

# Controlled Functionalization and Multistep Chemical Manipulation of Covalently Modified Si(111) Surfaces<sup>1</sup>

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**Abstract:** A hydrogen-terminated Si(111) surface has been covalently modified by UV irradiation in the presence of ethyl undecylenate leading to a Si(111)-C<sub>10</sub>H<sub>20</sub>CO<sub>2</sub>Et surface. It is possible to carry out a diverse range of chemical manipulations of the ester group on the surface. For example, reduction with sodium borohydride provides a surface terminated with a primary alcohol. Reaction with an alkyl Grignard reagent gives a tertiary alcohol that can be acylated with acetyl chloride. Finally, hydrolysis of the ester leads to a carboxylic acid terminated surface that can be coupled to an amino acid using a standard solid phase amide coupling protocol. The surface density of the ester function can be controlled by dilution of the reacting ester with a long-chain alkene. This has the beneficial effects of minimizing the disruption of the alkyl chain packing in the monolayers and avoiding steric blocking of the ester group. It is expected that the ability to precisely control the average distance between large biomolecules on surfaces will impact on future molecular electronic, sensor, and biochip technologies.

The covalent attachment of monolayers to semiconductor surfaces is of growing interest for potential applications from surface passivation to the incorporation of chemical/biochemical functionality at interfaces for use in biosensors or biosensor arrays. It is possible to prepare covalently modified Si(111) surfaces from the thermal, catalyzed, or photochemical reaction of hydrogen-terminated Si(111) or Si(100) with alkenes,<sup>2–7</sup> Grignard reagents,<sup>8</sup> or aldehydes<sup>9,10</sup> and by the electrochemical reduction of aryldiazonium ions.<sup>11,12</sup> Similar reactions have been reported for modification of porous silicon.<sup>13–17</sup> In addition, covalently modified surfaces also may be prepared from the

reaction of alkyl Grignard or alkyllithium reagents with the halogenated Si(111) surface.<sup>18–21</sup> In many of these examples the reactions lead to organic films that are terminated with a methyl group. While this is useful for passivation and chemical stabilization, the low reactivity of the terminal methyl group makes further manipulation of the surface physical or chemical properties difficult. Other workers have demonstrated the possibility of creating a functionalized organic film on a single crystal<sup>4,11–14,22</sup> surface, but only in a few cases have the sequential reactions of the organic film been investigated.<sup>2,3,6</sup> To incorporate more complex organic or bioorganic structures at the interface new strategies to increase the chemical functionality of the surface must be devised. Chemical approaches to this end-group manipulation should be both predictable and reproducible.

Chidsey and co-workers addressed this problem using a two-step process in which a methyl terminated the surface is first chlorosulfonated by a photoinitiated free radical reaction followed by sulfonamide formation by reaction of the sulfonyl chloride with an amine. Using this approach it was possible to functionalize the surface with a diverse range of amines including those containing DNA<sup>2</sup> and dendrimers.<sup>3</sup> They also reacted the methyl-terminated surfaces with singlet carbenes.<sup>2</sup> While these studies represent an important advance in our ability to design and control surface chemical properties, in both cases the extent of chemical reaction appeared to be difficult to control as it depends on a number of factors including the concentration of reagents and the intensity and spectrum of the light source. The incorporation of biocomponents such as single-strand DNA or proteins onto these surfaces will require the distance (at least average distance) between reactive centers to be carefully

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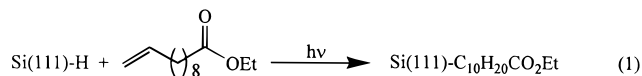
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controlled to reduce steric interference while at the same time optimizing the sensitivity of a device, a problem that represents a significant challenge to burgeoning biochip initiatives.<sup>23</sup>

Sieval et al. made the first advance that opened the possibility of carrying out more traditional solid-phase synthetic procedures from these modified surfaces.<sup>6</sup> They reported the thermal reaction of alkenes terminated with ester groups with the Si(100) hydrogen-terminated surface that could be hydrolyzed to form a carboxylic acid modified surface or reduced with LiAlH<sub>4</sub> to form an alcohol-modified surface. The carboxylic acid surface could be re-esterified by refluxing the surface in an acidified solution of a different alcohol. While this demonstrated the possibility of carrying out sequential chemical transformations on the surface, poor signal to noise in the carbonyl region made it difficult to assess the overall chemical yields and, perhaps more importantly, the reaction conditions were too harsh to be compatible with most biological materials.

We have taken a similar approach to the functionalization of the covalently bonded alkyl monolayers. The photochemical reaction of ethyl undecylenate with Si(111)-H (reaction 1) offers



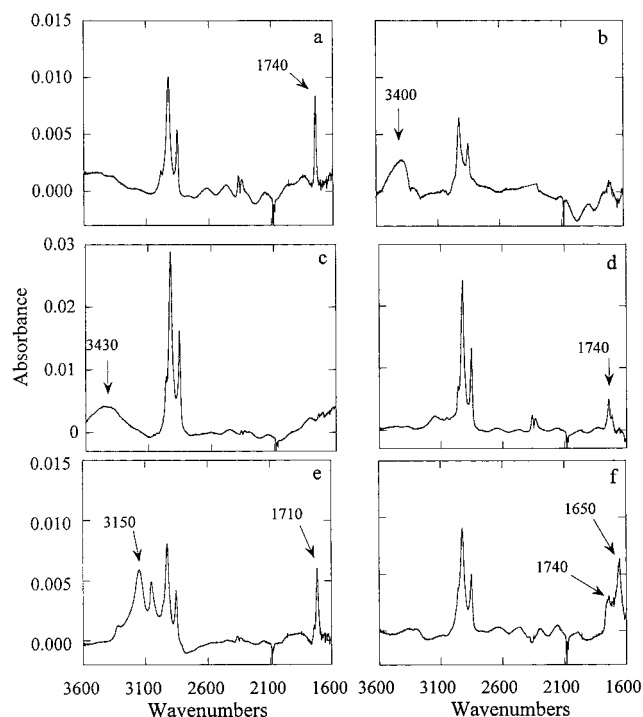
a convenient, mild route to ester-terminated monolayers which, as we will show, can easily be manipulated chemically to generate a wide range of surface functionalities under conditions compatible with biological molecules. This approach has the advantage that the surface coverage of the ester group can be predetermined by diluting the undecylenate with unreactive alkenes (e.g. 1-decene). Although the incorporation of the terminal ester is likely random, it should be straightforward to incorporate very low coverage of the reactive ester group with a known average intermolecular distance with high precision and without sacrificing the high chemical stability of the Si-C link.

Silicon ATR crystals were cleaned then hydrogen terminated by etching in deoxygenated ammonium fluoride as previously described.<sup>8,24</sup> The freshly hydrogen-terminated crystal was placed in a Pyrex tube containing the neat, previously deoxygenated alkene or mixture of alkenes and irradiated at 300 nm in a Rayonet reactor for 3 h. The ATR crystal was then rinsed with 1,1,1-trichloroethane to remove physisorbed hydrocarbons. The FTIR spectrum (Figure 1a) of the modified surface is characterized by absorptions in the alkyl C-H stretching region (2922 cm<sup>-1</sup>) and the carbonyl region (1740 cm<sup>-1</sup>). The integrated intensity at 2922 cm<sup>-1</sup> is consistent with a coverage similar to that obtained in a reaction of 1-decene.<sup>8,25</sup> Under similar conditions, a mixture of the ester and 1-decene reacts to incorporate both molecules in a ratio that is the same as the molar ratio of the mixture (Figure 2a) within the limits of detection (about 20 mol % of ester). Co-reaction with 1-decene allows the C<sub>11</sub> ester group to protrude above the plane of methyl groups (Figure 2b). This has the beneficial effects of minimizing the disruption of the alkyl chain packing in the monolayers and allowing access to the ester group by reagents.

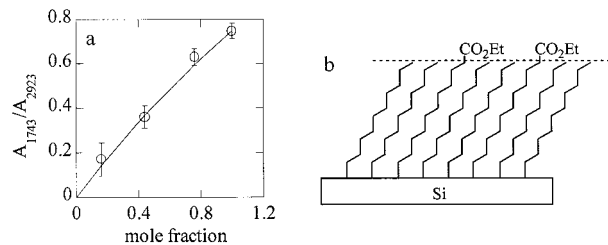
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(25) On the basis of XPS and STM results our best estimate of the surface coverage of the alkyl groups is 30-40% of the silicon atom density (Lopinski, G. P.; Boukherroub, R.; Wayner, D. D. M.; Wolkow, R. A., in preparation). This is approaching the limit of about 50% based on the radius of the methylene chain proposed by Chidsey.<sup>4</sup>

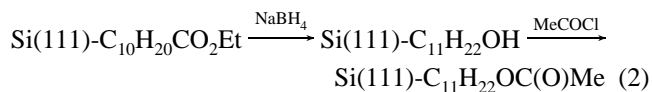


**Figure 1.** FTIR spectra of (a) Si(111)-C<sub>10</sub>H<sub>20</sub>CO<sub>2</sub>Et, (b) Si(111)-C<sub>11</sub>H<sub>22</sub>-OH, (c) Si(111)-C<sub>10</sub>H<sub>20</sub>C(C<sub>10</sub>H<sub>21</sub>)<sub>2</sub>OH, (d) Si(111)-C<sub>10</sub>H<sub>20</sub>C(C<sub>10</sub>H<sub>21</sub>)<sub>2</sub>-OC(O)CH<sub>3</sub>, (e) Si(111)-C<sub>10</sub>H<sub>20</sub>CO<sub>2</sub>H, and (f) Si(111)-C<sub>10</sub>H<sub>20</sub>C(O)NHCH<sub>2</sub>-CO<sub>2</sub>CH<sub>3</sub>. The negative peak at 2084 cm<sup>-1</sup> is the Si-H stretch from the Si(111)-H surface that was used as the reference for background subtraction. The experiments were carried out using 25 × 10 × 1 mm<sup>3</sup> ATR elements. The absorbance scale represents the total of 25 reflections.



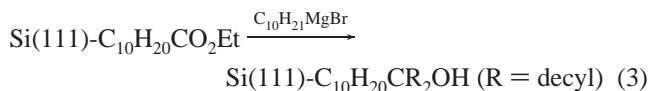
**Figure 2.** (a) Ratio of the ester carbonyl stretch to the total methylene asymmetric stretch as a function of the mole fraction of ethyl undecylenate in 1-decene. (b) Schematic of the packing of a Si(111)-C<sub>10</sub>H<sub>21</sub> monolayer containing a small amount of Si(111)-C<sub>10</sub>H<sub>20</sub>CO<sub>2</sub>Et.

We have carried out a number of chemical transformations on this surface prepared from the neat ethyl undecylenate to demonstrate the flexibility and utility of the terminal ester group. Borohydride reduction (4 h, 0.5 M solution at 85 °C, Supporting Information) leads to an alcohol-terminated surface, i.e., Si(111)-(CH<sub>2</sub>)<sub>11</sub>OH (reaction 2) similar to LiAlH<sub>4</sub> reduction

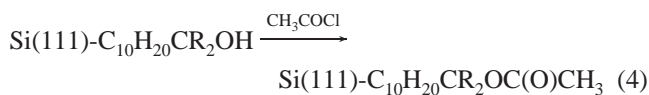


reported by Sieval et al.<sup>6</sup> The ester absorption at 1740 cm<sup>-1</sup> disappeared and was replaced by a broad absorption at 3450 cm<sup>-1</sup> attributed to internally hydrogen bonded O-H (Figure 1b). This alcohol-modified surface could be esterified by reaction with acetyl chloride (Supporting Information). Sieval et al. reported that acylation with acetic anhydride did not appear to go to completion.<sup>6</sup>

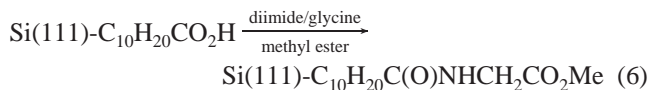
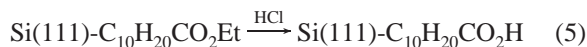
It is also possible to carry out multistep reactions with high overall conversion. Reaction of the ester-modified Si(111) with decylmagnesium bromide leads to the formation of the tertiary alcohol (reaction 3, Figure 1c). Evidence for the complete



reaction with 2 mol of Grignard is based on the loss of the carbonyl stretch, the appearance of an O–H stretch at ca. 3400  $\text{cm}^{-1}$ , and the expected 3-fold increase in the absorbance in the methylene C–H region compared to the starting surface. This tertiary alcohol can be acylated using acetyl chloride (reaction 4, Figure 1d) resulting in the reappearance of the carbonyl stretch at 1740  $\text{cm}^{-1}$  at close to its original intensity and disappearance of the O–H stretch.



It has previously been shown that the Si-C modified surface is stable toward exposure to HCl and even HF.<sup>4,8</sup> Consequently, it is possible to hydrolyze the ester to form a carboxylic acid modified surface (reaction 5) that can be coupled to an amino acid (in this case glycine methyl ester) using a standard amide coupling protocol (reaction 6, Supporting Information).<sup>26</sup>



Again, the spectroscopic evidence for the successful reaction is based on the disappearance of the ester stretch at 1740  $\text{cm}^{-1}$  and the appearance of the carboxylic acid stretch (1711  $\text{cm}^{-1}$ ) and OH stretch (3300, 3200  $\text{cm}^{-1}$ ). The coupling to glycine methyl ester results in the disappearance of the absorptions from the carboxylic acid and the appearance of now two carbonyl stretches corresponding to the amide stretch at 1680  $\text{cm}^{-1}$  and

the methyl ester stretch at 1740  $\text{cm}^{-1}$ . Rinsing in dilute HCl had no effect on the FTIR spectra ruling out the possibility of carboxylate formation. Further evidence for amide formation comes from XPS results which give a C:N:O ratio consistent with the glycine-terminated surface and show the expected two chemically shifted oxygen peaks and four chemically shifted carbon peaks. There is no evidence for  $\text{SiO}_2$  on the surface. The overall conversion is high (>90%) as judged by changes in the FTIR absorption spectra.

Thus, we have shown that it is possible to control the surface concentration of reactive ester sites on a covalently modified silicon surface. Additionally, we have shown that the terminal ester function can be manipulated using standard chemical and solid-phase chemical procedures. In principle this will allow the incorporation of virtually any chemical functionality at the surface at a well-defined density. It is expected that the ability to precisely control the average distance between large biomolecules on surfaces will impact on future molecular electronic, sensor, and biochip technologies. Future work will focus on further elaborating the chemistry at these interfaces and determining the distribution of ester groups from reactions of mixtures of alkenes. In addition, the ability to chemically pattern reactive regions for applications in microsensor arrays will be explored.

**Supporting Information Available:** Experimental details, a table of XP intensity data for the  $\text{Si(111)-C}_{10}\text{H}_{20}\text{C(O)NHCH}_2\text{CO}_2\text{Me}$  surface, and figures giving XP survey spectrum of the  $\text{Si(111)-C}_{10}\text{H}_{20}\text{C(O)NHCH}_2\text{CO}_2\text{Me}$  surface, high-resolution XP spectra of  $\text{Si}_{2p}$ ,  $\text{O}_{1s}$ ,  $\text{C}_{1s}$ , and  $\text{N}_{1s}$  peaks, and the contact made AFM image of the ester modified surface,  $\text{Si(111)-C}_{10}\text{H}_{20}\text{CO}_2\text{H}$  (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(26) Sieval et al. report two carbonyl peaks for the carboxylic acid terminated surface which they assign to free and hydrogen-bonded carboxylic acid. One of these peaks appears to be coincident with the origin ester so they point out that it is difficult to rule out the possibility of incomplete hydrolysis. We observe only a single peak in the carbonyl region that corresponds to a hydrogen-bonded carboxylic acid. It is possible that differences in the morphology of the Si(111) which is atomically flat (Supporting Information) and Si(100) which is more rough also could lead to differences in the spectroscopy.