Monolayers of 1-Alkynes on the H-Terminated Si(100) Surface

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Monolayers of a series of 1-alkynes, from 1-dodecyn to 1-octadecyn, have been prepared on the hydrogen-terminated Si(100) surface via a thermal reaction of the organic compound with this Si surface. An efficient procedure is presented for the synthesis of 1-alkynes from the corresponding 1-alkenes. The resulting monolayers were characterized by water contact angle measurements, ATR infrared spectroscopy, and X-ray reflectivity. The results show that these 1-alkynes give well-ordered, covalently bonded monolayers, which are at least as ordered as those of the corresponding 1-alkenes. The exact binding geometry of the 1-alkyne to the Si surface was investigated. The results from IR spectroscopy and X-ray reflectivity measurements indicate that the 1-alkynes form two Si–C bonds to the surface per reacting molecule. Quantum mechanical calculations confirm that this formation of two Si–C bonds is not only chemically possible but also energetically much more favorable than formation of only one Si–C bond per reacting molecule.

Introduction

Covariently attached, organic monolayers on silicon surfaces, without the interfacial silicon oxide layer, are an interesting new class of monolayers on solid substrates.1,2 These monolayers can be prepared by different routes.2 Probably the easiest and technologically most promising method is the hydrosilylation reaction of 1-alkenes with hydrogen-terminated (H-terminated) Si surfaces (Figure 1). This reaction has been successfully performed on both H-terminated Si(111)3,4,5 and Si(100)6,7,8 surfaces and on porous silicon.9

Covalent, organic monolayers on silicon surfaces have been prepared from a variety of functionalized compounds compared to other reagents, like PCl5 and Grignard reagents, that are to be used in other wet-chemical procedures.15 Recently, it was shown that the monolayers can also be prepared with dilute solutions of the 1-alkyne in organic (aromatic) solvents. This eliminates the previously required use of neat 1-alkynes and yields a 20–40-fold reduction of the required amount of the organic reagent.16

Although most of the research on the hydrosilylation of Si surfaces has been done on 1-alkenes, the reaction works equally well for 1-alkynes.3,5,9–13 However, so far no systematic investigations have been done on surface modifications with this latter class of compounds. Besides, the monolayers that are reported were also almost all prepared under different conditions. This has resulted in a remarkable observation: the 1-alkyne C≡C bond has been found to react either once3,5,9–12 or twice13 with a surface...
Si–H group, depending on the reaction conditions used. On the H-terminated Si(111) surface, on which each Si surface atom bears only one hydrogen atom, the peroxide-catalyzed thermal reaction of 1-hexadecyne and the photochemical reaction of 1-octyne and phenylacetylene resulted in alkynyl groups bound to the surface. A weak C=C stretch vibration was observed with infrared spectroscopy, which was interpreted to indicate the formation of only one Si–C bond per alkyne molecule. The same reactivity of 1-alkynes was reported for porous silicon, if the reaction was induced with an Al catalyst, or with white light. For all these reactions of 1-alkynes on porous silicon a C=C vibration was clearly visible in the IR spectrum of the modified silicon material.

In contrast, the thermal reaction of 1-octyne with porous silicon, this time without any catalyst, has been reported to give two Si–C bonds per molecule, as no alkene vibration was visible with IR spectroscopy. The formation of a certain amount of such doubly bonded structures has also been suggested to occur in the case of the RhI-catalyzed reaction of 1-alkynes with porous silicon, which makes the reactivity of this H-terminated Si(100) surface comparable to that of porous silicon. Thus, it could well serve as a model surface to study the reaction of 1-alkynes under more controlled conditions. In addition, the structure of the H-terminated Si(100) surface is relatively well-known compared to that of porous silicon, which facilitates the interpretation of experimental results.

If 1-alkynes can indeed form two Si–C bonds per molecule, this would also be relevant for an interesting application of monolayers of these compounds. It has been shown that monolayers of 1-alkenes on Si surfaces can be used for surface passivation. Formation of two stable Si–C bonds per molecule, instead of only one as in the case of alkenes, will reduce the number of available surface sites for further reactions and is therefore expected to improve the passivation properties.

In this paper, we present the first investigation of the thermal reaction of 1-alkynes with the H-terminated Si(100) surface. Four nonfunctionalized 1-alkynes of various lengths were used: 1-undecyne (I), 1-hexadecyne (II), 1-tetradecyne (III), and 1-dodecyne (IV). The properties of the resulting monolayers are compared to those of monolayers of the corresponding 1-alkenes, which are also prepared and investigated. All reactions were performed in refluxing mesitylene, which has been shown to be the solvent of choice for the thermal modification of H-terminated Si surfaces with 1-alkenes. The monolayers were characterized by water contact angle measurements, attenuated total reflection (ATR) infrared spectroscopy, and X-ray reflectivity. To get more insight into the way in which the 1-alkynes are bound to the Si(100) surface, several possible binding structures were also investigated with molecular mechanics and quantum mechanical calculations.


**General Information**

The 1-alkynes I–IV were synthesized according to the procedure described below. All 1-alkynes and 1-alkenes used in the monolayer preparations were distilled under reduced pressure and stored at <20 °C, except for 1-oc-tadecyne, which was recrystallized from methanol and stored at room temperature under vacuum. Mesitylene (Acros, 99% or Fluka, 99%) was distilled at atmospheric pressure and stored on CaCl₂.

All glassware for the distillations and the monolayer preparations was cleaned with distilled solvents only. All other chemicals are commercially available and were used as received, unless noted otherwise. The reaction substrates were either pieces of double-polished silicon (Si(100), n-type, 250 µm thickness), spheres (~3 cm) of single-polished silicon (Si(100), n-type, 500 µm thickness), or Si(100) parallelogram plates (ATR-plates) designed for multiple internal reflection spectroscopy (Harrick Scientific, 45°, 50 × 10 × 1 mm³, 50 reflections).

**1-alkyne Synthesis.**

All 1-alkynes were synthesized by the route depicted in Figure 3. The synthesis of 1-hexadecyne (II) is described here as an example; the analogous syntheses of the other 1-alkynes are described in the Supporting Information. The general route is depicted in Figure 3.21 The synthesis of 1-hexadecyne (II).

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**1,2-Dibromohexadecane.**

A solution of 44.8 g (0.20 mol) of 1-hexadecene in 200 mL of dry cyclohexane was cooled to 0 °C. After this cleaning, drops of water spread completely on the polished silicon (Si(100), n-type, 250 µm thickness). Subsequently, the sample was removed from the solution and cleaned.6,16

**1-Hexadecyne (II).**

In a large, three-necked flask fitted with a mechanical stirrer were either pieces of double-polished silicon (Si(100), n-type, 250 µm thickness), spheres (~3 cm) of single-polished silicon (Si(100), n-type, 500 µm thickness), or Si(100) parallelogram plates (ATR-plates) designed for multiple internal reflection spectroscopy (Harrick Scientific, 45°, 50 × 10 × 1 mm³, 50 reflections).

**Supporting Information.**

Details of the flask and procedure used can be found in the Supporting Information.

**General route for the synthesis of the 1-alkynes.**

**Experimental Section**

General route for the synthesis of the 1-alkynes. (b) Klein, J.; Gurfinkel, E.

**Figure 3.** General route for the synthesis of the 1-alkynes.
any C–H vibrations. This indicates that the monolayer was completely removed.

**Contact Angle Measurements.** Water contact angles were determined by the Wilhelmy plate method as described previously. All samples were prepared in triplicate, and for each sample at least seven measurements were made for both advancing and receding contact angles. The reported values are the averages of the three samples. The reproducibility of the advancing contact angles is ±1°, and that of the receding angles is ±1°–2°.

**Infrared Spectroscopy.** Infrared spectra of the monolayers were recorded on a Perkin-Elmer 1725X FT-IR spectrophotometer, equipped with a liquid nitrogen-cooled MCT detector, using a fixed angle multiple reflection attachment (Harrick Scientific). The infrared beam was incident on one of the 45° bevels of the ATR crystal. Spectra of the monolayers were recorded with s- and p-polarized light. Measurement conditions were as follows: resolution 0.25 cm⁻¹, with 512 scans. A clean, untreated Si ATR crystal was used as a background. All crystals were cleaned with chloroform. During the measurement they were kept in a cell which was continuously evacuated in order to avoid contamination through air exposure. The X-ray reflectivity data were obtained from a combination of water contact angle and infrared spectroscopy measurements. In Table 1 the contact angles as determined for the 1-alkyne and 1-alkene monolayers are listed (columns 2 and 3, respectively). From these results it is evident that all four 1-alkynes I–IV give ordered monolayers on the Si(100) surface (column 2). The advancing contact angles (θa = 106°–110°) are indicative of ordered monolayers that are terminated with methyl groups, as they are well-compared with the experimental resolution, which is assumed to be of Gaussian statistics.

**Mechanical Properties Measurement.** All measurements were performed with the MSI program Cerius 2 (version 3.5).27 The monoclinic-modified crystal, was measured as a background. All crystals were cleaned with chloroform. Before starting a measurement, the samples were rinsed in chloroform. During the measurement they were kept in a cell which was continuously evacuated in order to avoid contamination through air exposure. The X-ray reflectivity data were corrected for the sample size effects at small incidence angles, as well as for the background scattering, and were normalized to unit incident intensity. They were analyzed according to an iterative matrix formalism derived from the Fresnel equations through air exposure. The X-ray reflectivity data were obtained from a combination of water contact angle and infrared spectroscopy measurements. In Table 1 the contact angles as determined for the 1-alkyne and 1-alkene monolayers are listed (columns 2 and 3, respectively). From these results it is evident that all four 1-alkynes I–IV give ordered monolayers on the Si(100) surface (column 2). The advancing contact angles (θa = 106°–110°) are indicative of ordered monolayers that are terminated with methyl groups, as they are well-compared with the experimental resolution, which is assumed to be of Gaussian statistics.
may be caused by differences in the orientation of the monolayers. The difference between the receding contact angle on the Si(100) surface. This indicates that the monolayers 98 using neat 1-alkenes.6 Comparing the results from the well-ordered monolayers prepared on the Si(100) surface £ the same holds for the receding angles (r, s = 98–101°).

The values for the 1-alkene monolayers prepared with our recently developed solution procedure16 (column 3) are all comparable to the values reported earlier for the well-ordered monolayers prepared on the Si(100) surface using neat 1-alkenes.6 Comparing the results from the monolayers of the 1-alkynes to those of the 1-alkenes shows that the average values for both the advancing and the receding contact angles as observed for the monolayers of 1-alkynes are slightly higher than those of the corresponding 1-alkenes (€ = 108–110° vs 108–109°; r, s = 98–101° vs 96–98°). They are also the highest values reported so far for any methyl-terminated alkyl monolayer on the Si(100) surface. This indicates that the monolayers of 1-alkynes are at least as well-ordered as these 1-alkene monolayers. The difference between the receding contact angles of the monolayers of the 1-alkynes and the 1-alkenes might be caused by differences in the orientation of the methyl groups.35,36

The results from the infrared spectroscopy measurements on the monolayers of the 1-alkynes I–IV are shown in Table 2. The antisymmetric methylene stretching vibrations appear near 2921 cm⁻¹, and the symmetric vibrations are near 2852 cm⁻¹. The antisymmetric CH₃ vibration is visible at 2960 cm⁻¹. As an example, the spectrum of a monolayer of II is shown in Figure 4. It is known that shifts occur for these vibrations on going from the liquid to the solid state. In long, linear n-alkanes the antisymmetric vibration shifts from approximately 2928 to 2920 cm⁻¹ and the symmetric vibration from 2856 to 2850 cm⁻¹.37 Consequently, the packing of the 1-alkyne molecules in the monolayers resembles that of the solid state of n-alkanes. This indicates that the molecules are closely packed and form a well-ordered monolayer.

The values for the monolayers of 1-octadecylene (I) and 1-hexadecyl (II) are also similar to those previously reported for the corresponding 1-octadecene and 1-hexadecene monolayers on the Si(100) surface, which gave values of 2920–2921 and 2851–2852 cm⁻¹, respectively.6

### Table 1. Water Contact Angles for the 1-Alkyn and 1-Alkene Monolayers (Columns 2 and 3, Respectively)

<table>
<thead>
<tr>
<th>Compound, R =</th>
<th>Θw/Θr (H₂O)° (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₀H₂₁</td>
<td>110/96</td>
</tr>
<tr>
<td>C₁₂H₂₅</td>
<td>110/101</td>
</tr>
<tr>
<td>C₁₄H₂₉</td>
<td>110/100</td>
</tr>
<tr>
<td>C₁₆H₃₃</td>
<td>108/98</td>
</tr>
</tbody>
</table>

a Advancing and receding contact angles for water.

### Table 2. Infrared Absorptions (in cm⁻¹) for the Antisymmetric (v₂) and Symmetric (v₁) Methylene Stretching Vibrations of the Monolayers of I–IV, Using p-Polarized Light

<table>
<thead>
<tr>
<th>Monolayer</th>
<th>v₂</th>
<th>v₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂C=CH₂ (I)</td>
<td>2921.1</td>
<td>2851.9</td>
</tr>
<tr>
<td>H₂C=CH₂ (II)</td>
<td>2921.4</td>
<td>2852.2</td>
</tr>
<tr>
<td>H₂C=CH₂ (III)</td>
<td>2921.9</td>
<td>2852.4</td>
</tr>
<tr>
<td>H₂C=CH₂ (IV)</td>
<td>2921.5</td>
<td>2852.2</td>
</tr>
</tbody>
</table>

### Table 3. Tilt Angles for the Monolayers of 1-Alkynes I–IV

<table>
<thead>
<tr>
<th>Monolayer</th>
<th>e₁ (deg)</th>
<th>e₂ (deg)</th>
<th>e₃ (deg)</th>
<th>e₄ (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.064</td>
<td>0.097</td>
<td>0.035</td>
<td>0.076</td>
</tr>
<tr>
<td>II</td>
<td>0.047</td>
<td>0.071</td>
<td>0.027</td>
<td>0.057</td>
</tr>
<tr>
<td>III</td>
<td>0.035</td>
<td>0.060</td>
<td>0.018</td>
<td>0.040</td>
</tr>
<tr>
<td>IV</td>
<td>0.059</td>
<td>0.084</td>
<td>0.035</td>
<td>0.065</td>
</tr>
</tbody>
</table>

### Figure 4. Infrared spectrum (C–H stretching region) of a monolayer of II on Si(100).

As values for a monolayer of 1-tetradecene were not available and the values previously reported for 1-dodecene are less reliable,6 these monolayers were prepared by the same procedure as that for the 1-alkyne monolayers. The methylene stretch vibrations of these monolayers of 1-tetradecene and 1-dodecene showed absorptions at ν₁/ν₃ = 2922.2/2852.6 cm⁻¹ and ν₁/ν₃ = 2922.1/2852.5 cm⁻¹, respectively, again indicative of ordered monolayers in which the alkyl chains will adopt an all-trans conformation. In general, the absorptions of these methylene stretching vibrations shift to slightly higher values for shorter molecules.38 The absorption values for the monolayers of 1-tetradecyne (III) and 1-dodecyne (IV) (Table 2) are well comparable to these values, which confirms that also the shorter 1-alkynes give well-ordered monolayers. Thus, on the basis of the results from the water contact angle measurements and IR spectroscopy it is concluded that all four 1-alkynes I–IV give well-ordered monolayers on the Si(100) surface and that the ordering of the alkyl chains in these monolayers is similar to, if not better than, that of the monolayers of the corresponding 1-alkenes.

The separate measurement of s- and p-polarized IR spectra of the 1-alkyne monolayers allows for an estimate of the tilt angle of the alkyl chains with respect to the surface normal. The differences between the absolute absorptances of the antisymmetric and symmetric methylene vibrations can be used for this purpose.6 The results are listed in Table 3. The calculated average tilt angles of the four 1-alkynes is 35 ± 5°, which agrees with the value of 30 ± 9° that was previously found for the 1-alkene
monolayers by the same method. This again confirms a high similarity between the structures of monolayers of 1-alkynes and 1-alkenones on the Si(100) surface.

X-ray Reflectivity. Further information about the packing of the molecules in the monolayer is obtained by X-ray reflectivity. This technique is based on the condition that the resulting wave vector transfer $Q$ is parallel to the surface normal of the sample. Thus, X-ray reflectivity probes changes in the electron density perpendicular to the monolayer surface, which are used to determine the following sample parameters: the layer thickness, the electron density of the layer, and the interfacial roughness of the monolayer.

Three of the monolayers, that is, of compounds I–III, were studied with X-ray reflectivity. The results are depicted in Figure 5, which shows the reflectivity profiles of the monolayers as a function of momentum transfer $Q_z$. The shape of the reflectivity curve is determined by two characteristic regions. An intensity plateau is typical for incident angles smaller than the critical angle for total reflection the electron density of the layers as obtained from these fit curves are listed in Table 4.

The results in Table 4 show that there is an approximately linear correlation between the calculated layer thickness and the length of the organic molecule, as can be expected for ordered alkyl layers on solid substrates. The monolayer of III is somewhat too thick compared to the length of the 1-tetradecyne molecule but still agrees with this linearity within experimental error, as this error is much larger in this case than that for the monolayers of I and II, because the second minimum in the reflectivity profile could not be observed. The layers of compounds I and II have an electron density of 0.31 and 0.32 e/Å³, respectively, which is well comparable to the previously found value of 0.30–0.32 e/Å³ for the monolayers of the corresponding 1-alkynes on the Si(100) surface. These values are also similar to those measured for the crystalline alkanes of 0.35 e/Å³. The electron density of the alkyl chains in the monolayers shows that they are densely packed, as was already found with IR spectroscopy. The electron density of 0.27 e/Å³ for the monolayer of III is somewhat lower compared to these values. This may indicate that this monolayer is slightly less densely packed, although the larger experimental error in this measurement compared to those of monolayers of I and II precludes definitive conclusions.

For all three monolayers the roughness of $\sim 4$ Å of the Si surface is comparable to the roughness of $\sim 3$ Å of the air–monolayer interface. This shows that a smooth, densely packed film has been formed on the Si surface. These values are also similar to those measured for the corresponding 1-alkyne monolayers on the Si(100) surface, which confirms the high similarity between the monolayers of 1-alkynes and of 1-alkenones on this Si surface, as already observed with contact angle measurements and IR spectroscopy.

As mentioned above, the fitting of the reflectivity profiles as measured for the monolayers of the 1-alkynes I–III required the introduction of a second layer, that is, an intermediate layer between the organic layer and the Si surface. Such a layer was not necessary for the corresponding 1-alkyne monolayers, which indicates that there is an important difference between the structure of the two layers. The calculated electron density of 1.21 e/Å³ of this intermediate layer is the same for all three samples. Interestingly, this value is much higher than that of the alkyl layer, and also above that of Si, which has a value of 0.71 e/Å³. This indicates that there must be a very high density of probably strongly electronegative atoms in this interfacial region between the Si surface and the alkyl chains.

It is known that the Si–H groups that remain unreacted are oxidized to Si–OH groups, but further oxidation of...
the Si surface to SiO₂ does not occur.³ The electron density of SiO₂ is comparable to that of Si itself⁴¹ and thus significantly lower than the calculated value for the intermediate layer. Besides, Si surface oxidation would generate a SiO₂ layer with a thickness of at least several angstroms. Thus, it can be assumed that this interfacial layer is not due to the presence of SiO₂.

A possible explanation for the presence of the intermediate layer is that the 1-alkynes are bound to the Si surface in a different way than that for the 1-alkenes (see Figure 2). The various possible structures, which will be discussed in more detail in the next section, are shown in Figure 6. If each 1-alkyne forms two bonds to the Si surface, there will be an increase in the electron density near this surface when compared to that of the rest of the alkyl chain. If both bonds are formed to the terminal carbon atom of the 1-alkyne (structure 6C), this carbon atom comes close to the Si surface and will also have a considerable negative charge (vide infra), which implies an increase in the electron density on this atom. A ball-and-stick model shows that the second carbon atom of the former acetylene moiety is in such a bonding situation in a plane not much above this first carbon atom and that it has limited flexibility, whereas the remaining methylene groups are highly flexible. Thus, the alkyl chains can be in an all-trans conformation, as found with IR spectroscopy, except for the first two carbon atoms. Consequently, a thin layer is formed between the Si surface and the alkyl tails, which has a higher electron density compared to that of these alkyl tails. A similar situation occurs when the two Si—C bonds are formed to the two different carbon atoms of the 1-alkyne. In this case these two atoms are both in the same plane and at the same height above the Si surface (structures 6D and 6E). If the 1-alkyne makes only one Si—C bond to the Si surface, such an electron-rich layer is not formed, as the two carbon atoms in the remaining C=C double bond are not in the same plane above the Si surface (structures 6A and 6B) and also have on average the same electron density as that of an alkyl chain (vide infra). Thus, this gives a plausible explanation for the presence of an electron-rich intermediate layer between the Si surface and the alkyl chains.

The presence of such an intermediate layer of increased electron density makes it difficult to obtain an accurate value for the tilt angle of the alkyl chains in the monolayers of 1—III. It can be reasoned that the interfacial region reduces the alkyl chain length by two methylene groups, as the first two carbon atoms of the former 1-alkyne are in this intermediate layer. Consequently, using the same formula as was used for the 1-alkenes⁶ (\( \phi_{X-ray} = \cos^{-1}(d - 0.77)/(2.52(n - 1)/2) \), with \( d \) = layer thickness and \( n \) = number of C atoms in the alkyl chain), the tilt angle of the alkyl chains in the monolayer of I would be 22°, and the monolayer of III would give a tilt angle of 20°. However, both values deviate significantly from the value of 35 ± 5° as determined with IR spectroscopy. It is known that IR dichroism can give large experimental errors in the calculated tilt angles,⁶,² which suggests that there is probably a significant uncertainty in this latter value. The tilt angles calculated from the X-ray measurements also differ significantly from those obtained for the monolayers of the corresponding 1-alkenes (29° and 26° for monolayers of 1-octadecene and 1-hexadecene, respectively).⁵ This also indicates that it is not realistic to calculate a tilt angle for the monolayer of III, because of the large uncertainty in the thickness of that monolayer.

Si—C Interface: One or Two Si—C Bonds per Molecule? The results shown above indicate that 1-alkynes form densely packed, well-ordered monolayers on the H-terminated Si(100) surface. However, although the results from the X-ray reflectivity suggest a significant difference between the monolayers of 1-alkynes and 1-alkenes, so far no experimental evidence has been obtained about the nature of the binding between the 1-alkyne and this Si surface, that is, whether the 1-alkynes form one or two Si—C bonds per reacting molecule (see Figure 2).

The binding structure of the 1-alkyne at the Si interface was investigated with infrared spectroscopy, as these measurements can reveal the presence of C=C and/or C=C—H vibrations in the monolayer. If the 1-alkyne reacts only once with a Si—H group, forming only one Si—C bond per molecule, such vibrations will be present; if the 1-alkyne reacts with two Si—H groups on the surface and a doubly bonded structure is formed, these vibrations will be absent.⁴²

No vibrations from alkene moieties were observed in any of the IR spectra of the 1-alkynes investigated here. As an example, the spectrum of a monolayer of 1-hexadecyne (II) is shown in Figure 7. This observation strongly suggests that alkene moieties are absent in the monolayers of 1-alkynes on the H-terminated Si(100) surface, as the C=C vibration has been detected with IR spectroscopy in the monolayer of a 1-alkyne on the H-terminated Si(111) surface.⁴²,⁵,⁶ Thus, the 1-alkynes seem to form two Si—C bonds per molecule to the Si(100) surface. However, it is known that the intensity of infrared absorptions in monolayers on solid substrates can be orientation-de-

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(41) The electron density is proportional to the mass density of a material. For Si and SiO₂ these mass densities are 2.33 and 2.23 g/cm³, respectively. This results in \( \rho_{el}(Si) = 0.71 e/\text{Å}^3 \) and in \( \rho_{el}(SiO₂) = 0.68 e/\text{Å}^3 \). In ref 39 a ratio of \( \rho_{el}(SiO₂)/\rho_{el}(Si) = 0.96 ± 0.01 \) has been found experimentally. More information can be found in ref 25.

(42) In principle, the presence or absence of vibrations from the resulting tertiary C—H groups (methyne groups) in the doubly bonded structures could also be investigated with IR spectroscopy. However, these vibrations will most likely be too difficult to detect, as they are usually weak. Besides, the antisymmetric methyne vibration coincides with the much stronger symmetric methyl vibration and will therefore not be visible.
pential, as has for example been observed for carboxyl groups in the case of thiol monolayers on gold.\textsuperscript{43} It is not known to which degree this may also occur for the C–C vibrations in these monolayers, and therefore, the results from IR spectroscopy on their own are not fully conclusive.

Theoretical calculations were therefore performed to obtain further insight in the way the 1-alkynes are bound to the Si(100) surface. The structure of monolayers of 1-alkynes on Si surfaces has been successfully investigated by molecular mechanics calculations, using two-dimensionally repeating boxes to describe the modified Si surface.\textsuperscript{44} Unfortunately, this molecular mechanics approach is not suitable here, as the predominant factor that determines the overall monolayer structure is formed by the long alkyl chains, while the precise binding geometry at the Si surface has only a small influence on the layer thickness.

Therefore, quantum chemical computations were performed on small silicon–alkyl clusters, for which the starting structures were obtained using molecular mechanics calculations. As a model system was chosen a Si$_{12}$C$_2$ cluster with a single alkyl molecule (1-butyne) bound in all chemically realistic geometries that could be designed on a three-dimensional ball-and-stick model of the surface. This Si cluster had four Si surface atoms that are terminated with two H atoms to describe the structure of the Si(100) surface (Figure 6, Si(H) cluster). The alkyl chain was always oriented above this Si surface.

Several different structures are possible for a 1-alkyne that is bound to the H-terminated Si(100) surface. The results from the molecular mechanics calculations showed that the relative order of stability of the structures depends on the force field that is used (see Supporting Information). Therefore, these molecular mechanics results are only suitable to select the structures that are chemically most realistic. In Figure 6 these structures are presented. If the Si–H bond indeed only once with a Si–H group, this leads to the formation of a 1-alkenyl type structure. This leaves two possibilities:\textsuperscript{10,11} structure 6A with the remaining C=H bond trans, and structure 6B with the C=C bond cis. If the 1-alkyne forms two Si–C bonds to the surface, only one structure (6C) is possible if both bonds are formed to the terminal carbon of the 1-alkyne (1,1-bridge). Several different structures are possible if the two Si–C bonds are formed to the two different carbon atoms of the former 1-alkyne (1,2-bridge), as the second carbon atom of the 1-alkynecan reach any of the surrounding Si surface atoms and form a covalent Si–C bond to it. Only the two most suitable ones of these structures were considered, as these 1,2-bridged structures already have an energy significantly higher than that of 6A–6C. They differ in the orientation of the remaining ethyl group: upward (axial) in structure 6D and sideward (equatorial) in structure 6E. The energy of all the other 1,2-bridged structures was considerably higher compared to that of 6D and 6E (\textgreek{b} 20 kcal mol$^{-1}$ difference). Therefore, they were eliminated from the present investigations.

More accurate calculations were performed by quantum mechanical B3LYP/6-31G(d) investigations of the structures 6A–6E. The PCFF-optimized structures described above were used as starting structures for this purpose.\textsuperscript{45} Quantum mechanical calculations have frequently been used to investigate the binding structure of small molecules adsorbed on Si surfaces under ultrahigh vacuum conditions.\textsuperscript{46} Usually, a small Si cluster of only \textgreek{a} 7–15 Si atoms is used to represent the Si surface, to reduce the time required for the computations. In the present calculations, however, a large cluster of 32 Si atoms was used. This has two advantages: (a) the underlying Si crystal structure is much better described by such a large Si cluster, and (b) the use of such a large cluster allows for an estimate of the positions of the valence and conduction bands of the semiconductor. This can be used to investigate possible shifts of these levels as a result of the binding of the organic molecule to the Si surface.

So far, these monolayers of 1-alkenes or 1-alkynes on H-terminated Si surfaces have not been investigated by quantum mechanical calculations, which means that there are no reference values available (e.g., for the binding energy). Therefore, three structures, that is, the H-terminated Si cluster shown in Figure 6, a 1-butene molecule, and a Si surface with a butyl group bound to the surface (i.e., the structure that is formed when 1-butene reacts with the H-terminated Si(100) surface), were also investigated. The results\textsuperscript{47} showed that it is energetically favorable to bind an organic molecule to the Si surface. The binding of a 1-butene molecule to the Si cluster, resulting in the formation of the covalent Si–C bond and rehybridization of the terminal 1-alkene from sp$^2$ to sp$^3$, yields 23.4 kcal mol$^{-1}$.

The results of the calculations on the various 1-alkyne structures are listed in Table 5, which shows the relative energies of the structures 6A–6E. It is found that the 1,1-bridged structure C has the lowest energy. It was calculated that the energy of 6C is 59.9 kcal mol$^{-1}$ lower than that of the separate 1-butene molecule plus the H-terminated Si cluster.\textsuperscript{48} The 1,2-bridged structures 6D and 6E

\begin{table}[h]
\centering
\caption{Relative Energies of the Structures 6A–6E As Obtained from B3LYP/6-31G(d) Calculations}
\begin{tabular}{|c|c|}
\hline
structure & $E_{\text{rel}}$ (kcal mol$^{-1}$) \\
\hline
6A & +19.57 \\
6B & +21.82 \\
6C & 0 \\
6D & +4.74 \\
6E & +7.33 \\
\hline
\end{tabular}
\end{table}

(45) The choice to use the PCFF results is somewhat arbitrary, as both force fields give rise to the same structures for the various clusters A–E.


(47) The 6-31G(d) calculations gave the following energies: Si(H) cluster = –9285.887 914 Hartree; 1-butene = –157.221 066 9 Hartree; butyl chain bound to Si(H) cluster = –9443.146 197 5 Hartree.

(48) The 6-31G(d) calculations gave the following energies: 1-butene = –155.966 868 4 Hartree; structure 6C = –9441.950 328 8 Hartree.
and 6E are the intermediate situations, with energies that are only 4.7 and 7.3 kcal mol\(^{-1}\) higher than that of 6C. The two 1-alkynyl structures 6A and 6B have the highest energies, being approximately 20 kcal mol\(^{-1}\) less favorable than the 1,1-bridged situation, since the C−C bond is weaker than a Si−C=O bond. The formation of two Si−C bonds, this time combined with the rehybridization of the carbon atoms of the triple bond from sp to sp\(^3\), is not only structurally feasible, as was already found with the molecular mechanics calculations, but is apparently energetically highly favorable despite the introduction of some ring tension in the resulting structure.

Binding of the organic molecule leads to changes in the charge distribution of the Si atoms in the cluster, especially those at the surface. Figure 8 shows the charges as calculated for selected atoms from the clusters. Binding of the alkyl chain results in a Si surface atom that is more positively charged compared to the Si surface atoms that are bonded to hydrogen atoms. This is expected on the basis of Pauling’s electronegativities for the various atoms: C = 2.5, H = 2.1, and Si = 1.8.\(^{49}\) The binding of the organic compound also results in a small change in the difference between the HOMO and the LUMO of the structures, which is reduced by \(-0.005\) eV (0.12 kcal mol\(^{-1}\)) compared to that for the hydrogen-terminated duster.

The results from the quantum mechanical calculations show that it is likely that upon reaction of a 1-alkyne with the H-terminated Si(100) surface two Si−C bonds will be formed per reacting molecule, as shown in Figure 2. The formation of the second Si−C bond is energetically favorable, which suggests that after the reaction no alkynyl-type structures will be left in the monolayer. This is in line with the results from infrared spectroscopy (vide supra), where no C−C vibrations were observed in the resulting monolayers of the 1-alkynes I−IV. These calculations also provide an explanation for the intermediate layer between the Si surface and the alkyl chains, as observed with X-ray reflectivity. In the 1,1-bridge structure 6C as well as in the 1,2-bridged structures 6D and 6E, the two carbon atoms closest to the Si surface are (nearly) in the same plane and together have a high negative charge. This generates a thin layer with a relatively high electron density, as found with X-ray reflectivity. The alkynyl-type structures 6A and 6B do not give such a layer with high electron density, as for this situation the charges on the C and Si atoms are approximately equal to those found for the above-mentioned 1-butyl group bound to the Si surface. The energy difference between the 1,1-bridged structure 6C and the 1,2-bridged structures 6D and 6E is small (≈5−7 kcal mol\(^{-1}\)), which does not allow for a definitive conclusion about which structure will be formed. However, because of the high reaction temperature (165 °C), the radical mechanism (Figure 2),\(^{17}\) and the roughness of the Si(100) surface, it is not unlikely that the two situations will also both be present to some degree in the monolayers. Thus, on the basis of the results from IR spectroscopy, the X-ray reflectivity measurements, and the quantum mechanical calculations, it must be concluded that in monolayers of 1-alkynes on the H-terminated Si(100) surface two Si−C bonds are formed to this surface per reacting molecule.

**Conclusions**

A series of four 1-alkynes, ranging from 1-dodecyn to 1-octadecyne, has been synthesized and used to prepare organic monolayers on the H-terminated Si(100) surface. The properties of these monolayers were compared to those of monolayers of the corresponding 1-alkenes. The monolayers were formed by a thermal reaction of the organic compound with the Si surface. Well-ordered monolayers were obtained for the 1-alkynes in all cases, as became evident from water contact angle measurements, ATR infrared spectroscopy, and X-ray reflectivity measurements. The properties of the monolayers, that is, the hydrophobicity, the tilt angles of the alkyl chains, and the packing density of the alkyl chains in the monolayers, show that they are at least as ordered as the previously investigated monolayers of 1-alkynes on the Si(100) surface.\(^{6}\)

On the H-terminated Si(100) surface the 1-alkynes can form either one or two Si−C bonds to the Si surface per reacting molecule. The results from IR spectroscopy showed the complete absence of any remaining C−C vibrations in the monolayers, which strongly suggests that the acetylene moiety had reacted twice with the Si−H groups on the surface. The X-ray reflectivity measurements indicated that the monolayers of 1-alkynes were considerably thinner, by \(\sim 1.5−2\) Å, compared to the corresponding monolayers of 1-alkenes. However, an intermediate layer was found to be present between the Si surface and the alkyl chains, which showed that there is a significant difference between the binding of 1-alkynes and 1-alkenes to the Si(100) surface. It was inferred that this intermediate layer is the result of the formation of two Si−C bonds per 1-alkyne molecule.

The binding geometry of the 1-alkynes was further investigated by quantum mechanical calculations. These results showed that the formation of two Si−C bonds per 1-alkyne is energetically much more favorable, by \(\sim 15−20\) kcal mol\(^{-1}\), than the formation of only one Si−C bond, which would leave C−C groups near the Si surface. The situation in which both bonds are to the former terminal carbon atom of the 1-alkyne (the 1,1-bridged situation 6C) is more favorable by \(\sim 5−7\) kcal mol\(^{-1}\) compared to the 1,2-bridged geometry (structures 6D and 6E). Combined with the results from IR spectroscopy and from X-ray reflectivity measurements on the monolayers, it is concluded that 1-alkynes form two Si−C bonds per reacting molecule on the hydrogen-terminated Si(100) surface.

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Supporting Information Available: A sketch of the flask used in the modification of the ATR crystals, detailed procedures for the synthesis of 1-octadecyne (I), 1-tetradecyne (II), and 1-dodecyne (IV), and a table of energies from molecular mechanics calculations for the structures 6A–6E (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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