible with existing microfabrication technology, and the surface can be selectively anodized with a scanning probe microscope.

Many articles have been published addressing hydrogen passivation. Early work was carried out by Yablonovitch[1] et al., who detected the existence of Si-H on a surface using Fourier transform infrared spectroscopy (FTIR) in attenuated total reflection mode (ATR). Later Higashi[2] et al. and Jakob[3] et al. developed an effective technique for obtaining atomically flat Si(111) surfaces with monohydride termination by treatment in a buffered HF or ammonium fluoride solution. Atomic images of a surface taken with scanning tunneling microscopy (STM) showed defects such as etch pits on terraces and kinks on step edges. A more reliable method of producing relatively defect-free silicon(111) was later developed by Sakaue[4] et al., who discovered that dissolved oxygen in NH4F caused atomic-scale defects on hydrogen-passivated silicon. This problem was solved by heating NH4F to 72°C, significantly reducing the concentration of dissolved oxygen. The result was an almost defect-free surface. Once researchers began to study hydrogen-terminated silicon using scanning tunneling microscopy, it was discovered that a local electric field resulted in oxidation of the surface.[5] This process, referred to as field-induced oxidation (FIO), can also be performed using an atomic force microscope. In FIO, a cantilever is brought into contact with the surface, and ambient moisture condenses, forming a water meniscus between the tip and the sample. This causes OH anions to concentrate at the surface and H- anions to be released. The result is selective areas of surface oxides surrounded by hydrogen-terminated areas. The earliest report of tip-induced oxidation was by Dagata et al.[5] Dagata and many others have demonstrated the use of FIO as a method of growing an oxide layer on hydrogen-terminated silicon substrates. Using FIO, oxide patterns can be generated on most semiconductors or metals. Most groups to date have used these oxides as a mask. Upon characterizations

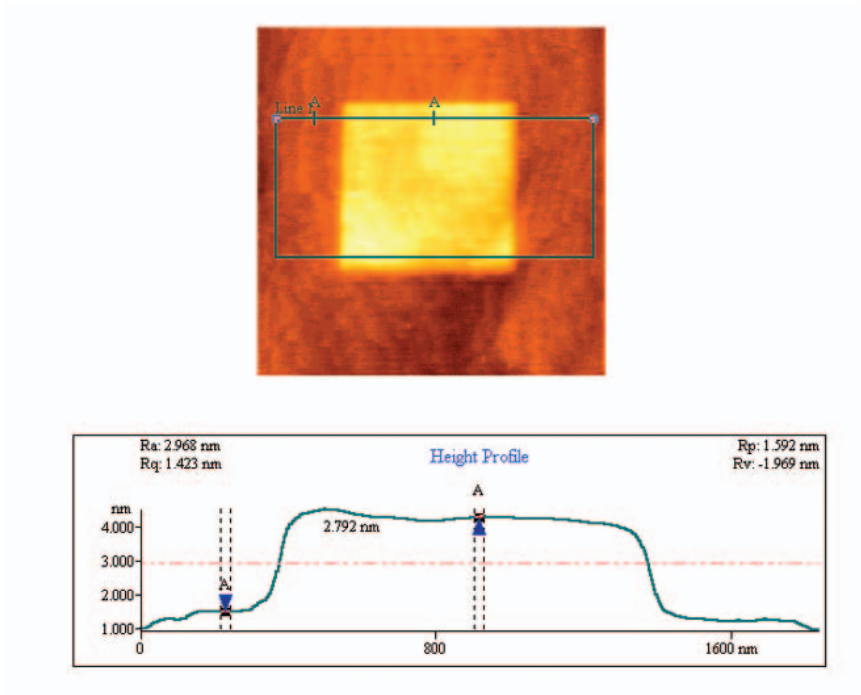


Figure 3: Height differential of FIO pattern on hydrogen-terminated silicon.

of FIO patterns using lateral-force microscopy, it can be shown that the patterns have high lateral friction, suggesting that the surface is hydrophilic (Figure 1). If that is true, then the oxide is likely —OH terminated, and this fact can be used for selective deposition of molecules that react with Si-OH moieties but not with Si-H moieties, such as silane coupling agents. Once the oxide pattern is developed, a method is needed to transition from silicon chemistry to organic chemistry. This is done through selective deposition of an organic linker molecule. Much research has been done on deposition of organosilane monolayers. One of the first was done by Maoz and Sagiv.[6] Due to the selective nature of the organosilane bonding, it is believed that a chlorosilane or a methoxysilane will bind specifically to oxide surfaces and not to hydrogen-terminated surfaces.

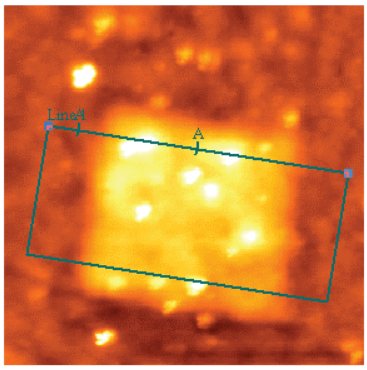
Organosilanes chosen have the silane group at one end and another reactive group at the other end. Once the silane adsorption step is complete, a reaction can be carried out using this reactive group. This includes DNA and protein immobilization and ring-opening metathesis polymerization (ROMP).[7,8]

Approach

The goal of this project is to make microarrays significantly smaller than presently available. To achieve this goal, an effective method of selectively patterning organic molecules on a surface is needed. This method can be broken into four steps. The first part is to prepare a substrate that can be easily patterned. Second, small areas of the substrate are selectively patterned using scanning probe lithography. Third, a linker molecule is adsorbed onto the patterned substrate. Finally, DNA or proteins are tethered to the linker, or a polymer can be grown from the surface using ROMP.

Substrate Preparation

For the substrate, hydrogen-terminated silicon(111) samples were prepared using the passivation technique developed by Sakaue.[4] The native oxide layer was stripped off by submerging a silicon sample in a 0.5% solution of hydrofluoric acid for 45 seconds. The sample was then placed in a 70:30 mixture of sulfuric acid:hydrogen peroxide mixture for 20 minutes to grow a new oxide. Finally, the sample was placed in a 40% aqueous solution of ammonium fluoride for 20 minutes to strip this new oxide layer. Aqueous ammonium fluoride contains dissolved oxygen, which is known to attack silicon. Argon was bubbled into



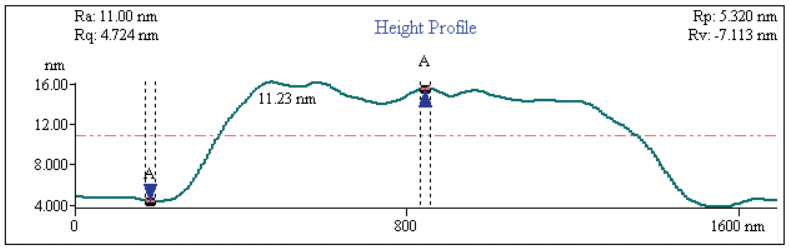


Figure 4: Height differential after norbornene polymerization.

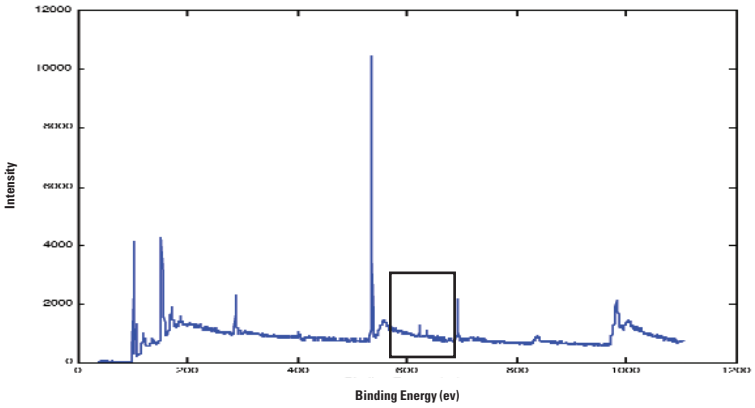


Figure 5: XPS Iodine Peak intensity for 10-minute exposure to EDA and 10-minute exposure to IPTMS. Iodine peak appears at approximately 680 ev.

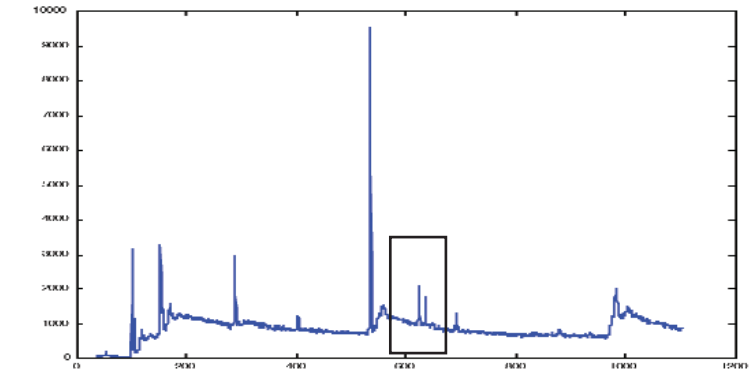


Figure 6: XPS Iodine peak intensity after 30 minutes of EDA exposure and overnight IPTMS exposure.

Rough Scan-45

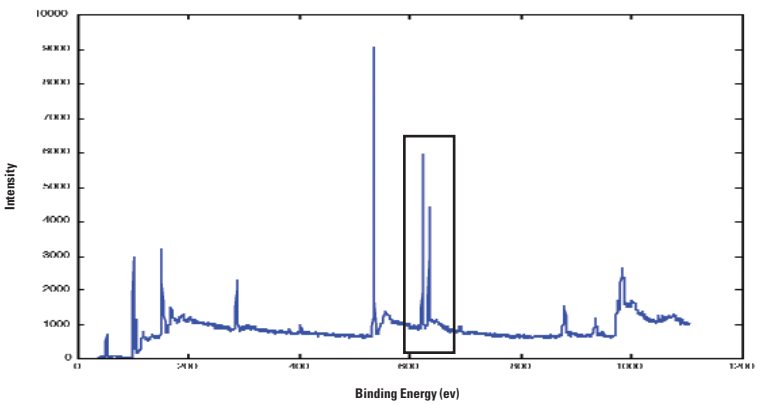


Figure 7: XPS Iodine peak intensity after overnight exposure to IPTMS.

the solution to displace this dissolved oxygen. After etching, residual ammonium fluoride was removed by dipping the sample in argon-bubbled, nano-pure water. This procedure resulted in a relatively defect-free hydrogen-terminated silicon sample (Figure 2).

Once the substrate was prepared, an atomic force microscope was used to selectively grow oxide patterns on the passivated silicon(111) as demonstrated by Dagata.[5] A 10 V bias was applied to the sample with the tip held at ground potential to create nine 1 x 1 µm boxes. The tip of the cantilever moved at 4 Hz, and the relative humidity was 48.7%. An organosilane was deposited to transition from the inorganic silicon chemistry to the organic molecular chemistry. Chlorosilanes and methoxysilanes are both suitable linkers. Both chemicals have a wide variety of functional groups, but their distinguishing characteristic is that they bind specifically to oxides and will not adhere to hydrogen-terminated silicon. This allows the selective deposition of these molecules. The deposition of the linker molecule was studied in two ways. The first method used an AFM to grow 1 x 1 µm oxide squares on hydrogen-terminated silicon samples. These samples were then taken into a nitrogen glove box. The patterned samples were dipped in a 1% solution of dry* triethylamine in toluene and allowed to dry. They were then place in a 1% solution of allyl trichlorosilane in dry toluene for one hour. A polymer was then grown from this surface using ROMP. After rinsing in toluene, the sample was dipped in a 0.5% solution of Grubb's catalyst (a ruthenium catalyst) and rinsed in toluene. Finally, the sample was immersed in a norbornene monomer in methylene chloride solution.

In the second method of studying linker deposition, monolayer deposition of silane coupling agents from the vapor phase was studied without using scanning probe-patterned substrates. Vapor-phase silanization is being explored because molecular interactions in the liquid phase can result in out-of-plane polymerization and poor surface coverage. The silicon was oxidized by immersing it in a 1:1 solution of HCL and methanol for 15 minutes. The sample was then sonicated in deionized water for five minutes and quickly immersed in a 70:30 solution of sulfuric acid:hydrogen peroxide mixture for 20 minutes. Excess chemical residue was removed with a five-minute sonication in deionized water. The sample was inserted into a holder and placed within a vapor-deposition chamber. Too much water on the surface of the oxidized silicon promotes out-of-plane polymerization, so the excess water was removed from the surface by heating the sample to 160°C for 30 minutes. The sample was then cooled to room temperature and dosed with ethylenediamine (EDA) for 10 to 30 minutes, followed by (3-iodopropyl)-trimethoxysilane (IPTMS) for times ranging from 10 minutes to 15 hours, following the method of Kanan[9] et al. IPTMS was chosen because the iodine group binds to cystine residues of proteins and polypeptides, making it a potentially useful linker. In later dosing experiments, the EDA dose was omitted to test its importance.

A final future step will be to bind protein to the IPTMS. This will be done using green fluorescent protein (GFP) synthesized at the University of Illinois by pipetting a dilute solution onto the surface. Once this has been demonstrated, the experiment can be repeated on a scanning probe-patterned substrate. Because the

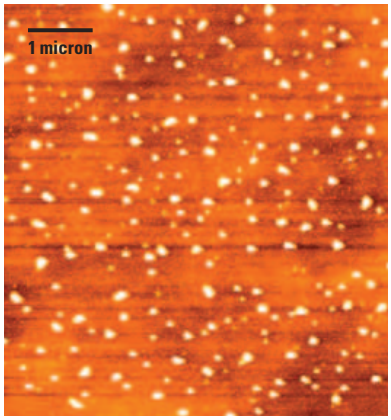


Figure 8: Out-of-plane polymerization after overnight exposure to IPTMS in VDC.

** The use of the word "dry" indicates that steps were taken to remove trace amounts of water contamination.*

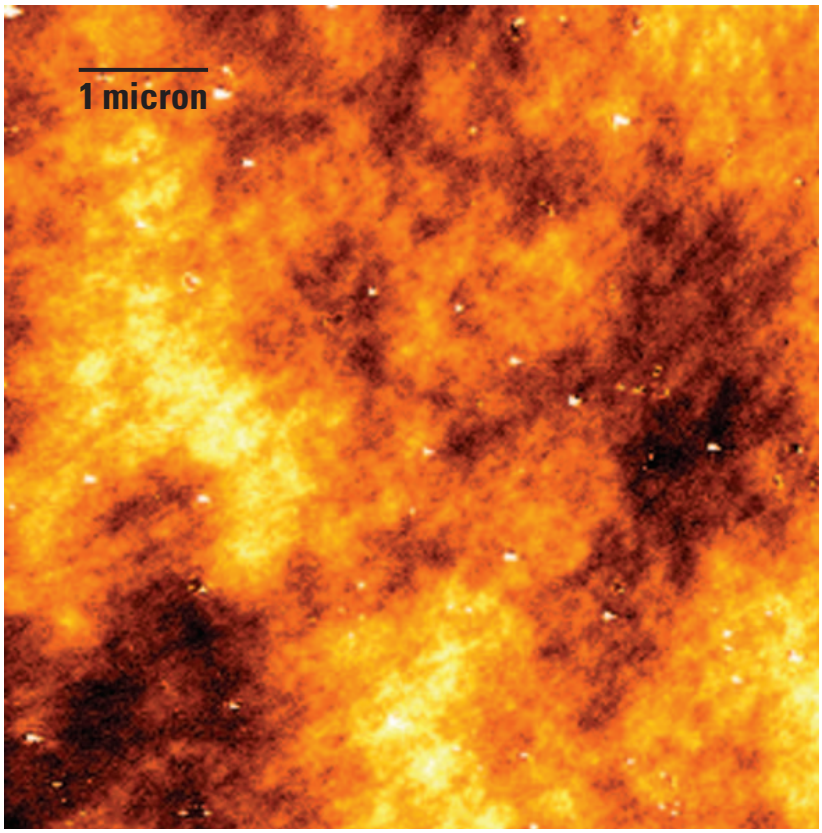


Figure 9: Reduced out-of-plane polymerization due to two-hour exposure to IPTMS.

linker molecule will be selectively patterned, the protein should selectively bind to the linker molecule, effectively patterning a biological molecule. The protein should be highly detectable using fluorescence microscopy.

Results

Substrate Preparation
For this step, the results were identical to those reported in previous journal articles. Using AFM, the distinctive step and terrace topography of hydrogen-terminated silicon was observed. A substrate with very few defects and very little contamination was successfully produced (Figure 2).

Patterning
Patterning also went according to literature. Upon analysis of the silicon substrate with AFM, it was shown that a 2 nm growth of oxide had been patterned. This oxide did not resemble its surroundings (no step and terrace feature), effectively showing the successful growth of an oxide layer (Figure 3).

Patterning of Polynorbornene
Topographic cross-sections reveal a noticeable height increase on the oxide layer after ROMP (Figure 4). However, there is also polymer growth on the hydrogen-terminated surface. Our preliminary assumption was that the polymer was simply adsorbed onto the surface. The first attempts at removing the adsorbed polymer consisted of a 15-minute sonication in methylene chloride. Little polymer was removed, and the sonication damaged the surface. The second attempt at removing adsorbed polymer involved boiling in tetrahydrofuran (THF) for 10 minutes. The norbornene polymer proved extremely soluble in this

solvent. Subsequent imaging by AFM revealed that all polymer had been removed from the surface by boiling in THF, including in the oxidized regions. This was likely due to the preceding sonication, which cleaved the bonds attaching the polynorbornene chains to the patterned substrate. Subsequent ROMP experiments on patterned substrates were followed by rinsing in THF. While the amount of adsorbed polymer was greatly reduced, appreciable adsorption on the hydrogen-passivated background persisted. The most likely cause of adsorbed polynorbornene on the hydrogen-terminated background is random oxidation during exposure to ambient conditions. To solve this problem, samples will be immersed in a solution of chlorotrimethylsilane to try to cap any oxides that may have spontaneously formed prior to FIO. This should cap spontaneous oxides and eliminate undesired sites of silanization.

Monolayer Deposition of IPTMS

The binding of IPTMS to an oxidized surface showed significant improvement. X-ray photoelectron spectroscopy (XPS) spectra were taken from many samples. In early vapor-phase deposition experiments, the chamber was evacuated to 10 millitorr, and the sample was dosed with EDA and then IPTMS until the pressure within the vacuum rose to 2,000 and 1,000 millitorr, respectively. Each vapor was allowed to stay in the chamber for 10 minutes, with a pump-down in between steps. Upon analysis with XPS, it was discovered that the iodine peak was not substantial enough to represent monolayer coverage[10] (Figure 5). This result was attributed to inadequate vapor pressure or dosing time of the IPTMS. Later experiments attempted to solve this problem by exposing the sample to the vapor for extended periods of time. The base was allowed to stay in the chamber for 30 minutes, followed by 15 hours of exposure to IPTMS. Using XPS analysis, it was shown that the iodine intensity was greatly increased but was still not representative of monolayer coverage (Figure 6). Recent literature suggested that silanization would be improved with the addition of the base EDA. As a test, the EDA dose was eliminated, and IPTMS was allowed to stay in the chamber for 15 hours. XPS spectra showed a great increase in iodine peak intensity (Figure 7). This was more representative of monolayer coverage.[9] Upon analysis using intermittent contact mode AFM, it was discovered that out-of-plane polymerization had occurred (Figure 8). This problem was solved by reducing the exposure time of IPTMS to two hours. XPS analysis showed almost identical peak intensity to the 15-hour exposure, but careful analysis with intermittent contact mode AFM showed very little out-of-plane polymerization (Figure 9).

Future Direction

Subsequent experiments will involve binding GFP to the IPTMS functionalized surface and will be characterized by fluorescence microscopy. Experiments will also be conducted on hydrogen-terminated silicon (111) to ensure that this surface is not reactive toward IPTMS. All of the individual steps will be combined using scanning probe-patterned substrates to nano-pattern GFP on an FIO-patterned substrate.

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