

Chemistry of Olefin-Terminated Homogeneous and Mixed Monolayers on Scribed Silicon

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We describe the preparation of homogeneous olefin-terminated monolayers on scribed silicon made from 1,9-decadiene, and mixed monolayers with varying degrees of olefin termination prepared from 1,9-decadiene and 1-decene or 1-octene, and their subsequent reactions with bromine, osmium tetroxide, dichlorocarbene, and Grubbs' catalyst. Each of these reagents contains a heteroatom, which allows straightforward monitoring of the surface reactions by X-ray photoelectron spectroscopy (XPS). Surface reactions of mixed monolayers made from 1,9-decadiene and 1-octene are consistently more efficient than surface reactions of mixed monolayers made from 1,9-decadiene and 1-decene, presumably because of steric effects. After chemisorption of Grubbs' catalyst, ring-opening metathesis polymerization (ROMP) of norbornene is demonstrated. The kinetics of Grubbs' catalyst adsorption and of polynorbornene growth is monitored by XPS and time-of-flight secondary ion mass spectrometry (ToF-SIMS). A principal components analysis (PCA) of the ToF-SIMS data is presented. Autoscaling is shown to be a relatively ineffective preprocessing method for this data. Polynorbornene features on patterned substrates effectively resist and direct the electroless deposition of copper.

Introduction

Silicon is arguably the most important material in the semiconductor and microelectronics industries, and because of this importance, numerous studies have been performed on its surface, which may be hydrogen-terminated, reconstructed, porous, or scribed.^{1–4} Chemomechanical modification of silicon (scribing)⁴ is an effective and convenient method for functionalizing the surface of silicon. In this method, a silicon surface is mechanically scribed in the presence of a reactive species. Scribing activates the surface so that it reacts immediately with the reagent it is in contact with. Scribed silicon reacts with 1-alkenes,^{5–7} 1-alkynes,^{5,7} alkyl halides (chlorides, bromides, and iodides),^{7,8} alcohols,⁶ epoxides,⁹ aldehydes,¹⁰ and acid chlorides¹¹ to produce

hydrophobic, methyl-terminated monolayers. Scribed silicon also reacts with bifunctional compounds, including 1,2,7,8-diepoxyoctane⁹ and suberoyl chloride,¹¹ to form amine-reactive epoxide and acid chloride monolayers, respectively. These reports are significant because of the rich and versatile chemistry of activated carboxyl and epoxy groups. The chemomechanical patterning method is straightforward, allowing both nanometer- and micrometer-sized features to be created.^{12–15} It is similar to the nanografting method developed by Xu and co-workers^{16,17} and to the micromachining/manipulation of surface wetting method developed by Abbott et al.¹⁸

The olefin group is found in numerous compounds and polymers of significance. It has important addition-reaction properties. Here, we explore the chemistry of homogeneous,

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Table 1. Compositions in Mole Percent of the Mixed Solutions Used To Prepare the Surfaces in Figure 1

component	compositions				
1,9-decadiene	0%	25%	50%	75%	100%
1-octene or 1-decene	100%	75%	50%	25%	0%

olefin-terminated monolayers made with a neat dialkene on scribed silicon,¹³ along with mixed monolayers prepared with a mixture of a dialkene and a monoalkene. To demonstrate the preservation of active carbon-carbon double bonds after monolayer formation, monolayers were exposed to three reagents that readily react with carbon-carbon double bonds: bromine (Br₂), osmium tetroxide (OsO₄), and dichlorocarbene (:CCl₂). A fourth reaction was also demonstrated: chemisorption of Grubbs' catalyst, followed by ring-opening metathesis polymerization (ROMP)^{19–26} to form an adsorbed polymer film (see Scheme 1). In ROMP, rings may be opened in a ruthenium carbene-catalyzed reaction, where the driving force is the relief of ring strain. ROMP on surfaces using Grubbs' catalyst has been demonstrated from olefin- or norbornenyl-terminated silicon oxide surfaces^{27–29} and porous silica³⁰ and from the surface of liposomes.³¹

Copper metallization, including electroless plating, has recently drawn significant attention because of its importance in the production of integrated devices,³² including interconnects in microelectronic circuits.³³ Electroless plating occurs by an autocatalytic redox process, in which the cation of the copper to be deposited is reduced chemically at the substrate. Here, we show that polynorbornene features produced by ROMP serve as masks for the electroless deposition of copper on silicon.

The results presented in this work are substantiated by many analytical methods, including wetting, X-ray photoelectron spectrometry (XPS), positive and negative ion time-of-flight-secondary ion mass spectrometry (ToF-SIMS), atomic force microscopy (AFM), scanning electron microscopy (SEM), and principal components analysis (PCA) of

ToF-SIMS data, which confirm monolayer formation and reactivity, polymer growth, and subsequent electroless metal deposition. Section analysis by AFM reveals that the thickness of the polymer layers is ca. 40 nm.

Experimental Section

Chemicals. All chemicals were reagent grade or the highest available commercial grade, unless otherwise specified, and were used as received as follows: 1,9-decadiene (Aldrich, 96%), 1-decene (Aldrich, 94%), 1-octene (Aldrich, 97%), 1.0 M bromine in trimethyl phosphate (Aldrich), 2.5 wt % osmium tetroxide solution in 2-methyl-2-propanol (Aldrich), 1.0 M potassium *t*-butoxide solution in 2-methyl-2-propanol (Aldrich), (Cy₃P)₂Cl₂Ru=CHPh, Cy = cyclohexyl (Grubbs' catalyst first generation, Aldrich).

Preparation for Patterning Silicon Surfaces. We employed two different scribing methods for chemomechanically patterning silicon. In the first, native oxide-terminated silicon was scribed and patterned using a diamond-tipped rod.^{5–11} The other method consisted of using a rigidly held 1/32" diameter tungsten carbide ball (McMaster-Carr, Cat. Nos. 9598K12).¹⁴ This ball was glued on a metal rod, which was attached to a flexible cantilever, and the cantilever was connected to a computer-controlled set of translation stages. The tungsten carbide ball was used for creating patterned lines on hydrogen-terminated silicon surfaces for AFM and SEM imaging. All surfaces were cleaned with a solution of H₂O₂(conc.)/NH₄OH(conc.) for 30–40 min, were rinsed with water, and were dried with a stream of nitrogen. Prior to scribing with the tungsten carbide ball, Si(100) surfaces were dipped in 2.5% HF for 5 min, were rinsed with water, and were dried with a stream of nitrogen gas. The hydrogen-terminated silicon samples were then wetted with reactive chemicals, were scribed with a tungsten carbide ball, were rinsed with acetone and water, and finally were dried with a stream of nitrogen gas. When the diamond tip was to be used as the scribing tool, the cleaned silicon surfaces were wetted directly with reactive chemicals, and then scribing was performed on a 6 mm × 6 mm area of the surface. Silicon samples with patterned monolayers on the surface were stored in nitrogen gas before the polymerization process.

Preparation of Monolayers. Mixed monolayers were prepared from solutions made from different proportions of 1-decene and 1,9-decadiene or from a mixture of 1-octene and 1,9-decadiene. No solvent was employed. The compositions of these solutions are given in Table 1.

Reaction with Bromine. Monolayers (see Table 1) were immersed in 1.0 M bromine in trimethyl phosphate for 12 h. After immersion, they were washed with acetone and then with soap and water with agitation from a soft camel hair brush. Finally, they were rinsed with DI water and Millipore water and were dried with nitrogen gas.

Reaction with OsO₄. Scribed silicon surfaces (see Table 1) were immersed for 30 min in a 2.5 wt % solution of osmium tetroxide in 2-methyl-2-propanol that had been diluted by the same solvent to 0.1 wt %. Finally, the surfaces were removed and washed with 2-methyl-2-propanol and then were dried with nitrogen gas.

Reaction with Dichlorocarbene. Silicon surfaces, which had been scribed with the reagents shown in Table 1, were immersed for 3.5 h in a stirred solution of 1.0 M potassium *t*-butoxide in 2-methyl-2-propanol that was diluted to 0.1 M with CHCl₃. The system was sealed and under nitrogen. After they were taken out, the surfaces were first washed with chloroform and then with DI water. Finally, they were rinsed with Millipore water and were dried with nitrogen gas.

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Reaction with Grubbs' Catalyst. Scribed silicon surfaces (see Table 1) were immersed in a 13 mM solution of the olefin metathesis catalyst (Grubbs' catalyst) in dichloromethane at room temperature for 30 min. After exposure to this catalyst, the surfaces were rinsed in CH_2Cl_2 .

Calculation of Reaction Yields. Yields of homogeneous 1,9-decadiene monolayers with different reagents were calculated using the following formulas that employ the heteroatom/C ratio, which can be directly measured by XPS: percent yield of the Br_2 reaction: $500 \cdot (\text{Br}/\text{C})$, percent yield of the OsO_4 reaction: $1000 \cdot (\text{Os}/\text{C})$, percent yield of the CCl_2 reaction: $1000 \cdot (\text{Cl}/\text{C}) / (2 - (\text{Cl}/\text{C}))$, and percent yield of the Grubbs catalyst reaction: $1000 \cdot (\text{Ru}/\text{C}) / (35 - (\text{Ru}/\text{C}))$. These formulas ignore attenuation of photoelectrons, which is a good assumption for the ultrathin films studied in this work. In practice, the "yield" for the control reaction of the given reagent with a 1-decene monolayer (12%, 3%, 19%, and 0.68%, respectively) was subtracted from the yield for the reaction of the reagent with the 1,9-decadiene monolayer to give the numbers reported in the text.

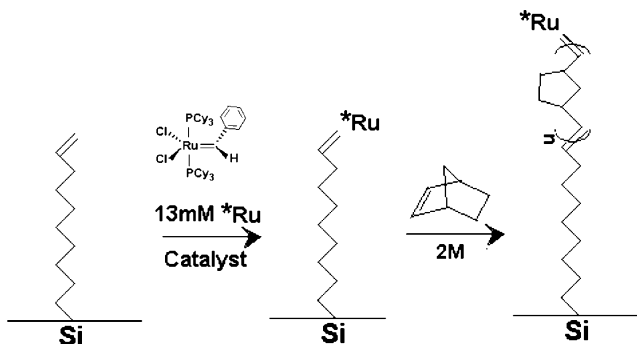
Polymerization. To grow polynorbornene on functionalized regions, the olefin-terminated/functionalized/patterned Si samples (prepared from 1,9-decadiene) were first immersed in a 13 mM solution of Grubbs' catalyst in dichloromethane at room temperature for 30 min. Samples were then removed from the solution, were washed thoroughly with dichloromethane, and were dried with a stream of dry nitrogen gas. The silicon samples were next immersed in a 2.0 M solution of norbornene monomer in toluene at room temperature for 40 min. Finally, the samples were removed from solution, were washed thoroughly with dichloromethane, and were dried with a stream of nitrogen gas. To study the kinetics of polymer growth, different reaction times were investigated.

Copper Deposition. Silicon samples that were patterned with 1,9-decadiene and then with polynorbornene were dipped in a solution of 0.01 M cupric sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), 0.01 M ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$), 0.005 M sodium potassium tartrate ($\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$), 30 vol % methanol, and 50 vol % ammonium fluoride (NH_4F 40%) at room temperature for 2–5 min³² to form a seed layer. The reaction is $\text{Si} + 6\text{F}^- + 2\text{Cu}^{2+} \rightarrow 2\text{Cu} + \text{SiF}_6^{2-}$. Electroless plating was used to grow copper on the seed layer in the unmasked areas. Glyoxylic acid was used as the reducing agent during electroless plating from a solution composed of 0.0305 M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 0.0351 M EDTA, 0.06–0.1 M glyoxylic acid, and 0.004 g/L RE-610 surfactant at pH = 12.5.³⁴ The electroless plating time was 10 min.

Instrumentation. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was performed with an ION-TOF TOF-SIMS IV instrument with monoisotopic 25 keV $^{69}\text{Ga}^+$ primary ions in "bunched mode." The primary ion (target) current was typically 1.3 μA , with a pulse width of 20 ns before bunching, and the raster area of the beam was $500 \times 500 \mu\text{m}^2$. X-ray photoelectron spectroscopy was performed with an SSX-100 X-ray photoelectron spectrometer with a monochromatic Al K α source and a hemispherical analyzer. No electron flood gun was employed. Survey scans as well as narrow scans were recorded with an $800 \times 800 \mu\text{m}^2$ spot size. Atomic force microscopy (AFM) was performed with a Dimension 3100 AFM, equipped with a motorized optical microscope and a motorized stage. Scanning electron microscopy (SEM) was performed with a JEOL JSM 840A instrument.

PCA Analysis of ToF-SIMS Data. The "peak list" feature in the ToF-SIMS instrument software was used to integrate (bin) spectral regions ± 0.3 mass units around each integer value along the abscissa. This operation effectively binned the data to unit mass

Scheme 1. Schematic of a Growing Polynorbornene Chain on a Patterned Silicon Surface. (Cy = Cyclohexyl)



resolution, and the positive and negative ion spectra were binned in this manner from 1–350 amu. The data were then exported into Microsoft Excel and were normalized and arranged into data matrices where the spectra were in rows and the variables (integrated regions) were in columns. Normalization, a row operation, was done with the "1-Norm", which divides each mass in a spectrum by the sum of masses from the row. Two matrices consisting of the positive ion spectra and the negative ion spectra were thus obtained. These matrices were then exported to the PLS_Toolbox 3.0 (Eigenvector Research, Inc., Wenatchee, WA) in Matlab. Four different processing methods were applied to these data. The first is normalization alone,³⁵ which may account for the differences between spectra collected under somewhat different instrumental conditions, for example, data collection times. Following normalization, which is a row operation, three other preprocessing methods were used for some of the analyses: mean centering, standardization, and logarithmic scaling. In mean centering,³⁵ a column operation, the mean of the values that correspond to each variable is subtracted from each value in that column. In standardization,³⁵ also a column operation, each data point is mean centered and then divided by the standard deviation of all of the data points in a column in the data matrix. Standardization has the effect of putting all of the variables on equal footing; it gives all variables unit variance. This method may be disadvantageous for ToF-SIMS data, which has many regions containing mostly noise. In logarithmic scaling, data points were replaced by their base 10 logarithms.

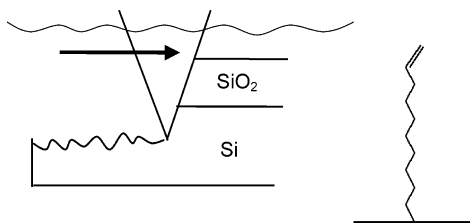
Results and Discussion

Chemical Verification of Olefin-Termination at the Monolayer Surface. On the basis of previous results,^{9,11,13} it was expected that olefin-terminated monolayers would be formed when scribing was performed in the presence of neat 1,9-decadiene (see Scheme 2) and that in mixed monolayers the degree of olefin termination at the monolayer–air interface could be controlled by varying the proportions of 1,9-decadiene and a 1-alkene in the liquid above the surface (see Scheme 3). Our first evidence for monolayer formation after scribing with 1,9-decadiene came from advancing water contact angle measurements of these surfaces. A silicon surface that has been scribed in the air has an advancing water contact angle of zero degrees; it is completely wet by water. However, a silicon surface that has been scribed in the presence of 1,9-decadiene has a water contact angle of 107°. The advancing water contact angle of a densely packed,

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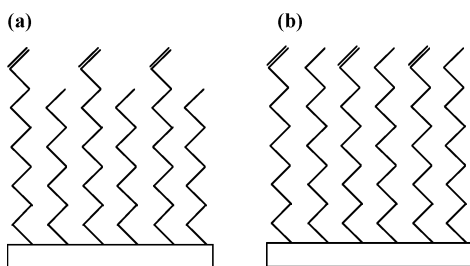
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Scheme 2. Schematic of the Scribing Method and an Olefin-Terminated Monolayer on a Patterned Silicon Surface That Was Prepared from a Diolefin^a



^a There remains some uncertainty in the way in which olefins attach to scribed silicon.

Scheme 3. Possible Arrangement of Alkyl Chains in Monolayers on a Silicon Surface Scribed under (a) 50% 1-Octene and 50% 1,9-Decadiene and (b) 50% 1-Decene and 50% 1,9-Decadiene



vinyl-terminated monolayer (on mica) prepared from $\text{CH}_2=\text{CH}(\text{CH}_2)_{18}\text{Si}(\text{OEt})_3$ has previously been reported to be 101° .³⁶ We attribute the higher water contact angle of our $\text{CH}_2=\text{CH}-$ terminated monolayer to surface roughness. X-ray photoelectron spectroscopy (XPS), which is a valuable surface analytical technique that provides elemental analysis and oxidation states of species in near-surface regions, showed that silicon scribed under 1,9-decadiene had monolayer quantities of carbon (vide infra).

To demonstrate the presence of a reactive double bond at the surface, homogeneous monolayers prepared from 1,9-decadiene and mixed monolayers made from 1,9-decadiene and 1-octene or 1-decene (see Table 1) were exposed to a variety of chemical reagents. That is, after scribing in the presence of these reactive liquids, the surfaces were allowed to react with bromine (Br_2), osmium tetroxide (OsO_4), and dichlorocarbene ($:\text{CCl}_2$). All of these reagents are known to react readily with carbon-carbon double bonds.³⁷ XPS proved particularly effective in monitoring these surface reactions, showing that as the fraction of 1,9-decadiene increases in the scribing liquid, the corresponding Br/Si , Os/Si , and Cl/Si ratios also increase (see Figure 1). For every pair of samples made from 1-octene and 1-decene, which employed the same fraction of 1,9-decadiene, the Br/Si , Os/Si , and Cl/Si ratios are always slightly higher for 1-octene than that for 1-decene (see Figure 1a, 1b, and 1c). These results are consistent with lower degrees of steric hindrance in mixed monolayers prepared with the shorter 1-alkene. The most reactive surfaces were made from 100% 1,9-decadiene. These results provide compelling evidence for formation of

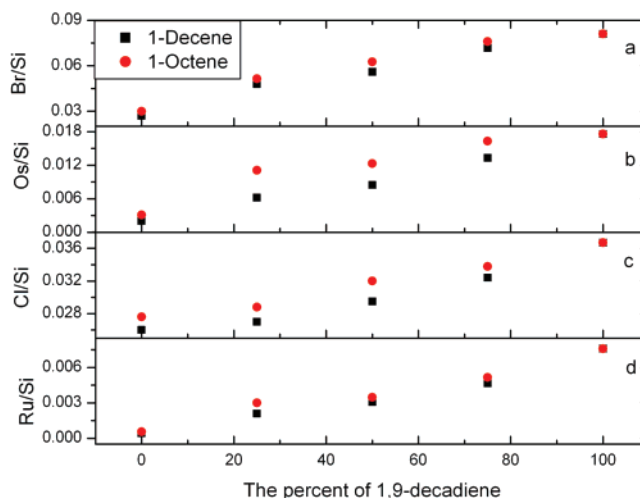


Figure 1. The XPS (a) Br/Si ratio, (b) Os/Si ratio, (c) Cl/Si ratio, and (d) Ru/Si ratio after exposure of the monolayers described in Table 1 to Br_2 , OsO_4 , CCl_2 , and Grubbs' catalyst, respectively.

olefin-terminated mixed monolayers on scribed silicon. However, the data in Figure 1 also suggest that Br_2 and especially dichlorocarbene react both specifically with double bonds at monolayer surfaces and also adsorb nonspecifically to these surfaces, presumably at the silicon-monolayer interface.

While the purpose of these studies was not to find optimal conditions for the reaction between these reagents and the double bonds at the surface, or to completely saturate the surface with these reagents, it was possible to use XPS to quantify the extent of reaction of these reagents with the surface prepared from neat 1,9-decadiene. If attenuation of photoelectrons is ignored, which is a good approximation for our ultrathin films, we find that the yields (percentage of tethered alkyl chains that react) are 43%, 19%, and 11% for the reactions with Br_2 , OsO_4 , and CCl_2 , respectively.

Reaction of Olefin-Terminated Monolayers with Grubbs' Catalyst. Another chemical verification of active carbon-carbon double bonds at the monolayer-air interface is their reaction with Grubbs' catalyst. Accordingly, the monolayers in Table 1 were immersed in a solution of Grubbs' catalyst for 30 min. XPS was then performed to verify that chemisorption had occurred. It was not possible to use the more intense Ru 3d peaks to verify surface reaction because of their overlap with the C 1s signal. However, the Ru $3p_{3/2}$ line was unobstructed and allowed determination of the yield of this surface reaction (19%), where this calculation included subtracting the intensity of the Ru 3d peaks from the C 1s peak. Clearly, the adsorption of Grubbs' catalyst follows the same trend as the chemisorption of Br_2 , OsO_4 , and CCl_2 on the mixed monolayers; as the fraction of 1,9-decadiene in the mixed monolayer increases, the corresponding Ru/Si ratio also increases. As was the case for the other adsorbates (see Figure 1) (1) for every pair of samples made from 1-octene and 1-decene that had the same fraction of 1,9-decadiene, the Ru/Si ratio is always higher for octene than that for decene (see Figure 1d), presumably because of less steric hindrance from tethered octyl chains, and (2) the homogeneous monolayer prepared from 1,9-decadiene adsorbed the largest amount of Grubbs' catalyst.

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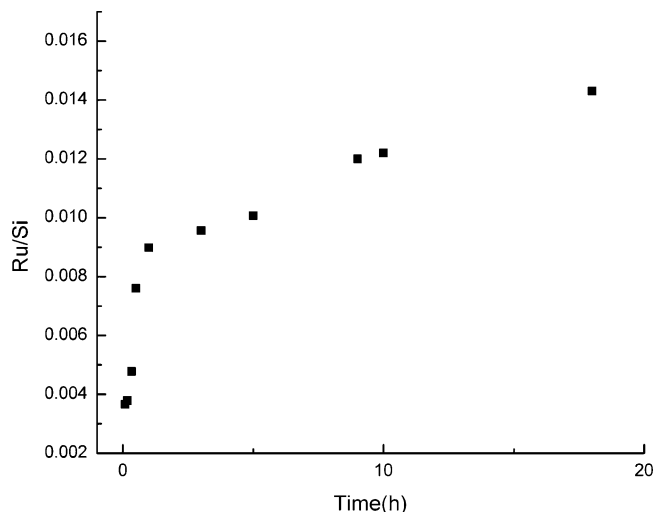


Figure 2. The XPS Ru/Si ratio measured after adsorption of Grubbs' catalyst onto a homogeneous 1,9-decadiene monolayer.

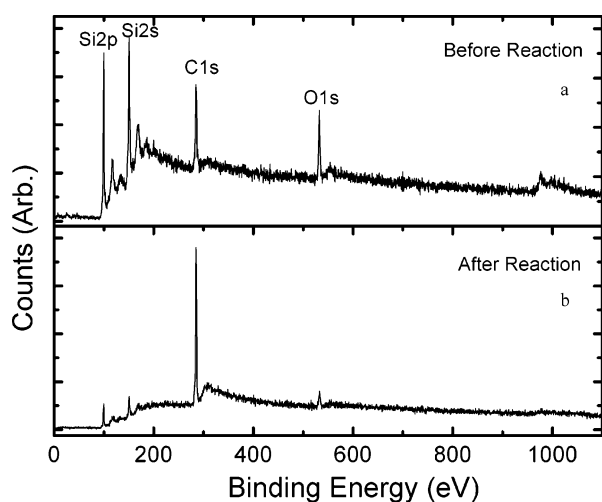


Figure 3. XPS of silicon scribed in the presence of 1,9-decadiene (functionalized area: 6 mm × 6 mm) (a) before and (b) after growth of polynorbornene onto the functionalized region.

The kinetics of adsorption of Grubbs' catalyst to a 1,9-decadiene monolayer was also studied. XPS results of the Ru/Si ratio in Figure 2 shows that Grubbs' catalyst adsorption occurs most quickly during the first 2 h of immersion in the catalyst solution and slower thereafter. It did not seem reasonable to continue this experiment for longer periods of time because after ca. 20 h the Grubbs' catalyst solution begins to darken, even if it is sealed under nitrogen gas and is kept out of the light. On the basis of these results, we used a 30-min immersion time for the monolayers in the catalyst solution.

Polymerization. Silicon samples scribed in the presence of 1,9-decadiene were immersed in a solution of Grubbs' catalyst for 30 min and were rinsed well with solvent. They were then immersed in a 2.0 M solution of norbornene monomer in toluene at room temperature for 40 min to grow the polymer. XPS survey spectra (see Figure 3) showed that after the reaction with norbornene the silicon and oxygen signals decreased dramatically and the carbon signal increased significantly compared to the spectrum before reaction. These results are consistent with growth of a polymer film that is about 100 Å thick.

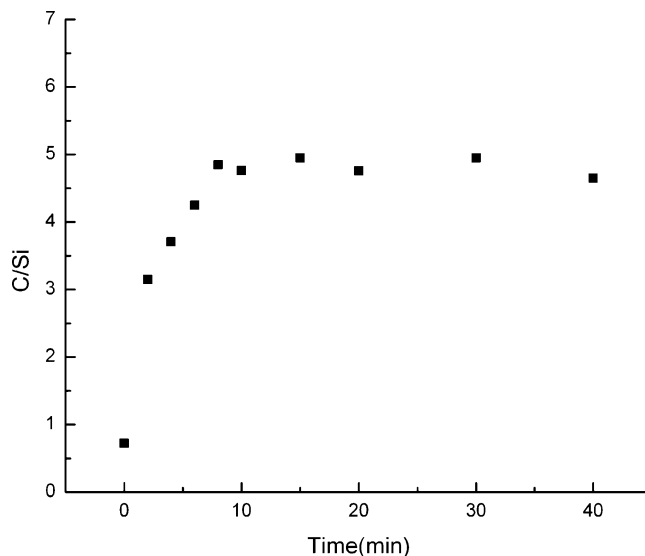


Figure 4. The XPS C/Si ratio of samples prepared by varying the reaction time of norbornene with 1,9-decadiene monolayers after adsorption of Grubbs' catalyst. Each point on this graph represents a different experiment.

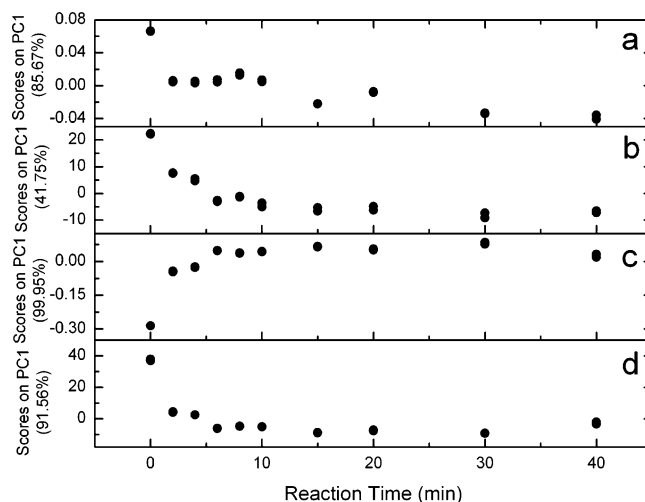


Figure 5. Scores on PC1 from a PCA analysis of ToF-SIMS data showing the combinations of positive and negative ion spectra with two different preprocessing methods (mean centering and autoscaling): (a) positive ion spectra and mean centering, (b) positive ion spectra and autoscaling, (c) negative ion spectra and mean centering, (d) negative ion spectra and autoscaling. Samples were made by (1) adsorption of Grubbs' catalyst onto 1,9-decadiene monolayers followed by (2) exposure of these samples to norbornene monomer for different periods of time. The values in parentheses give the fraction of the variance captured by each PCA analysis.

The following control experiment was performed to verify that carbon-carbon double bonds at the surface were responsible for binding Grubbs' catalyst and subsequent polynorbornene growth. A monolayer prepared from 1-decene, which should be terminated with methyl groups, was immersed in a solution of Grubbs' catalyst followed by immersion in a solution of norbornene, exactly as the surface that was prepared with 1,9-decadiene was treated. There is essentially no change in the XPS spectrum of this surface before exposure to catalyst and after exposure to Grubbs' catalyst and monomer. These spectra look essentially the same as the survey spectrum shown in Figure 3a, that is, the spectra consist of Si 2s and Si 2p peaks from the substrate, a C 1s peak that suggests monolayer quantities of alkyl chains, and a small O 1s peak, presumably because of

Table 2. Ten Largest Peaks from the Loadings Plots of PC1 from a PCA Analysis of Positive Ion Spectra of Samples (Homogeneous 1,9-Decadiene Monolayers with Adsorbed Grubbs' Catalyst) after Different Reaction Times with Norbornene^a

PC1					
mean centering			autoscaling		
m/z	loadings	species	m/z	loadings	species
28	0.5911	Si	51	-0.109	C ₄ H ₃
29	0.5288	SiH	65	-0.1084	C ₅ H ₅
23	-0.4592	Na	78	-0.1082	C ₆ H ₆
91	-0.1366	C ₇ H ₇	77	-0.108	C ₆ H ₅
67	-0.1361	C ₅ H ₇	91	-0.108	C ₇ H ₇
77	-0.1329	C ₆ H ₅	52	-0.1078	C ₄ H ₄
43	0.1206	SiCH ₃ , C ₃ H ₇	53	-0.1078	C ₄ H ₅
39	-0.1191	C ₃ H ₃	92	-0.1069	C ₇ H ₈
45	0.1059	SiHO	39	-0.1067	C ₃ H ₃
79	-0.0989	C ₆ H ₇	83	0.1065	SiC ₄ H ₇

^a See Figures 5 and 6.

Table 3. Ten Largest Peaks from the Loadings Plots of PC1 from a PCA Analysis of Negative Ion Spectra of Samples (Homogeneous 1,9-Decadiene Monolayers with Adsorbed Grubbs' Catalyst) after Different Reaction Times with Norbornene

PC1					
mean centering			autoscaling		
m/z	loadings	species	m/z	loadings	species
1	0.8316	H	35	0.0738	Cl
35	-0.4732	Cl	37	0.0738	³⁷ Cl
17	-0.159	OH	47	0.0738	CCl
37	-0.1492	³⁷ Cl	153	0.0738	unknown
16	-0.1261	O	168	0.0738	unknown
13	0.113	CH	169	0.0738	unknown
25	0.077	C ₂ H	170	0.0738	unknown
12	0.033	C	171	0.0738	unknown
24	0.0264	C ₂	186	0.0738	unknown
14	0.0111	CH ₂	193	0.0738	unknown

^a See Figures 5 and 6.

mild oxidation of the silicon substrate, which is regularly observed in monolayers on scribed silicon.⁴

Kinetics of Polynorbornene Growth as Studied by XPS and ToF-SIMS. XPS and time-of-flight secondary ion mass spectrometry (ToF-SIMS) were used to study the kinetics of polynorbornene growth on 1,9-decadiene monolayers on scribed silicon surfaces. The C 1s/Si 2p XPS ratio showed that polymer growth was complete within ca. 10 min of exposure to monomer (see Figure 4).

ToF-SIMS provides complementary information to XPS in the form of hundreds of atomic and molecular fragments from surfaces. Because of the complexity of ToF-SIMS spectra, principal components analysis (PCA) was applied to the positive and negative ion spectra obtained from polynorbornene samples made with different exposure times to monomer. Chemometrics methods like PCA are increasingly used in ToF-SIMS data analysis to rapidly find the variation between such complicated spectra.³⁸ Four different preprocessing methods were applied to the data: normalization, mean centering, autoscaling, and log scaling. Figure 5a and 5b shows the scores on the first principal component (PC1) using mean centering and autoscaling preprocessing of the positive ion spectra from polynorbornene growth. The other two preprocessing methods used on the positive ion

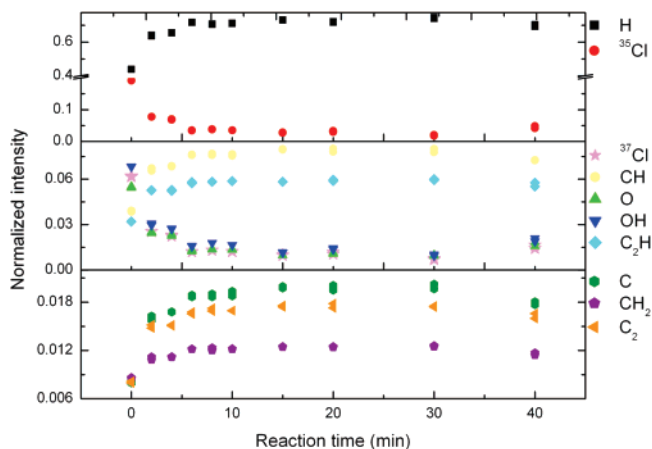


Figure 6. Normalized intensities of the 10 largest peaks in the PC1 loadings plot of a PCA analysis of ToF-SIMS negative ion spectra, the same mean-centered data that were used to make Figure 5c.

data (normalization and log scaling) show essentially the same trends. Figure 5c and 5d shows the scores on PC1 of the negative ion spectra using mean centering and autoscaling preprocessing, respectively, for the polymer growth samples. The negative ion spectra preprocessed with the other two processing methods again show essentially the same trends as those in Figure 5c and 5d. All of these ToF-SIMS results are similar to the XPS results shown in Figure 4. That is, after approximately 10 min, little if any change in the surface chemistry is observed.

Scores on principal components often show graphically the relationships between samples. Loadings, on the other hand, reveal the chemical bases for these relationships. Table 2 shows the 10 largest peaks from the loadings on PC1 of the positive ion data using mean centering and autoscaling. Here, we see that the loadings of pure hydrocarbon fragments, such as C₆H₅⁺, C₅H₇⁺, C₇H₇⁺, C₃H₃⁺, C₆H₇⁺, C₄H₃⁺, C₅H₅⁺, C₆H₆⁺, C₄H₄⁺, C₄H₅⁺, and C₇H₈⁺ are negative. These peaks are expected to come from the polynorbornene brushes. In contrast, the peaks that contain silicon, such as Si⁺, SiH⁺, SiHO⁺, and SiC₄H₇⁺, which are expected to come from the substrate, have the opposite polarity, that is, they have positive values. These data, combined with the scores on PC1 in Figure 5, paint a consistent picture of polynorbornene growth on scribed silicon. That is, the data from surfaces with negative scores on PC1 (see Figure 5a and b), that is, the surfaces with thicker polynorbornene layers, are richer in the peaks in the loading plots with negative polarity, that is, the hydrocarbon peaks. In contrast, the surfaces with positive scores on PC1 (see Figure 5a and b), that is, the surfaces with thinner polynorbornene layers, are richer in the peaks in the loading plots with positive polarity, that is, the silicon-containing peaks that are expected from the substrate. We have previously shown that ToF-SIMS spectra of alkyl monolayers of varying thickness on scribed silicon behave similarly, that is, thicker monolayers were richer in hydrocarbon peaks and thinner monolayers were richer in silicon-containing substrate peaks.³⁵ Please note that the polarity (positive or negative) of the scores and loadings is completely arbitrary because of the well-known sign ambiguity in PCA. That is, in PCA a data matrix, **S**, is decomposed into a scores matrix, **T**, and a loadings matrix,

(38) Wagner, M. S.; Graham, D. J.; Ratner, B. D.; Castner, D. G. *Surf. Sci.* **2004**, *570*, 78.

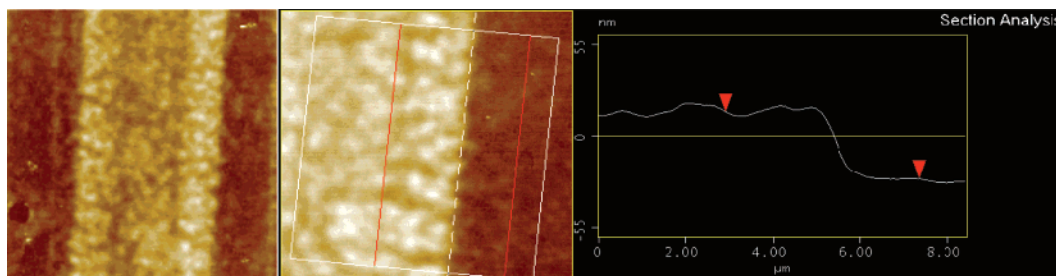


Figure 7. Left: AFM image of a polynorbornene line on a patterned silicon surface. Center and right: AFM section analysis of a polynorbornene line on a patterned silicon surface that shows that the thickness of the polynorbornene is about 40 nm.

$\mathbf{P:S} = \mathbf{TP}^T$. However, it is also true that $\mathbf{S} = (-\mathbf{T})(-\mathbf{P}^T)$.

Table 3 shows the loadings plots from PC1 of the 10 largest peaks and their likely assignments from negative ion spectra (see Figure 5c and d) preprocessed by mean centering and autoscaling. The results for mean centering are similar to those found in Table 2 and Figure 5a and b. That is, in Figure 5c, the thicker polynorbornene films show positive scores and these correspond to the peaks with positive loadings in Table 3, which include fragments expected from a hydrocarbon layer: H^- , CH^- , C_2H^- , C^- , C_2^- , and CH_2^- . Conversely, the surfaces with thinner polymer layers have negative scores (Figure 5c) and loadings (Table 3), and these loadings peaks correspond to species that would be expected from the substrate: $^{35}\text{Cl}^-$, OH^- , $^{37}\text{Cl}^-$, and O^- , where chloride is a common contaminant on surfaces.

The autoscaling results in Table 3 are more difficult to interpret. Autoscaling is a less than ideal method for preprocessing our data because a large fraction of our binned regions contain mostly noise, and autoscaling makes these regions as significant as those that contain real information. In addition, the large number of binned regions we analyze makes it increasingly likely that one or more of these noisy regions will correlate well with the data from real peaks and that these regions will, by chance, emerge as significant in the analysis. Thus, some of the loadings predicted by autoscaling should be unreliable. To check this hypothesis, we examined the raw data at m/z 153, 168, 169, 170, 171, 186, and 193. The binned regions at m/z 153, 168, 169, 170, and 171 appear to contain only noise. Those at m/z 186 and 193 appear to contain small signals.

While the PCA results represent an important, total analysis of the data, it remains essential to stay close to the original data during data analysis. Figure 6 shows the normalized intensities of the 10 largest peaks in the negative ion data (see Table 3). All of these peaks show the expected trends: as polynorbornene growth occurs, signals from ions expected from the substrate decrease in intensity ($^{35}\text{Cl}^-$, $^{37}\text{Cl}^-$, O^- , and OH^-), while signals from ions expected from the polynorbornene film increase in intensity (H^- , CH^- , C_2H^- , C^- , CH_2^- , C_2^-).

Polymer Growth on and Electroless Copper Deposition outside of Patterned Features. It has previously been shown that the chemomechanical method can be used to produce fine, flat lines by drawing an immobilized tungsten carbide ball over the surface of hydrogen-terminated silicon that has been wet with a reactive liquid.¹⁴ Accordingly, this method was performed with 1,9-decadiene to make olefin-terminated lines on silicon. This surface was then immersed in a solution

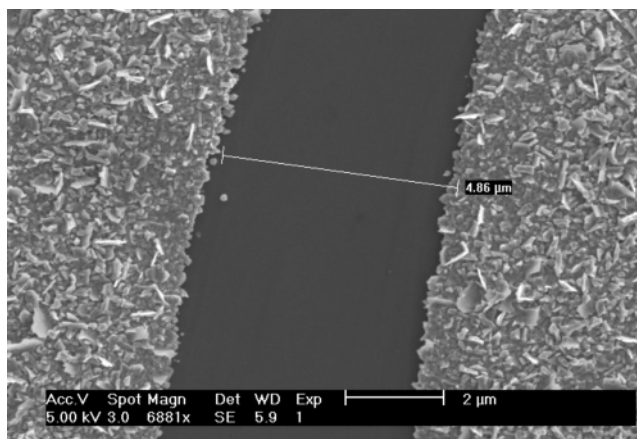


Figure 8. SEM micrograph showing electroless copper deposition adjacent to a polynorbornene line (center) formed by chemomechanical patterning with 1,9-decadiene and Grubbs' polymer growth.

of Grubbs' catalyst, was rinsed, and was immersed in a second solution of norbornene. Figure 7 shows the AFM images of a line and its section image. Polymer growth appears to occur exclusively on the functionalized feature. The thickness of the polynorbornene line is about 40 nm, which is greater than the minimum thickness of the polymer suggested by XPS. Nevertheless, the AFM view of polymer growth also suggests a fair amount of heterogeneity in polymer formation, that is, thicker and thinner spots, which would be more consistent with the XPS results.

We end this paper by discussing an application for polynorbornene features on scribed silicon: the electroless deposition of copper on surface regions unprotected by polynorbornene.³⁹ To attain this end, patterned polymer lines grown with Grubbs' catalyst on 1,9-decadiene monolayers were used as resist layers. As shown in the scanning electron micrograph (SEM) in Figure 8, essentially no copper was deposited on a ca. 5- μm polynorbornene line at the center of the image, while thick copper layers were grown on either side of it. These results illustrate in-situ resist growth, where the polynorbornene mask layer is grown in place after patterning.

Conclusions

In summary, olefin-terminated monolayers and mixed monolayers with terminal olefin functionality have been prepared by chemomechanically modifying silicon. That a

(39) Monolayers chemomechanically patterned onto silicon surfaces using 1-hexadecene and a tungsten carbide ball similarly functioned as resist layers for the electroless deposition of copper.

terminal double bond is present at the monolayer surfaces and that this double bond remains reactive was demonstrated by reactions with bromine, osmium tetroxide, and dichlorocarbene. Grubbs' catalyst was also shown to bind to these surfaces, which then underwent polynorbornene growth by ROMP. The kinetics of Grubbs' catalyst adsorption and polynorbornene growth were investigated. ToF-SIMS gave additional chemical characterization and confirmation of polynorbornene growth as a function of time. Grubbs'

polymer growth was demonstrated on patterned surfaces, and patterned features were found to effectively resist electroless deposition of copper.

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