

Theoretical Investigation of the Structure and Coverage of the Si(111)–OCH₃ Surface

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The surface structure, strain energy, and charge profile of the methoxylated Si(111) surface, Si(111)–OCH₃, has been studied using quantum mechanics, and the results are compared to those obtained previously for Si(111)–CH₃ and Si(111)–C₂H₅. The calculations indicate that 100% coverage is feasible for Si(111)–OCH₃ (similar to the methylated surface), as compared to only ~80% coverage for the ethylated surface. These differences can be understood in terms of nearest-neighbor steric and electrostatic interactions. Enthalpy and free energy calculations indicate that the formation of the Si(111)–OCH₃ surface from Si(111)–H and methanol is favorable at 300 K. The calculations have also indicated the conditions under which stacking faults can emerge on Si(111)–OCH₃, and such conditions are contrasted with the behavior of Si(111)–CH₃ and Si(111)–CH₂CH₃ surfaces, for which stacking faults are calculated to be energetically feasible when etch pits with sufficiently long edges are present on the surface.

Silicon surfaces have been functionalized with a wide variety of organic reagents through a number of methods including reactions with alkyllithium or alkyllithium reagents, electrochemical functionalization, ultraviolet light-initiated reactions,^{1–5} chemical free-radical activation,^{6,7} thermal activation,^{7–13} hydrosilylation reactions,^{14–18} or through reactions with alcohols.^{19–25} In general, the reported reactions can be divided into those producing surfaces having the functionalized Si in the formal Si(0) oxidation state, with Si–C–R bonding, or those producing surfaces having the functionalized Si in the Si(I) oxidation state, with Si–O–R bonding. The alkylated Si(111) surfaces are the most characterized to date.^{2–4,6,7,11,21,22,26–34} Simple molecular modeling considerations indicate that –CH₃ groups are the only saturated straight-chain alkyl that, on steric grounds, can terminate every atop Si site on an unreconstructed Si(111) surface. Consistently, recent low-temperature (4 and 77 K) atomic resolution scanning tunneling microscopy (STM) images of the methyl-terminated Si(111) surface prepared through a two-step chlorination/alkylation process^{26,27} have revealed a well-ordered structure with a nearest-neighbor spacing equal to 3.8 Å, corresponding to 100% coverage on the unreconstructed 1 × 1 Si(111) surface.³⁴ The relaxed geometry obtained from quantum mechanics (QM) calculations for Si(111)–CH₃ (Figure 1) is in accord with the experimental data on such systems.^{35,36} In contrast, STM images at 77 K of the Si(111)–C₂H₅ surface, prepared through the same method, indicate that the ethyl surface coverage is only ~80%.³⁷ At 100% coverage, QM calculations indicate that the ethyl-terminated Si(111) surface should contain a significant amount of strain, with large bond angles and short nonbond distances.³⁷ The equilibrium C–C–Si and C–Si–Si bond angles calculated at 100% coverage are $\alpha = 130.8^\circ$ and $\beta = 123.8^\circ$, respectively (Figure 2), which are appreciably larger than the tetrahedral value of 109.4°. The nonbond H···H distances were calculated to be as

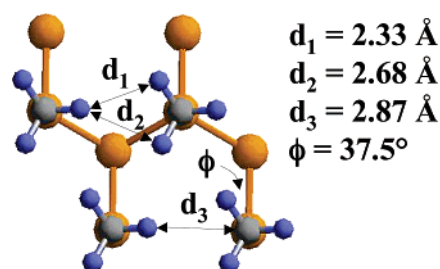


Figure 1. Top view atomistic model showing four adjacent surface sites of the 1 × 1 Si(111)–CH₃ surface at 100% coverage with the most relevant nonbond distances (d_1 , d_2 , and d_3) and the torsion angle of the methyl group with respect to the silicon surface, obtained from quantum mechanics calculations.³⁵ The color code is as follows: blue = hydrogen, gray = carbon, and orange = silicon.

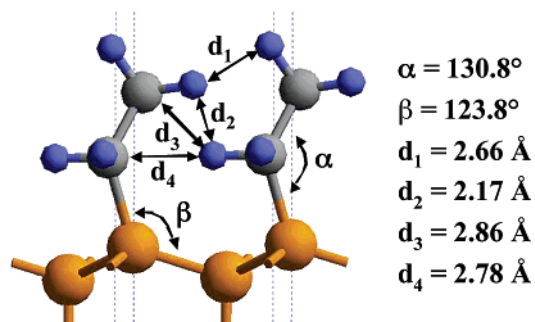


Figure 2. Side view atomistic model showing two adjacent surface sites of the 1 × 1 Si(111)–C₂H₅ surface at 100% coverage with the most relevant bond angles (α and β) and nonbond distances (d_1 , d_2 , d_3 , and d_4), obtained from quantum mechanics calculations.³⁷ The color code is as follows: blue = hydrogen, gray = carbon, and orange = silicon.

low as 2.17 Å, much shorter than the calculated values for hydrogen atoms on neighboring methyl groups of Si(111)–CH₃

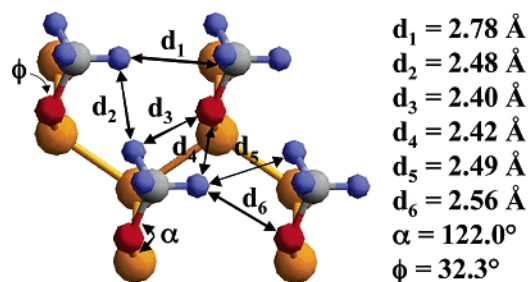


Figure 3. Top view atomistic model showing four adjacent surface sites of the 1×1 Si(111)-OCH₃ surface with the most relevant nonbond distances (d_1 , d_2 , d_3 , and d_4), and the bond and torsion angles (α and ϕ , respectively), obtained from quantum mechanics calculations. The color code is as follows: blue = hydrogen, gray = carbon, red = oxygen, and orange = silicon.

(2.33 Å) or for hydrogen atoms on neighboring carbon atoms within bulk crystalline polyethylene (2.51 Å).³⁷ These expectations are therefore also in accord with STM data of C₂H₅-terminated Si(111) surfaces.

In this work, we focus on the structure of the Si(111)-OCH₃ surface. Alkoxyated Si surfaces have been prepared by the slow room-temperature reaction of porous or roughened Si(111)-H surfaces with alcohols,^{19,20,23} by the rapid, oxidatively driven reaction of Si(111)-H with alcohols,^{21,22,38} or by reaction of alcohols with Cl-terminated Si(111) surfaces.²² Methoxylated Si surfaces are also of interest, because a common method of electrically passivating Si(111) is to immerse it into I₂ in CH₃OH,^{39–43} which forms, at least in part, Si-OCH₃ as well as Si-I bonds.^{44–46} We are interested in modeling the Si(111)-OCH₃ and Si(111)-I surfaces to calculate the geometry, to estimate the maximum surface coverage that is feasible, and to compare the results to those obtained for Si(111)-CH₃ and Si(111)-C₂H₅.

SeqQuest software⁴⁷ with Gaussian double- ζ plus polarization basis sets, pseudopotentials, and the PBE⁴⁸ approximation of density functional theory (DFT) was used for all periodic calculations. The details on the basis sets, including the Gaussian decay constants and associated contraction coefficients, pseudopotentials, and k-points are provided in the Supporting Information. Unless otherwise indicated, all calculations reported here correspond to full geometry optimizations. These are the same methods that were used to study the methylated and ethylated surfaces.^{34,35,37}

To calculate the Si(111)-OCH₃ surface at 100% coverage, geometry optimization was performed on an infinitely repeated 2D periodic 1×1 unit cell that consisted of six layers of bulk silicon atoms, a hydrogen atom terminating the bottom surface, and a -OCH₃ group terminating the top surface. Thus, the unit cell contains a total of twelve atoms, of which only the bottom hydrogen was kept fixed during the geometry optimization. This number of bulk silicon layers resting on a fixed hydrogen layer has been shown previously to be an optimal compromise between accuracy and computation cost through extensive QM geometry optimization calculations on reconstructed Si(111) surfaces.⁴⁹ These calculations yielded the equilibrium surface geometry (Figure 3), as well as the partial charges of the surface atoms as calculated through a Mulliken populations analysis (Figure 4). The surface charge profile is as expected from the electronegativity of the atoms involved. DFT calculations were also performed in the presence of electric fields in the range of -10 to +10 MV/cm, but negligible effects were observed. As shown in Figure 3, the CH₃ groups in the -OCH₃ moiety are calculated to be tilted, having a Si-O-C angle, α , of 122.0°, consistent with expectations based on nearest-neighbor interac-

tions between -OCH₃ groups and between these groups and the Si(111) surface. Figure 5 shows the behavior of the surface energy as a function of the torsion angle, yielding a minimum in energy for a Si-Si-O-C torsion angle, ϕ , of 32.3°.

To quantify the surface strain as a function of the -CH₃, -C₂H₅, and -OCH₃ surface coverage on Si(111), periodic PBE DFT calculations were performed on 1×1 (surfaces with 100% coverage), 2×2 (surfaces with 100%, 75%, 50%, and 25%), and 3×3 (surfaces with 66.7% coverage) unit cells of Si(111)-CH₃, Si(111)-C₂H₅, and Si(111)-OCH₃ surfaces having functional group coverage amounts ranging from 25% to 100% of the Si atop sites. Comparison of the calculations performed on 1×1 and 2×2 unit cells at 100% coverage gave similar values of the strain energy for all three functional groups considered, indicating that the 1×1 symmetry is preferred. All structures contained six bulk silicon layers resting on a layer of hydrogen atoms fixed at their lattice sites, as before. In each case, the remaining Si atop sites were terminated with hydrogen atoms. For each surface, the average bond energy of the appropriate functional group was compared to its bond energy on a Si(111) surface site modeled as a Si₁₀H₁₅ cluster having no nearest neighbors (Figure 4), with the bond to this cluster taken as the reference and assigned zero strain (i.e., the strain energy was calculated as the difference between the average bond energy of the functional group to the surface and the bond energy to the cluster, as summarized in Table 1 for the methoxylated surface). As expected, the calculated strain energy was greater in the ethylated surface than in the other two cases, especially for surface coverages above 67% (Figure 6). At 100% coverage, the amount of strain in the Si(111)-C₂H₅ surface is three times greater than for Si(111)-CH₃ and ten times greater than for Si(111)-OCH₃. In fact, the calculated strain was lowest in Si(111)-OCH₃ for all values of the surface coverage.

While the strain vs coverage curves for the Si(111)-CH₃ and Si(111)-OCH₃ surfaces are smooth, the curve calculated for Si(111)-C₂H₅ had a distinct jump between 67% and 75% coverage, at which point the ethyl groups could no longer fit on the surface unless their C-C-Si angle was significantly increased to allow them to have a nearly vertical orientation with respect to the surface (at 100% coverage, each functional group is forced to occupy only one unit cell). On the basis of the structural similarity between the Si(111)-CH₂-CH₃ and Si(111)-O-CH₃ surfaces, it is somewhat surprising that the Si(111)-OCH₃ surface has such low surface strain. Although the methoxylated surface structure would be expected to involve steric repulsions between hydrogen and oxygen atoms, whose nearest-neighbor nonbond distances can be as low as 2.40 Å (Figure 3), this interaction is not as repulsive as that between hydrogen atoms of a terminal -CH₃ group of an ethyl molecule with the -CH₂- groups on a neighboring ethyl group, because the hydrogen and oxygen atoms in the Si(111)-OCH₃ overlayer have atomic charges of different signs, which results in a favorable Coulomb interaction of 20.7 kcal/mol (in a vacuum), thus compensating for part of the nearest-neighbor repulsion energy.

The strain energy calculations as well as the equilibrium geometry suggest that 100% surface coverage of -OCH₃ groups is feasible. Experimental observations indicate that -OCH₃ groups can be added to the surface through a relatively slow but spontaneous reaction of methanol with Si(111)-H surfaces in the dark. One possible reaction mechanism could be Si(111)-H + CH₃-OH → Si(111)-OCH₃ + H₂.²⁴ Free energy and enthalpy calculations on this reaction were therefore performed using *nonperiodic* QM (Jaguar software, Schrödinger,

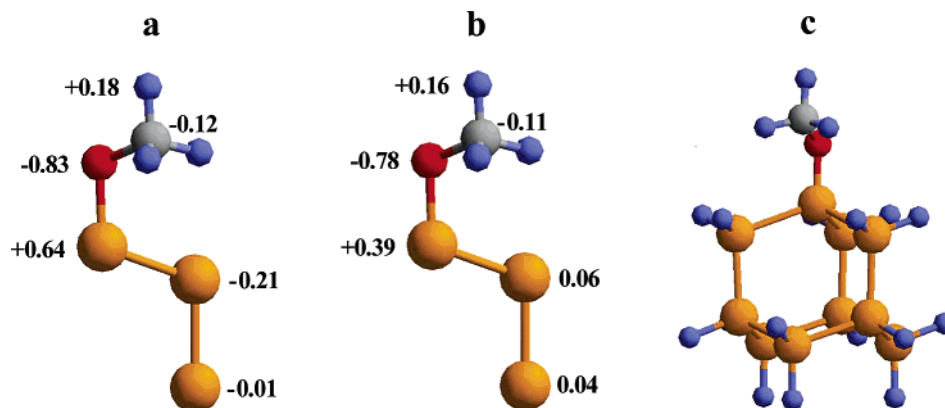


Figure 4. Atomic charges from Mulliken populations analysis (in a vacuum) for Si(111)–OCH₃ using an infinitely repeated periodic surface unit cell (a) and using a Si₁₀H₁₅–OCH₃ cluster (b and c). The atomic charge in the fourth Si layer of the surface unit cell (not shown) is less than 0.01. The charges of the –OCH₃ substituent are similar for the cluster and the periodic structure. The silicon charges differ because the cluster was terminated with hydrogen atoms.

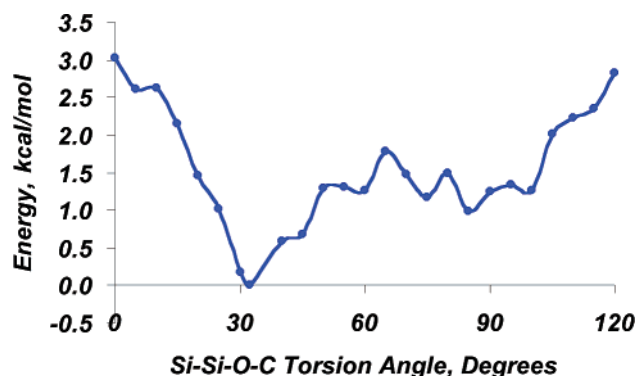


Figure 5. Surface energy as a function of the Si–Si–O–C torsion angle, ϕ , of the Si(111)–OCH₃ surface. The energy values were obtained by changing the torsion angle of the equilibrium surface structure (with all other parameters kept constant) and performing single-point energy DFT calculations (without relaxation). The equilibrium minimum-energy torsion angle is 32.3°.

TABLE 1: Bond and Strain Energy of –OCH₃ Bonded to the Si(111) Surface and to the Si₁₀H₁₅ Cluster Shown in Figure 4c^a

surface model	average ^b bond energy of –OCH ₃ (kcal/mol)	average strain energy of –OCH ₃ (kcal/mol)
Si ₁₀ H ₁₅ cluster	81.84	reference
2 × 2 Si(111)–OCH ₃ 100% coverage	80.64	1.20
2 × 2 Si(111)–OCH ₃ 75% coverage	80.30	1.55
2 × 2 Si(111)–OCH ₃ 50% coverage	80.15	1.69
2 × 2 Si(111)–OCH ₃ 25% coverage	80.33	1.52

^a This cluster was taken as the reference and assigned zero strain.

^b These energies represent the average for all the functional groups in the unit cell. For example, the 2 × 2 Si(111)–OCH₃ surface with 75% coverage contains three –OCH₃ groups and one surface hydrogen (not including the hydrogen atoms terminating the bottom of the slab model used), so the average bond energy is the difference in energy between the functionalized surface and the resulting structure where the three –OCH₃ groups are dissociated and located at infinity with respect to the surface (which now contains three Si atoms with dangling bonds), divided by 3 (since there are three –OCH₃ groups).

Portland, OR) at the B3LYP level of theory with 631G** basis sets and the Poisson–Boltzmann continuum solvation model (assuming for methanol a dielectric constant of 33.62 and a solvent radius of 2.0 Å). For this calculation, energies for each reactant and product were calculated as surrounded by the dielectric of methanol, and the Si(111) surface sites were modeled as Si(SiH₃)₃ clusters to which –H or –OCH₃ groups

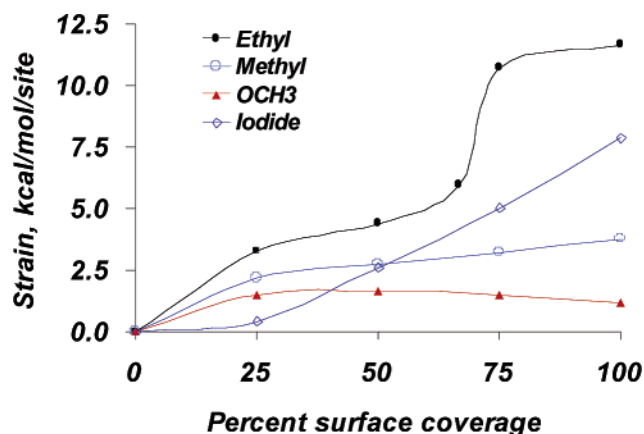


Figure 6. Strain energy per occupied surface site for Si(111)–C₂H₅, Si(111)–CH₃, and Si(111)–OCH₃ as a function of surface coverage from quantum mechanics calculations. The sites not occupied with ethyl, methyl, or methoxy were terminated with hydrogen atoms. The reference is a functional group bonded to a 1 × 1 site Si₁₀H₁₅ cluster with no nearest neighbors (cf. Figure 4). The results for ethyl and methyl surfaces have been reported previously.³⁵ The results for the I-terminated surface are included, since this is a byproduct in one of the synthetic routes used to prepare the Si(111)–OCH₃ surface.

were bonded. The values obtained were $\Delta G^{298^\circ} = -4.9$ kcal/mol and $\Delta H^{298^\circ} = -5.8$ kcal/mol, confirming the feasibility of a spontaneous reaction to alkoxyate the surface from alcohols. Electrochemical experiments indicate that, while the hydrogen-terminated silicon surface can be oxidized at –0.6 V vs a standard calomel electrode,³⁸ the oxidation of a model compound, tris(trimethylsilyl)silane, H–Si[Si(CH₃)₃]₃, does not occur within the solvent window of methanol. These experiments indicate that the valence band energy is significantly higher in energy than the HOMO for the model compound and that the free energy for spontaneous reaction of the H–Si(111) surface with methanol may be significantly more exothermic than suggested by the calculations on the H–Si(SiH₃)₃ cluster.

Because most experimental surfaces contain etch pits and step edges, with surface sites located on the edges, strain energy calculations were also performed on unit cells that contained steps. Previous calculations³⁵ have indicated that a full stacking fault is energetically favorable on the terraces of the Si(111)–CH₃ surface when etch pits with sufficiently long edges are present on the surface. The stacking fault, which changes the step edge terminations from a <112> step edge to a structure similar to the <1̄12> step edge,⁵⁰ minimizes the total strain energy of the surface by significantly lowering the strain at edge sites.³⁵

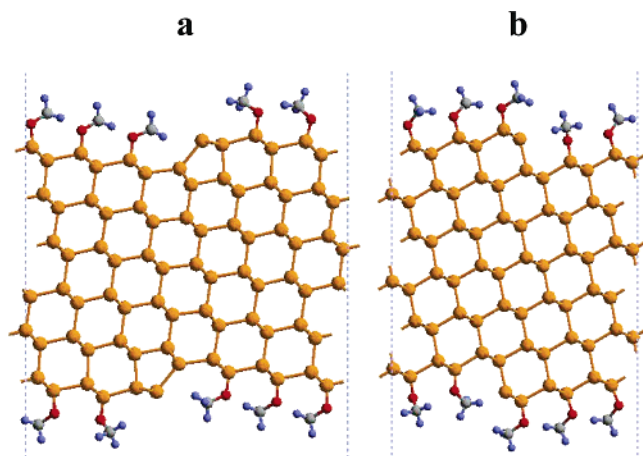


Figure 7. Unit cells used for the strain energy calculations on the Si(111)–OCH₃ surface in the presence of step edges. The unit cell containing a $\langle 11\bar{2} \rangle$ step edge (a) was obtained by cutting the silicon crystal along the $\langle 668 \rangle$ plane, and the unit cell containing a $\langle \bar{1}\bar{1}2 \rangle$ step edge (b) was obtained by cutting the silicon crystal along the $\langle 664 \rangle$ plane. The step edge surface sites are shown in the pictures without functionalization.

Because ethyl groups are even larger than methyl groups, the Si(111)–C₂H₅ surface is expected to undergo the same transformation, but it is not clear whether such a transformation can also occur for Si(111)–OCH₃. Hence, strain energy calculations were performed for –OCH₃ groups bonding to surface sites on $\langle 11\bar{2} \rangle$ and $\langle \bar{1}\bar{1}2 \rangle$ step edges (Figure 7). The bond energy to $\langle 11\bar{2} \rangle$ was calculated to be *more* favorable than to the isolated binding site by 0.15 eV/site, while the bond energy to $\langle \bar{1}\bar{1}2 \rangle$ was *less* favorable by 0.53 eV/site. Binding to $\langle \bar{1}\bar{1}2 \rangle$ is thus preferred by ~ 0.68 eV/site with respect to the bond energy to $\langle 11\bar{2} \rangle$. The calculated energy cost of a stacking fault is ~ 0.074 eV/site, approximately twice the cost of a stacking fault in the Si(111)–CH₃ surface. From the high strain energy of the sites on the $\langle 11\bar{2} \rangle$ step edge, and the difference between bonding to $\langle 11\bar{2} \rangle$ and bonding to $\langle \bar{1}\bar{1}2 \rangle$, we conclude (using similar arguments to those presented previously³⁵) that at 100% coverage the step edges cannot be functionalized with –OCH₃ groups unless a stacking fault occurs on the terraces. For a stacking fault to be energetically favorable, however, the ratio of terrace sites to edge sites must be *lower* than the ratio of the difference in energy between bonding to $\langle 11\bar{2} \rangle$ and bonding to $\langle \bar{1}\bar{1}2 \rangle$ to the stacking fault energy cost, equal to ~ 9 (as compared to ~ 19 for the methylated surface). For the methylated surface, the energy barrier to the emergence of the stacking fault could be overcome by the large amount of free energy released during the Grignard reaction used to add methyl groups to the Si(111)–Cl surface ($\Delta G^{298^\circ} = -41.0$ kcal/mol), which in turn was prepared from the Si(111)–H surface.³⁵ In the case of the Si(111)–OCH₃ surface prepared through the reaction of Si(111)–H with methanol, no such large change in free energy is present for the reaction, making it unlikely that a stacking fault can occur. In this system, it is more likely that to reduce the strain as the surface approaches 100% coverage the edge sites simply remain functionalized with hydrogen atoms, which do not experience significant strain at the edges.³⁵ Note that the hydrogen-terminated site could be located on the edge itself or at one of the sites immediately adjacent to it, one on the terrace and one in the etch pit. The calculations show that having the hydrogen-terminated site on the edge is more favorable than having the H-terminated site on the adjacent terrace or pit sites by 2.51 and 2.25 kcal/mol, respectively. However, the formation of a stacking fault may still be a possibility for other synthetic

routes involving more aggressive surface reactions with a sufficiently low ratio of terrace to edge sites.

In summary, we have shown that the Si(111)–OCH₃ surface can, in principle, afford a route to achieve full termination of terrace atop Si sites on an unreconstructed Si(111) surface, offering 100% coverage of functional groups with minimal strain in the alkoxyl overlayer. Relative to the Si(111)–CH₃ surface, the chemical and electrical properties of the Si(111)–OCH₃ surface should therefore at complete reaction reflect differences solely arising from changing the Si–C–R bonds into Si–O–C–R bonds, as opposed to coverage, packing density, or other major chemical differences arising from residual Si–H bonds, at least on the terraces of such functionalized surfaces.

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Supporting Information Available: Additional data on pseudopotentials and basis sets, and discussion of k-points and spin polarization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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