

# Passivation and Secondary Functionalization of Allyl-Terminated Si(111) Surfaces

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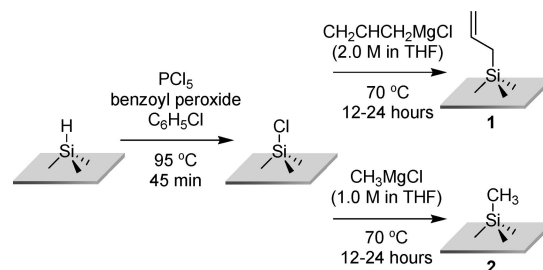
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Synthesis of passivated silicon surfaces with tunable properties requires formation of a monolayer that includes a synthetically useful functional group, such as an alkene. Thus, Si(111) surfaces have been chemically and electrically passivated by attachment of an allyl monolayer. The structure of the monolayer was confirmed using infrared spectroscopy. The allyl-functionalized surface exhibited resistance to oxidation and had a low density of surface trap states. Metal-catalyzed reactions, in particular, Heck coupling and ruthenium-catalyzed olefin cross-metathesis, allowed attachment of small molecules despite the steric constraints of the dense surface-bound layer. Allyl-terminated silicon surfaces thus offer a means of attaching a variety of chemical moieties to a silicon surface through a short linking group, enabling applications in energy conversion, catalysis, and sensing.

## Introduction

Functionalization of silicon surfaces with short alkyl chains effects chemical and electrical surface passivation while minimizing the barrier to electron transfer across the passivating layer.<sup>1–4</sup> Functionalization with such species has proven useful because of their high attainable packing densities and short chain lengths. However, the suitability of such modified surfaces as substrates for secondary functionalization is limited because saturated hydrocarbons undergo few reactions under mild conditions. Expansion of the variety of surface-bonded functionalities is desirable for tuning the properties of the resulting surfaces, attachment of species for catalytic or sensing applications,<sup>5–7</sup> and formation of covalent contacts to metallic or semiconducting materials. We describe herein the introduction of unsaturated functional groups onto Si surfaces and the use of organic synthetic reactions to further enhance the functionality of the resulting chemisorbed overlayers. Specifically, two reactions commonly employed in solution chemistry for the coupling of olefins, the Heck reaction<sup>8</sup> and olefin cross-metathesis,<sup>9</sup> have been performed on an allyl-terminated

## Scheme 1. Synthesis of Allyl- and Methyl-Functionalized Si(111) Surfaces



monolayer on a Si(111) surface (surface **1**, Scheme 1), enabling further chemical elaboration of such surfaces.

Several recent studies have focused on attachment of small unsaturated groups to silicon surfaces.<sup>10–13</sup> Surface **1** has been used as a substrate for ring-opening metathesis polymerization,<sup>14</sup> and infrared (IR)-absorption and high-resolution electron energy loss spectra of an allyl-terminated silicon surface have recently been reported.<sup>11</sup> Although the allyl Grignard reagent can, in principle, undergo hydrosilylation at the hydrogen-terminated silicon surface, the primary reaction pathway has been shown to involve attachment of the allyl group at the saturated carbon.<sup>11</sup> This approach thus offers the possibility of utilizing the remaining olefinic functionality on such surfaces for subsequent chemical reactions, as described herein. The methyl-terminated surface (surface **2**, Scheme 1), used here as a control because of its anticipated inertness toward metal-catalyzed coupling reac-

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tions, has been characterized in detail. X-ray photoelectron spectroscopy (XPS),<sup>15,16</sup> IR spectroscopy,<sup>15</sup> scanning tunneling microscopy and spectroscopy,<sup>17,18</sup> electron diffraction,<sup>15</sup> photoconductivity measurements,<sup>3</sup> and a variety of electrochemical measurements<sup>4,19</sup> have demonstrated that surface **2** is chemically and electrically passivated. Studies using these techniques have demonstrated that methylation by a two-step chlorination/alkylation process produces surfaces consisting of an ordered monolayer with a methyl group attached to nearly every silicon atop atom on an unreconstructed Si(111) surface. In this work, surface **1** prepared by a chlorination/Grignard reaction has been characterized by XPS, surface recombination velocity measurements, and IR spectroscopy. Additionally, the reactivity of this surface toward C–C bond formation has been compared to that of surface **2**.

### Experimental Section

**Primary Functionalization of Si(111).** Silicon wafers (float zone, n-type, phosphorus-doped wafers, polished on both sides, either from Silicon Quest International with a resistivity of 63–77  $\Omega$  cm and a thickness of 450–430  $\mu\text{m}$  or from Topsil with a resistivity of 4000–8000  $\Omega$  cm and a thickness of 375–325  $\mu\text{m}$ ) were cleaned by immersion in piranha acid (7:3 v/v concentrated  $\text{H}_2\text{SO}_4/30\%$   $\text{H}_2\text{O}_2$ ) and rinsed with deionized water having a resistivity of 18.3 M $\Omega$  cm. (**Caution!** Piranha solution is corrosive and reacts violently with organic materials.) These wafers were rinsed sequentially with water, methanol, acetone, methanol, and water immediately before etching in 11 M  $\text{NH}_4\text{F}$ (aq) (Transene, Inc., degassed with ultrahigh purity Ar for 15 min) followed by a water rinse. The samples were rapidly transferred to a nitrogen-purged flush box that contained <10 ppm of  $\text{O}_2$ . A chlorine-terminated surface was produced by immersing the sample in a saturated solution of  $\text{PCl}_5$  (Sigma-Aldrich, 95%, or Riedel-de Haën,  $\geq 99\%$ ) in chlorobenzene (Aldrich, anhydrous, 99.8%) to which several grains of benzoyl peroxide (Aldrich reagent grade, 97%) had been added. The solution was heated at  $\sim 90$  °C for 45 min. The samples were then rinsed with chlorobenzene and tetrahydrofuran (THF) (Aldrich, anhydrous,  $\geq 99.9\%$ , inhibitor-free). The Si samples were then immersed in a solution of a Grignard reagent in THF, either  $\sim 1$  M  $\text{CH}_3\text{MgCl}$  (Aldrich, diluted from 3.0 M) to form surface **2** or 2.0 M  $\text{CH}_2\text{CHCH}_2\text{MgCl}$  (Aldrich) to form surface **1**, and heated at 60–70 °C for 12–24 h. The samples were then rinsed with anhydrous THF followed by a rinse with  $\text{CH}_3\text{OH}$  (Aldrich, anhydrous, 99.8%). The samples were removed from the flush box and sonicated sequentially in  $\text{CH}_3\text{OH}$  and in water.

**Secondary Functionalization of Si(111).** Heck Reaction. A sample of either allyl- or methyl-terminated silicon (surface **1** or **2**, respectively) was immersed in a solution of  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$  [tris(dibenzylideneacetone)dipalladium(0)· $\text{CHCl}_3$ , Alfa Aesar, 98%, 3 mg  $\text{mL}^{-1}$  in anhydrous THF], to which 0.3–0.5 mL of dried triethylamine and 0.3–0.5 mL of 1-iodo-4-trifluoromethylbenzene were added. The reaction mixture was heated to 90–110 °C in a pressure vessel for 12–16 h. The samples were then rinsed and sonicated repeatedly and sequentially in THF,  $\text{CH}_2\text{Cl}_2$ , and  $\text{CH}_3\text{OH}$ .

**Cross-Metathesis Reaction.** A sample of either allyl- or methyl-terminated silicon was immersed in a solution of Grubbs' first-generation catalyst (11 mg  $\text{mL}^{-1}$  in anhydrous  $\text{CH}_2\text{Cl}_2$ ) and heated to reflux. After 3–12 h, 0.3–0.5 mL of 4-fluorostyrene was added, and the reaction mixture was heated for another 12–16 h. The samples were then rinsed and sonicated repeatedly and sequentially in THF,  $\text{CH}_2\text{Cl}_2$ , and  $\text{CH}_3\text{OH}$ .

**Photoelectron Spectroscopy.** XPS data were acquired using an M-Probe X-ray photoelectron spectrometer operated under ultrahigh vacuum (UHV) at  $10^{-9}$ – $10^{-8}$  Torr, as described previously.<sup>15</sup> The incident X-ray beam was generated by an Al K $\alpha$  source (1486.6 eV), and ejected electrons were measured at 35° from the surface normal. Periodic calibrations were performed using Au standards with their Au 4f peaks at 84 and 87 binding eV. The spectrometer resolution was  $\sim 0.9$  eV, as determined by the full width at half-maximum of the Au 4f<sub>7/2</sub> line. Data were collected using ESCA 2000 E Capture software, version 102.04 (Service Physics). Wide-energy scans from 0 to 1000 binding eV were performed to identify the elements present on the surface. High-resolution spectra, employing scan times of up to 2.5 h, were captured as necessary for the Si 2p, C 1s, and F 1s regions (96–106, 280–290, and 693–683 eV scan ranges, respectively).

The surface coverage of silicon oxide was determined by measurement of the ratio of the area under the oxygen-shifted Si 2p peak ( $\sim 103$  binding eV) to the combined area of the bulk Si 2p peaks (i.e., the 2p<sub>3/2</sub> and 2p<sub>1/2</sub> emissions at 100 and 99 binding eV, respectively). Peak shapes were fit to Voigt functions fixed at 80% Gaussian and 20% Lorentzian line shapes using ESCA 2000 A Analysis version 102.04 integration software. On the basis of the substrate-overlayer model, the monolayer coverage of oxide species was determined according to the following equation:<sup>20</sup>

$$d_{\text{ov}} = (\lambda \sin \theta) \left\{ \ln \left[ \left( \frac{I_{\text{ov}}}{I_{\text{Si}}} \right) \left( \frac{I_{\text{Si}}^0}{I_{\text{ov}}^0} \right) + 1 \right] \right\} \quad (1)$$

where  $d_{\text{ov}}$  is the overlayer thickness,  $\lambda$  is the escape depth of the generated electrons ( $\lambda = 2.6$  nm),  $\theta$  is the takeoff angle used in collecting the XPS data ( $\theta = 35^\circ$ ),  $I_{\text{Si}}^0/I_{\text{ov}}^0$  is a normalizing factor for the particular instrument used (equal to 1.3 for this instrument), and  $I_{\text{ov}}/I_{\text{Si}}$  is the ratio of the peak area of the oxide-shifted silicon signal to the area of the bulk silicon peaks. Monolayer coverages were determined by the ratio of  $d_{\text{ov}}$  to the thickness of one monolayer of oxide (3.5 Å).

The coverage of surface **1** by silicon-bonded carbon was determined from a comparison of the ratio of the area of the C–Si peak in the C 1s region to that of the bulk Si 2p peak for surface **1** with the corresponding ratio for the methylated surface **2**, which was assumed to have a monolayer of Si–C bonds on its surface.<sup>17,18</sup> The region of the carbon 1s peak was fit to three peaks, representing silicon-bonded carbon at 284.0(1) eV, carbon-bonded carbon at 284.9(1) eV, and oxygen-bonded carbon at  $\sim 286$  eV.

Monolayer coverages of fluorine with respect to silicon were calculated according to eq 2, which was obtained following the derivation in Haber et al.<sup>21</sup>

$$\ln \left[ \left( \frac{I_{\text{ov}}}{I_{\text{Si}}} \right) \left( \frac{F_{\text{Si}}}{F_{\text{ov}}} \right) \left( \frac{\rho_{\text{Si}}}{\rho_{\text{ov}}} \right) + 1 \right] \lambda \sin \theta = d_{\text{ov}} \quad (2)$$

where  $I_{\text{ov}}/I_{\text{Si}}$  is the ratio of the area of overlayer peak to the area of the Si 2p peak,  $F_{\text{Si}}$  and  $F_{\text{ov}}$  are the modified sensitivity factors for the Si 2p peak and the chosen overlayer peak, respectively, and  $\rho_{\text{Si}}$

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and  $\rho_{ov}$  are the densities of the silicon substrate and overlayer, respectively. Here,  $\lambda = 2.6$  nm and  $\theta = 35^\circ$ ,  $\rho_{Si} = 5.00 \times 10^{22}$  atoms  $\text{cm}^{-3}$ ,  $\rho_F = 5.28 \times 10^{22}$  atoms  $\text{cm}^{-3}$ ,  $F_{Si2p} = 0.90$ , and  $F_{F2p} = 3.4$ . Note that because of possible attenuation of the Si signal by the intervening carbon layers, the reported F coverages may be underestimates. The reaction yield with respect to the attached allyl groups was obtained by multiplying the F coverage with respect to the silicon atoms by the allyl surface coverage.

**Photoconductivity Decay Measurements.** A contactless radio frequency (RF) conductivity apparatus was used to measure surface recombination velocities. Electron-hole pairs were photogenerated using a Coherent pulsed diode laser (828.7 nm, 50  $\mu\text{s}$  pulses, 10 Hz, 0.3 mJ pulse $^{-1}$ ) whose beam was passed through neutral density filters ( $2 \times 3\%$  and  $2 \times 50\%$ ) prior to striking the sample. The photoinduced conductivity in the Si sample was monitored using the reflected signal from a radio frequency coil (495 MHz). The conductivity decreased as the charge carriers recombined with surface-localized trap states. The bulk charge-carrier lifetimes reported by the manufacturer ( $\sim 6$  ms) were much longer than those measured here, indicating that the observed decay rate was due to recombination of charge carriers at the surfaces of the sample. Charge-carrier lifetimes ( $\tau$ ) were extracted from the absorbed RF signal (128 trace average) by fitting the data to a single-exponential decay:

$$A = y_0 + ae^{-t/\tau} \quad (3)$$

The surface recombination velocity,  $S$ , is related to  $\tau$  through the equation

$$\frac{1}{\tau} = \frac{1}{\tau_B} + \frac{2S}{d} \quad (4)$$

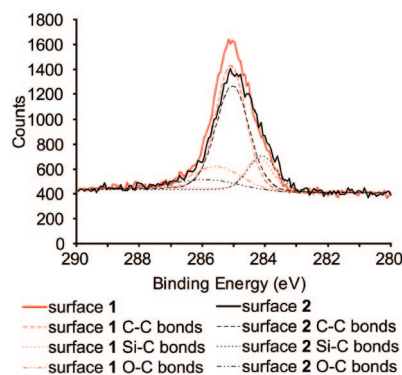
where  $\tau_B$  is the bulk lifetime and  $d$  is the sample thickness. Both surfaces of the sample were treated identically, so both surfaces contribute equally to charge-carrier recombination. Because  $\tau_B \gg \tau$ , eq 4 can be rearranged to give

$$S \approx \frac{d}{2\tau} \quad (5)$$

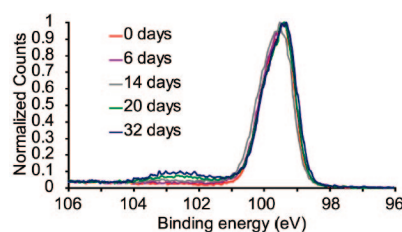
**Infrared Spectroscopy of Si(111) Surfaces.** IR spectra were collected using a Thermo Scientific Nicolet 6700 Optical Spectrometer with a DTGS-TEC detector and a purified-air purge. Si wafers with resistivities of 66–73  $\Omega$  cm (described above) were cut to approximately 1.6 cm  $\times$  3 cm and positioned at an angle of  $74.6^\circ$  from normal to the beam. Background spectra of silicon oxide- and hydrogen-terminated surfaces were collected for each wafer. The hydrogen-terminated surface was used as a background for the allylated sample. Reported spectra represented averages of 3000 scans with a 4  $\text{cm}^{-1}$  resolution collected after 40 min of purging.

## Results and Discussion

The initial functionalization of Si(111) surfaces was carried out using a process (Scheme 1) similar to that reported previously (see the Experimental Section for details).<sup>14</sup> Briefly, oxide-coated Si(111) surfaces were etched with  $\text{NH}_4\text{F}(\text{aq})$  to create large terraces of hydrogen-terminated Si(111).<sup>22</sup> These surfaces were chlorinated using a  $\text{PCl}_5$  solution. The Cl–Si(111) surfaces were then immersed in either an allyl magnesium chloride solution (to produce the



**Figure 1.** XPS data for the C 1s region of surface 1 (red) and surface 2 (black). The peak fitting illustrates the C–Si (284 eV), C–C (285 eV), and C–O (285.5–286 eV) signals. The ratio of the C–Si peak to the bulk Si 2p peak for surface 1 is less than that for surface 2, corresponding to a monolayer coverage of  $\sim 75\%$  of Si–C bonds on surface 1.



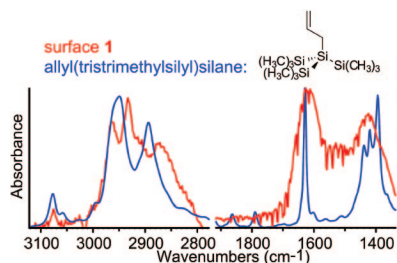
**Figure 2.** XPS data for the Si 2p region of surface 1, collected after varying times of exposure to an ambient atmosphere. Oxidation (as detected by the presence of the Si–O $_x$  peak at  $\sim 103$  eV) was observable only after 20 days, and no signal was observable after 2 weeks of exposure.

allyl-functionalized surface 1) or a methyl magnesium chloride solution (to produce the methyl-terminated surface 2 used as a control).

The fractional monolayer coverage of surface 1 by allyl groups was determined using XPS by comparing the ratio of the area of the C 1s peak produced by the silicon-bound carbon atoms to that of the bulk Si 2p peak with the analogous peak-area ratio observed for the methylated surface 2 (Figure 1). This method indicated that carbon was bound to  $75 \pm 20\%$  of the silicon atop atoms of surface 1. As expected, the greater steric bulk of the allyl group resulted in an allyl surface coverage lower than that for methyl groups. However, chemical and electrical surface passivation has been achieved using bulky groups that do not cover every atop silicon.<sup>1</sup> Furthermore, lateral access to the chemisorbed olefins, which may be beneficial during secondary functionalization, is a likely result of the  $< 100\%$  coverage of allyl groups on Si atop sites of surface 1 (see the Supporting Information for a possible model structure).

The allyl-functionalized Si surface exhibited resistance to oxidation as well as good electrical properties. When samples of the surface were stored under ambient conditions, no Si–O $_x$  peak was observed for at least two weeks, and 20 days of exposure was required before  $19 \pm 3\%$  of a monolayer of oxide was observed (Figure 2). Thus, functionalization with allyl groups extended by several weeks the oxide-free lifetime of Si(111) surfaces compared with the behavior in air of the hydrogen-terminated Si(111) surface. RF photoconductivity measurements of surface 1 applied to high-purity, high-resistivity silicon with long bulk

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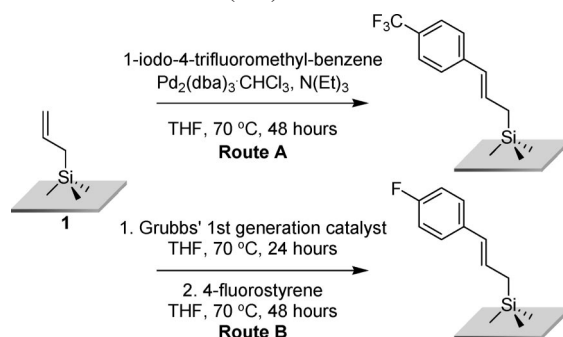
**Figure 3.** IR spectra of surface **1** (red) and allyltris(trimethylsilyl)silane (blue), showing the overlap of peaks indicative of the olefin group: the C–H stretch at  $3077\text{ cm}^{-1}$ , C=C stretch at  $1623\text{ cm}^{-1}$ , and C=C–H out-of-plane bend at  $1418\text{ cm}^{-1}$ .

charge-carrier lifetimes<sup>3,23</sup> yielded photogenerated charge-carrier lifetimes of  $280 \pm 20\ \mu\text{s}$ , indicating a surface recombination velocity of  $50\text{ cm s}^{-1}$ . Assuming a geometric cross section for the trap states on the surface implies a density of electrically active defects for such surfaces of 1 per  $10^6$  surface atoms.<sup>23</sup>

IR spectroscopy showed that the allyl groups on surface **1** were attached to the silicon surface by the  $\text{sp}^3$ -hybridized carbon. Peaks due specifically to a methyl group (e.g., the  $-\text{CH}_3$  umbrella mode at  $1250\text{ cm}^{-1}$ ), which would indicate attachment via hydrosilylation, were not observed. However, peaks indicative of olefins [ $3077$ ,  $1623$ , and  $1418\text{ cm}^{-1}$  (C–H stretch, C=C stretch, and C=C–H bend, respectively)] and  $\text{sp}^3$  C–H stretches ( $2964$ ,  $2932$ ,  $2907$ , and  $2869\text{ cm}^{-1}$ ) were observed. These peaks agree with the previously reported spectra of allyl-terminated Si(111) surfaces synthesized without the use of a Si–Cl intermediate surface,<sup>11</sup> with small shifts attributed to the much greater density of allyl groups on the surface produced using the two-step reaction pathway. Furthermore, peaks in the spectrum of surface **1** due to C=C and C=C–H absorptions appeared at positions close to those observed for the small-molecule analog allyltris(trimethylsilyl)silane (Figure 3). The broad C=C stretches observed for surface **1** suggest that the allylic moieties exist in a variety of environments, indicating that the monolayer was not highly ordered.

Given the utility of allylsilanes in organic synthesis,<sup>24</sup> the allyl surface **1** should offer a versatile, reactive layer for chemical elaboration. The Heck reaction<sup>8</sup> and olefin cross-metathesis<sup>9</sup> are commonly employed in solution-phase chemistry to form new C–C bonds with terminal olefins. These reactions are catalyzed by various metal-containing compounds, can be carried out under relatively mild conditions, and retain the carbon–carbon double bonds of the reactants. The Heck reaction generally involves coupling between an olefin and an aryl iodide in the presence of a homogeneous palladium catalyst, while cross-metathesis exchanges carbons of two different olefins, commonly with the assistance of an organometallic ruthenium catalyst. In this work, both types of reactions were successfully utilized to attach a fluorine-containing moiety to the silicon surface, with the fluorine serving as an unambiguous marker for XPS.

## Scheme 2. Secondary Functionalization of Allyl-Terminated Si(111) Surfaces



While cross-metathesis has been demonstrated for monolayers on silicon produced by hydrosilylation reactions with long-chain hydrocarbons,<sup>25</sup> the steric demands of such surfaces, which have less than 50% of the silicon atop atoms bonded to organic groups, are smaller than that of surface **1**. Given the size of the catalysts employed, crowding of the reactive olefin site could substantially impede the progress of both the Heck and cross-metathesis reactions on **1**.

To demonstrate the functionalization process, a Heck reaction (Route A, Scheme 2) was performed on **1** by immersing the sample in a THF solution that contained  $\text{N}(\text{C}_2\text{H}_5)_3$ , 1-iodo-4-(trifluoromethyl)benzene, and  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$  as a catalyst.  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$  was used because it has been successfully employed on vinylsilanes without cleavage of the C–Si bond,<sup>26</sup> it is recommended for oxidatively sensitive materials,<sup>27</sup> and the zerovalent Pd reduces the number of necessary mechanistic steps. After treatment under the Heck reaction conditions (Route A) with the fluorine-tagged aryl iodide, surface **1** exhibited a significant F 2p peak ( $688\text{ eV}$ ) in the XPS data (Figure 4A). The F signal did not disappear after repeated washing, consistent with covalent attachment of the F-containing group to the surface. For surface **1**, the ratio of the areas under the F 1s and Si 2p peaks<sup>21</sup> indicated an aryl-group coverage of 13% of a monolayer with respect to the surface silicon sites ( $\sim 10\%$  with respect to silicon-bound allyl groups) after correction for the fact that three fluorines were present on each attached aryl group.

The spectrum for surface **1** after treatment by Route A was markedly cleaner than that obtained for the identically treated control sample **2**. In addition to the expected Si 2p ( $98.7\text{ eV}$ ) and 2s ( $150.0\text{ eV}$ ), C 1s ( $284.3\text{ eV}$ ), O 1s ( $531.7\text{ eV}$ ), and F 1s ( $687.7\text{ eV}$ ) peaks, a small amount of contamination by I (the 3d peaks at  $630.9$  and  $619.7\text{ eV}$  were most prominent) and Pd (the 3d peaks at  $335.9$  and  $341.1\text{ eV}$  were most prominent) was observed for surface **1**. In contrast, surface **2** consistently exhibited a greater degree of contamination by Pd and I than did surface **1**. F was observed on surface **2**, along with Pd and I. With repeated vigorous cleaning of surface **2**, the F, Pd, and I peaks all

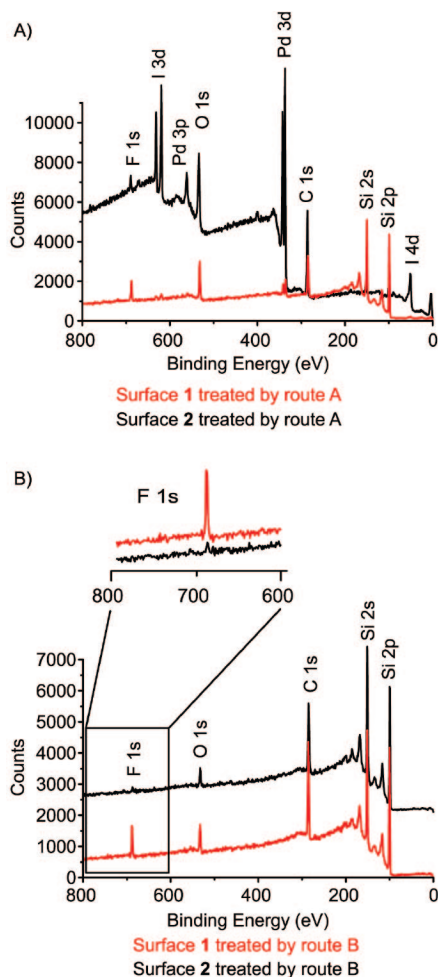
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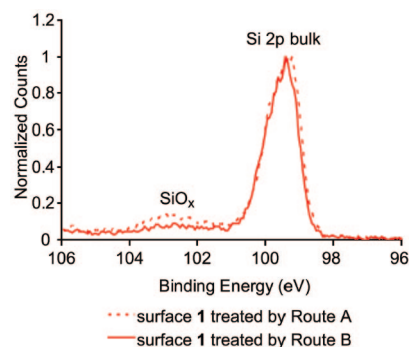
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**Figure 4.** XPS data for allyl- and methyl-functionalized Si(111) surfaces [1 (red) and 2 (black), respectively] treated with (A) Heck or (B) cross-metathesis reaction conditions, as in Scheme 2. Fluorine was incorporated into surface 1 in larger amounts and/or more cleanly (without the presence of an equivalent amount of I) than into surface 2, indicating successful attachment of fluorine-containing moieties to the monolayer. Surface 2 exhibited either (A) incorporation of fluorine accompanied by large amounts of impurities, suggesting that the fluorine peak on that surface arose from a species in which the fluorine was still bound to a group that also contained iodine, or (B) a small amount of fluorine incorporation.

decreased in intensity. Furthermore, the ratio of F to I in the spectra of surface 2 after treatment by Route A was  $\leq 1$ , after correcting for the sensitivity factors (Figure 4A and Supporting Information). Both of these results indicate that a 4-trifluoromethylbenzene group was not chemically bonded to surface 2. Although the presence of F on the methylated control surface 2 could be explained by sorption of a variety of species, the fluorine on the allylated surface 1 apparently originated from chemical attachment of the 4-trifluoromethylbenzene group produced by a successful Heck reaction. After the Heck reaction, surfaces 1 and 2 both exhibited a comparable amount of oxidation ( $\sim 50\%$  of a monolayer; see the Supporting Information).

A sample of allyl-functionalized 1 and a control sample of methyl-terminated 2 were also treated with a Grubbs first-generation catalyst solution followed by addition of 4-fluorostyrene (Route B). The first-generation Grubbs catalyst was selected because it has worked well in related systems.<sup>14,25</sup> XPS of the resulting surfaces (Figure 4B) indicated that significant amounts of F (1s, 687.8) were observed only when



**Figure 5.** XPS data for the Si 2p region of surface 1 after treatment by Route A (the Heck reaction, dashed line) or Route B (olefin cross-metathesis, solid line). The  $\text{SiO}_x$  peak area was greater for Route A ( $50 \pm 40\%$  of a monolayer) than for Route B ( $20 \pm 10\%$  of a monolayer), indicating that the olefin-metathesis route is generally less damaging to the Si surfaces than is the Heck reaction route.

the allyl-functionalized surface was used. The elements Si (2p and 2s, 99.9 and 151.1 eV, respectively), C (1s, 285.4 eV), and O (1s, 532.7 eV) were also observed on the allyl-functionalized surfaces. The only elements observed in XPS of surfaces subjected to the cross-metathesis reaction were Si, C (chemisorbed and adventitiously physisorbed), O (adventitiously physisorbed), and F, indicating that this was a much cleaner reaction than the Heck reaction. Calculations of the F coverage<sup>21</sup> gave values of 37% of a monolayer with respect to the underlying silicon, implying that  $\sim 30\%$  of the attached allyl groups had reacted. The density of reacted sites provides insight into the properties of polymers grown off the surface by ring-opening metathesis polymerization (ROMP).<sup>14</sup> ROMP from the surface results in a polymer film covering the silicon surface, but the number of polymer chains and the density with which they are attached to the silicon surface are difficult to determine. However, on the basis of the mechanistic and experimental similarities between the cross-metathesis and ROMP reactions, the density observed here for attachment of fluorostyrene suggests that an even, dense polymer film results from such a surface modification procedure. The extent of Si surface oxidation induced by the cross-metathesis reaction ( $20 \pm 10\%$  of a monolayer) was significantly less than that observed for the Heck reaction (Figure 5). The cleanliness and improved yield of the cross-metathesis reaction may make this method of coupling to an olefin-terminated surface preferred over the Heck reaction.

## Conclusion

Allyl termination of Si(111) has been demonstrated to impart chemical and electrical passivation while affording a facile means of chemical elaboration of the Si surface. The allyl treatment provides resistance to oxidation and maintains low rates of photogenerated charge-carrier recombination on such Si(111) surfaces. In addition to passivating the silicon surfaces toward oxidation and imparting to them a low surface-recombination velocity, allyl termination enables metal-catalyzed organic transformations to be performed on these systems. Both the Heck reaction and olefin cross-metathesis, which are commonly employed in the solution-phase chemistry of olefins, were successfully implemented

on the allyl-terminated surfaces despite the significant steric demands generated by the packing of the allyl monolayer onto the silicon surface. Olefin metathesis produced particularly clean surfaces with a large amount of F incorporation. This work thus demonstrates methods by which a variety of molecules can be attached to silicon surfaces, providing straightforward opportunities for functionalization of such systems with biomolecules, catalysts, or nanoparticles.

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**Supporting Information Available:** Computational model of surface **1**, an additional set of XPS data comparing surfaces **1** and **2** after treatment by Route A, and XPS data illustrating the relative oxidation of surfaces **1** and **2** after treatment by Route A (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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