

Chemomechanical Functionalization and Patterning of Silicon

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ABSTRACT

The chemomechanical method has emerged as a straightforward and convenient tool for simultaneously functionalizing and patterning silicon. This technique simply consists of wetting (or exposing) a silicon surface to a reactive chemical and then scribing. Scribing activates the surface and leads to monolayer formation. The properties of the monolayers are dependent on the reactive chemicals used, and mixed monolayers and functionalized monolayers are easily produced with mixed chemicals or α,ω -bifunctional compounds, respectively. Both micrometer and nanometer sized functionalized features have been created. It has been shown that this technique has potential in a variety of applications.

Introduction

The importance of the semiconductor and microelectronics industries has made silicon one of the most important of all materials. Therefore, to better understand its chemistry, numerous studies have been performed on reconstructed, hydrogen-terminated, porous, and chemomechanically modified silicon.^{1–5} Chemomechanical modification, or scribing, of silicon, which is the subject of this Account, is arguably the least expensive and most rapid approach for *simultaneously* functionalizing and patterning silicon.^{6–22} This method consists of wetting a silicon surface with a reactive compound and then scribing the surface. Scribing breaks through silicon's passivation layer (oxide or hydrogen) to expose a highly reactive surface that appears to react immediately with the reagent with which it is in contact (Figure 1). In general, excellent

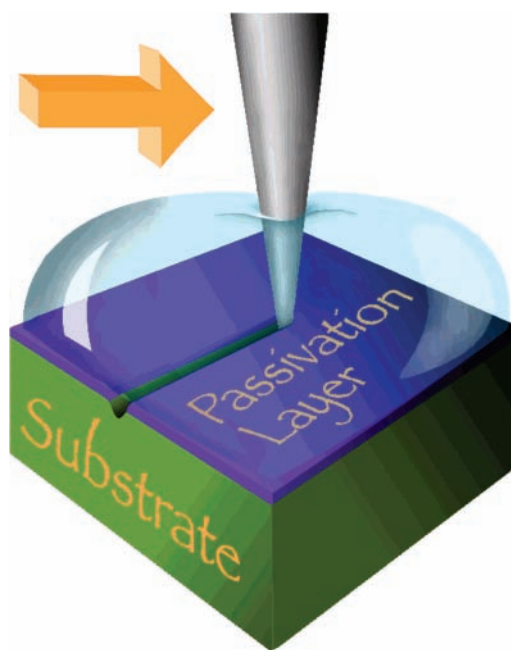


FIGURE 1. Schematic of chemomechanical surface modification. Figure courtesy of Melissa Gardner Wolf.

results are obtained in an open laboratory using compounds that have not been degassed or otherwise specially treated.

In 1992,²³ Abbott, Folkers, and Whitesides created 0.1–1 μm lines on thiol-coated gold surfaces by scribing with a scalpel or carbon fiber.^{23–25} Immersion of these scribed surfaces into a thiol solution led to monolayer formation on the exposed gold. Enclosures of hydrophobic lines on a hydrophilic background were shown to confine droplets of water.²⁶ They noted that, in theory, either atomic force microscopy (AFM) or scanning electron microscopy (SEM) could be similarly used to pattern monolayers on gold.²⁴

In 1997, Liu and Xu not only used AFM to scribe/pattern monolayer-coated gold, but they did so in the presence of another thiol, inducing monolayer formation in exposed regions.^{27,28} They termed this seminal work “nanoshaving” or “nanografting”. The method described in this Account bears a clear resemblance to the Whitesides and Liu approaches.

Before leaving graduate school in 1996, Linford showed that monolayer-coated particles could be prepared by grinding silicon in the presence of 1-hexadecene. A provisional patent was filed on this work in early 1997, and a patent was ultimately issued.²⁹ In this study, the reagent was degassed, and grinding was performed manually in a glovebox.

Other tip-based approaches for surface modification include nanometer-scale lithography on H-passivated Si(100),³⁰ nanopatterning of alkyl monolayers on Si(111),³¹ the modification of self-assembled monolayers by scanning tunneling microscopy (STM),^{32,33} dip-pen nanolithography,³⁴ and control of lipid bilayers on glass.³⁵

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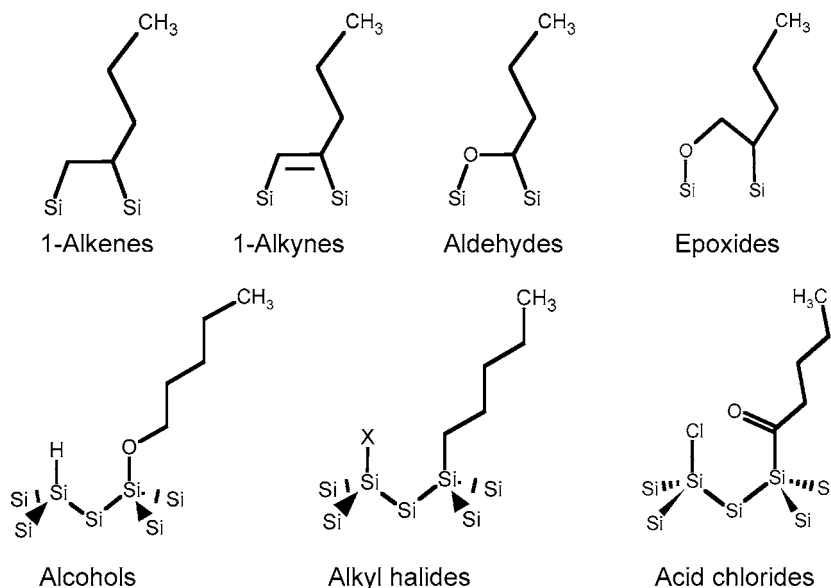


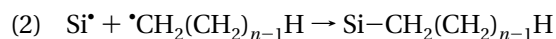
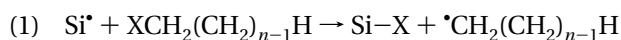
FIGURE 2. Proposed structures of 1-alkenes, 1-alkynes, aldehydes, epoxides, alcohols, alkyl halides, and acid chlorides bonded to Si_{scr} .

Mechanism of Monolayer Formation

Monolayers on scribed silicon (Si_{scr}) have been produced by scribing in the presence of 1-alkenes,^{6,7,9} 1-alkynes,^{6,9} aldehydes,¹² alcohols,⁷ alkyl halides,^{8,9,15} epoxides,¹⁰ and acid chlorides.¹³ Si_{scr} is believed to be similar to $\text{Si}(100)\text{-}2 \times 1$ and $\text{Si}(111)\text{-}7 \times 7$, the two most important reconstructions of silicon, which are also known to react with all of these species,^{36–46} except the epoxides and acid chlorides.^{1–3} To the best of our knowledge, our reports of the reactions of Si_{scr} with epoxides¹⁰ and acid chlorides¹³ are the first to show the reactivity of any bare silicon surface with these compounds.

1-Alkenes and 1-alkynes are believed to react with Si_{scr} to form two carbon–silicon bonds,⁶ and alkyl halides are believed to react to form one carbon–silicon bond,⁸ as shown in Figure 2. The reaction of 1-alkenes and 1-alkynes with Si_{scr} may be through a [2 + 2] addition to surface dimers, as is the case for addition to the $\text{Si}(100)\text{-}2 \times 1$ surface.^{1–3} It is also possible that two adjacent surface radicals react with a double or triple bond to form the structures shown in Figure 2. The stability of monolayers on Si_{scr} made from 1-alkenes and alkyl halides¹⁴ is consistent with adsorbates bound to the surface through silicon–carbon bonds,^{47,48} which are not readily hydrolyzed (see Figure 2). Monolayers on hydrogen-terminated silicon and porous silicon with C–Si linkages have similar stabilities.^{49,50}

It was proposed that silicon reacts with alkyl halides in a two-step mechanism consisting of halogen abstraction by the surface, followed by condensation of the resulting alkyl radicals with the surface,⁸ as shown below.



This process should be driven by the difference in bond strengths between carbon–halogen and silicon–halogen bonds (see Table 1). In support of the first step of this

Table 1. Bond Strengths between Carbon–Halogen and Silicon–Halogen Bonds

X	$D_{298}^{\circ}(\text{C-X})$, ^a kJ/mol	$D_{298}^{\circ}(\text{Si-X})$, ^a kJ/mol	approx $\Delta D^{\circ d}$
Cl	$397 \pm 29^{b,c}$	$406,^b 456 \pm 42^c$	34
Br	$280 \pm 21^{b,c}$	$367.8 \pm 10^b, 343 \pm 50^c$	75.4
I	$209 \pm 21^{b,c}$	$293,^b 339 \pm 84^c$	107

^a D_{298}° is the bond dissociation energy at 298 K. ^b From the Handbook of Chemistry and Physics (CRC), 2000. ^c From Lange's Handbook of Chemistry, 15th ed., 1999. ^d $D_{298}^{\circ}(\text{C-X}) - D_{298}^{\circ}(\text{Si-X})$.

mechanism, X-ray photoelectron spectroscopy (XPS) shows surface halogen, and time of flight secondary ion mass spectrometry (ToF–SIMS) shows SiX^+ species.⁸ High-resolution XPS suggests a Si–Br and a C–Br species in silicon scribed under 1,4-dibromobutane.⁸ ToF–SIMS further shows strong SiCH_3^+ and SiC_2H_5^+ signals from silicon scribed under CH_3I and $\text{C}_2\text{H}_5\text{I}$, respectively.⁹ However, it did not show $\text{C}_x\text{H}_y\text{X}^+$ type fragments, which also supports covalent bonding between halogen atoms and Si.^{8,9}

If the proposed mechanism for formation of monolayers from alkyl halides were operative, it was reasoned that not every alkyl radical would return and react with the surface. Some radicals would diffuse away from the surface where they would dimerize or disproportionate. To confirm this hypothesis, silicon was ground in the presence of different alkyl halides, and the unreacted liquid was analyzed by gas chromatography–mass spectrometry (GC–MS). The expected dimerization and disproportionation products were indeed observed.¹⁵

While there appears to be some complexity in the reaction between Si_{scr} and alcohols, we believe that alcohols, ROH, primarily react dissociatively to form Si–H and Si–OR species. ToF–SIMS provides direct evidence for this possibility in the form of quasi-molecular, $[\text{M} - 1]^-$, ions ($\text{C}_3\text{H}_7\text{O}^-$, $\text{C}_4\text{H}_9\text{O}^-$, or $\text{C}_8\text{H}_{17}\text{O}^-$) from silicon scribed in the presence of 1-propanol, 1-butanol, or 1-octanol, respectively.⁷

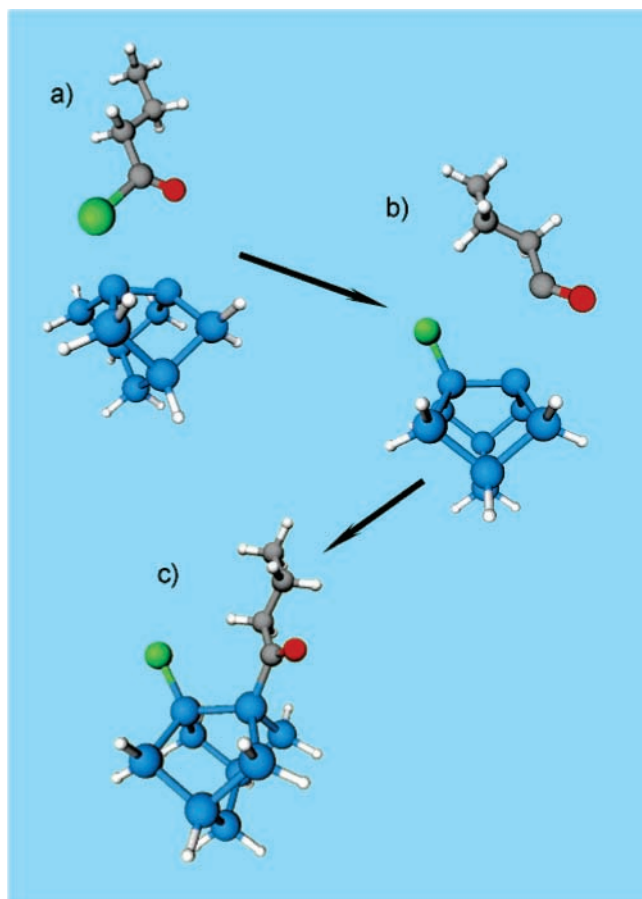
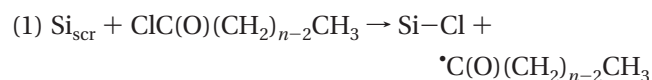


FIGURE 3. Structures of (a) a Si_9H_{12} cluster and butanoyl chloride, (b) the species in panel a after chlorine abstraction, and (c) the final product showing the chemisorbed chlorine and acyl radicals. Geometry minimizations were performed with Hartree–Fock theory using the 6-31+G* basis sets. Blue atoms represent silicon, green chlorine, red oxygen, white hydrogen, and gray carbon. Reproduced with permission from *Langmuir* **2005**, *21*, 2093–2097 (Copyright 2005 American Chemical Society).

Aldehydes are proposed to react with Si_{scr} in the same way that they do with $\text{Si}(100)-2 \times 1$,^{44,46} that is, by cycloaddition to produce four-membered rings (see Figure 2).¹²

Three possible mechanisms for the reaction between epoxides and Si_{scr} were proposed.¹⁰ Ab initio calculations were most consistent with a silicon surface radical attacking the oxygen of an epoxide ring to form a strong silicon–oxygen bond, followed by ring opening and then by Si–C bond formation between a carbon-centered radical on the alkyl chain and a surface silicon radical (see Figure 2).

Si_{scr} is proposed to first react with acid chlorides by chlorine abstraction to form Si–Cl bonds. The acyl radical formed in this process then returns to the surface to condense with a silicon radical. Ab initio calculations (see Figure 3) were consistent with this mechanism:¹³



Also in support of step 1 in this mechanism, XPS shows chlorine on these surfaces. ToF–SIMS of surfaces pre-

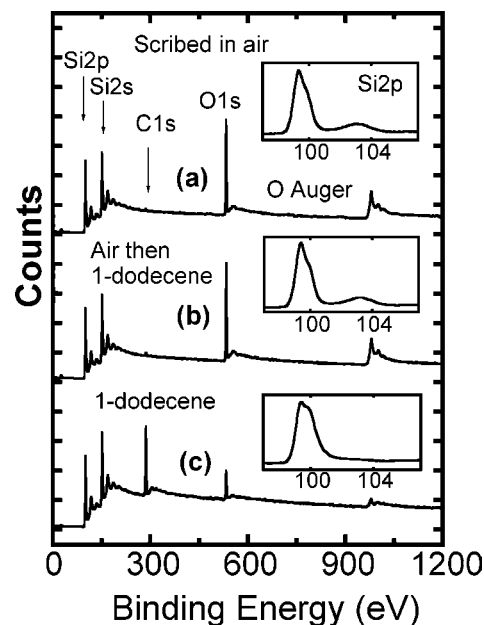


FIGURE 4. XPS spectra of silicon (a) scribed in air, (b) scribed in air and then wet with 1-dodecene, and (c) scribed while wet with 1-dodecene.

pared from both mono- and diacid chlorides shows $\text{Si}^{35}\text{Cl}^+$ and $\text{Si}^{37}\text{Cl}^+$ species.¹³

XPS of Monolayers on Si_{scr}

XPS provides direct evidence for monolayer formation on Si_{scr} .^{6–8,10,12} Figure 4 shows XPS survey spectra with Si 2p narrow scans (insets) of (a) a control experiment in which clean, dry silicon was scribed in the air, (b) another control experiment in which silicon was first scribed in the air and then immediately wet with 1-dodecene, and (c) silicon that was wet with 1-dodecene and then scribed. The control surfaces show small C 1s signals, strong O 1s signals, and chemically shifted Si 2p peaks (~ 103 eV), which indicate silicon oxide. In contrast, the silicon surface wet with 1-dodecene prior to scribing shows a very significant C 1s signal with correspondingly less oxygen and silicon oxide. These latter results suggest alkyl monolayer formation.

Figure 5a shows XPS C 1s/Si 2p ratios of 1-alkenes with different chain lengths, including silicon scribed under a jet of ethylene.^{7,16} The obvious trend is that the carbon signals increase with increasing alkyl chain length of the adsorbate in a linear fashion. As a comparison to help the reader interpret these C 1s/Si 2p ratios, three monolayer hydrogen-terminated $\text{Si}(111)$ were made by heating neat, degassed 1-hexadecene to 150 °C for 1 h.^{49,51} The resulting ellipsometric thicknesses, advancing water contact angles, and XPS C 1s/Si 2p ratios were 15.64 ± 0.03 Å, $98.6^\circ \pm 2.3^\circ$, and 1.27 ± 0.03 , respectively. This C 1s/Si 2p ratio is about the same as the values we previously obtained from silicon scribed under 1-hexadecene.^{6,7} Although surface roughness is a complication in interpreting the XPS results from scribed surfaces, this comparison

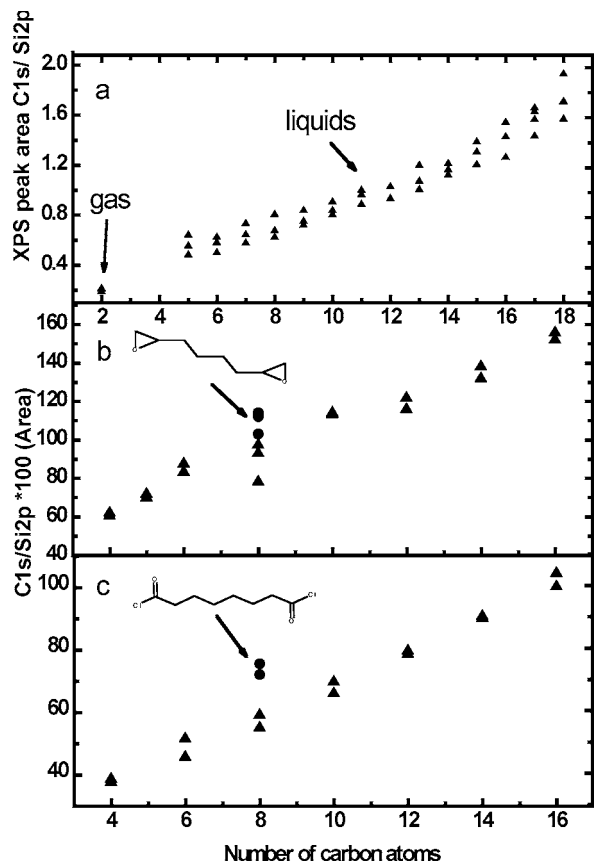


FIGURE 5. XPS C 1s/Si 2p ratios of homologous series of (a) 1-alkenes, (b) monoepoxides and 1,2,7,8-diepoxyoctane, and (c) monoacid chlorides and suberoyl chloride. Adapted in part from *Langmuir* **2005**, *21*, 2093–2097 (Copyright 2005 American Chemical Society) and *Angew. Chem., Int Ed.* **2003**, *42*, 4046–4049 (Copyright 2003 Wiley-VCH).

study suggests that complete, or nearly complete, monolayers are produced when silicon is scribed under reactive reagents.

The trend observed by XPS for 1-alkenes is also found for 1-alkynes,⁶ 1-haloalkanes,⁸ epoxides (Figure 5b),¹⁰ acid chlorides (Figure 5c),¹³ and aldehydes.¹² In Figure 5b,c, somewhat higher C 1s/Si 2p ratios are found for 1,2,7,8-diepoxyoctane and suberoyl chloride compared to 1,2-epoxyoctane and octanoyl chloride, respectively. These results are most likely a reflection of higher densities of functional groups in the neat bifunctional liquids, compared to the monofunctional compounds.

High-resolution XPS has also been used to characterize monolayers on scribed silicon. For example, the fits to the C 1s narrow scans from silicon scribed under octanoyl chloride and suberoyl chloride ($\text{ClCO}(\text{CH}_2)_6\text{COCl}$) are consistent with chemisorption of these species (see Figure 6). The spectrum from suberoyl chloride contains one large peak and three small peaks of nearly equal area.¹³ The large peak is assigned to chemically unshifted carbon (C–C, C–H). The peak shifted +2.0 eV from the main peak is consistent with a carbonyl carbon bonded to silicon. The small peak shifted +4.5 eV from the main silicon peak is consistent with an acyl chloride carbon. The other small peak is due to carbon adjacent to an acyl chloride, which

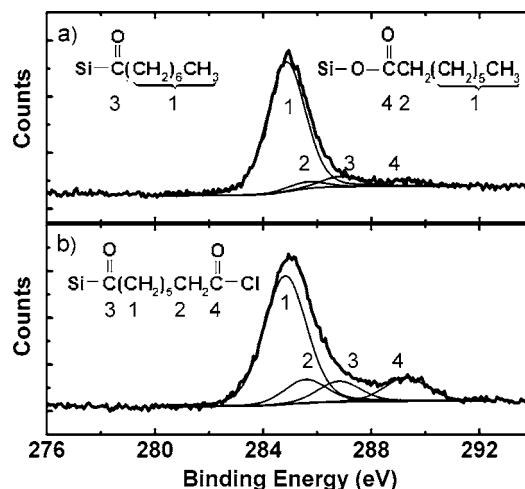


FIGURE 6. C 1s XPS narrow scans of silicon scribed under (a) octanoyl chloride and (b) suberoyl chloride. Reproduced with permission from *Langmuir* **2005**, *21*, 2093–2097.

is secondarily shifted by +0.75 eV. The ratio of the Si–C(O)–R and –COCl peaks to the other two signals is 1:3.5, which is in reasonable agreement with the expected ratio of 1:3. The extra carbon in the main peak may be due to decarbonylation of the reagent.

Wetting of Monolayers on Si_{scr}

The formation of monolayers on Si_{scr} from monofunctional hydrocarbons should result in hydrophobic surfaces. Figure 7 shows water contact angles for homologous series of 1-alkenes, epoxides, and acid chlorides.^{6,10,13,16} For the shorter chain adsorbates, the surface hydrophobicity increases with alkyl chain length. However, the values plateau at around 10 carbon atoms. These data suggest that after a certain thickness water droplets cannot “feel” the underlying substrate. Analogous behavior has also been reported for alkyl monolayers of thiols on gold and silanes on silicon oxide.^{52–54}

Typical methyl-terminated monolayers from long-chain adsorbates on planar substrates have water contact angles of 111° – 115° .^{52,54} The abnormally high values observed on monolayers on Si_{scr} are attributed to surface roughness. The relatively low contact angles from the surfaces prepared with bifunctional adsorbates, compared to their monofunctional analogues, that is, 1,2,7,8-diepoxyoctane (Figure 7b) and suberoyl chloride (Figure 7c), are consistent with polar headgroups, that is, an oxirane ring and an acyl chloride moiety, at the top of the monolayers.

ToF–SIMS of Monolayers on Si_{scr}

ToF–SIMS spectra from monolayers on Si_{scr} made from various adsorbates generally contain a large number of hydrocarbon (C_xH_y^+) and silicon–hydrocarbon (SiC_xH_y^+) fragments. The presence of SiC_xH_y^+ type fragments suggests covalent bonding of alkyl chains to the silicon surfaces through Si–C bonds. Studies of monolayers of 1-alkenes,⁹ 1-alkynes,⁹ alkyl halides,⁹ aldehydes,¹² and acid chlorides¹³ on Si_{scr} reveal that in general the relative intensities of these fragments for a homologous series

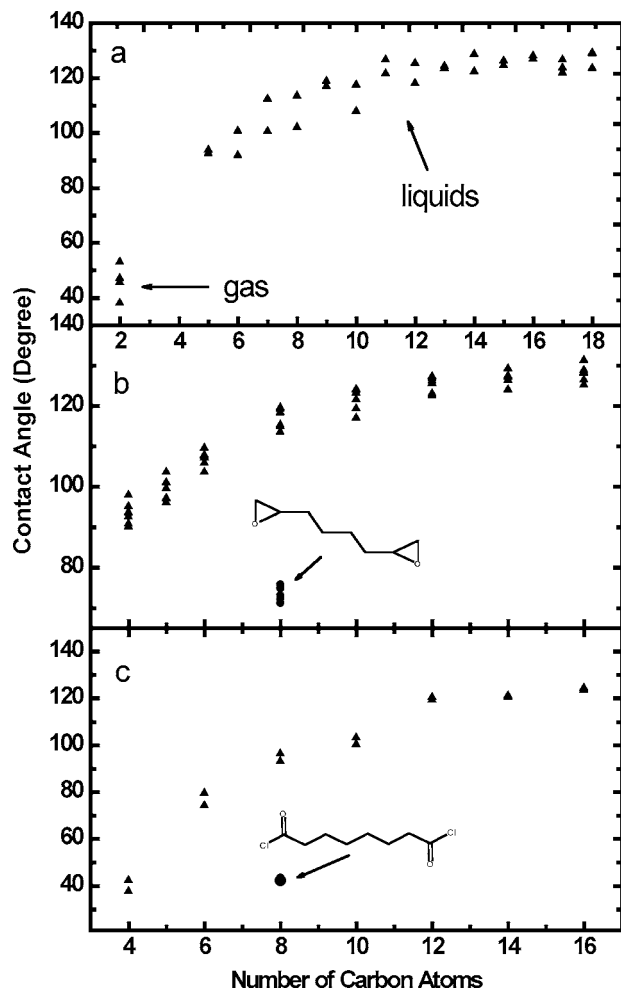


FIGURE 7. Sessile water contact angles of (a) 1-alkenes, (b) monoepoxides and 1,2,7,8-diepoxyoctane, and (c) monoacid chlorides and suberoyl chloride. Adapted with permission in part from *Langmuir* **2005**, *21*, 2093–2097 (Copyright 2005 American Chemical Society) and *Angew. Chem., Int Ed.* **2003**, *42*, 4046–4049 (Copyright 2003 Wiley-VCH).

increase with increasing alkyl chain length, which is consistent with XPS and wetting results.^{9,13}

Consistent with their lower water contact angles (see Figure 7), ToF–SIMS of monolayers prepared from 1,2,7,8-diepoxyoctane shows more oxygen-containing peaks (CHO^+ , CH_2O^+ , $\text{C}_2\text{H}_3\text{O}^+$, $\text{C}_3\text{H}_5\text{O}^+$, and $\text{C}_4\text{H}_7\text{O}^+$) than surfaces prepared under 1,2-epoxyoctane.¹⁰

Principle Components Analysis of ToF–SIMS Data

Although a univariate approach to data analysis is often valid, it may miss or ignore much of the information in ToF–SIMS spectra. Principal components analysis (PCA) better considers all, or at least a larger fraction, of the variation.⁵⁵ A PCA analysis of the positive ion, negative ion, and concatenated (linked) positive and negative ion spectra of monolayers on Si_{scr} was performed.²² The analysis of all of the positive ion spectra revealed a good correlation between the number of carbon atoms in all of the adsorbates and the scores on PC1. PCA of all of the negative ion spectra and the concatenated positive and

negative ion spectra showed a correlation based on the number of carbon atoms in the adsorbate and the class of the adsorbate. These results imply that the positive ion spectra are most sensitive to monolayer thickness, while the negative ion spectra are sensitive to the nature of the substrate–monolayer interface and monolayer thickness. Loadings of monolayers made with homologous series show an inverse relationship between inorganic fragments that are expected from the substrate and organic fragments expected from the monolayer. These latter results, which strongly suggest increasing film thickness with increasing carbon number of the adsorbate, are significant because optical ellipsometry is not possible on rough scribed surfaces.

Mixed Monolayers and Functionalized Monolayers on Si_{scr}

Varying the ratio of adsorbates in mixed monolayers is a means of tailoring surface properties.^{54,56,57} However, unlike mixed monolayers of thiols on gold, the ratios of adsorbates in mixed monolayers on Si_{scr} , for example, 1-decene and 1-octadecene,⁷ 1-decene and 1-decanol,⁷ and 1,2-epoxyoctane and 1,2,7,8-diepoxyoctane,¹⁰ appear to closely resemble the ratios in the scribing liquids. These results are not unexpected because the strong covalent bonds that are believed to form between Si_{scr} and adsorbates (Figure 2) would be more consistent with kinetic, and not thermodynamic, control in monolayer formation.^{7,10}

Surfaces with reactive functional groups are important in a variety of applications, and a straightforward method for preparing functionalized monolayers on Si_{scr} is with homobifunctional reactive species. Functionalized monolayer formation has been demonstrated with 1,4-dibromobutane ($\text{Br}(\text{CH}_2)_4\text{Br}$),⁸ 1,2,7,8-diepoxyoctane,¹⁰ and suberoyl chloride ($\text{ClCO}(\text{CH}_2)_6\text{COCl}$).¹³ XPS, wetting, ToF–SIMS, and chemical reactivity provide evidence for formation of functionalized monolayers (vide supra, see also Figures 5, 7, and 8).

The amine reactivity of epoxide- and acid chloride-terminated monolayers has also been demonstrated.^{10,13} Figure 8 shows XPS and wetting of mixed monolayers prepared from binary solutions of 1,2,7,8-diepoxyoctane and 1,2-epoxyoctane before and after reaction with octylamine. After reaction, XPS C 1s/Si 2p (Figure 8a), XPS N 1s/Si 2p (Figure 8b), and water contact angles (Figure 8c) increase with increasing mole fraction of 1,2,7,8-diepoxyoctane in the solution.

For acid chloride-terminated monolayers made from suberoyl chloride,¹³ yields as high as 60% between a terminal acyl chloride group and piperazine, morpholine, and octylamine were found. BSA also bound to this surface.

Different Patterning Tips

Chemomechanical surface modification on silicon was first performed with a diamond-tipped rod that scribed native oxide-coated silicon.^{6–8} In all of these experiments,

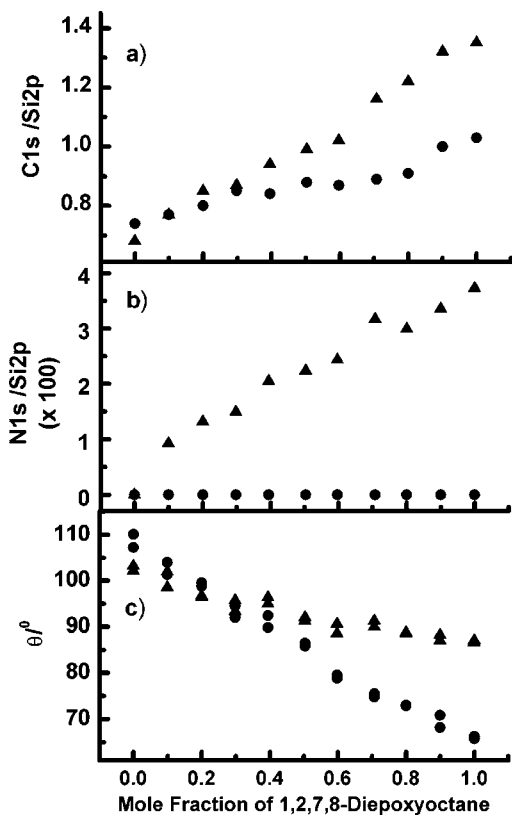


FIGURE 8. Physical properties of mixed monolayers prepared by scribing silicon under binary solutions of 1,2-epoxyoctane and 1,2,7,8-diepoxyoctane before (●) and after (▲) reaction with octylamine: (a) C 1s/Si 2p XPS uncorrected area ratio; (b) N 1s/Si 2p XPS uncorrected area ratio; (c) sessile water contact angles. Reproduced with permission from *Angew. Chem., Int Ed.* **2003**, *42*, 4046–4049 (Copyright 2003 Wiley-VCH) and *Nonconventional lithography and patterning: techniques and applications*; Bucknall, D., Ed.; Woodhead Publishing: Cambridge, U.K., 2005; Chapter 4 (Copyright 2005 Woodhead Publishing).

the feature depths were much greater than the thickness of the native oxide (ca. 2 nm), which suggests that the native oxide has very little to do with the reactions that are observed. The features produced with a diamond tip (with 2–3 N force) were irregular, broad ($\sim 100 \mu\text{m}$), and deep ($\sim 5 \mu\text{m}$) (Figure 9a). An improved tip holder, or end-effector, was developed to better control the force on the tip.^{19,20} Using a diamond-tipped rod in the end-effector, one can produce narrower features (1–10 μm), although surface roughness remains an issue.²¹ To further improve feature quality, a miniature tungsten carbide ball (1/32 in. in diameter) was affixed to a metal rod and pulled over a hydrogen-terminated silicon surface. (At reasonable forces, the tungsten carbide ball was incapable of penetrating the native oxide on silicon.) Surface features that were less than 50 μm wide and that had submicrometer edge roughness were made in this manner (Figure 9b). More remarkably, the features are only a few nanometers deep.¹¹ Unlike features scribed with a diamond tip, surface features made with a tungsten carbide ball are invisible to the naked eye, although their presence is apparent by AFM, SEM, and imaging ToF–SIMS.

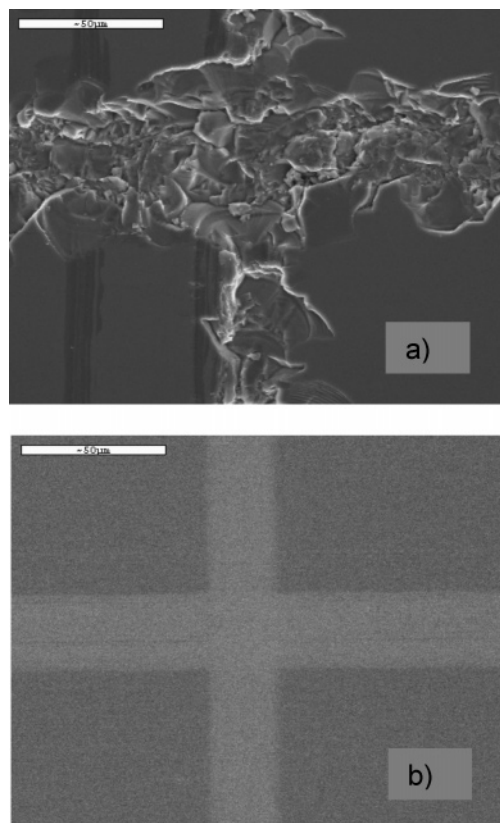


FIGURE 9. SEM of a silicon surface scribed with (a) a diamond-tipped rod and (b) a tungsten carbide ball. The scale bars represent 50 μm . Reproduced with permission from *Langmuir* **2003**, *19*, 985–988.

Scribing Silicon at Nanometer Dimensions

An important goal for patterning silicon by the chemomechanical method is to make surface features with nanometer dimensions. A smaller tip and better control of forces on the tip should allow attainment of this goal. Therefore, AFM, which uses very small forces (micronewton to piconewton) on very small probes (ca. 20 nm tip radii) was employed to chemomechanically pattern hydrogen-terminated silicon surfaces.¹⁷ The widths of the resulting features were controlled by the force on the tip and ranged from 30 to 100 nm (Figure 10). In these studies, an AFM fluid cell was required to immerse the AFM probe and silicon surface in a reactive chemical.

Gas-Phase Modification of Si_{scr}

A disadvantage of the chemomechanical method is the need to remove unreacted liquid from surfaces after scribing. Recently, silicon was scribed under a jet of a reactive gas: ethylene, acetylene, or air (a control).¹⁶ XPS (Figure 5a), wetting (Figure 7a), and ToF–SIMS, including a principal components analysis, show functionalization of Si_{scr} by these reagents. Thermal desorption spectroscopy (TDS) also provides direct evidence for chemisorption.

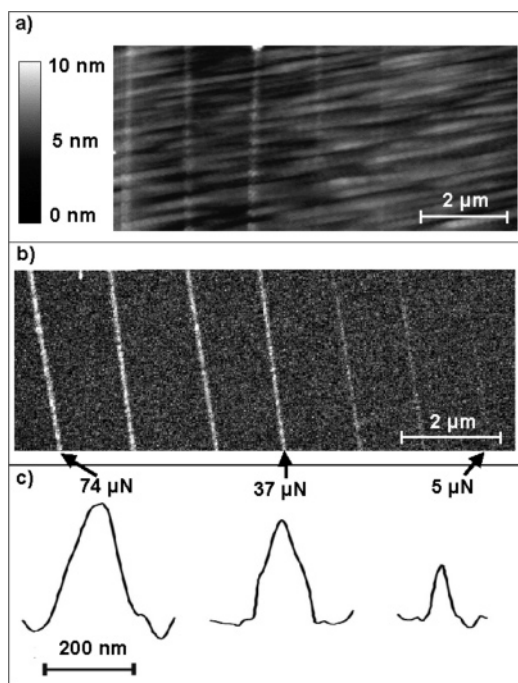


FIGURE 10. (a) In situ AFM and (b) corresponding SEM images of seven lines scribed on silicon in the presence of $\text{CF}_3(\text{CF}_2)_7\text{CH}=\text{CH}_2$. Forces were, starting from the left, 74, 62, 49, 37, 25, 12, and 5 μN , and the tip speed was 10 $\mu\text{m/s}$. (c) Profile plots of three of the lines in part b. The arrows indicate the line from which each of the plots were made, and the labels refer to the force used to scribe the lines. The vertical axis is the grayscale value. Reprinted with permission from *Appl. Phys. Lett.* **2003**, *82*, 808–810. Copyright 2003 American Institute of Physics.



FIGURE 11. Hydrophilic silicon substrate containing hydrophobic lines after a rinse with DI water. *Lab Chip* **2004**, *4*, 553–557—Reproduced by permission of The Royal Society of Chemistry.

Applications for Chemomechanically Patterned Silicon

Hydrophobic corrals are enclosures of hydrophobic lines on a hydrophilic background that hold droplets of water and other liquids (Figure 11).^{6,18} Polyelectrolyte multilayer growth has been demonstrated in a single hydrophobic corral⁶ and over an array of hydrophobic corrals.¹⁸ Colloidal carbon, semiconductor nanocrystals, and DNA have also been loaded into hydrophobic corrals made with a

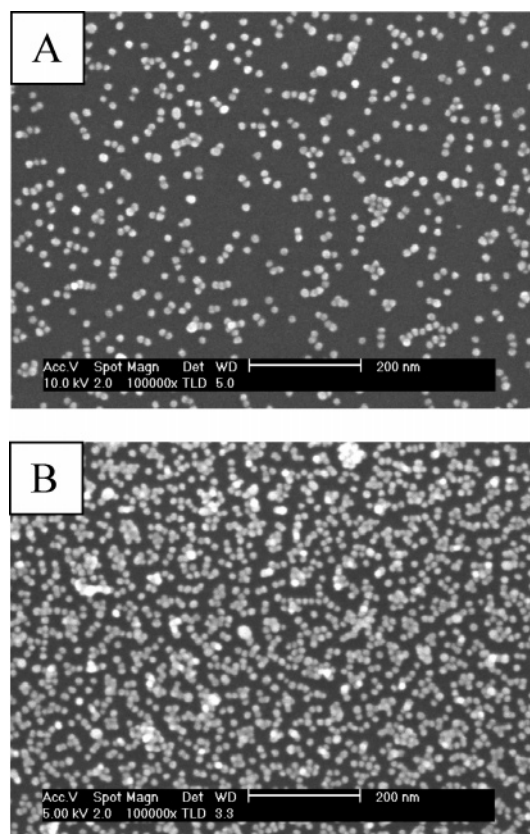


FIGURE 12. SEM images of polyelectrolyte multilayers in hydrophobic corrals on a single silicon chip after exposure to a solution of 13 nm Au nanoparticles for (A) 10 min and (B) 60 min. Scale bars are 200 nm. *Lab Chip* **2004**, *4*, 553–557—Reproduced by permission of The Royal Society of Chemistry.

tungsten carbide ball.¹¹ An array of hydrophobic corrals on a single surface has been used to study the kinetics of gold nanoparticle deposition onto polyelectrolyte surfaces (Figure 12).¹⁸

Two other applications of scribing are noteworthy. First, it was shown that hydrophilic anchor plates for matrix-assisted laser desorption ionization (MALDI) mass spectrometry can be prepared in a simple and straightforward manner by scribing a hydrophobic silanized silicon surface in the presence of water.⁵ Similar anchor plates had been previously developed to improve MALDI's poor spot-to-spot reproducibility by focusing sample onto a single hydrophilic patch on a surface.⁵⁸ MALDI from ca. 200 μm hydrophilic anchors (patches) on silanized silicon showed good signal sensitivity and reproducibility compared to conventional MALDI, and interestingly, the signal from a test peptide depended on the shape of the anchor.

Scribing has also been used to prepare masters for microcontact printing⁵⁹ with 1–12 μm features (Figure 13). In this method, glass microscope slides are scribed with a diamond tip held in the end-effector, which was attached to a computer numerically controlled (CNC) milling machine.²¹ CNCs with ca. 1 μm resolution in the plane are widely available, increasing the accessibility of the chemomechanical approach. The resulting patterns are then transferred to poly(methyl methacrylate) (PMMA) by

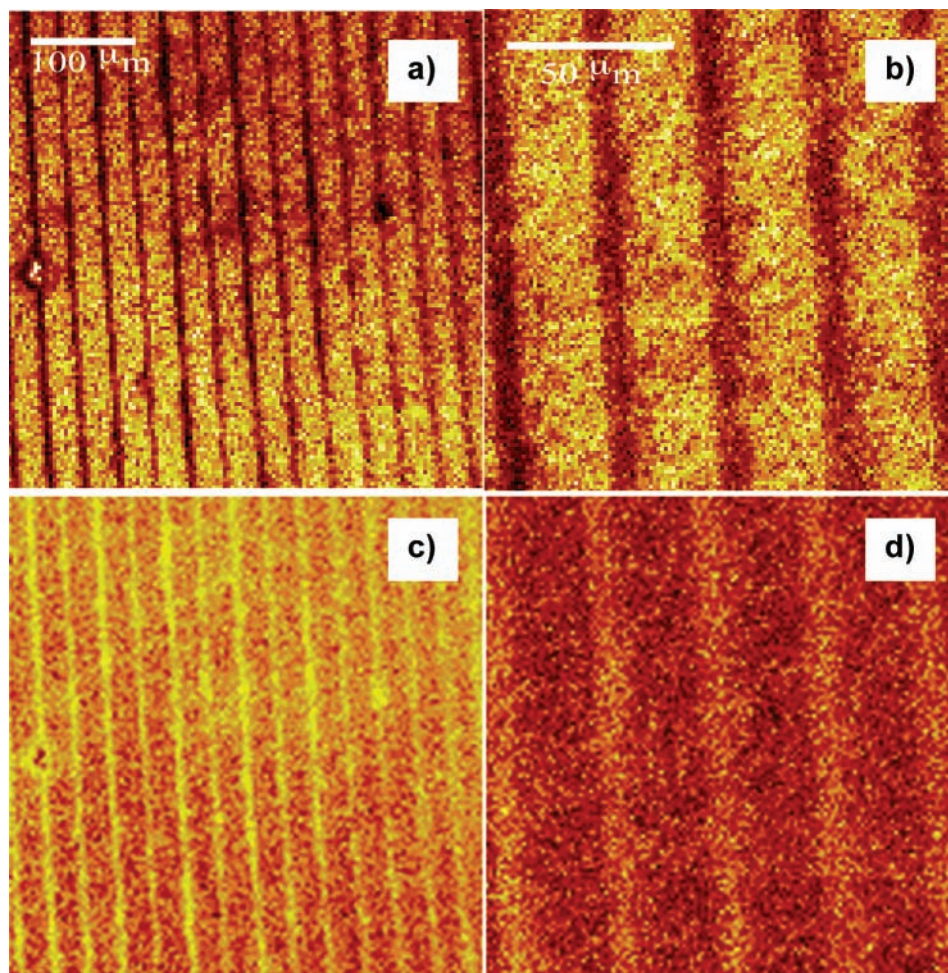


FIGURE 13. Microcontact printing using a stamp produced from a scribed master: (a) ToF-SIMS F^- ion image of a microcontact printed silicon surface; (b) a close up of image a—the brighter lines indicate higher concentrations of F^- ; (c,d) the first principal component of a PCA analysis of the mass spectra from which images a and b were taken, respectively, which further demonstrate the expected chemical contrast of the patterned surface. Reprinted with permission from *Rev. Sci. Instrum.* **2004**, *75*, 3065–3067. Copyright 2004 American Institute of Physics.

embossing. Finally, elastomeric stamps of poly(dimethylsiloxane) (PDMS) are cast from the PMMA negatives to make a replica of the original scribed surface. This entire process only takes a few hours. Microcontact printing using the PDMS stamps is confirmed with ToF-SIMS. In this approach, no clean room, clean room equipment, or lasers, which to date have been needed to prepare masters for microcontact printing,^{59–61} are needed.

The Future

A number of frontiers exist for the chemomechanical method. One is improved characterization to shed greater light on the structure and mechanism of formation of monolayers. For example, TDS has played an important role in understanding the chemistry of bare reconstructed silicon^{1,2} and should similarly prove useful in understanding monolayers on Si_{scr} from most of the adsorbates that have been studied. Vibrational spectroscopy will also increase our understanding of these new materials. Another frontier is improved surface patterning. The most important direction in this regard is better control and

understanding of AFM patterning. New surface chemistry also remains a priority, especially the chemistry of monolayers with pendant reactive groups.

References

- (1) Buriak, J. M. Organometallic Chemistry on Silicon and Germanium Surfaces. *Chem. Rev.* **2002**, *102*, 1271–1308.
- (2) Hamers, R. J.; Wang, Y. Atomically-Resolved Studies of the Chemistry and Bonding at Silicon Surfaces. *Chem. Rev.* **1996**, *96*, 1261–1290.
- (3) Bent, S. F. Organic functionalization of group IV semiconductor surfaces: principles, examples, applications, and prospects. *Surf. Sci.* **2002**, *500*, 879–903.
- (4) Sieval, A. B.; Linke, R.; Zuilhof, H.; Sudhölter, E. J. R. High-Quality Alkyl Monolayers on Silicon Surfaces. *Adv. Mater.* **2000**, *12*, 1457–1460.
- (5) Linford, M. R.; Davis, R. C.; Magleby, S. P.; Howell, L. L.; Jiang, G.; Thulin, C. D. Chemomechanical surface modification of materials for patterning. In *Nonconventional lithography and patterning: techniques and applications*; Bucknall, D., Ed.; Woodhead Publishing: Cambridge, U.K., in press, 2005.
- (6) Niederhauser, T. L.; Jiang, G.; Lua, Y.-Y.; Dorff, M. J.; Woolley, A. T.; Asplund, M. C.; Berges, D. A.; Linford, M. R. A New Method of Preparing Monolayers on Silicon and Patterning Silicon Surfaces by Scribing in the Presence of Reactive Species. *Langmuir* **2001**, *17*, 5889–5900.

- (7) Niederhauser, T. L.; Lua, Y.-Y.; Jiang, G.; Davis, S. D.; Matheson, R.; Hess, D. A.; Mowat, I. A.; Linford, M. R. Arrays of Chemomechanically Patterned Patches of Homogeneous and Mixed Monolayers of 1-Alkenes and Alcohols on Single Silicon Surfaces. *Angew. Chem., Int. Ed.* **2002**, *41*, 2353–2356.
- (8) Niederhauser, T. L.; Lua, Y.-Y.; Sun, Y.; Jiang, G.; Strossman, G. S.; Pianetta, P.; Linford, M. R. Formation of (Functionalized) Monolayers and Simultaneous Surface Patterning by Scribing Silicon in the Presence of Alkyl Halides. *Chem. Mater.* **2002**, *14*, 27–29.
- (9) Lua, Y.-Y.; Niederhauser, T. L.; Matheson, R.; Bristol, C.; Mowat, I. A.; Asplund, M. C.; Linford, M. R. Static Time-of-Flight Secondary Ion Mass Spectrometry of Monolayers on Scribed Silicon derived from 1-Alkenes, 1-Alkynes and 1-Haloalkanes. *Langmuir* **2002**, *18*, 4840–4846.
- (10) Lua, Y.-Y.; Lee, M. V.; Fillmore, W. J. J.; Matheson, R.; Sathya-palan, A.; Asplund, M. C.; Fleming, S. A.; Linford, M. R. Amine-Reactive Monolayers on Scribed Silicon with Controlled Levels of Functionality: Reaction of a Bare Silicon Surface with Mono- and Diepoxides. *Angew. Chem., Int. Ed.* **2003**, *42*, 4046–4049.
- (11) Lua, Y.-Y.; Niederhauser, T. L.; Wacaser, B. A.; Mowat, I. A.; Woolley, A. T.; Davis, R. C.; Fishman, H. A.; Linford, M. R. Chemomechanical Production of Submicron Edge Width, Functionalized, $\sim 20\ \mu\text{m}$ Features on Silicon. *Langmuir* **2003**, *19*, 985–988.
- (12) Lua, Y.-Y.; Fillmore, W. J. J.; Linford, M. R. Aldehydes react with scribed silicon to form alkyl monolayers. Characterization by ToF-SIMS suggests an even-odd effect. *Appl. Surf. Sci.* **2004**, *231–232*, 323–327.
- (13) Lua, Y.-Y.; Fillmore, W. J. J.; Yang, L.; Lee, M. V.; Savage, P. B.; Asplund, M. C.; Linford, M. R. The First Reaction of a Bare Silicon Surface with Acid Chlorides, and a One-Step Preparation of Acid Chloride Terminated Monolayers on Scribed Silicon. *Langmuir* **2005**, *21*, 2093–2097.
- (14) Jiang, G.; Niederhauser, T. L.; Davis, S. D.; Lua, Y.-Y.; Cannon, B. R.; Dorff, M. J.; Howell, L. L.; Magleby, S. P.; Linford, M. R. Stability of alkyl monolayers on chemomechanically scribed silicon to air, water, hot acid, and X-rays. *Colloids Surf., A* **2003**, *226*, 9–16.
- (15) Jiang, G.; Niederhauser, T. L.; Fleming, S. A.; Asplund, M. C.; Linford, M. R. Evidence for a Radical Mechanism in Monolayer Formation on Silicon Ground (or Scribed) in the Presence of Alkyl Halides. *Langmuir* **2004**, *20*, 1772–1774.
- (16) Lee, M. V.; Richards, J.; Linford, M. R.; Casey, S. M. Chemomechanical Modification of Silicon with Gas-Phase Reagents. *J. Vac. Sci. Technol., B*, submitted for publication, 2005.
- (17) Wacaser, B. A.; Maughan, M. J.; Mowat, I. A.; Niederhauser, T. L.; Linford, M. R.; Davis, R. C. Chemomechanical surface patterning and functionalization of silicon surfaces using an atomic force microscope. *Appl. Phys. Lett.* **2003**, *82*, 808–810.
- (18) Owen, J. I.; Niederhauser, T. L.; Wacaser, B. A.; Christenson, M. P.; Davis, R. C.; Linford, M. R. Automated, controlled deposition of nanoparticles on polyelectrolyte coated silicon from chemomechanically patterned droplet arrays. *Lab Chip* **2004**, *4*, 553–557.
- (19) Cannon, B. R.; Magleby, S. P.; Howell, L. L.; Jiang, G.; Niederhauser, T. L.; Linford, M. R. Influence of Scribe Speed and Force on Chemomechanical Nanofunctionalized Features. Presented at the ASME International Mechanical Engineering Congress and Exposition, 2002, New Orleans, LA.
- (20) Cannon, B. R.; Lillian, T. D.; Magleby, S. P.; Howell, L. L.; Linford, M. R. A compliant end-effector for microscribing. *Precis. Eng.* **2005**, *29*, 86–94.
- (21) Zilch, L. W.; Hussein, G. A.; Lua, Y.-Y.; Lee, M. V.; Gertsch, K. R.; Cannon, B. R.; Perry, R. M.; Sevy, E. T.; Asplund, M. C.; Woolley, A. T.; Linford, M. R. A rapid and convenient method for preparing masters for microcontact printing with 1–12 μm features. *Rev. Sci. Instrum.* **2004**, *75*, 3065–3067.
- (22) Yang, L.; Lua, Y.-Y.; Jiang, G.; Tyler, B. J.; Linford, M. R. A Multivariate Analysis of ToF-SIMS Spectra of Monolayers on Scribed Silicon. *Anal. Chem.* **2005**, *77*, 4654–4661.
- (23) Abbott, N. L.; Folkers, J. P.; Whitesides, G. M. Manipulation of the Wettability of Surfaces on the 0.1 to 1 Micrometer Scale Through Micromachining and Molecular Self-Assembly. *Science* **1992**, *257*, 1380–1382.
- (24) Abbott, N. L.; Kumar, A.; Whitesides, G. M. Using Micromachining, Molecular Self-Assembly, and Wet Etching to Fabricate 0.1–1 μm -Scale Structures of Gold and Silicon. *Chem. Mater.* **1994**, *6*, 596–602.
- (25) Abbott, N. L.; Rolison, D. R.; Whitesides, G. M. Combining Micromachining and Molecular Self-Assembly To Fabricate Microelectrodes. *Langmuir* **1994**, *10*, 2672–2682.
- (26) Abbott, N. L.; Whitesides, G. M.; Racz, L. M.; Szekely, J. Using Finite Element Analysis To Calculate the Shapes of Geometrically Confined Drops of Liquids on Patterned, Self-Assembled Monolayers: A New Method To Estimate Excess Interfacial Free Energies gsv-gsl. *J. Am. Chem. Soc.* **1994**, *116*, 290–294.
- (27) Xu, S.; Liu, G.-Y. Nanometer-Scale Fabrication by Simultaneous Nanoshaving and Molecular Self-Assembly. *Langmuir* **1997**, *13*, 127–129.
- (28) Liu, G.-Y.; Xu, S.; Qian, Y. Nanofabrication of Self-Assembled Monolayers Using Scanning Probe Lithography. *Acc. Chem. Res.* **2000**, *33*, 457–466.
- (29) Linford, M. R. Producing coated particles by grinding in the presence of reactive species. U.S. Patent, 2000.
- (30) Lee, H. T.; Oh, J. S.; Park, S.-J.; Park, K.-H.; Ha, J. S.; Yoo, H. J.; Koo, J.-Y. Nanometer-scale lithography on H-passivated Si(100) by atomic force microscope in air. *J. Vac. Sci. Technol., A* **1997**, *15*, 1451–1454.
- (31) Ara, M.; Graaf, H.; Tada, H. Nanopatterning of alkyl monolayers covalently bound to Si(111) with an atomic force microscope. *Appl. Phys. Lett.* **2002**, *80*, 2565–2576.
- (32) Lercel, M. J.; Redinbo, G. F.; Craighead, H. G.; Sheen, C. W.; Allara, D. L. Scanning tunneling microscopy based lithography of octadecanethiol on Au and GaAs. *Appl. Phys. Lett.* **1994**, *65*, 974–976.
- (33) Perkins, F. K.; Dobisz, E. A.; Brandow, S. L.; Koloski, T. S.; Calvert, J. M.; Rhee, K. W.; Kosakowski, J. E.; Marrian, C. R. K. Proximal probe study of self-assembled monolayer resist materials. *J. Vac. Sci. Technol., B* **1994**, *12*, 3725–3730.
- (34) Piner, R. D.; Zhu, J.; Xu, F.; Hong, S.; Mirkin, C. A. “Dip-Pen” Nanolithography. *Science* **1999**, *283*, 661–663.
- (35) Cremer, P. S.; Boxer, S. G. Formation and Spreading of Lipid Bilayers on Planar Glass Supports. *J. Phys. Chem. B* **1999**, *103*, 2554–2559.
- (36) Lu, X. Diradical Mechanism for the [2 + 2] Cycloaddition of Ethylene on Si(100) Surface. *J. Am. Chem. Soc.* **2003**, *125*, 6384–6385.
- (37) Lopinski, G. P.; Moffatt, D. J.; Wayner, D. D. M.; Wolkow, R. A. How Stereoselective Are Alkene Addition Reactions on Si(100)? *J. Am. Chem. Soc.* **2000**, *122*, 3548–3549.
- (38) Liu, Q.; Hoffmann, R. The Bare and Acetylene Chemisorbed Si(001) Surface, and the Mechanism of Acetylene Chemisorption. *J. Am. Chem. Soc.* **1995**, *117*, 4082–4092.
- (39) Taylor, P. A.; Wallace, R. M.; Cheng, C. C.; Weinberg, W. H.; Dresser, M. J.; Choyke, W. J.; Yates, J. T., Jr. Adsorption and Decomposition of Acetylene on Si(100)-(2 \times 1). *J. Am. Chem. Soc.* **1992**, *114*, 6754–6760.
- (40) Chen, Y.; Liu, Z.; Zhang, Q.; Feng, K.; Lin, Z. Effect of atomic hydrogen on the acetylene adsorbed Si(100)(2 \times 1) surface. *Appl. Phys. Lett.* **1995**, *67*, 2936–2938.
- (41) Bronikowski, M. J.; Hamers, R. J. Atomically Resolved Scanning Tunneling Microscopy Study of the Adsorption and Dissociation of Methylchloride on Si(001). *J. Vac. Sci. Technol., A* **1995**, *13*, 777–781.
- (42) Keeling, L. A.; Chen, L.; Greenlief, C. M.; Mahajan, A.; Bonser, D. Direct Evidence for β -hydride elimination on Si(100). *Chem. Phys. Lett.* **1994**, *217*, 136–141.
- (43) Zhang, L.; Carman, A. J.; Casey, S. M. Adsorption and Thermal Decomposition Chemistry of 1-Propanol and Other Primary Alcohols on the Si(100) Surface. *J. Phys. Chem. B* **2003**, *107*, 8424–8432.
- (44) Lu, X.; Zhang, Q.; Lin, M. C. Adsorption of methanol, formaldehyde and formic acid on the Si(100)-2 \times 1 surface: A computational study. *Phys. Chem. Phys.* **2001**, *3*, 2156–2161.
- (45) Casaletto, M. P.; Zanoni, R.; Carbone, M.; Piancastelli, M. N.; Aballe, L.; Weiss, K.; Horn, K. Methanol adsorption on Si(1 0 0)2 \times 1 investigated by high-resolution photoemission. *Surf. Sci.* **2002**, *505*, 251–259.
- (46) Bu, Y.; Breslin, J.; Lin, M. C. Adsorption and Thermal Decomposition of Acetaldehyde on Si(111)-7 \times 7. *J. Phys. Chem. B* **1997**, *101*, 1872–1877.
- (47) Song, J. H.; Sailor, M. J. Functionalization of Nanocrystalline Porous Silicon Surfaces with Aryllithium Reagents: Formation of Silicon–Carbon Bonds by Cleavage of Silicon–Silicon Bonds. *J. Am. Chem. Soc.* **1998**, *120*, 2376–2381.
- (48) Song, J. H.; Sailor, M. J. Reaction of Photoluminescent Porous Silicon Surfaces with Lithium Reagents to Form Silicon–Carbon Bound Surface Species. *Inorg. Chem.* **1999**, *38*, 1498–1503.
- (49) Linford, M. R.; Fenter, P.; Eisenberger, P. M.; Chidsey, C. E. D. Alkyl Monolayers on Silicon Prepared from 1-Alkenes and Hydrogen-Terminated Silicon. *J. Am. Chem. Soc.* **1995**, *117*, 3145–3155.
- (50) Buriak, J. M.; Allen, M. J. Lewis Acid Mediated Functionalization of Porous Silicon with Substituted Alkenes and Alkynes. *J. Am. Chem. Soc.* **1998**, *120*, 1339–1340.

- (51) Sieval, A. B.; Opitz, R.; Maas, H. P. A.; Schoeman, M. G.; Meijer, G.; Vergeldt, F. J.; Zuilhof, H.; Sudhölter, E. J. R. Monolayers of 1-Alkynes on the H-Terminated Si(100) Surface. *Langmuir* **2000**, *16*, 10359–10368.
- (52) Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. Formation of Monolayer Films by the Spontaneous Assembly of Organic Thiols from Solution onto Gold. *J. Am. Chem. Soc.* **1989**, *111*, 321–335.
- (53) Offord, D. A.; Griffin, J. H. Kinetic Control in the Formation of Self-Assembled Mixed Monolayers on Planar Silica Substrates. *Langmuir* **1993**, *9*, 3015–3025.
- (54) Ulman, A. *An Introduction to Ultrathin Organic Films: from Langmuir–Blodgett to Self-Assembly*; Academic Press: Boston, MA, 1991.
- (55) Brereton, R. G. *Chemometrics. Data Analysis for the Laboratory and Chemical Plant*; John Wiley & Sons Ltd.: Chichester, U.K., 2003.
- (56) Laibinis, P. E.; Nuzzo, R. G.; Whitesides, G. M. Structure of Monolayers Formed by Coadsorption of Two *n*-Alkanethiols of Different Chain Lengths on Gold and Its Relation to Wetting. *J. Phys. Chem.* **1992**, *96*, 5097–5105.
- (57) Chapman, R. G.; Ostuni, E.; Yan, L.; Whitesides, G. M. Preparation of Mixed Self-Assembled Monolayers (SAMs) That Resist Adsorption of Proteins Using the Reaction of Amines with a SAM That Presents Interchain Carboxylic Anhydride Groups. *Langmuir* **2000**, *16*, 6927–6936.
- (58) Schuerenberg, M.; Luebbert, C.; Eickhoff, H.; Kalkum, M.; Lehrach, H.; Nordhoff, E. Prestructured MALDI-MS sample supports. *Anal. Chem.* **2000**, *72*, 3436–3442.
- (59) Xia, Y.; Whitesides, G. M. Soft Lithography. *Annu. Rev. Mater. Sci.* **1998**, *28*, 153–184.
- (60) Xia, Y.; Whitesides, G. M. Soft Lithography. *Angew. Chem., Int. Ed.* **1998**, *37*, 550–575.
- (61) Grzybowski, B. A.; Haag, R.; Bowden, N.; Whitesides, G. M. Generation of Micrometer-Sized Patterns for Microanalytical Applications Using a Laser Direct-Write Method and Microcontact Printing. *Anal. Chem.* **1998**, *70*, 4645–4652.

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