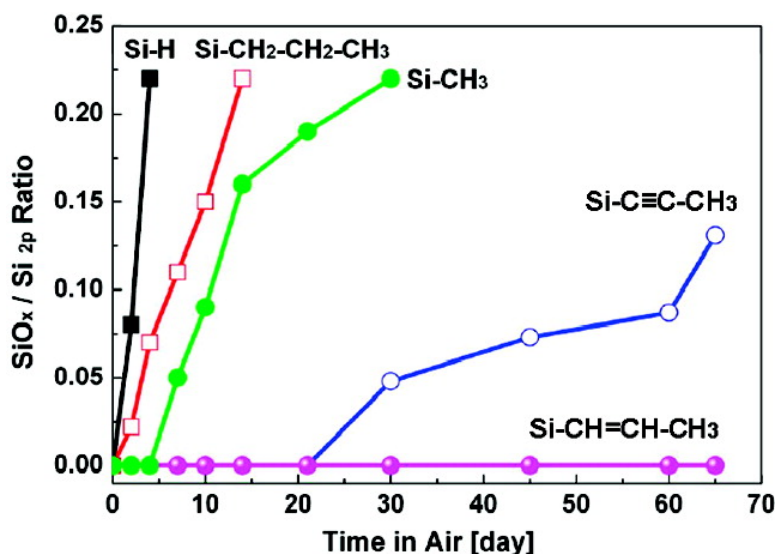


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Sreenivasa Reddy Puniredd, Ossama Assad, and Hossam Haick

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Highly Stable Organic Modification of Si(111) Surfaces: Towards Reacting Si with Further Functionalities while Preserving the Desirable Chemical Properties of Full Si–C Atop Site Terminations

Sreenivasa Reddy Puniredd, Ossama Assad, and Hossam Haick*

Department of Chemical Engineering and Russell Berrie Nanotechnology Institute, Technion, Israel Institute of Technology, Haifa 32000, Israel

Received February 3, 2008; E-mail: hhossam@technion.ac.il

Densely packed organic layers bonded covalently to crystalline silicon (Si) surfaces, without an interfacial silicon oxide (SiO_2) layer, have received an increasing interest, mainly because of their variety of applications in micro- and nanoelectronics as well as in (bio)chemical sensors.^{1,2} For example, attachment of organic species on a Si substrate could significantly reduce the density of trap states on Si surfaces³ as well as the diffusion of oxygen into Si during formation of insulating or high-dielectrics layers.⁴ To this end, formation of Si–C bonds is particularly attractive owing to their kinetic inertness as compared to Si–O or Si–H bonds.¹ Si–C bonds are chemically more stable than Si–O bonds, because they are less polarized and thus less susceptible to nucleophilic substitution reactions.¹ Complete coverage of Si atop sites was achieved by CH_3 termination of Si(111), through the two-step chlorination/alkylation process.^{5–7} Though CH_3 termination gives full coverage, further functionalization (by reaction with other molecules) is not possible. To provide a reactive functionality for further chemical modification of the Si surfaces, Si(111) surfaces have been terminated with acetylenic functionality, via Si–C bonding.⁸ The obtained coverage of these molecules was identical to that of the CH_3 -terminated Si(111) surface, namely, full termination of the Si atop sites. Yet, surfaces terminated with acetylenic functionality oxidize after a certain period of time (cf. ref 8 and Figure 2A and related discussion below).

Here, we report on the functionalization of Si(111) surfaces with various organic molecules having similar backbone but different in their C–C bond close to the Si surface (i.e., C–C vs C=C vs C≡C bonds). We show that functionalization of Si surfaces with $\text{CH}_3\text{–CH=CH–MgBr}$ organic molecules gives nearly full coverage of the Si atop sites. Furthermore, we show that Si surfaces with $\text{CH}_3\text{–CH=CH–MgBr}$ molecules are more robust for surface oxidation and more stable against water attacks than $\text{CH}_3\text{–C≡C–MgBr}$ and $\text{CH}_3\text{–MgBr}$, which give nearly full coverage too.

Prior to chemical modification, all Si(111) surfaces were cleaned by a sequential rinse with DI water, methanol, acetone, dichloromethane, 1,1,1-trichloroethane, acetone, methanol, and DI water. Samples were then dried under a stream of $\text{N}_{2(g)}$. H-terminated Si(111) surfaces were obtained through wet chemical etching for 20 min in 40% $\text{NH}_4\text{F}_{(aq)}$. The samples were agitated periodically to minimize the formation of etch pits. Following etching, the monohydride-terminated surfaces were rinsed with flowing H_2O and dried under a stream of $\text{N}_{2(g)}$. Si–H samples were alkylated using the two-step chlorination/alkylation protocol.^{3,7} First, H–Si(111) surfaces were immersed in a saturated solution of PCl_5 in chlorobenzene for 50 min at 90 ± 10 °C. The chlorinated samples were rinsed sequentially with chlorobenzene and tetrahydrofuran (THF) and the samples were transferred to a N_2 -purged glovebox. The samples were subsequently immersed for 27 h at 120–130 °C in a THF solution of 0.5 M 1-propenylmagnesium bromide ($\text{CH}_3\text{–CH=CH–MgBr}$) and 1-propynylmagnesium bromide ($\text{CH}_3\text{–C≡C–MgBr}$) for producing Si–CH=CH– CH_3 and Si–C≡C– CH_3 surfaces, respectively. A diethyl

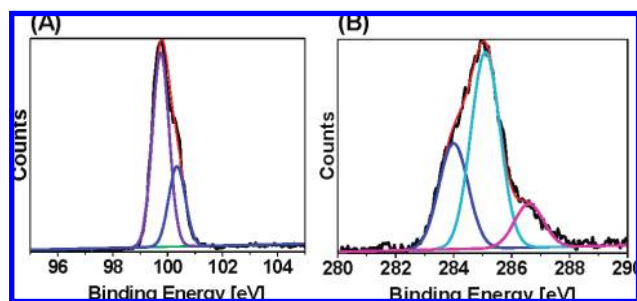


Figure 1 (A) XPS of Si2p region for Si–CH=CH– CH_3 , showing Si2p_{3/2} (purple) and Si2p_{1/2} (blue); (B) XPS of C1s region, showing C–Si (blue), C–C (cyan), and C–O (magenta) peaks for Si–CH=CH– CH_3 .

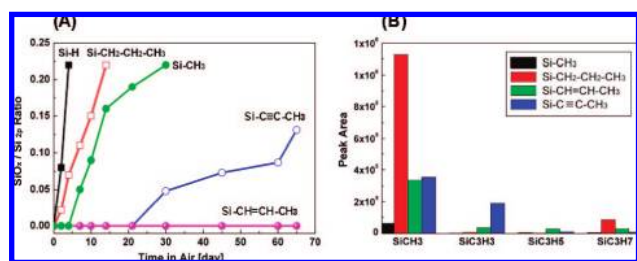


Figure 2 (A) Ratio of the oxidized Si2p peak area to the bulk Si2p peak area for the different surface modifications of Si(111) surfaces, exposed to air over extended time periods; (B) SiC_xH_y^+ peak intensities of ToF-SIMS spectra of the different Si(111) surfaces.

ether solution of 2.0 M of propylmagnesium chloride ($\text{CH}_3\text{–CH}_2\text{–CH}_2\text{–MgCl}$) was used to produce the Si– $\text{CH}_2\text{–CH}_2\text{–CH}_3$ surface. A 10 h immersion in 3.0 M THF solution of methyl magnesium chloride (CH_3MgCl) was used for producing the CH_3 -terminated Si surface (Si– CH_3).⁵ Alkylated Si samples were rinsed with flowing THF and then immersed in methanol. The alkylated samples were transported out of the glovebox and further rinsed with methanol, sonicated in fresh methanol and 1,1,1-trichloroethane, rinsed with H_2O , and dried under a stream of $\text{N}_{2(g)}$. The resulting functionalized surfaces were characterized by high resolution X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectroscopy (ToF-SIMS) analysis.

Figure 1 shows a high resolution XPS scan of Si2p and C1s region of Si–CH=CH– CH_3 surface. The Si2p spectrum (Figure 1A) shows Si2p_{3/2} and Si2p_{1/2} with the expected 2:1 area ratio and 0.6 eV energy separation. No oxidized Si between 101.0 and 103.5 eV was observed, confirming the absence of SiO_2 after alkylation (Figure 1A). Three peaks were observed at 284.0, 285.2, and 286.6 eV in the C1s spectrum (Figure 1B). The peaks at 285.2 and 286.6 eV are common to all alkylated and H-terminated Si surfaces,⁷ whereas the low binding energy peak at 284.0 eV is unique to alkylated Si surfaces. Hence, the first peak at 284.0 eV can be assigned to emission from core-level electrons of carbon atoms covalently bonded to the relatively electro-

positive silicon (C–Si).^{8,9} The second C1s peak, characterized by an energy emission at 285.2 eV, can be ascribed to carbon bonded to either hydrogen or another carbon atom. The third C1s peak, characterized by a binding energy at 286.6 eV, is ascribed to adventitious carbon bonded to oxygen from the wet chemical processing with THF solvent and THF/methanol rinse after functionalization, from carbonaceous materials present in the laboratory environment, and/or from the transportation of samples to the XPS chamber. The two peaks at higher energy may also contain contributions from vibrational excitations associated with lower energy peaks.^{3,7,8} All C1s emissions located at 284.0, 285.2, and 286.2 eV and Si2p peaks were also observed for propyl, propynyl, and methyl-functionalized silicon surfaces.^{3,7,8} The ratio of C–Si/Si2p peak area can provide quantitative coverage with a suitable reference system.⁷ Methylation (Si–CH₃) has been shown by various methods to provide a nearly complete monolayer on the Si(111) surface.^{7,8} Si–CH=CH–CH₃ surfaces showed a C–Si/Si2p peak ratio of 110 ± 10% relative to that of CH₃–Si surface, indicating that the Si–CH=CH–CH₃ can be packed at very high density by this two-step alkylation method. The XPS peak area analysis in Figure 1B shows that the stoichiometric ratio between the C atom bonded directly to the Si (at 284.0 eV) and to the two C atoms bonded far away from the Si surface (at 285.2 eV) is 1:2, indicating that these XPS peaks are due to Si–CH=CH–CH₃ molecule per se. Similarly, C–Si/Si2p peak ratio for Si–C≡C–CH₃ and Si–CH₂–CH₂–CH₃ produced 105 ± 10% and 50 ± 10%, respectively, relative to that of CH₃–Si surface.

Figure 2A, shows the oxidized Si2p peak area to the bulk Si2p peak area for the functionalized Si(111) surfaces, exposed to ambient air over extended time periods. Oxidation of the Si surface was monitored by the growth of a broad SiO₂ peak between 101.0 and 105.0 eV.^{3,7} Relative to H-terminated Si, Si–CH=CH–CH₃ surfaces exposed to ambient air over a period of more than two months showed no surface oxidation. This result is significant because adventitious oxidation degrades the electronic properties of the Si surface.⁴ The Si–C≡C–CH₃ surface showed no oxidation up to 25 days. Yet, beyond that period, the oxidation rate increased with time. The Si–CH–CH–CH₃ surface showed more oxidation than Si–CH=CH–CH₃, Si–C≡C–CH₃, and Si–CH₃, mostly due to its lower surface coverage (~50% as compared with ~100% surface coverage of the other molecules).¹⁰

To further study the quality of monolayers, we investigated their stability in water. We immersed the samples in water for 24 h and then dried and characterized them by XPS. The XPS results did not show any SiO₂ peak for the Si–CH=CH–CH₃ surface. However, prominent peaks of SiO₂ were observed in case of Si–C≡C–CH₃ (ca. half-monolayer of SiO₂), Si–CH–CH–CH₃ (ca. one monolayer of SiO₂), and Si–CH₃ surfaces (ca. half-monolayer of SiO₂). The constant C–Si/Si2p ratio for the Si–CH=CH–CH₃ surface in XPS before and after exposure to water indicated that the layer was not removed. These results provide further evidence that stable Si–CH=CH–CH₃ monolayers were formed if compared to Si–C≡C–CH₃, Si–CH₂–CH₂–CH₃ and Si–CH₃ monolayers, thus widening the range of potential applications.

Figure 2B presents summary of the ToF-SIMS Si_xC_yH_z⁺ peak intensities for all samples having nearly complete coverage (as determined by the XPS analysis). The Si₃C₃H₅⁺ cations are more easily produced for the monolayers with Si–C≡C–CH₃ molecules, suggesting an easily sputtered-induced decomposition of the near surface region by ToF-SIMS.¹² This provides an additional evidence for surface oxidation with air and the stability with water of Si–C≡C–CH₃ molecules. In contrast, the Si₃C₃H₅⁺ cations for the Si–CH=CH–CH₃ molecules are not easily sputtered by ToF-SIMS

showing that the monolayers of alkyl chains are densely packed and more robust. When compared to other molecules (Si₃C₃H₅⁺, Si₃C₃H₇⁺, Si₃C₃H₉⁺) Si–CH=CH–CH₃ is producing less Si₃C₃H₅⁺ cations after sputtering, indicating for their superior stability.

Our results indicate that a possible mechanism for the high stability of the Si–CH=CH–CH₃ molecules is that of π–π interaction between the molecules.¹³ In the case of Si–C≡C–CH₃ molecules, π–π interactions occur between the adjacent molecules but leave one pair of electrons free. This pair of free electrons might easily transfer to the atop Si site (beneath the molecule) and interact with oxidizing agents (e.g., water, O₂, etc.).¹¹ Our ToF-SIMS results indicate that direct interaction between the free electron pair and oxidizing agent is possible too, mostly for ca. 10% of the molecules on the surface. In the case of Si–CH₂–CH₂–CH₃ molecules, neither full (100%) coverage nor π–π interactions exist, thus explaining their low resistance to oxidation processes.

In summary, we demonstrated passivation of the Si(111) surface using Si–CH=CH–CH₃ alkyl chains and the binding of each Si surface atom with one Si–C bond. Also, we showed that the Si–CH=CH–CH₃ molecule is more robust than the Si–C≡C–CH₃, Si–CH₂–CH₂–CH₃ and Si–CH₃ surfaces. On the basis of these findings, Si–CH=CH–CH₃ monolayer can provide an avenue to protect the surface from oxidation while eliminating interfacial trap states. Also, Si–CH=CH–CH₃ molecules offer an avenue for introducing well-defined “molecular wires” between Si surfaces and micro- or macrocontacts.¹⁴ The ability to react the Si further with other functionalities opens up avenues to Si functionalization while maintaining the desirable chemical and electrical properties of full Si–C atop site termination on the Si(111) surface.² Of great interest, Si substrates that are covered with Si–CH=CH–CH₃ molecules, or with further reacted functionalities, can be used credibly not only in ambient (gaseous environment) conditions, but also in liquid solutions.

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