Formation of (Functionalized) Monolayers and Simultaneous Surface Patterning by Scribing Silicon in the Presence of Alkyl Halides

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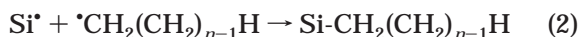
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Silicon is arguably the most important material in modern technology and there has been much recent interest in chemically modifying its surface.[1,2]

Linford and co-workers[3] recently published a new method of simultaneously preparing alkyl monolayers on silicon and patterning silicon by scribing it with a diamond-tipped rod while it is wet with 1-alkenes or 1-alkynes. They proposed that scribing creates highly active Si species that condense with unsaturated molecules. Here, we report that monolayers on Si can also be produced and Si surfaces concomitantly patterned by scribing Si that is wet with 1-chloro-, 1-bromo-, and 1-iodoalkanes.[4] As before,[3] this process takes place under ambient conditions, without the need to degas reagents. A dry Si surface with its thin (10−20 Å) native oxide layer is simply wet with an alkyl halide and the surface is scribed. We propose that surface species on scribed silicon, which may include Si=Si (double) bonds and Si dangling bonds (Si•), as are present on Si(100)−(2 × 1) and Si(111)−(7 × 7), respectively,[2] react with alkyl halides to produce Si−X (X is Cl, Br, or I) and Si−alkyl species. This process is shown below for Si•: homolytic scission of a C−X bond is followed by condensation of Si• with an alkyl radical.

$$Si^\bullet + XCH_2(CH_2)_{n-1}H \rightarrow Si\text{-}X + {}^\bullet CH_2(CH_2)_{n-1}H \quad (1)$$

$$Si^\bullet + {}^\bullet CH_2(CH_2)_{n-1}H \rightarrow Si\text{-}CH_2(CH_2)_{n-1}H \quad (2)$$

While ${}^\bullet CH_2(CH_2)_{n-1}H$ could diffuse away from the surface, it is likely that it will return to it by a random walk (a cage effect would also increase the likelihood of reaction with the surface). Bond strength tabulations support this mechanism—the CH_3-X[5] and $C-X$[6] bonds

are weaker than the Si−X bond. Step (2) is clearly energetically favorable.[5] Bronikowski and Hamers[7] similarly suggested the following mechanism to explain the 2-fold excess of −Cl over −CH₃ on Si(001) dosed with gaseous CH_3Cl:

$$CH_3Cl(g) + Si=Si \rightarrow Si\text{-}Cl(s) + Si(s) + CH_3(g) \quad (3)$$
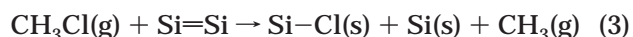
A number of reports on unpassivated silicon[2] and on monolayer formation on silicon[1] and gold serve as important precedents to this work. Abbott, Folkers, and Whitesides[8] removed regions of thiol monolayers on gold by micromaching techniques, for example, with a scalpel or a carbon fiber, and subsequently formed a second thiol monolayer in the exposed regions. Xu and Liu[9] used an AFM tip to scrape away areas of a thiol monolayer on gold while it was immersed in a solution of a different thiol. They showed that the thiol in solution adsorbs in the exposed regions. Linford[10] has shown that functionalized particles can be produced in a single step by grinding silicon in the presence of reactive compounds. CH_3I,[11] CH_3Cl,[7,12] and CH_3CH_2Br[13,14] undergo dissociative adsorption onto Si(100)−(2 × 1) under ultrahigh vacuum to form Si−X and Si−CH_3 (or Si−CH_2CH_3) species. Sailor and co-workers[15] derivatized both planar and porous silicon by electrochemical reduction of haloalkanes. Monolayers on planar and/or porous Si have been prepared by reacting H-terminated Si with diacylperoxides,[16] alkenes,[17−20] alkynes,[17,21] alcohols,[22] aldehydes,[22] alkylmagnesium bromides,[19] and alkyllithiums[23] and by reacting chlorinated Si with Grignard and alkyllithium reagents.[24] In contrast to these earlier preparations of monolayers on silicon, both here and in our earlier report[3] we demon-

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(4) Preliminary results from our laboratory also indicate that monolayers are formed by scribing silicon in the presence of alcohols ($CH_3(CH_2)_nOH$) and carboxylic acids ($CH_3(CH_2)_nCOOH$).
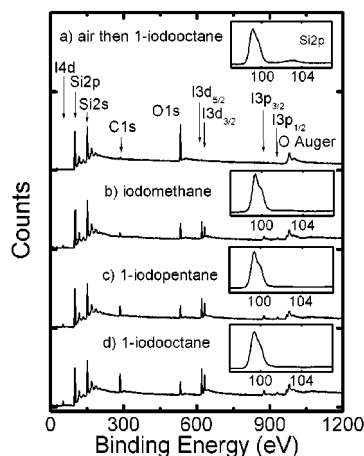(5) Dean, J. A. *Lange's Handbook of Chemistry*; McGraw-Hill: New York, 1999.
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Figure 1. X-ray photoelectron spectra of scribed silicon.

Figure 2. Ratio of areas[30] of C 1s to Si 2p XP peaks (solid symbols) and ratio of O atoms per alkyl chain (open symbols). Squares, circles, and triangles correspond to alkyl iodides, alkyl bromides, and alkyl chlorides, respectively.

strate for the first time a direct, wet-chemical preparation of monolayers on Si that does not require a hydrogen-terminated silicon intermediate.

Figure 1 shows X-ray photoelectron (XP) spectra of Si surfaces that were (a) scribed in the air and then wet with $I(CH_2)_7CH_3$ and (b)−(d) wet with three different alkyl iodides and then scribed. Prior to scribing, the clean Si was completely hydrophilic. After scribing, the control surface (a) was hydrophilic, but the others were hydrophobic. Details of preparing and analyzing samples were previously reported[3] (see also Supporting Information). The C 1s peaks in Figure 1b−d show monolayer quantities of alkyl chains,[25−27] and the peak areas are proportional to the number of carbons in the alkyl halide. Surfaces scribed under iodoalkanes have smaller O 1s peaks than the control surface (a) and significant I signals. The narrow scans of the Si 2p region (Figure 1b−d insets) show less oxide at ≈103 eV[28] than the control (Figure 1a). Because the Si−X bond is easily hydrolyzed in most molecular compounds, it might be considered surprising that I is present on surfaces that had been rinsed with water as part of the cleaning procedure. However, Cl-terminated Si(111) has been found to hydrolyze slowly in the air or even when immersed in water.[29]

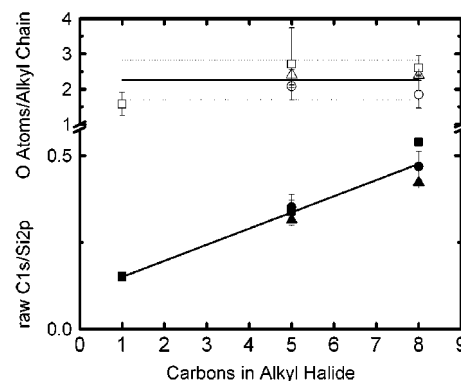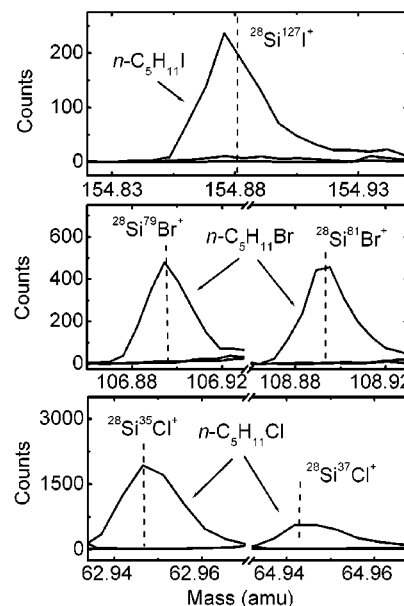The XP spectra of Si scribed under 1-bromoalkanes and 1-chloroalkanes also had significant halogen sig-

Figure 3. TOF−SIMS spectra of silicon scribed under 1-iodo, 1-bromo, and 1-chloropentane.

nals, little oxidized Si, and C 1s signals similar to those in Figure 1. The linear fit of the ratio of C 1s to Si 2p peak areas for all of the 1-haloalkane data is (C 1s)/(Si 2p) = 0.047 × (carbons in alkyl halide) + 0.10, and the ratio of O atoms per alkyl chain is roughly constant (2.26 ± 0.56) and essentially equal to the value reported for 1-alkenes and 1-alkynes[3] (see Figure 2).

Evidence for the formation of surface Si−X species was provided by static time-of-flight secondary ion mass spectrometry (ToF−SIMS). Figure 3 shows positive ion spectra of Si surfaces scribed under 1-halopentanes (1-halooctanes gave the same result), where dashed vertical lines show theoretical masses of $^{28}SiX^+$ cations. The top panel shows that $Si^{127}I^+$ is only present in the spectrum of the $I(CH_2)_4CH_3$-derived surface, and not in the spectra of the Br- and Cl−$(CH_2)_4CH_3$-derived surfaces. The middle and bottom panels show that $Si^{79}Br^+$ and $Si^{81}Br^+$ are only in the $Br(CH_2)_4CH_3$-derived surface spectrum and that $Si^{35}Cl^+$ and $Si^{37}Cl^+$ are only in the spectrum from the $Cl(CH_2)_4CH_3$-derived surface. The Br- and Cl-containing peaks in Figure 3 correlate well with the natural isotopic abundances of ^{79}Br (51%) and ^{81}Br (49%) and ^{35}Cl (76%) and ^{37}Cl (24%). Peaks from CH_nX^+ ($n = 0-3$) and $C_2H_nX^+$ ($n = 0-5$) were not

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(27) The different morphologies of monolayers on scribed and planar silicon do not allow XPS results to be directly compared, and thicker (C_{18}) monolayers cause greater attenuation of silicon photoelectrons than thinner films (C_8). With those caveats stated, we note that the (C 1s)/(Si 2p) ratio (using peak heights) from XPS of densely packed monolayers of 1-octadecene on planar silicon[25,26] suggests that 63−75% of an alkyl monolayer of 1-halooctane chains, for (C 1s)/(Si 2p) = 0.5, are formed by the methods presented here. Earlier work[3] and Figure 1 in the Supporting Information show that silicon scribed under 1-alkenes and 1-alkynes has higher (C 1s)/(Si 2p) ratios than does silicon scribed under 1-haloalkanes with the same number of carbon atoms.

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(30) Although data were taken with two different XP spectrometers with different takeoff angles, we were unable to differentiate between the sets of data from these rough surfaces.
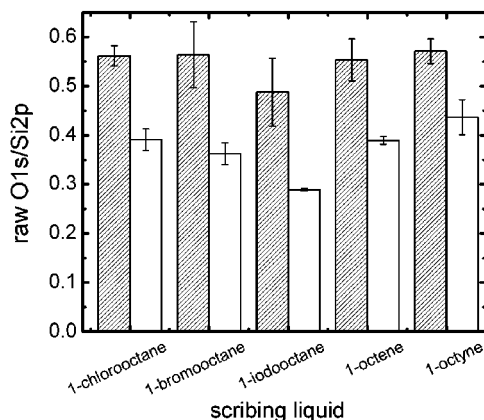
Figure 4. Ratio of the areas of the O 1s to Si 2p peaks from silicon scribed under five scribing liquids in the air (dark columns) and in a glovebox (white columns). The height of the columns gives the average of two data points, which are at the ends of the error bars.

observed. These data support the hypothesis that halogen atoms covalently bind to Si when Si is scribed under alkyl halides. (A variety of $SiC_xH_y{}^+$-type fragments were also observed in SIMS spectra.)

A particular strength of this scribing technique is that silicon functionalization takes place under ambient conditions and without the need to degas scribing liquids. However, silicon oxidizes readily and so it is reasonable to expect that dissolved oxygen would compete with the scribing liquid for surface sites, as has been proposed for silicon scribed under 1-alkenes and 1-alkynes.[3] Thus, to better understand the role of oxygen in monolayer formation on scribed silicon, silicon was scribed under 1-chlorooctane, 1-bromooctane, 1-iodo-octane, 1-octene, and 1-octyne in the air and in a glovebox with degassed compounds. Figure 4 shows the ratio of XPS peak areas of oxygen (O 1s) to silicon (Si 2p) for the resulting surfaces. It is clear for all of these compounds that more oxygen is present when silicon is scribed in the air than in an inert atmosphere. In this same set of experiments the (C 1s)/(Si 2p) ratio was generally somewhat higher for silicon scribed in the glovebox than in the air, the amounts of chlorine (from 1-chlorooctane) were roughly the same under oxygen-free conditions and the air, and the amount of Br and I was greater for silicon scribed in a glovebox (see Supporting Information). We attribute the lower oxygen levels and the higher bromine and iodine signals of silicon scribed in the air under 1-bromo- and 1-iodo-octane to the weakness of the C−Br and C−I bonds.

Up to this point we have described the preparation of what we believe are methyl-terminated monolayers on silicon. However, without a functional group such monolayers are of limited utility in many applications. In an attempt to create a useful leaving group on the surface, silicon was scribed under $Br(CH_2)_4Br$. Figure 5 shows XP spectra taken on Beamline 8-2 at the
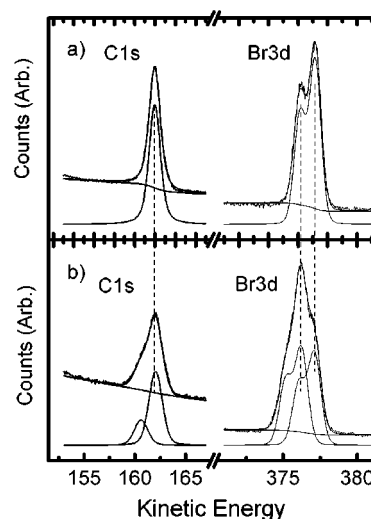

Figure 5. C1s and Br3d XP spectra of silicon scribed in the presence of (a) 1-bromopentane and (b) 1,4-dibromobutane.

Stanford Synchrotron Radiation Laboratory and fits to the data for Si scribed under (a) $Br(CH_2)_4CH_3$ and (b) $Br(CH_2)_4Br$. The lower C 1s spectrum (unlike the upper) has two components. We attribute the smaller peak in (b), which is 26% of the fit area, to C−Br species and the larger to the remaining C atoms. The Br 3d signals in Figure 5 from $Br(CH_2)_4CH_3$-derived surfaces are fit to a single doublet, but those from the $Br(CH_2)_4Br$-derived surface are well fit with a pair of doublets, indicating two chemical states for Br, that is, Si− Br and C−Br. These results suggest that functionalized monolayers consisting of Si−$(CH_2)_nX$ and Si−X moieties, where both X's could act as leaving groups, can be prepared by scribing Si under α,ω-dihaloalkanes.

In addition to the patches of scribed silicon that were studied above by XPS and ToF−SIMS, silicon was patterned with checkerboard arrays of hydrophobic lines (0.5 cm apart), as was previously done with 1-alkenes and 1-alkynes.[3] As before, the resulting square enclosures, or hydrophobic corrals,[8] were probed with 20-μL test droplets of methanol−water mixtures with different surface tensions, and corrals made from alkyl halides with longer chain lengths held test droplets with lower surface tensions. The following list gives the scribing liquid followed by the lowest surface tension of a test droplet (held) and the highest surface tension (not held) by corrals: $Cl(CH_2)_4CH_3$ (40.5 ± 3.3, 37.5 ± 3.7), $Br(CH_2)_4CH_3$ (38.5 ± 3.9, 35.8 ± 4.2), $I(CH_2)_4CH_3$ (42.5 ± 4.6, 39.2 ± 4.8), $Cl(CH_2)_7CH_3$ (34.9 ± 0.0, 32.0 ± 0.0), $Br(CH_2)_7CH_3$ (36.8 ± 2.7, 33.7 ± 2.6), and $I(CH_2)_7CH_3$ (32.7 ± 1.3, 30.2 ± 1.1).