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Patterning by Etching at the Nanoscale (PENs) on Si(111) through the Controlled Etching of PDMS

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Patterned polymer brushes were grown from organic monolayers on Si(111) using ring-opening metathesis polymerization catalyzed by the Grubbs' first generation catalyst. The Grubbs' catalyst reacted through cross metathesis with an olefin-terminated monolayer on Si(111) such that it was attached to the monolayer. Next, a polydimethylsiloxane slab patterned in bas-relief was placed on this surface to form microchannels. Undecenoic acid was added to the microchannels to react with and remove the Grubbs' catalyst from the surface exposed in the microchannels. Next, the microchannels were etched by tens of nanometers to several micrometers with F^-. This etching exposed fresh monolayers on the silicon terminated with the Grubbs' catalyst. A solution of bicyclo[2.2.1]hept-5-ene-2-carboxylic acid was added to the microchannels and polymer brushes grew by ring-opening metathesis polymerization only on the newly exposed surface. A range of polymer brushes with widths from 70 nm to several micrometers was fabricated. This method is exciting because an entire surface can be patterned simultaneously and it is not limited by the wavelength of light. Rather, the width of the polymer brushes is determined by the amount of polydimethylsiloxane that is etched from the microchannels. In addition, this method can be used to pattern surfaces inside of existing microchannels. These polymer brushes were characterized by a combination of methods including X-ray photoelectron spectroscopy, scanning Auger spectroscopy, scanning electron microscopy, and optical microscopy.

Introduction

Nanometer to micrometer wide patterns of well-defined organic compounds on surfaces have accelerated advances in nanoscience in fields ranging from medicine to molecular electronics.[1−9] These patterns allow for the spatial engineering of smart surfaces to display well-defined arrays of molecules that can recognize metals, DNA, RNA, or proteins in solution; act as molecular wires; or provide the basis for devices fabricated for molecular electronics. Numerous methods to pattern surface chemistries on the micrometer-size scale exist, but patterning surfaces with nanometer-sized dimensions is considerably more challenging. Current methods to pattern surfaces with nm-sized features of organic molecules include dip pen lithography,[10,11] electron-beam lithography,[12−14] focused ion beam lithography,[15,16] nanoimprint lithography,[17−19] and microcontact printing.[20] These methods are exciting alternatives to photolithography as they combine patterning on the nanometer-size scale with the placement of well-defined and tailored organic functional groups on a surface and exploit the opportunity to generate many patterns quickly without the need for new chrome masks to be manufactured. This combination of patterning on the nanometer-size scale with well-defined chemistries is critical for new applications in nanoscience.

In this article, we report a mild method to pattern polymer brushes from 70 nanometers to several micrometers from

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monolayers on Si(111) using ring opening metathesis polymerization (ROMP) catalyzed by the Grubbs' first generation catalyst. This method uses F^- to etch polydimethylsiloxane (PDMS) microchannels to pattern an entire silicon wafer with polymer brushes that are readily integrated with microfluidic systems. Although these polymers were decorated with carboxylic acids or anhydrides, a wide range of functional groups is possible because ROMP is insensitive to many functional groups. Recently, polymers have been synthesized with ROMP that exposed alcohols, carboxylic acids, Pd catalysts, anhydrides, esters, amides, sugars, ethylene glycols, and ethers, to name a few examples.[21−25] Clearly, ROMP is an important polymerization method that can be used to grow polymers displaying many functional groups. In this article, we choose to grow polymer brushes exposing anhydrides and carboxylic acids as these functional groups demonstrate our method and they can be further reacted in subsequent steps. We call this method "patterning by etching at the nanoscale," or PENs for short.

We choose to use PDMS microchannels and silicon for two reasons. First, silicon is the most important electronic material; yet methods to pattern and control its surface chemistry lag behind that of coinage metals and glass.[26−44] Combining the successes of nanotechnology with silicon technology will open up opportunities to fabricate materials with new properties that take advantage of the semiconducting properties of silicon.[45−53] Patterning with polymer brushes is exciting as they combine the selectivity of organic chemistry with the multiplying effect of polymers. Polymer brushes can be used to add more functional groups per unit area of surface than monolayers and still maintain atomic level control over surface chemistry. Second, PDMS microfluidic channels have gained widespread acceptance as a useful tool. Our work is exciting because we are growing well-defined polymer brushes inside of microfluidic channels that will allow their surface chemistries to be patterned from the nanometer to micrometer scales in new ways that will extend the applications of these microchannels.

Experimental Section

Materials. We purchased 10-undecanoic acid (98%), 48% HF, cyclooctene, bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (98% pure as an endo/exo mixture), norbornene, the Grubbs' first generation catalyst, and all solvents from Aldrich or Acros chemicals and used as received. Exo-7-oxa-bicyclo(2.2.1)-heptane-2,3-dicarboxylic anhydride was synthesized according to literature precedent.[54] Single-side polished Si(111) wafers (n-type) were purchased from Silicon Inc, Boise, ID.

Instrumentation. A Hitachi S-4000 scanning electron microscope was used to gather the SEM images. An accelerating voltage of 5 kV was used to image the patterns on the surface. A micromaster optical microscope with image-capturing software (Micron) was used to obtain the optical micrographs of the surface.

The samples were studied by XPS and scanning Auger spectroscopy using a Kratos Axis Ultra at the University of Iowa. For XPS, the dimension of the image area was 300 μm by 700 μm and the takeoff angle was 45°. The pass energy on the survey scan (0−1100 eV) was 160 eV. High-resolution scans of Si(2p) (92−108 eV binding energy), C(1s) (274−300 eV binding energy), O(1s) (523−539 eV binding energy), and F(1s) (680−696 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). For scanning Auger spectroscopy, the voltage was 5 kV and the lateral resolution was 200 nm.

Patterning of Polymer Brushes. We will describe how we patterned polymer brushes with Bu_4NF and bicyclo[2.2.1]hept-5-ene-2-carboxylic acid, this method was followed for all patterns. The Grubbs' catalyst was removed from a glove box, where it was stored under N_2 and exposed to ambient atmosphere. All further

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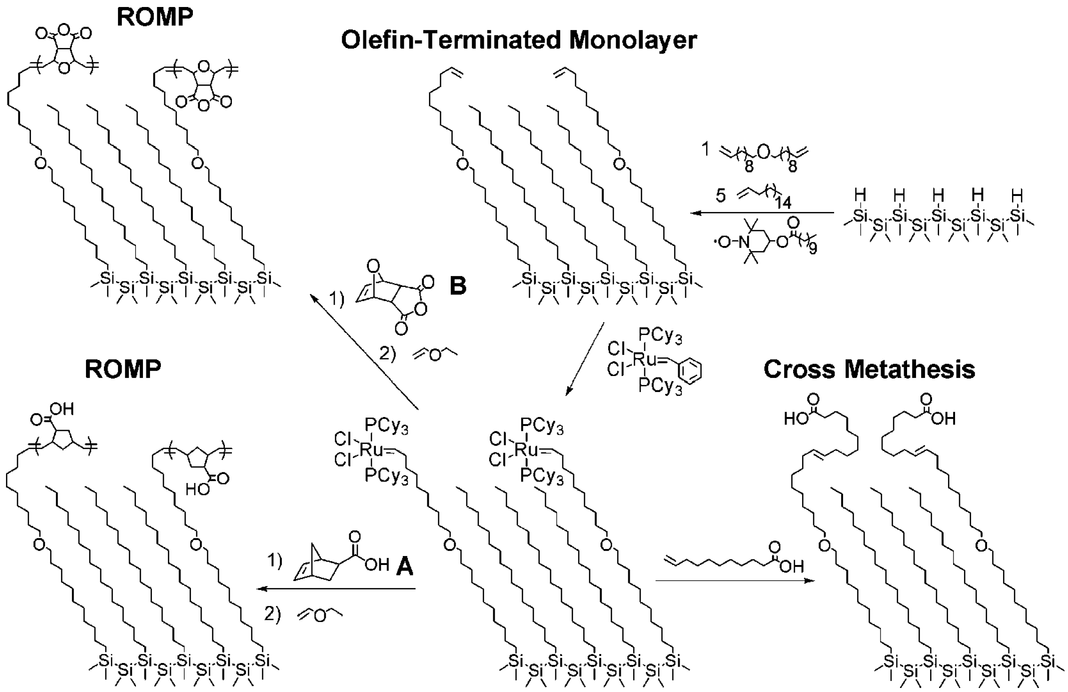

Figure 1. Reactions and monolayers used in this study; the full characterization and reactions conditions are reported in the literature. Monolayers terminated with olefins and methyl groups were assembled directly on Si(111) without an intervening layer of silicon dioxide. We first synthesized hydrogen-terminated Si(111) and reacted this surface with 1-octadecene and a diolefin with 0.1 mol % TEMPO-C_{10}. Next, these surfaces were exposed to a solution of the Grubbs' catalyst to yield a surface with this catalyst covalently bonded to it. This monolayer was reacted with 10-undecenoic acid to yield a carboxylic acid-terminated monolayer by cross metathesis. Alternatively, it was reacted with bicyclo[2.2.1]hept-5-ene-2-carboxylic acid, **A**, or exo-7-oxa-bicyclo-(2.2.1)-heptane-2,3-dicarboxylic anhydride, **B**, to yield polymer brushes by ROMP.

steps in this procedure were carried out under ambient conditions. We mixed a 1.22 mM solution of the Grubbs' first generation catalyst in CH_2Cl_2 and immersed a silicon wafer with an olefin-terminated monolayer in it for 30 min. The wafer was removed from the solution of catalyst and rinsed. A PDMS stamp was placed on the monolayer and a 0.48 M solution of undecenoic acid in nitromethane was added to the microchannels for 60 min. The undecenoic acid reacted with the Grubbs' catalyst on the surface to yield an acid-terminated monolayer that was free of the Grubbs' catalyst. 0.5 M Bu_4NF in THF/nitromethane was added to the microchannels for different periods of time. This solution was removed from the channels with fresh nitromethane. A 58 mM solution of the monomer in DMF was added to the microchannels for 3−33 h. This addition of monomer resulted in polymer brushes only along the newly exposed Grubbs' catalyst-terminated monolayer. The polymerization time varied to obtain clear images by optical microscopy or scanning electron microscopy. The microchannels were rinsed with fresh nitromethane and the PDMS stamp was removed. The surface was rinsed and imaged by optical and scanning electron microscopy.

Results and Discussion

Our method to pattern micrometer- to nanometer-sized polymer brushes begins with the assembly of an olefin-terminated monolayer on Si(111) as shown in Figure 1. The assembly and characterization of these monolayers was reported in a previous publication, and we will repeat only the important details here. We assembled mixed monolayers of a diolefin and 1-octadecene to form monolayers terminated with olefins and methyl groups. We demonstrated that these monolayers readily react by cross metathesis or ring-opening metathesis polymerization (ROMP) with the Grubbs' first-generation catalyst.[55−57] Metathesis is an important class of organic reactions that can be used to synthesize small molecules and large polymers.[58−67] In our previous work, we used cross metathesis and ROMP to pattern surfaces with carboxylic acid-terminated monolayers and polymer brushes.[55] These monolayers on Si(111) are stable to atmospheric conditions for months and to immersion in aqueous or organic solvents for days to weeks. They are stable enough to have a wide range of application in fields that currently use monolayers on electrically conducting substrates such as gold or electrically insulating substrates such as glass.

Method to Fabricate Polymer Brushes Inside Microfluidic Channels. In this paper, we report a method to pattern polymer brushes on monolayers on Si(111). This method

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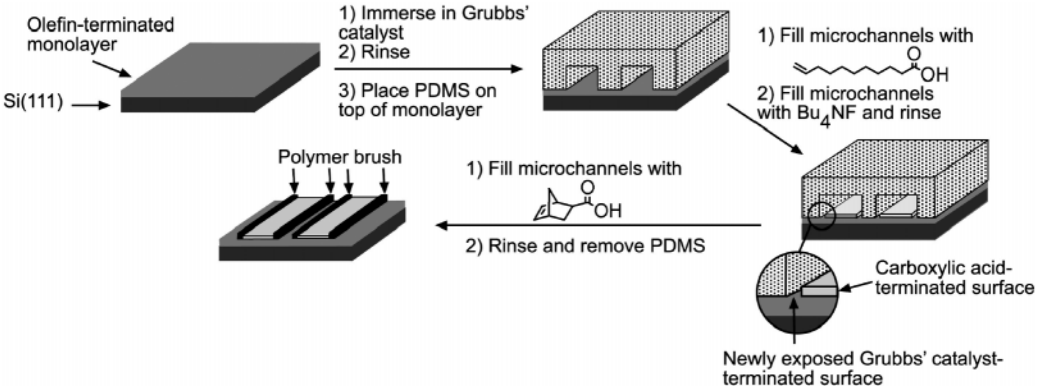

Figure 2. Growth of patterned polymer brush lines began with the assembly of an olefin-terminated monolayer as shown in Figure 1. The silicon wafer is immersed in a solution of the Grubbs' first generation catalyst and removed. The Grubbs' catalyst reacts with the olefins on the surface and is bonded to the monolayer. After being rinsed with fresh solvent, a PDMS slab with microchannels is placed on the surface. The microchannels are filled with undecenoic acid to cross metathesize with exposed Grubbs' catalyst and remove it from the surface. Bu_4NF or HF is added to the PDMS microchannels to etch the walls and expose fresh Grubbs' catalyst-terminated surface. A solution of monomer for ROMP is added to the microchannels to grow polymer brushes only on the newly exposed surface. The entire method outlined here is performed outside of a glove box under ambient conditions.

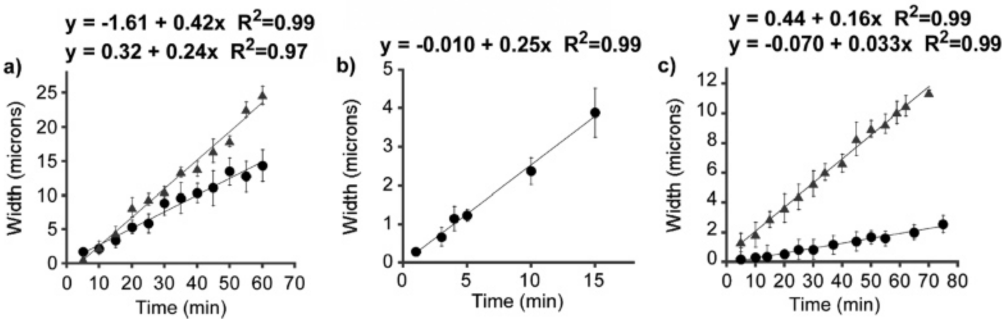

Figure 3. Amount of PDMS that was etched under a variety of conditions. The equations above each graph describe the linear fits to the data as shown by the lines through the data. (a) Calibration curves for etching PDMS microchannels in 0.5 M Bu_4NF after the PDMS was immersed in 10% by volume solution of undecenoic acid in $MeNO_2$ for 60 min (●) and without exposure to undecenoic acid (▲). (b) Width of polymer brushes fabricated using the 0.5 M Bu_4NF as the etchant and as measured from SEM micrographs. (c) Calibration curves for etching PDMS microchannels in 5% HF after the PDMS was immersed in a 10% by volume solution of undecenoic acid in nitromethane for 60 min (●) and without exposure to undecenoic acid (▲). The error bars are the standard deviations for at least 10 measurements at each point.

relies on the controlled etching of PDMS by HF or Bu_4NF within microfluidic channels (Figure 2). PDMS is a commercially available polymer that is extensively used in "soft lithography" for numerous applications including patterning of monolayers or as scaffolds to generate microfluidic channels.[68−70] A PDMS mold maintains its shape when placed on a surface and it is flexible enough to seal in conformal contact with a surface. Thus, fluids flowing through PDMS microchannels do not come into contact with surfaces covered with PDMS.

The structure of cross-linked PDMS is comprised of strong silicon−oxygen bonds (formula: $(-O-SiMe_2-)$) with a bond-dissociation energy of approximately 522 kJ mol^{-1}.[71] These bonds are unreactive toward most reagents with an important exception of the fluoride ion, F^-, which readily cleaves the polydimethylsiloxane network into small molecules. We took advantage of this property of PDMS and passed solutions of HF or Bu_4NF through PDMS microfluidic channels to etch PDMS. By controlling the time of exposure of the channels to a solution of certain $[F^-]$, we were able to control how much PDMS was etched to reveal a fresh surface of Grubbs' catalyst-terminated monolayer that subsequently could be functionalized by ROMP. Two key features of this method is its potential to pattern sub-100 nm wide lines on a surface because it is not limited by the wavelength of light, and its potential to pattern an entire wafer concurrently.

Our method demonstrates the tolerance of the Grubbs' catalysts to these conditions. Only the Grubbs' catalysts are stored in a glove box; the remaining steps are carried out under ambient conditions. The Grubbs' catalysts bonded to the monolayer are exposed to aqueous solutions of HF or Bu_4NF and O_2, yet they still catalyze the growth of polymer brushes from the surface. This result is unexpected but welcome as it makes the formation of patterned polymer brushes rather simple and easy to carry out.

Rates of Etching of PDMS. We first measured the rate at which PDMS is etched when immersed in either 0.5 M Bu_4NF dissolved in 1/1 v/v $MeNO_2$/THF or 5% HF in H_2O (Figure 3). To measure the amount of PDMS that was etched, we cut a slab of PDMS that was patterned in bas-relief with microchannels to expose a series of features raised by 50 μm on PDMS. We measured the widths of at least 10

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microchannels before and after etching the PDMS to learn how much had been removed. From our results it is clear that 0.5M Bu_4NF etches PDMS faster than 5% HF ($[F^-] = 4$ M). These results indicate that PDMS can be readily etched with Bu_4NF, but to etch sub-micrometer wide stripes of PDMS from the walls of microchannels, it is better to use 5% HF.

Interestingly, if we immerse PDMS into a solution of undecenoic acid in nitromethane prior to etching, the amount of PDMS that was etched was lowered relative to slabs of PDMS that had not been immersed in undecenoic acid. Undecenoic acid can diffuse into PDMS and affect the etching rate by buffering the F^-. It is well-known that the rate at which SiO_2 is etched is highly dependent on the pH of the solution with acidic solutions more reactive than basic solutions. Also, undecenoic acid can affect the rate at which F^- reacts with PDMS by offering a barrier through which it must diffuse to react. The reasons for the retarded rate is unknown and is beyond the scope of this paper. It is important to note that undecenoic acid had an important effect and that it must be taken into consideration when etching PDMS. In the next section, we will further describe how the width of the polymer brush patterns closely match the calibration curve set using PDMS immersed in undecenoic acid prior to etching. This result is not unexpected, as undecenoic is flown through the microfluidic channels prior to etching.

Growth of Polymer Brushes and Characterization by Optical Microscopy and SEM. After treatment with etchant solution, polymer lines were grown on the newly exposed surface according to the procedure of Figure 2 and characterized by optical and scanning electron microscopy (Figure 4). For these experiments we used monomer **A** in Figure 1 to synthesize a polymer brush exposing carboxylic acids. There is a limitation in viewing these patterns by SEM as the lines are narrow (widths of tens of nanometers to several micrometers) and do not show up well at low magnifications. Therefore, we grew thick polymers that were easily viewed as bright lines under optical microscopy and show SEM micrographs at high and low magnifications where the lines were still clearly visible.

We wished to show that this technique works over a large area for both straight and curvy microchannels. The images in Figure 4 are representative of what we observed over numerous samples, the polymer lines were continuous over the entire length of the microchannels—greater than a centimeter in length. Although there were very few defects on these surfaces, occasionally a microchannel did not fill with the liquid so a polymer line was not patterned in it. In addition, it is clear from Figure 4e that curvy channels can be patterned. Figure 4d shows polymer lines that followed the contours of the end of the microchannels. This method is both robust over large areas and can be used to pattern polymer brushes in straight and curvy microchannels.

To better characterize the polymer lines, we imaged them under high magnification by SEM (Figures 4f−i). These images clearly demonstrate that the lines were continuous. The walls of the microchannels were not smooth (as expected from the use of transparency masks to create the microchannels), and the polymer brushes followed their uneven contours. Thus, this method successfully replicated the contours of the walls of the microchannels. It is forgiving of imperfections in the roughness of the walls and allows curves on the submicrometer to tens of micrometers scale to be patterned.

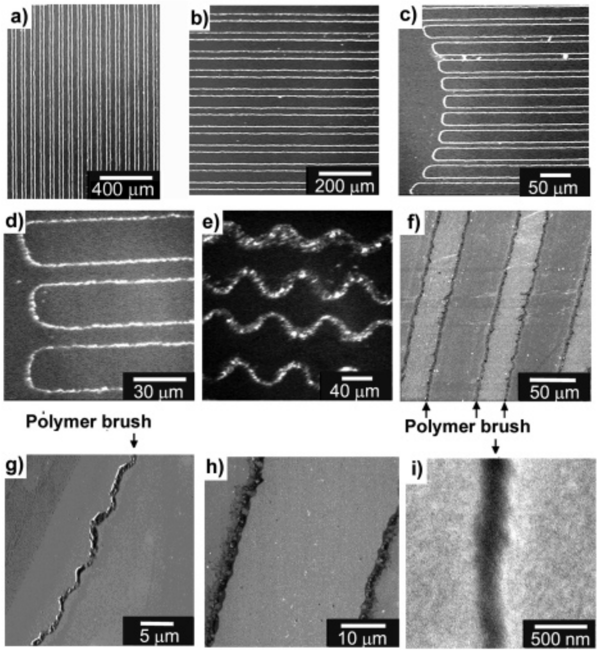

Figure 4. Optical micrographs of polymer brushes (bright lines) that were grown in (a−d) straight and (e) curvy microchannels. In (c) and (d), we show the ends of the microchannels to emphasize that the polymer lines followed the curves of their shapes. (f−i) SEM micrographs of polymer brushes (dark lines). The polymer lines appear curvy under high magnification due to imperfections in the walls of the PDMS microchannels used to fabricate them. (i) SEM micrograph of a polymer brush with a width of 270 nm. In each of these experiments, we used monomer **A** from Figure 1 to synthesize the polymers.

The widths of the patterns were measured as a function of time that the microchannels were exposed to Bu_4NF and the data were plotted in Figure 3b. The agreement between the measured widths of the lines and the amount of PDMS etched after exposure to undecenoic acid was excellent (slopes of 0.25 and 0.24 μm per min) and demonstrated that this method could be used to grow patterned polymer brushes with widths from 270 nm to at least 3.7 μm. Control experiments where we did not add monomer to the microchannels after etching did not show any polymer lines.

To grow polymer brushes with widths of less than 250 nm we had to use an etchant solution different from 0.5 M Bu_4NF. On the basis of the calibration curves, to etch 100 nm from microchannel walls they must be exposed to 0.5 M Bu_4NF for only 26 s, a time that we found challenging to control. Decreasing the concentration of Bu_4NF did not provide reproducible results for the widths of polymer brushes, so we switched to 5% HF as the etchant because of its slower rate of etching, as shown in Figure 3c. With this etchant 100 nm of PDMS would be etched from the microchannel walls upon exposure to HF for approximately 5 min. In Figure 5, we show polymer brushes with widths of 70, 90, and 140 nm that were fabricated by following the

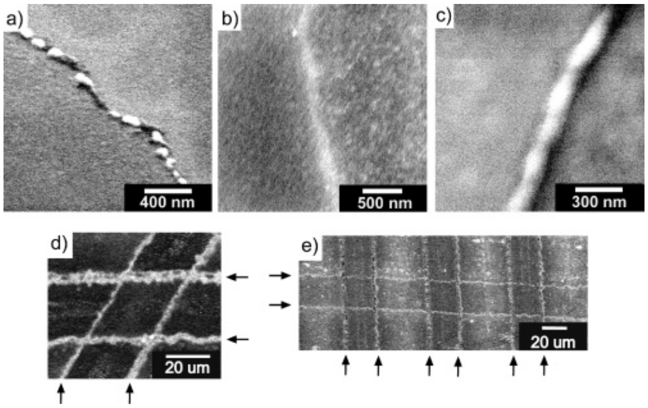

Figure 5. SEM micrographs of patterned polymer brushes that were grown from PDMS microchannels after etching with 5% HF and using monomer **B** in Figure 1. The polymer brush lines had widths of (a) 70, (b) 90, and (c) 140 nm. (d, e) Crossed polymer brush lines that were fabricated by growing one set of polymer lines, removing the PDMS, immersing the wafer in a solution of the Grubbs' catalyst, and following the method in Figure 2 to grow a second set of polymer lines on the surface. The arrows point to the lines of polymer brushes.

method outlined in Figure 2 and replacing the etchant with 5% HF in H_2O. From the results in Figures 4 and 5, it is clear that the edge resolution of the polymer brushes increases with their widths. For the smallest lines the edge resolutions were much less than 50 nm, but for the widest lines exceeding 1 μm the edge resolution increased to over 50 nm.

To further demonstrate the potential of this method, we patterned crossed lines of different polymer brushes by first growing polymer brushes of monomer **A** in Figure 1 along microchannels of PDMS. Next, the surface was immersed in a solution of the Grubbs' catalyst again to bond Grubbs' catalyst throughout the entire surface. The PDMS stamp was rotated and placed back on the surface. The procedure outlined in Figure 1 was repeated to grow polymer brushes of monomer **B** at an angle relative to the first lines. Because we replenished the Grubbs' catalyst on the surface prior to growing the second set of polymer brushes, we grew crossed polymer lines as shown in Figures 5d and e.

Characterization of Polymer Brushes by XPS and Auger Spectroscopy. We further characterized these polymer brushes by XPS and Auger spectroscopy. We first looked at these surfaces by XPS to characterize the change in the C(1s) peak that would show evidence of growth of polymer. Polymer brushes of monomer **A** were grown on the entire surface of a Si(111) wafer for measurements by XPS. A nonpatterned surface was imaged because our polymer brushes were narrower than the smallest pixel size that could be measured by scanning XPS. In Figure 6, we show the evolution of the C(1s) peak in the original monolayer, the Grubbs' catalyst-terminated surface, and the polymer brush. These results demonstrate that we are growing polymers that were bonded to the surface (they were not removed with extensive washing in organic solvents). In addition, the Ru(3p) and Ru(3d) peaks clearly show that the Grubbs' catalyst was bonded to the monolayer as described in Figure 1.

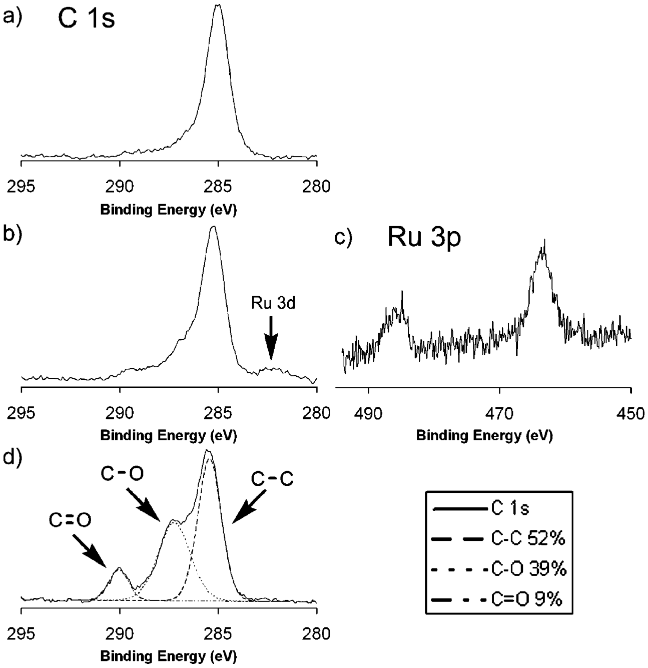

Figure 6. Change of the C(1s) peak in the XPS spectra for (a) a mixed monolayer terminated with methyls and olefins, (b) after reaction with the Grubbs' catalyst, and (d) after reaction of the surface with monomer. (c) The Ru(3p) peak clearly shows that it is bonded to the surface.

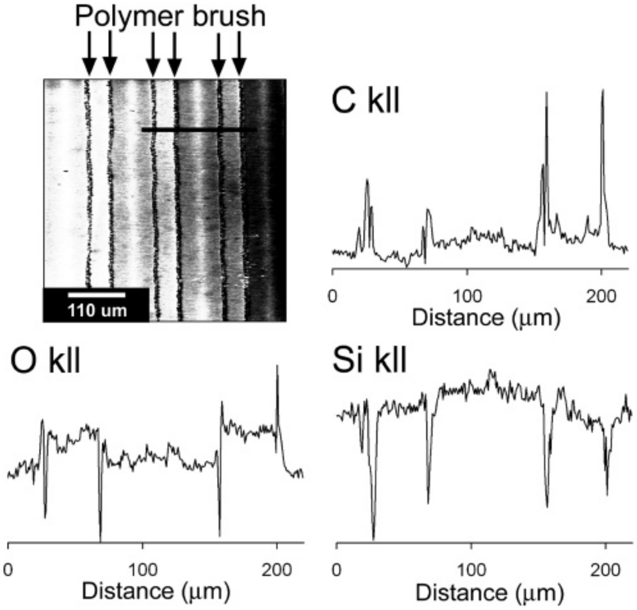

Figure 7. SEM of a patterned surface taken in the Auger spectrometer. The gradient in darkness is due to the unoptimized location of the detector due to the location of the XPS detector. The dark vertical lines are the polymer brushes and the one dark horizontal line is where the surface was imaged by Auger spectroscopy. The C(kll), O(kll), and Si(kll) scans show spikes where the polymer brushes were found.

Because XPS is a bulk measurement over a large (approximately 0.24 mm^2) section of a surface, we grew patterned polymer brushes using monomer **A** and imaged them by scanning Auger spectroscopy. Auger spectroscopy has the advantage that it can be image small area with a lateral resolution approaching 200 nm. In Figure 7, we show a SEM of a patterned surface with a dark, horizontal line that indicates where the surface was imaged by scanning Auger spectroscopy. When the Auger imaged the polymer brush, it detected a spike in the amount of C and a decrease in the amount of O and Si. These results are consistent with the growth of a polymer brush with high amounts of C that shields the Si peak. The O(kll) peak decreases when the polymer brush is imaged because the area between the polymer brushes the surface is terminated with acids, as described in Figure 1.

Conclusions and Summary

We report a new method to pattern polymer brushes inside of PDMS microchannels with widths from several micrometers down to 70 nm. All of the steps of this method are carried out under ambient conditions using simple PDMS slabs. This method uses the controlled etching of PDMS with different sources of F^- to expose fresh surfaces of Grubbs' catalyst-terminated monolayer within microchannels. Although we patterned lines with widths down to 70 nm, this method probably can be extended to patterns with smaller widths by using lower exposures to F^- or low-molecular-weight polymer brushes. We expect that the true widths of the polymer lines where they attach to the surface is smaller than the widths measured here because polymer brushes will spread onto adjacent surfaces that did not grow polymer brushes. The spreading of polymer brushes and increasing difficulty of imaging nanometer-wide polymer lines by SEM kept us from learning the lower limit of this method.

Growing polymer brushes patterned along the edges of microfluidic channels is exciting for several reasons. One potential application will be the study of fluid flow directly along the edges of complex microchannels. Because our method relies on etching the PDMS walls with continually refreshed sources of F^-, it should be possible to study how fluid flows along the walls of microchannels through the width of polymer brushes along the surface. Another exciting option with this method is control of spatial chemistry inside of microfluidic devices for use in micro total analysis systems (μTAS). In "these lab on a chip" systems, the increasingly small dimensions of the microfluidic channels increases the importance of controlling their surface chemistry. To pattern the surface chemistry inside of a microfluidic device, the surface is either patterned and then another slab is bonded onto the surface to form channels or the channels are modified using lamellar flow in the channels. These patterned surfaces can direct the flow of liquids or the growth of substrates in the channels. Our method allows the edges of the channels to be patterned selectively from the rest of the surface and will allow for further control over the surface chemistry. Finally, we can imagine coating the newly formed polymer brushes with other nanomaterials or inorganics. A hard shell could be grown over the polymer brush lines, and after the polymers are etched, a new nanofluidic device would remain that would be readily integrated with a microfluidic channel. This method is also promising because it can be integrated with monolayers on coinage metals. In future work, we will explore some of these applications, study the lower limits of line widths of polymer brushes that can be obtained with this method, and investigate the growth of block copolymer brushes.

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