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# Modification and chemical transformation of Si(1 1 1) surface

Yang Liu [a,b], Shoko Yamazaki [a,b,*], Suguru Izuhara [a]

[a] Department of Chemistry, Nara University of Education, Takabatake-cho, Nara 630-8528, Japan
[b] The Core Research for Evolutional Science and Technology, The Japan Science and Technology Agency (JST), Kawaguchi, Saitama, Japan

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**Abstract**

Modification of hydrogen-terminated Si(1 1 1) surfaces by hydrosilylation of activated alkenes and further chemical transformation of the modified surfaces is reported. A Si(1 1 1)–H surface was reacted with activated alkenes such as acrylate esters, acrylonitrile, and maleic anhydride under mild conditions to give modified surfaces with terminal functional groups. A modified surface with a terminal ester group was reduced by $LiAlH_4$ to give a hydroxy-terminated surface, and the hydroxy-terminated surface was transformed to a bromo-terminated surface. XPS analysis revealed that the brominated surface (≡Si(1 1 1)–$CH_2CH_2CH_2Br$) had 32% coverage with the 3-bromopropyl group. Ester and amide formation reactions were carried out on hydroxy- and carboxy-terminated Si surfaces by reaction with *tert*-butoxycarbonyl glycine, glycine *tert*-butyl ester, 2,2,2-trifluoroethanol and 4-trifluoromethylbenzyl alcohol in the presence of carbodiimide. XPS characterization indicated that the esters and amide were successfully formed with coverage ranging from 16% to 58%. Coverage ratios of octadecyl ester modified surfaces were also estimated by combination of surface reduction and gas chromatography analysis to be 25–35%.
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*Keywords:* Hydrosilylation; Silicon surface; Chemical transformation of modified surfaces; Acrylate esters; Propiolate esters

## 1. Introduction

Organic modification of silicon surfaces through formation of Si–C covalent bonds has been intensively studied [1]. Because the modified surfaces usually possess enhanced oxidative stability and novel functionalities and properties compared with a hydrogen-terminated Si surface [2,3], they are considered to be potential semiconducting substrates for fabrication of electronic devices or biosensors [4]. Various modification methods based on wet-chemistry have been explored to form Si–C bonded organic monolayers on silicon surfaces, such as hydrosilylation of alkenes or alkynes initiated by a free-radical initiator [2], hydrosilylation activated by thermal or UV irradiation [2,5], hydrosilylation mediated by Lewis acids [6], and alkylation with Grignard or organolithium reagents [3]. Significant improvement of Si surface modification under milder conditions suitable for binding labile or bioactive functional groups onto the silicon surface has been achieved. Zuilhof et al. reported a mild attachment of saccharides onto a hydrogen terminated silicon surface by visible light [7]. We have recently reported a mild modification of hydrogen terminated Si(1 1 1) surfaces by activated alkynes at room temperature without addition of catalyst [8].

In this study, we investigated the modification of a hydrogen-terminated Si(1 1 1) surface with various activated alkenes and further transformation of the surface functionalities of the organic monolayer modified surfaces. By further chemical transformation, surfaces with new reactive functional terminal groups were obtained without breaking the Si–C bond linkage or the Si–Si back-bond.

Although modification techniques have been rapidly developed, quantitative analysis especially estimation of the monolayer coverage of organic groups bonded on silicon surfaces is still a crucial subject. Quantitative infrared

* Corresponding author. Address: Department of Chemistry, Nara University of Education, Takabatake-cho, Nara 630-8528, Japan. Tel.: +81 742 9193; fax: +81 742 27 9289.
*E-mail address:* yamazaks@nara-edu.ac.jp (S. Yamazaki).

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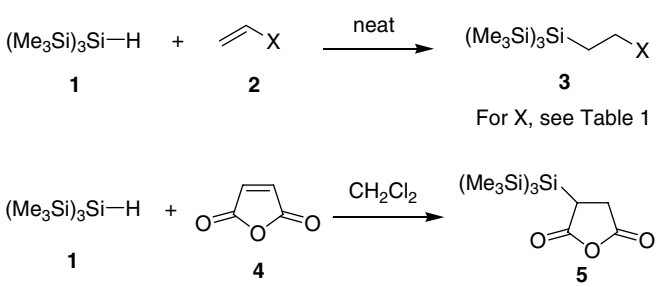
spectroscopy (IR) [6,9] and X-ray photoelectron spectroscopy (XPS) [5,10] characterization are most often used to estimate the monolayer coverage of modified surfaces. However, the accuracy of XPS analysis in estimation of coverage of an organic monolayer is usually decreased by surface contaminated carbon. In order to prevent complication by surface contamination, we have previously used fluorine or nitrogen containing alkynes to modify the Si surface and estimated the monolayer coverage by quantitative analysis of the relative intensities of fluorine or nitrogen photoelectrons to silicon photoelectrons [8]. Determination of surface coverage by a stepwise procedure including detachment of fluorescence probes from the surface monolayer and quantitative fluorescence analysis was recently reported [11]. In this report, we have attempted determination of the coverage ratios of ester modified surfaces by quantitative analysis of the corresponding alcohols reductively liberated from ester monolayers, using gas chromatography.

## 2. Results and discussion

### *2.1. Modification of a hydrogen-terminated Si(1 1 1) surface with activated alkenes*

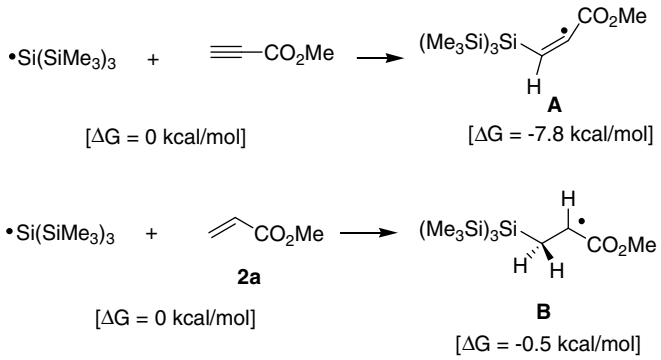
We have reported that a hydrogen-terminated Si(1 1 1) surface was easily modified by activated alkynes such as propiolate esters and propionitrile. This surface modification was directed by model reactions of activated alkynes and tris(trimethylsilyl)silane (**1**), a molecular model of the Si–H group on hydrogen terminated Si(1 1 1) surface [8,12].




Scheme 1.

In this study, we have investigated the reactions of the model tris(trimethylsilyl)silane (**1**) and the Si(1 1 1)–H surface with various activated alkenes such as acrylate esters, acrylonitrile and maleic anhydride (**4**). Reactions of silane **1** and alkenes **2** and **4** gave β-silylated addition products **3** and **5** (Scheme 1). Compared to the corresponding propiolate esters and propionitrile [8], acrylate esters and acrylonitrile showed relatively lower reactivity with silane **1**. Reactions of alkenes **2b**–**c** and **2e**–**f** gave moderate yields of hydrosilylation products, and reaction **2b** and **2d**–**f** required a slightly higher reaction temperature and prolonged reaction times (Table 1).

This hydrosilylation is considered to proceed through a radical chain mechanism [12]. The initiation step included an autoxygenation reaction of silane group by adventitious in situ oxygen and a hydrogen abstraction reaction to generate a silicon radical. In general, alkynes are less reactive than alkenes in radical addition reactions [13]. Rate constants for the reaction of $Et_3Si$ radicals to alkynes compared to alkenes also shows that alkynes are slightly less reactive [14]. Possible radical intermediates **A** and **B** were calculated by UB3LYP/6-31G* calculations [15] (Scheme 2 and Fig. 1). **A** has a quasi-linear (∠C=C–C is 158°) and slightly more compact structure than **B**. The highly bulky $(Me_3Si)_3Si$ group [16] may destabilize the slightly sterically hindered radical **B** compared to radical **A**. The explanation is supported by the calculated free energy differences $\Delta G_{298}$ of **A** (−7.8 kcal/mol) [17] and **B** (−0.5 kcal/mol) referred to $(Me_3Si)_3Si$ and methyl propiolate




Scheme 2.

Table 1
Reaction of Tris(trimethylsilyl)silane (**1**) and alkenes **2**

| Entry | Substrate | X | Reaction conditions | Product (yield[b], %) |
|---|---|---|---|---|
| 1 | **2a** | X = $CO_2Me$ | r.t.[a], 20 h | **3a** (79) |
| 2 | **2b** | X = $CO_2CH_2CH_2OH$ | r.t. ~40°C, 48 h | **3b** (52) |
| 3 | **2c** | X = $CO_2CH_2CF_3$ | r.t., 20 h | **3c** (62) |
| 4 | **2d** | X = $CO_2(CH_2)_{17}CH_3$ | r.t. ~40°C, 72 h | **3d** (87) |
| 5 | **2e** | X = $CO_2CH_2$–$C_6H_4$ – *p*–$CF_3$ | r.t. ~40 °C, 48 h | **3e** (57) |
| 6 | **2f** | X = CN | r.t., 72 h | **3f** (50) |
| 7 | **4** | | r.t., 20 h | **5** (87) |

[a] Room temperature ~25–30 °C
[b] Isolated yield.

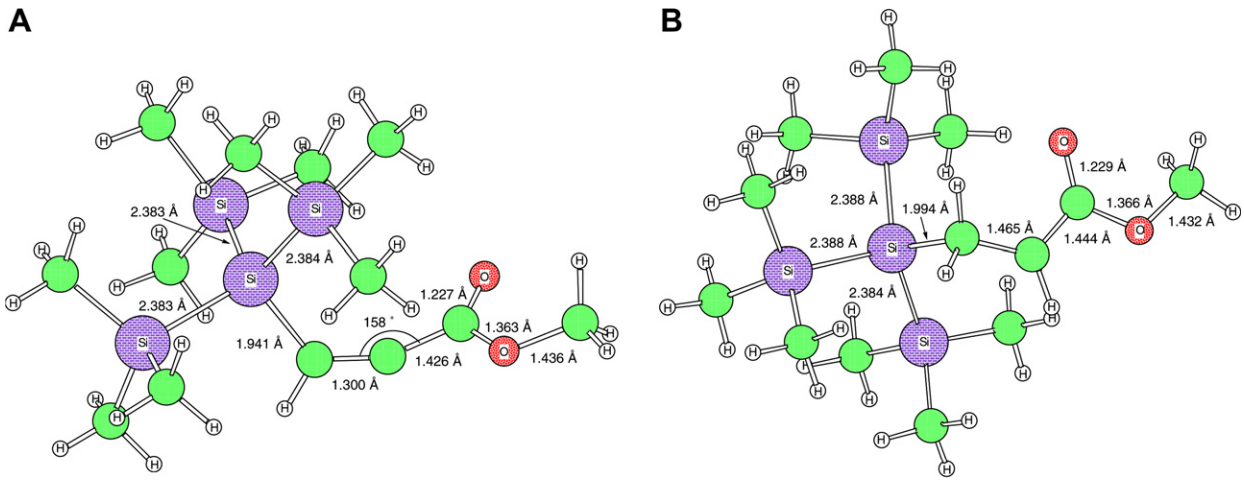
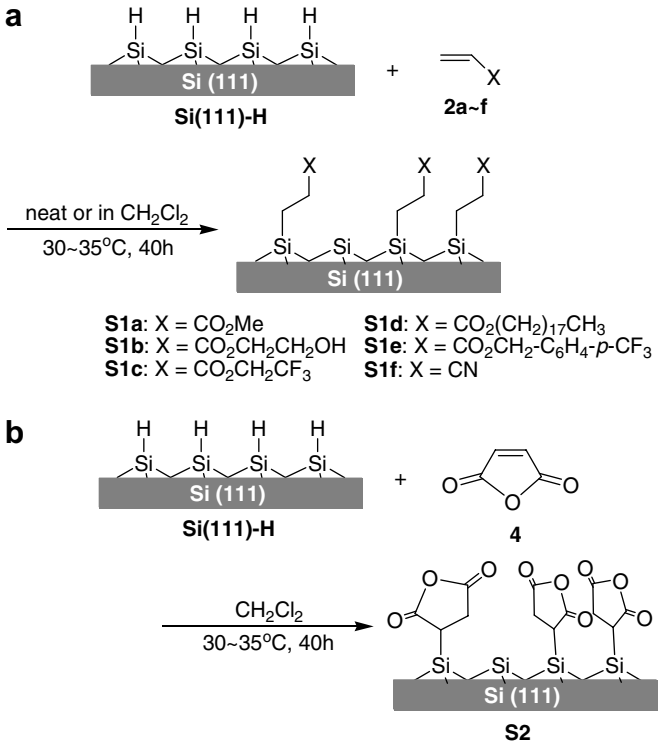



Fig. 1. B3LYP/6-31G*-optimized geometries of A and B in Scheme 2.

(≡–$CO_2Me$) or **2a**. Even so, comparatively mild reaction conditions (r.t. to 40 °C) are enough to promote the reaction of $(Me_3Si)_3Si^{\cdot}$ and activated alkenes because of stabilization of the intermediate radical by spin delocalization with the $CO_2R$ group.

The hydrosilylation of activated alkenes was applied to Si(1 1 1)–H surface modification. Hydrogen-terminated Si(1 1 1) surface was prepared by etching oxidized Si surface in HF and $NH_4F$ solutions, as described previously [8]. The freshly prepared Si(1 1 1)–H surface was immersed in neat alkene or in a dichloromethane solution and the reaction mixture was kept at 30–35 °C for 40 h to give the modified surface with Si–C bonded organic monolayer (Scheme 3)




Scheme 3.

[18,19]. Slightly higher temperature was used because more steric hindrance with alkenes than alkynes is considered to exist also on the surface.

The various alkene-modified surfaces were characterized by XPS. XPS spectra of modified surfaces **S1e** and **S2** are shown in Fig. 2. Peak of fluorine 1s photoelectrons at a binding energy of 688.9 eV for trifluoromethylbenzyl ester modified surface **S1e** indicates that the organic monolayers were successfully formed on the silicon surface. In the high resolution carbon 1s spectra, peaks of $CF_3$ carbon and carbonyl (C=O) carbon were also identifiable [8,20]. $CF_3$ group on **S1e** gave the typical C 1s peak at high binding energy of 293.6 eV, and carbonyl group showed C 1s peaks at 289.8 eV [21]. Peaks of C–Si (around 284–5 eV) [10a] and C–C species in the C 1s spectra are overlapped and not resolved in this measurement condition. Si 2p spectrum of XPS for **S2** shows that the Si 2p peak at ca. 103 eV corresponding to Si oxidation [22] is small ($\text{Equiv.}_{\text{ml}}$ of $SiO_x$ [23] 0.23).

Monolayer coverage of modified surfaces containing fluorine and nitrogen atoms were estimated by calculation of the relative intensities of F 1s peaks and N 1s peaks with respect to the Si 2p peaks according to the method previously reported [8,24]. The estimated coverage ratios of **S1c** and **S1e–f** range from 19% to 39% (Table 2) [25].

The mechanism of hydrosilylation of activated alkenes with a Si(1 1 1)–H surface may be similar to that of alkynes previously reported [8,26]. The silicon radical would react with alkene (**2** or **4**) to form Si–C bond, leading to a carbon radical. The carbon radical abstracts a hydrogen from an adjacent Si–H group to regenerate a surface Si radical to propagate the chain reaction [27].

### 2.2. Chemical transformation of surface functional groups

Further chemical transformations of free carboxyl, ester and hydroxy-terminated Si surfaces were carried out, in order to prepare various functionalized surfaces which may be difficult to prepare by hydrosilylation reactions.

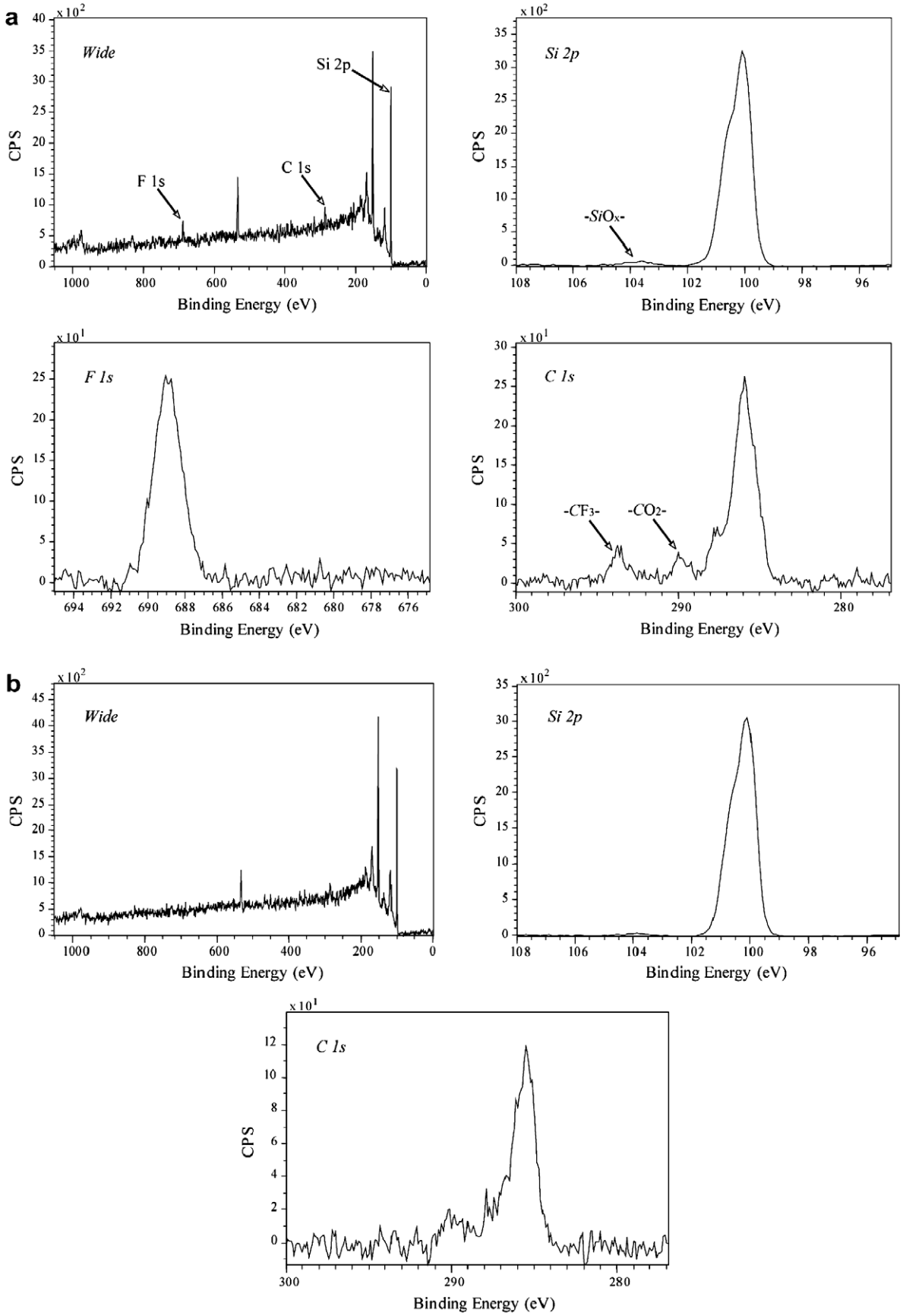
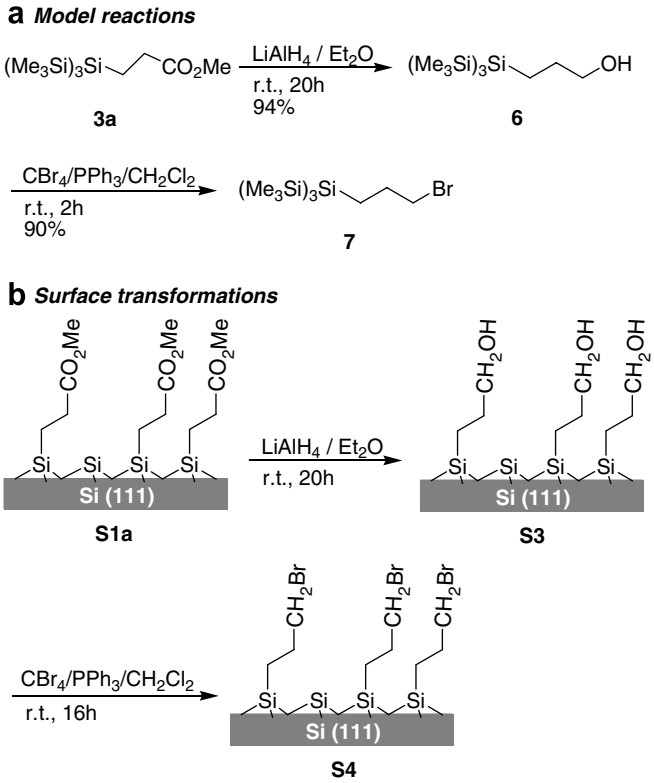



Fig. 2. (a) XPS spectra of modified Si(111) surface **S1e**. (b) XPS spectra of surface **S2**.

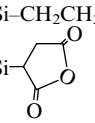
(1) *Ester reduction and bromination*: Ester-terminated surface was reduced to a hydroxy-terminated surface by $LiAlH_4$ [28]. Furthermore, the hydroxy terminal group was readily transformed to a bromoalkyl-terminated surface by bromination reaction.
The transformation was first investigated with model compounds. Methyl ester **3a** was reduced in diethyl ether by a suspension of $LiAlH_4$ to give alcohol **6**, and **6** was brominated by $CBr_4$ and $PPh_3$ to give **7** (Scheme 4). Both **6** and **7** were obtained in good yields without cleavage of the Si–Si bond. Next, methyl acrylate modified surface **S1a** was examined by immersing in an ether suspension of $LiAlH_4$ at room temperature overnight to give the reduced surface **S3**. The proof of successful reduction of the methyl ester group was shown by XPS analysis. Comparing the carbon 1s spectra of **S1a** and the reduced derivative **S3** (Fig. 3a), disappearance of the C 1s peak for carbonyl carbon at 289.7 eV indicated that the ester reduction was almost complete. Moreover, the water contact angle changed from 66° (**S1a**) to 48° (**S3**) after reduction (Tables 3 and 5). This may arise from higher hydrophilicity of the hydroxy group than ester group. This hydroxy-terminated surface was then treated with a mixture of $CBr_4$, $PPh_3$ in dichloromethane to transform the hydroxy group to a bromo group. XPS analysis of the obtained surface **S4** verified the existence of bromine. Br 3d photoelectrons showed two peaks at 70 and 71 eV, which are the spin-splitting peaks of Br $3d^{5/2}$ and $3d^{3/2}$ lines [29]. In the C 1s spectrum of **S4**, a peak at 286.9 eV with a chemical shift of 1.2 eV from the carbon centerline was assigned to $-CH_2Br$ (Fig. 3b) [30]. In a comparison, the C 1s peak assigned to $-CH_2OH$ of **S3** appeared at 287.0 eV which had a chemical shift of 1.7 eV from the centerline. The monolayer coverage calculated from the relative intensities of Br 3d to Si 2p photoelectrons was 32% (Table 4). Thus, these results indicated that the transformation of hydroxy group to bromine proceeded smoothly.

(2) *Ester and amide formation*: Silicon surfaces with terminal functionalities such as hydroxyl, carboxy or amine are of interest for immobilization of DNA strands or proteins [4a,4b,4c,31] towards biotechnological applications. Ester and amide formations are the most basic reactions for covalent immobilization of biomolecules. Esterification of a hydroxy-terminated surface has been reported by reaction with acetic anhydride [28a] or acetyl chloride [28b] to give acetate termination. In this work, a mild esterification using 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (EDCI) and 4-*N*,*N*-dimethylaminopyridine (DMAP) was carried out. Model compounds **3b**, **6** and **8** react with *tert*-butoxycarbonyl (Boc) glycine in the presence of EDCI/DMAP. Esters **9a**–**c** were obtained in high yields after overnight reactions at room temperature (Scheme 5a).




Scheme 4. Ester reduction and bromination.

Table 2
Surface hydrosilylation and the estimated monolayer coverages by XPS

| Surface | Surface group | Coverage (%) | Equiv.$_{ml}$ of $SiO_x$ [23] |
|---|---|---|---|
| **S1c** | $\equiv$Si–$CH_2CH_2CO_2CH_2CF_3$ | 39[a] | 1.07 |
| **S1e** | $\equiv$Si–$CH_2CH_2CO_2CH_2$–$C_6H_4$ – *p*–$CF_3$ | 19[a] | 0.38 |
| **S1f** | $\equiv$Si–$CH_2CH_2CN$ | 38[b] | 1.62 |
| **S2** | $\equiv$Si–  | 14[c] | 0.23 |

[a] Determined by F 1s/Si 2p peaks.
[b] Determined by N 1s /Si 2p peaks.
[c] Determined by C 1s (C=O) /Si 2p peaks.

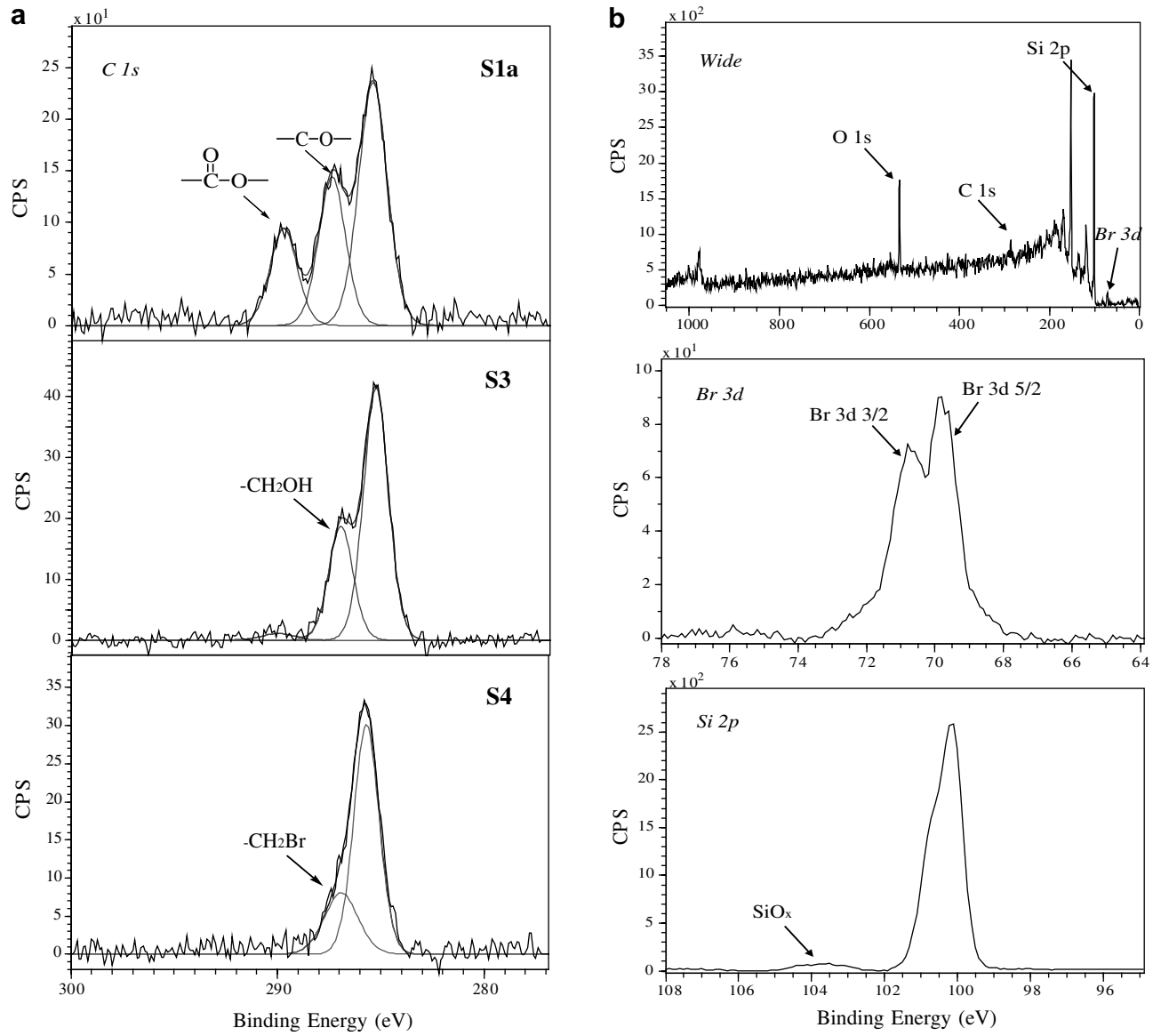
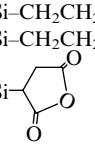



Fig. 3. (a) C 1s XPS region spectra of surfaces **S1a** and **S3**–**4**. (b) XPS survey scan spectrum and region spectra (Br 3d and Si 2p) of **S4**.

Table 3
Static water contact angles of modified surfaces

| Surface | Surface group | Contact angle (°) | Standard error (°) |
|---|---|---|---|
| **S1a** | $\equiv$Si–$CH_2CH_2CO_2CH_3$ | 66 | 0.3 |
| **S1b** | $\equiv$Si–$CH_2CH_2CO_2CH_2CH_2OH$ | 53 | 0.4 |
| **S1c** | $\equiv$Si–$CH_2CH_2CO_2CH_2CF_3$ | 69 | 0.5 |
| **S1d** | $\equiv$Si–$CH_2CH_2CO_2(CH_2)_{17}CH_3$ | 86 | 0.9 |
| **S1e** | $\equiv$Si–$CH_2CH_2CO_2CH_2$–$C_6H_4$ – *p*–$CF_3$ | 72 | 0.5 |
| **S1f** | $\equiv$Si–$CH_2CH_2CN$ | 64 | 0.4 |
| **S2** | $\equiv$Si–  | 52 | 0.7 |

Next, this esterification method was applied to hydroxy-terminated Si surfaces, **S3**, **S1b** and **S5** (Scheme 5b). After immersion in a mixture of a dichloromethane solution of Boc-glycine, EDCI and DMAP at room temperature for 20 h, the obtained surfaces were characterized by XPS and contact angle measurement. XPS analysis of surface **S6a** derived from **S3** proved that nitrogen was contained in the monolayer while the N 1s photoelectrons showed its peaks at 401.3 eV. In the C 1s spectrum, the peak for the carbonyl carbon appeared at 290.3 eV is further proof of the successful introduction to Boc-glycine on the hydroxy-terminated surface through ester formation. Similarly, XPS spectra of surfaces **S6b** and **S6c** confirmed the formation of an ester linked monolayer of Boc-glycine (for surface **S6c**, see Fig. 4). Based on quantitative XPS results, monolayer coverages of **S6a**–**c** calculated from relative intensities of N 1s peak to Si 2p peak were in a range of 34–57%. Measured water contact angles of **S6a**–**c**

Table 4
XPS estimated monolayer coverages of Si surfaces after chemical transformation

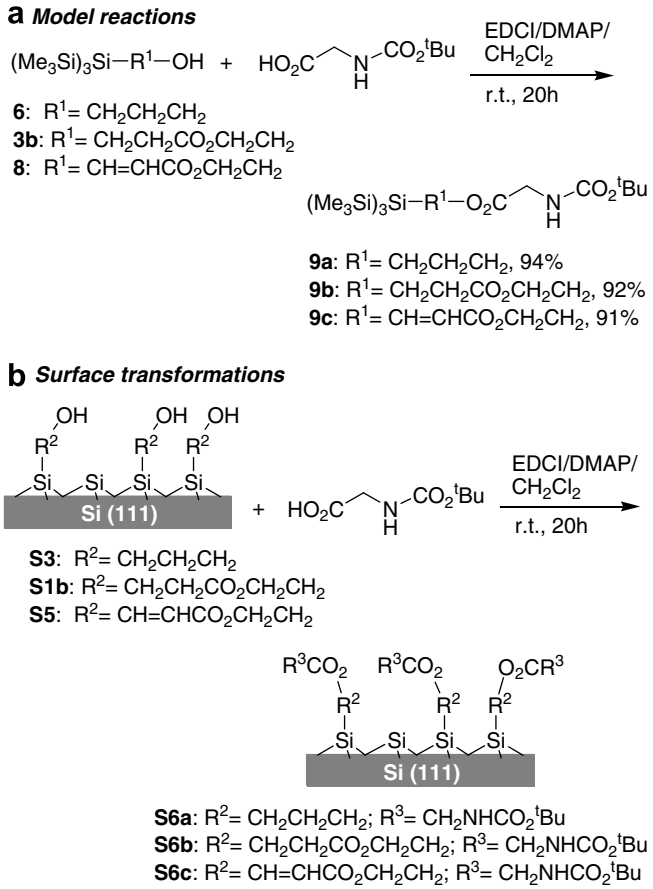
| Surface | Surface group | Coverage (%) | Equiv.$_{ml}$ of $SiO_x$ [23] |
|---|---|---|---|
| **S4** | ≡Si–$CH_2CH_2CH_2Br$ | 32 | 0.54 |
| **S6a** | ≡Si–$CH_2CH_2CH_2OC(O)CH_2NH–CO_2{}^tBu$ | 42 | 2.03 |
| **S6b** | ≡Si–$CH_2CH_2CO_2CH_2CH_2OC(O)CH_2NH–CO_2{}^tBu$ | 35 | 0.41 |
| **S6c** | ≡Si–CH=$CHCO_2CH_2CH_2OC(O)CH_2NH–CO_2{}^tBu$ | 58 | 0.43 |
| **S9a** | ≡Si–CH=$CHCO_2CH_2CF_3$ | 16 | 0.87 |
| **S9b** | ≡Si–CH=$CHCO_2CH_2–C_6H_4–p-CF_3$ | 22 | 0.88 |
| **S9c** | ≡Si–CH=CHC(O)NH–$CH_2CO_2{}^tBu$ | 27 | 0.51 |

Table 5
Static water contact angles of modified surfaces

| Surface | Surface group | Contact angle (°) | Standard error (°) |
|---|---|---|---|
| **S3** | ≡Si–$CH_2CH_2CH_2OH$ | 48 | 0.4 |
| **S4** | ≡Si–$CH_2CH_2CH_2Br$ | 52 | 0.4 |
| **S6a** | ≡Si–$CH_2CH_2CH_2OC(O)CH_2NH–CO_2{}^tBu$ | 62 | 0.3 |
| **S6b** | ≡Si–$CH_2CH_2CO_2CH_2CH_2OC(O)CH_2NH–CO_2{}^tBu$ | 57 | 0.3 |
| **S6c** | ≡Si–CH=$CHCO_2CH_2CH_2OC(O)CH_2NH–CO_2{}^tBu$ | 58 | 0.3 |
| **S9a** | ≡Si–CH=$CHCO_2CH_2CF_3$ | 47 | 0.4 |
| **S9b** | ≡Si–CH=$CHCO_2CH_2–C_6H_4–p-CF_3$ | 60 | 0.4 |
| **S9c** | ≡Si–CH=CHC(O)NH–$CH_2CO_2{}^tBu$ | 59 | 0.5 |

ranged from 57° to 62°, which were a little higher than them of the hydroxy-terminated surfaces (44°–53° for **S1b**, **S3** and **S5**).

It has been reported that esterification of free carboxylic acid-terminated Si surfaces was carried out in boiling acidic propanol [28a]. Ester formation reaction using EDCI/DMAP was applied to a carboxy-terminated surface [28b]. As shown in Scheme 6, ester and amide formation of carboxyl group with EDCI were investigated with both model compounds and Si surface. Acid model compound **10** reacted with 2,2,2-trifluoroethyl alcohol (**11a**) and 4-trifluoromethylbenzyl alcohol (**11b**) in the presence of EDCI and DMAP to give corresponding esters **12a** and **12b** in 93% and 78% yields, respectively. For amide formation, reaction of **10** and glycine *tert*-butyl ester (**11c**) was carried out in the presence of EDCI and 1-hydroxybenzothiazole (HOBT). Amide **12c** was obtained in 83% yield after 20 h reaction at room temperature. Then, model reactions were applied to carboxy-terminated Si surface. Free carboxylic acid-terminated surface **S8** was prepared by two-step procedure in order to avoid possibility to react with Si–H group to form silyl ester (Si–OC(O)) bond [28a,31,32]. Surface **S7** was prepared first by modification of Si(1 1 1)–H surface with *tert*-butyl propiolate. **S7** was then treated with trifluoroacetic acid (TFA)/dichloromethane solution to cleave the *tert*-butyl group to give free carboxy-terminated surface **S8** (Fig. 5) [33,8]. Thereafter, ester and amide formation reactions were carried out on surface **S8** with alcohols **11a,b** and amine **11c** under the same condition of model reactions. Surface **S9a** obtained from esterification with trifluoroethanol showed F 1s peak and the typical C 1s peak for $CF_3$ group in the XPS spectra (Fig. 6).




Scheme 5.

Monolayer coverage of trifluoroethyl ester estimated by XPS was 16% (Table 4). The contact angle of **S9a** was 47° (Table 5) which is lower than that of the same surface

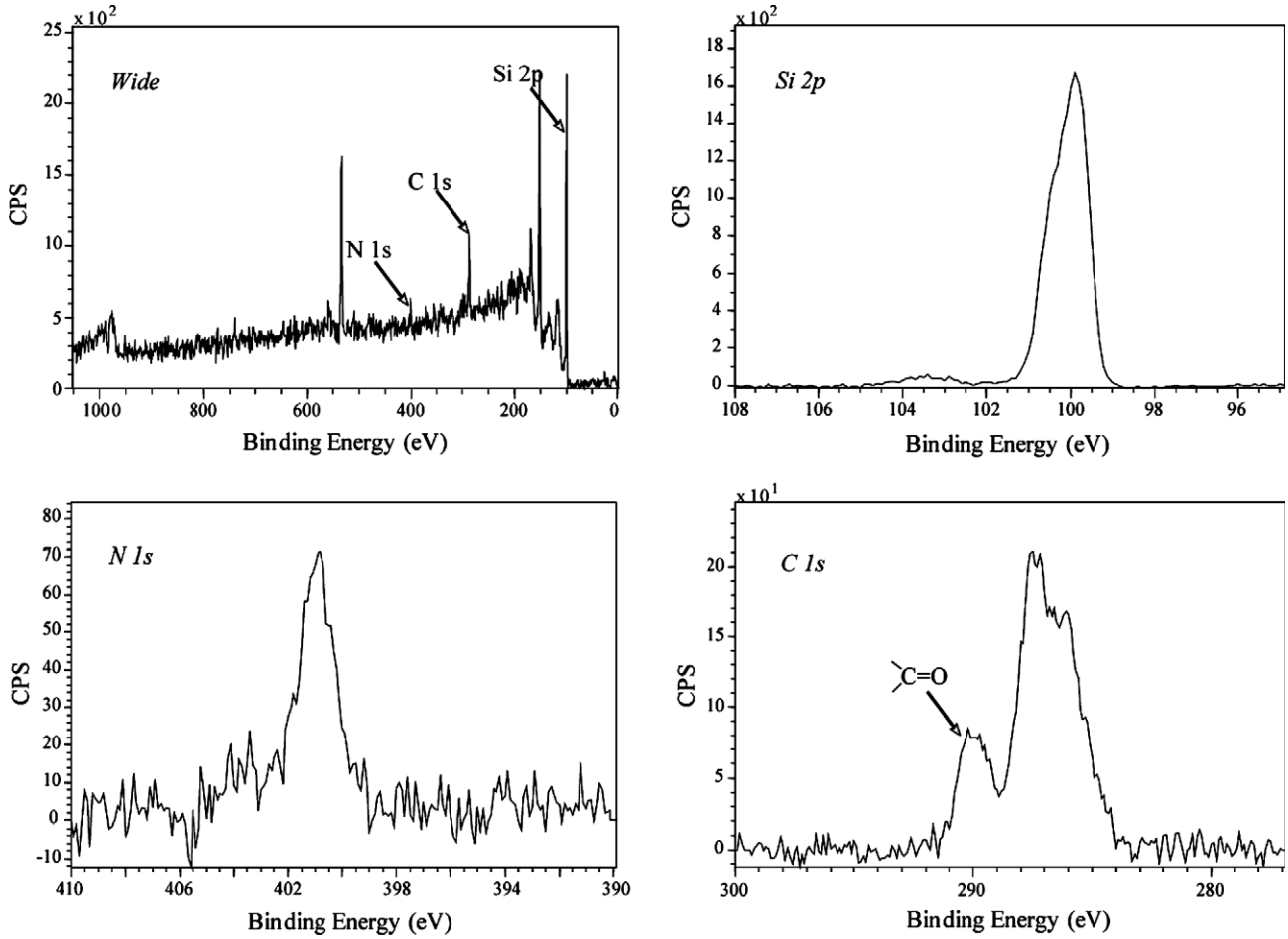



Fig. 4. XPS spectra of surface **S6c**.

prepared directly from propiolate ester (contact angle 75°, coverage 56%) [8]. The left unreacted carboxy groups and higher degree of the surface oxidation [34] may be responsible to this low contact angle. Similarly, **S9b** containing fluorine has a coverage of trifluoromethylbenzyl ester group estimated to be 22% by XPS. Formation of amide group on surface **S9c** was also proved by quantitative analysis of nitrogen composition by XPS. From Fig. 7, it can be found that the N 1s peak clearly appeared at 400.8 eV. The coverage of amide group was estimated to be 27% based on N 1s XPS data, and the water contact angle was measured to be 59° (Table 5).

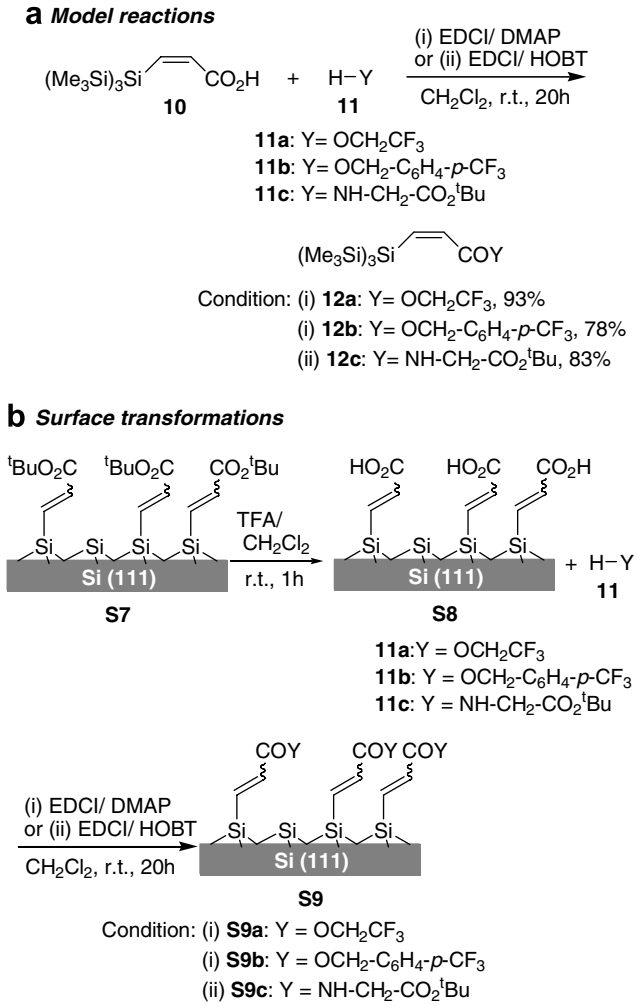
The chemical transformation presented in this work sometimes leads to significant oxidation of the silicon surface, as estimated using fractional monolayer coverage (Equiv.$_{ml}$) of $SiO_x$ by XPS (Tables 2 and 4) [23]. Such oxide formation may be a serious issue so as to render the interface useless for electronic applications. Study to solve the problem is under investigation [35].

### 2.3. Estimation of monolayer coverage by ester reduction and GC analysis

IR and XPS spectra for estimation of the coverage ratio of modified surfaces have limited applicability to selected functional groups and inclusion of heteroatom such as fluorine or nitrogen. In order to explore the complementary methods to the well known techniques, we have attempted determination of the coverage ratios by combination of chemical transformation and gas chromatography.

In the former section, the reduction of surface ester group with $LiAlH_4$ transforms an ester-terminated surface to a hydroxy-terminated surface. In the reduction of **S1a**, methanol is liberated. When the surface ester group is completely reduced, it is possible to detect the liberated alcohol quantitatively and calculate the absolute coverage ratio of the starting ester group. The concentration of Si–H group on an ideal Si(1 1 1) surface is about $1.3 \times 10^{-9}$ mol/cm$^2$ [2,36]. For detection of the alcohol liberated from Si surface, the gas chromatography (GC) with flame-ionization detectors (FID) was used.

The ester modified Si surfaces, surfaces **S1d** and **S10** ($\equiv$Si(1 1 1)–CH=CH–$CO_2(CH_2)_{17}CH_3$) [37] were prepared for estimation of monolayer coverage by combination of ester reduction and GC analysis. The ester modified surface was then reduced by $LiAlH_4$ in $Et_2O$ at room temperature for 20 h. The liberated alcohol, octadecyl alcohol was extracted and concentrated to a certain volume of *n*-propanol solution, and this solution was used for quantitative GC analysis to determine the concentration (Scheme 7).




Scheme 6.

GC diagram of the sample and the reference solutions is shown in Fig. 8. The concentration of the sample solutions obtained from surface reduction was determined by integration of the peak areas [38]. Using the determined concentration, the monolayer coverage was calculated as following equation:

$$\text{Coverage} = (C \cdot V)/\left[(1.3 \times 10^{-9}) \cdot S_{\text{surface}}\right]$$

where ($C$ (mol/L) is the concentration of the sample solution; $V$ (L) is the volume of the sample solution; $S_{\text{surface}}$ ($cm^2$) is the total surface area of the Si wafer.)

The estimated coverages of surfaces **S1d** and **S10** were 25% and 35%, respectively (Table 6) [39]. Coverages of surfaces **S1d** and **S10** by GC are comparable to those values estimated by C 1s (C=O) spectra of XPS. Because XPS determination of C 1s spectra may be not very accurate by the contaminated carbons, GC method can be suitable for octadecyl ester modified surfaces.

In summary, a mild modification of hydrogen-terminated silicon surface by hydrosilylation of activated alkenes was investigated. This surface modification resulted in the formation of Si–C bonded organic monolayer with functional terminal groups. The further chemical transformation of the surface functional groups was also carried out based on the reactions such as ester reduction, bromination, esterification and amide formation. Developments of modification and chemical transformation on silicon surface are of interest and important to tailor the surface structures and properties for a variety of applications. We have investigated the combination of ester reduction and GC analysis to estimate the monolayer coverage of ester modified Si surfaces. This method can be used as a complement for XPS and ATR-IR spectroscopies.

## 3. Experimental

### 3.1. Model reactions

*General methods:* Melting points are uncorrected. IR spectra were recorded in the FT-mode. $^1$H NMR spectra were recorded at 400 MHz. $^{13}$C NMR spectra were recorded at 100.6 MHz. $^1$H chemical shifts are reported in ppm relative to $Me_4Si$. $^{13}$C chemical shifts are reported in ppm relative to $CDCl_3$ (77.1 ppm). Mass spectra were recorded at an ionizing voltage of 70 eV by EI or FAB. All reactions were carried out under a nitrogen atmosphere.

*Materials:* Substrates **1**, **2a**–**d**,**f**, **4**, **11a**–**c** were purchased and used without further purification. **8** and **10** were prepared according to the previous report [8] Spectral data of **3a**, **3f**, **5**, **7a** and**7b** were in accord with reported data [40].

*4-Trifluoromethylbenzyl acrylate (**2e**):* To a mixture of acrylic acid (360 mg, 5.0 mmol) and 4-(trifluoromethyl)benzyl alcohol (1.05 g, 6.0 mmol) in 5.0 ml dichloromethane was added 4-(dimethylamino)pyridine (122 mg, 1.0 mmol) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (1.15 g, 6.0 mmol). After stirring at room temperature for 20 h, the reaction mixture was diluted with dichloromethane and washed with water. The organic phase was dried ($MgSO_4$) and evaporated in vacuo. The residue was purified by column chromatography over silica gel eluting with hexane–ether (10:1) to give the title compound (593 mg, 52%) ($R_f$ = 0.2). Colorless liquid; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 5.25 (s, 2H), 5.89 (dd, 1H, $J = 10.4$, 1.4 Hz), 6.18 (dd, 1H, $J = 17.2$, 10.4 Hz), 6.48 (dd, 1H, $J = 17.2$, 1.4 Hz), 7.49 (d, 2H, $J = 8.1$ Hz), 7.63 (d, 2H, $J = 8.1$ Hz); $^{13}$C NMR (100.6 MHz, $CDCl_3$) $\delta$ 65.4, 124.1 (q, $-CF_3$, $J_{F-C} = 272.0$ Hz), 125.6 (q, $J_{F-C} = 3.8$ Hz), 128.0, 128.2, 130.5 (q, $J_{F-C} = 32.5$ Hz), 131.7, 139.9, 165.9 ($-CO_2-$); IR (neat) 1734, 1635, 1622, 1408, 1327, 1296, 1269, 1170, 1125, 1067, 1020, 984, 822, 809 $cm^{-1}$. MS (EI) $m/z$ 230 ($M^+$), 211 ($M^+-F$), 175 ($M^+-CH_2{=}CHC(O)-$), 159 ($M^+-CH_2{=}CHCO_2-$); exact mass $M^+$ 230.0554 (calcd for $C_{11}H_9F_3O_2$, 230.0555).

Hydrosilylation of alkenes with tris(trimethylsilyl)silane **1** was carried out through a similar procedure reported for alkynes [12]. Reaction of **2b**,**d**,**e** with **1** was performed at

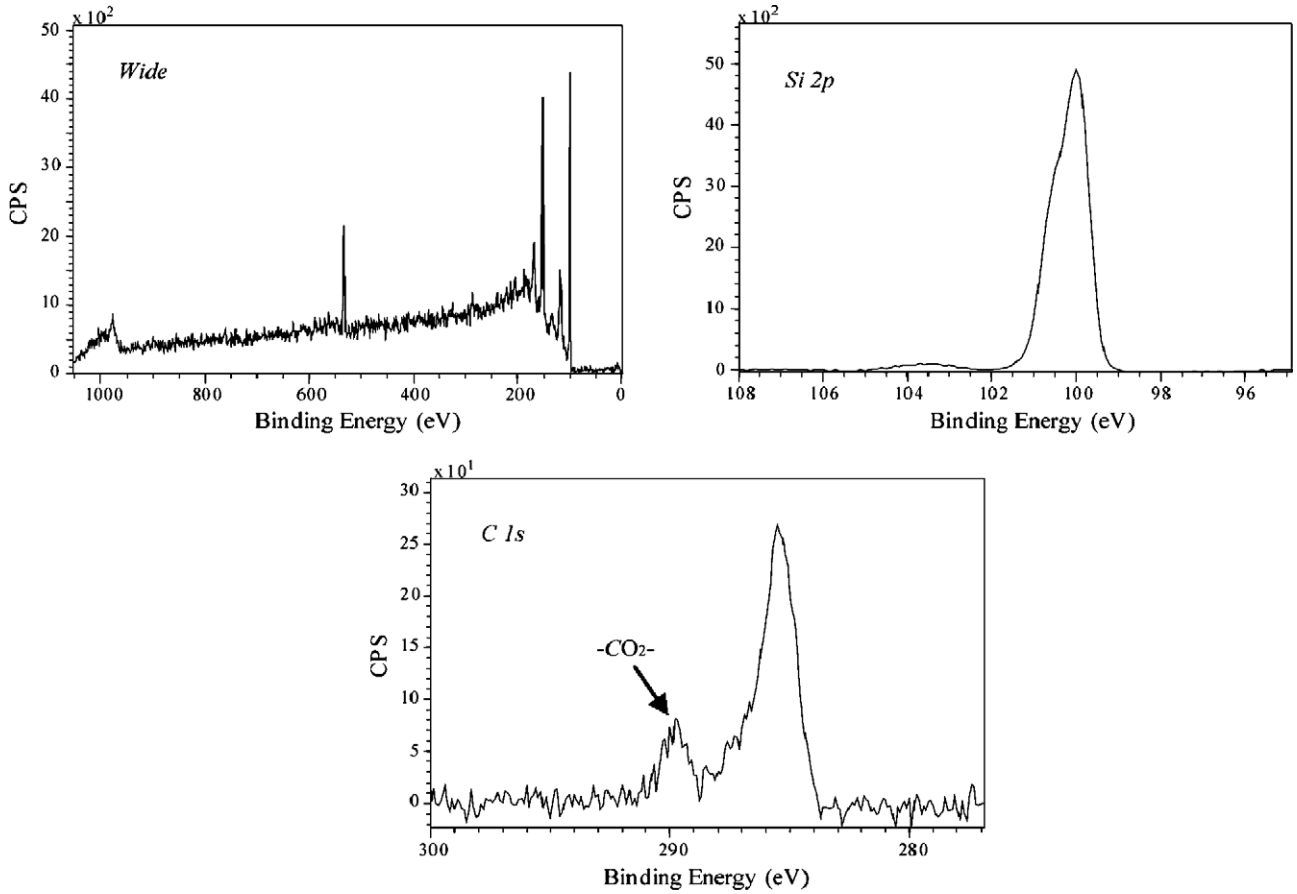



Fig. 5. XPS spectra of surface **S8**.

room temperature overnight and followed by warming to 40 °C until the high conversion of the alkenes was reached.

*2-Hydroxyethyl 3-[tris(trimethylsilyl)silyl]propionate (**3b**):* (52%) Column chromatography: hexane–ether = 2/1, $R_f = 0.1$. Colorless crystals; m.p. = 98–99 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.18 (s, 27H), 1.11 (m, 2H), 2.38 (m, 2H), 3.84 (m, 2H), 4.22 (m, 2H); $^{13}$C NMR (100.6 MHz, $CDCl_3$) $\delta$ 1.2 (–Si*C*H$_3$), 2.9, 33.2, 61.5, 66.3, 175.2 (–*C*OO–); IR (KBr) 3349, 2947, 2892, 1736, 1246, 1202, 1156, 1081, 834, 688, 623 cm$^{-1}$. MS (FAB) *m/z* 387 (M$^+$+Na); exact mass M$^+$+Na 387.1614 (calcd for $C_{14}H_{36}NaO_3Si_4$, 387.1639).

*2,2,2-Trifluoroethyl 3-[tris(trimethylsilyl)silyl]propionate (**3c**):* (62%) Column chromatography: hexane/ethyl acetate = 40/1, $R_f = 0.25$. Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.18 (s, 27H), 1.12 (m, 2H), 2.42 (m, 2H), 4.46 (q, 2H, $J_{F-H} = 8.4$ Hz); $^{13}$C NMR (100.6 MHz, $CDCl_3$) $\delta$ 1.1 (–Si*C*H$_3$), 2.8 (Si–*C*H$_2$–CH$_2$–), 32.6 (Si–CH$_2$–*C*H$_2$–), 60.4 (q, –*C*H$_2$–CF$_3$, $J_{F-C} = 36.6$ Hz), 123.1 (q, –CH$_2$–*C*F$_3$, $J_{F-C} = 277.0$ Hz); IR (neat) 2950, 2895, 1764, 1411, 1282, 1246, 1170, 1130, 834, 689, 622 cm$^{-1}$. MS (EI) *m/z* 403 (M$^+$+1), 387 (M$^+$–CH$_3$), 329 (M$^+$–Si(CH$_3$)$_3$), 73 ((CH$_3$)$_3$Si$^+$); Anal. Calc. for $C_{14}H_{33}F_3O_2Si_4$: C, 41.75; H, 8.26. Found: C, 41.55; H, 8.31%.

*Octadecyl 3-[Tris(trimethylsilyl)silyl]propionate (**3d**):* (87%) Column chromatography: hexane, $R_f = 0.3$. Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.17 (s, 27H), 0.88 (t, 3H, 1.11 m, 2H), 1.25–1.31 (broad, 30H), 1.76 (m, 2H), 2.31 (m, 2H), 4.05 (t, 2H, $J = 6.8$ Hz); $^{13}$C NMR (100.6 MHz, $CDCl_3$) $\delta$ 1.2 (–Si(CH$_3$)$_3$), 3.0, 14.2, 22.8, 26.0, 28.7, 29.4, 29.5, 29.6, 29.7, 29.8, 32.0, 33.4, 64.7, 174.9 (–*C*O$_2$–); IR (neat) 2925, 2854, 1739, 1467, 1337, 1245, 1198, 1148, 836, 688, 622 cm$^{-1}$. MS (FAB) *m/z* 571 (M$^+$−H); exact mass M$^+$−H 571.4219 (calcd for $C_{30}H_{67}O_2Si_4$, 571.4218).

*4-Trifluoromethylbenzyl 3-[tris(trimethylsilyl)silyl]propionate (**3e**):* (57%) Column chromatography: hexane–ether = 20:1, $R_f = 0.15$. Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.15 (s, 27H), 1.10 (m, 2H), 2.37 (m, 2H), 5.13 (s, 2H), 7.44 (d, 2H, $J = 8.1$ Hz), 7.60 (d, 2H, $J = 8.1$ Hz); $^{13}$C NMR (100.6 MHz, $CDCl_3$) $\delta$ 1.1 (–Si(*C*H$_3$)$_3$), 3.0 (Si–*C*H$_2$CH$_2$–), 33.2 (Si–CH$_2$*C*H$_2$–), 65.4 (–*C*H$_2$–C$_6$H$_4$– CF$_3$), 124.1 (q, $J_{F-C} = 272.4$ Hz), 125.6 (q, $J_{F-C} = 3.8$ Hz), 128.3, 130.4 (q, $J_{F-C} = 32.3$ Hz), 140.2, 174.4 (–*C*O$_2$–); IR (neat) 2950, 2894, 1744, 1623, 1420, 1326,1246, 1167, 1131, 1068, 1020, 836, 747, 689, 623 cm$^{-1}$. MS (EI) *m/z* 477 (M$^+$−H), 463 (M$^+$−CH$_3$), 405 (M$^+$−Si(CH$_3$)$_3$), 159 ($^+$CH$_2$C$_6$H$_4$CF$_3$), 73 ((CH$_3$)$_3$Si$^+$); exact mass M$^+$−H 477.1745 (calcd for $C_{20}H_{36}O_2F_3Si_4$, 477.1744).

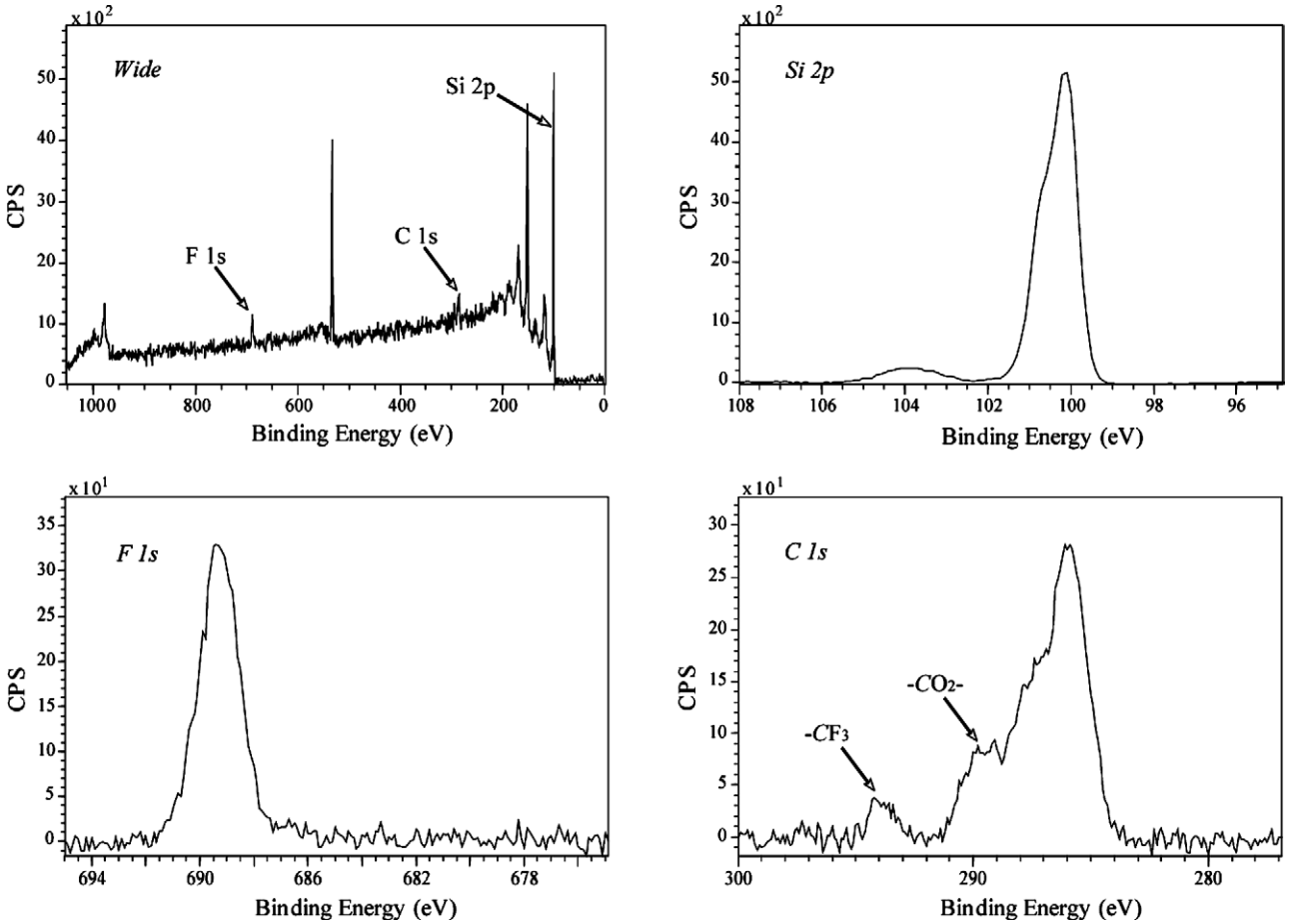



Fig. 6. XPS spectra of surface **S9a**.

*3-[Tris(trimethylsilyl)silyl]propanol (**6**):* $LiAlH_4$ in saturated ether solution (ca. 1 N, 8.0 mL) was transferred to a 25 ml flask containing **3a** (320 mg, 1.0 mmol). After stirring at room temperature for 20 h, the mixture was carefully poured into cold aqueous solution of hydrogen chloride (1 N) and then extracted by ether. The extract was dried ($MgSO_4$) and evaporated in vacuo. The residue was purified by column chromatography over silica gel eluting with hexane–ether (5:1) to give the title compound (288 mg, 94%) ($R_f = 0.1$). Colorless crystal, m.p. = 49–51 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.16 (s, 27H), 0.76 (m, 2H), 1.62 (m, 2H), 3.57 (t, 2H, $J = 6.7$Hz); $^{13}$C NMR (100.6 MHz, $CDCl_3$) $\delta$ 1.2 (–Si*C*H$_3$), 3.3 (–Si*C*H$_2$–), 32.3 (–SiCH$_2$*C*H$_2$–), 66.1 (–*C*H$_2$–OH); IR (KBr) 3348, 2947, 2892, 1243, 1052, 835, 746, 686, 623 cm$^{-1}$. MS (EI) *m/z* 305 ($M^+$–H), 291 ($M^+$–$CH_3$), 233 ($M^+$–Si$(CH_3)_3$), 73 ($(CH_3)_3Si^+$); exact mass $M^+$ 306.1679 (calcd for $C_{12}H_{34}OSi_4$, 306.1687). Anal. Calc. for $C_{12}H_{34}OSi_4$: C, 47.02; H, 11.18. Found: C, 46.99; H, 11.17%.

*1-Bromo-3-[tris(trimethylsilyl)silyl]propane (7):* $CBr_4$ (166 mg, 0.5 mmol) and $PPh_3$ (131 mg, 0.5 mmol) was added to a solution of **6** in dichloromethane (1.0 mL). The reaction mixture was stirred at room temperature for 2 h. After addition of 2 mL of water and stirring for 10 min, the mixture was extracted by dichloromethane (15 mL × 3). The extract was washed by brine, dried ($MgSO_4$) and evaporated in vacuo. The residue was purified by column chromatography over silica gel eluting with hexane to give the title compound (134 mg, 90%) ($R_f = 0.65$). Colorless wax; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.17 (s, 27H), 0.87 (m, 2H), 1.91 (m, 2H), 3.38 (t, 2H, $J = 6.9$ Hz); $^{13}$C NMR (100.6 MHz, $CDCl_3$) $\delta$ 1.2 (–Si*C*H$_3$), 6.7 (–Si*C*H$_2$–), 32.7 (–SiCH$_2$*C*H$_2$–), 37.2 (–*C*H$_2$–Br); IR (KBr) 2948, 2893, 1431, 1396, 1492, 1245, 831, 742, 687, 622, 562 cm$^{-1}$. MS (EI) *m/z* 370, 368 ($M^+$), 355, 353 ($M^+$–$CH_3$), 297, 295 ($M^+$–Si$(CH_3)_3$), 73 ($(CH_3)_3Si^+$); exact mass $M^+$ 370.0817, 368.0846 (calcd for $C_{12}H_{33}{}^{81}BrSi_4$, 370.0822; $C_{12}H_{33}{}^{79}BrSi_4$, 368.0843).

*3-[Tris(trimethylsilyl)silyl]propyl(tert-butoxycarbonylamino)acetate (**9a**):* (94%) Column chromatography: hexane–ether = 2:1, $R_f = 0.3$. Colorless crystal, m.p. = 48–50°C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.16 (s, 27H), 0.75 (m, 2H), 1.45 (s, 9H), 1.70 (m, 2H), 3.92 (d, 2H, $J = 5.5$ Hz), 4.07 (t, 2H, $J = 6.9$ Hz), 5.01 (broad, 1H); $^{13}$C NMR (100.6 MHz, $CDCl_3$) $\delta$ 1.2 (–Si*C*H$_3$), 3.5 (–Si*C*H$_2$–), 28.0 (–SiCH$_2$*C*H$_2$–), 28.4 (–C(*C*H$_3$)$_3$), 42.5 (–*C*H$_2$NH–), 68.1 (CH$_2$*C*H$_2$O–), 80.0 (–C(*C*H$_3$)$_3$), 155.7 (–NH–*C*O$_2$–), 170.5 (–CH$_2$*C*O$_2$–); IR (KBr) 3308, 2948,

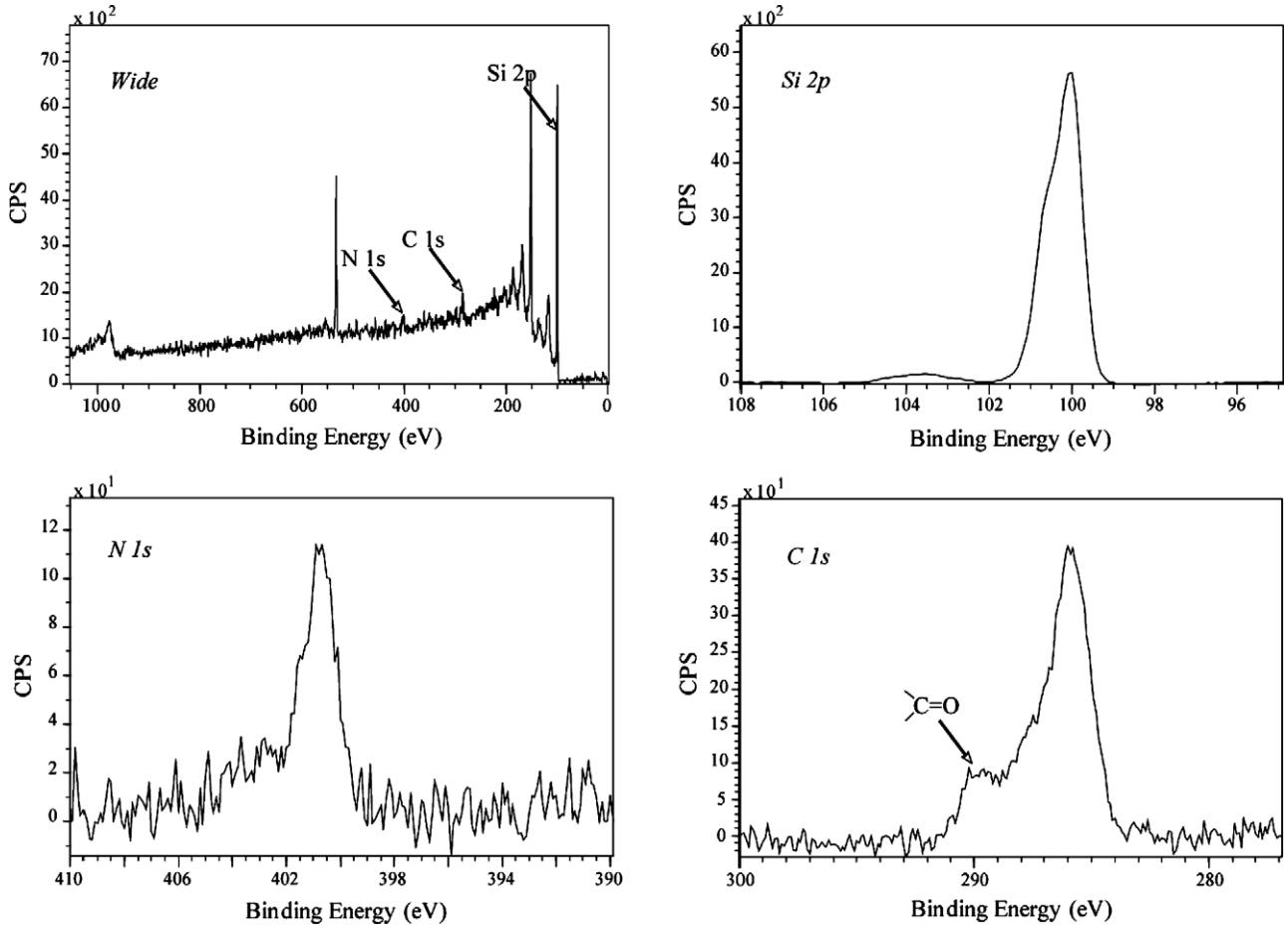
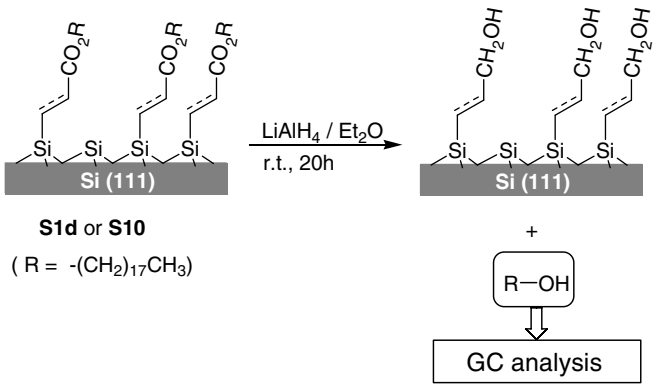



Fig. 7. XPS spectra of surface **S9c**.




Scheme 7.

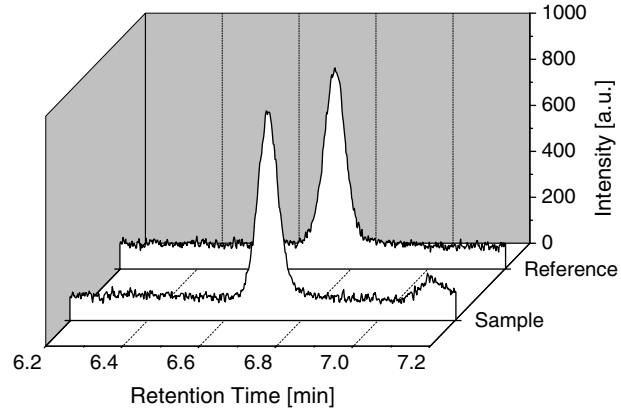



Fig. 8. Typical GC diagrams of a sample solution from surface reaction and a reference solution (1-octadecanol (concentration of reference solution, $1.0 \times 10^{-4}$ mol/L)).

2892, 1758, 1689, 1540, 1417, 1392, 1365, 1301, 1244, 1206, 1167, 1052, 980, 834, 688, 622 $cm^{-1}$. MS (FAB) *m/z* 486 ($M^+$+Na); exact mass $M^+$+Na 486.2320 (calcd for $C_{19}H_{45}NO_4Si_4Na$, 486.2323). Anal. Calc. for $C_{19}H_{45}NO_4Si_4$: C, 49.19; H, 9.78; N, 3.02. Found: C, 49.15; H, 9.90; N, 3.16%.

*2-[(2-tert-Butoxycarbonylamino)acetoxy]ethyl 3-[tris(trimethylsilyl)silyl]propionate (**9b**):* (92%) Column chromatography: hexane–ether = 2:1, $R_f = 0.3$. Colorless wax; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.16 (s, 27H), 1.09 (m, 2H), 1.44 (s, 9H), 2.34 (m, 2H), 3.93 (d, 2H, $J = 5.7$ Hz), 4.28 (m, 2H), 4.34 (m, 2H), 5.02 (broad, 1H); $^{13}$C NMR (100.6 MHz, $CDCl_3$) $\delta$ 1.1 (–Si*C*H$_3$), 2.7 (Si–*C*H$_2$CH$_2$–), 28.3 (–C(*C*H$_3$)$_3$), 33.0 (Si–CH$_2$*C*H$_2$–), 42.3 (–NH*C*H$_2$–), 62.0 and 63.1 (–O–*C*H$_2$*C*H$_2$–O–), 80.1 (–*C*(CH$_3$)$_3$), 155.7 (–NH–*C*O$_2$–), 170.3 (–NHCH$_2$*C*O$_2$–), 174.5 (–CH$_2$CH$_2$*C*O$_2$–); IR (neat) 3384, 2949, 2894, 1742, 1723, 1513, 1367, 1246, 1168, 1057, 836, 689, 622 $cm^{-1}$.

Table 6
Monolayer coverages of ester modified Si surfaces by reduction and GC analysis

| Surface | Surface group | Coverage estimated by GC (%) | Coverage estimated by XPS (%)[a] |
|---|---|---|---|
| **S1d** | $\equiv$Si–$CH_2CH_2CO_2(CH_2)_{17}CH_3$ | 25 | 38 |
| **S10** | $\equiv$Si–CH=$CHCO_2(CH_2)_{17}CH_3$ | 35 | 31 |

[a] Determined by C 1s (C=O)/Si 2p peaks.

MS (EI) *m/z* 506 ($M^+-CH_3$), 448 ($M^+-Si(CH_3)_3$), 247 ($(TMS)_3Si^+$), 73 ($(CH_3)_3Si^+$); exact mass $M^+$ 521.2485 (calcd for $C_{21}H_{47}O_6NSi_4$, 521.2480).

*[(2-tert-Butoxycarbonylamino)acetoxy]ethyl 3-[tris(trimethylsilyl)silyl]acrylate (**9c**):* (91%) Column chromatography: hexane–ether = 2:1, $R_f = 0.3$. Colorless crystal, m.p. = 60–61 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.17 (s, 27H), 1.45 (s, 9H), 3.94 (d, 2H,$J = 5.7$ Hz), 4.32 (m, 2H), 4.36 (m, 2H), 4.99 (broad, 1H), 6.59 (d, 1H, $J = 13.7$ Hz), 6.81 (d, 1H, $J = 13.7$ Hz); $^{13}$C NMR (100.6 MHz, $CDCl_3$) $\delta$ 1.4 (–Si*C*H$_3$), 28.4 (–C(*C*H$_3$)$_3$), 42.4 (–H*C*H$_2$–), 61.4 and 63.3 (–O–*C*H$_2$*C*H$_2$–O–), 80.2 (–*C*(CH$_3$)$_3$), 133.8 (Si–*CH*=CH–), 150.5 (Si–CH=*C*H–), 155.7 (–NH–*C*O$_2$–), 166.2 (–CH=CH–*C*O$_2$–), 170.4 (–NHCH$_2$*C*O$_2$–); IR (KBr) 3364, 2978, 2950, 2893, 1743, 1709, 1522, 1380, 1369, 1247, 1193, 1172, 1050, 836, 687 cm$^{-1}$. MS (FAB) *m/z* 542 ($M^+$+Na); exact mass $M^+$+Na 542.2221 (calcd for $C_{21}H_{45}O_6NSi_4Na$, 542.2222). Anal. Calc. for $C_{21}H_{45}NO_6Si_4$: C, 48.51; H, 8.72; N, 2.69. Found: C, 48.47; H, 8.83; N, 2.67%.

*tert-Butyl [[(Z)-3-tris(trimethylsilyl)silyl]acryloylamino]acetate (**12c**):* **11c** (84 mg, 0.5 mmol), HOBT (68 mg, 0.5 mmol), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDCI, 115 mg, 0.6 mmol) and triethylamine (36 mg, 0.5 mmol) was added to a solution of **10** (160 mg, 0.5 mmol), in dichloromethane (1.0 mL). After stirring at room temperature for 20 h, the reaction mixture was diluted with dichloromethane and washed with saturated aqueous solution of $NaHCO_3$ and water. The organic phase was dried ($MgSO_4$) and evaporated in vacuo. The residue was purified by column chromatography over silica gel eluting with hexane–ether (2:1) to give the title compound (178 mg, 83%) ($R_f = 0.5$). Colorless crystal, m.p. = 92–94 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.16 (s, 27H), 1.47 (s, 9H), 3.97 (d, 2H, $J = 4.9$ Hz), 5.87 (br, 1H), 6.51 (d, 1H, $J = 13.4$ Hz), 6.59 (d, 1H, $J = 13.4$ Hz); $^{13}$C NMR (100.6 MHz, $CDCl_3$) $\delta$ 1.4 (–Si*C*H$_3$), 28.1 (–C(*C*H$_3$)$_3$), 42.0 (–NH–*C*H$_2$–), 82.2 (–*C*(CH$_3$)$_3$), 136.0 (Si–*C*H=CH–C(O)–), 144.0 (Si–CH=*C*H–), 165.8 (–*C*(O)NH–), 169.6 (–*C*OO–); IR (KBr) 3421, 2947, 2892, 1735, 1670, 1515, 1392, 1240, 1167, 837, 755, 687, 623 cm$^{-1}$. MS (EI) *m/z* 431 ($M^+$), 416 ($M^+-CH_3$), 374 ($M^+-C(CH_3)_3$), 358 ($M^+-Si(CH_3)_3$), 330 ($M^+-CO_2C(CH_3)_3$), 302 ($M^+-Si(CH_3)_3-CH_2=C(CH_3)_2$); exact mass $M^+$ 431.2155 (calcd for $C_{16}H_{38}O_2Si_4$, 431.2164). Anal. Calc. for $C_{16}H_{38}O_2Si_4$: C, 50.06; H, 9.57; N, 3.24. Found: C, 50.17; H, 9.66; N, 3.29%.

### 3.2. Si(1 1 1) surface modification

Single-crystal n-Si(1 1 1) wafers (resistivity of 0.5–1.5 Ω cm and thickness of 500 ± 25 μm), polished on one side or both sides, were used in all surface reactions. Preparation of hydrogen-terminated Si(1 1 1) surface was followed by the previously reported method [8]. All surface modifications were carried out under nitrogen atmosphere, and all solutions used for surface modification were predeoxygenated by nitrogen bubbling for 30 min. XPS spectra were obtained with a KRATOS-AXIS-165 spectrometer, with a Mg Kα line (1253.6 eV) or a monochromated Al Kα line (1486.6 eV) used as the X-ray source. An analyzer pass energy of 80 eV was used for survey scans, and that of 40 eV was used for fine scans of specific elements. Static water contact angle was measured by an ERMA G-1 contact angle meter. A drop of pure water (~1 μL) was put on the surface using a micro-syringe. Five measurements were made at different spots for each sample surface. GC analysis was performed on a Yanaco G-6800 gas chromatography using a capillary column (30 m × 0.25 mm, supelcowax 10) with flame-ionization detectors.

#### 3.2.1. Hydrosilylation of alkene on Si(1 1 1)–H surface

A piece of freshly prepared Si(1 1 1)–H wafer was immersed in neat alkene (**2a**–**c**,**f**) or a dichloromethane solution of alkene (**2d**,**e** or **4**, 1.0 mol/L) in a reaction tube. The reaction mixture was gently warmed and kept at 30–35 °C for 40 h. The immersed wafer was successively rinsed with dichloromethane, ethanol (for **4**), sonicated in dichloromethane, and dried under vacuum. Preparation of **S5** was reported in the previous paper [8].

#### 3.2.2. Reduction by $LiAlH_4$

A freshly prepared ester-modified surface was immersed in ether solution of $LiAlH_4$ at room temperature for 20 h. The obtained surface was successively washed with 1 N aqueous solution of HCl and Milli-Q water, rinsed with dichloromethane, sonicated in dichloromethane, and dried under vacuum.

#### 3.2.3. Bromination of S3

Freshly prepared surface **S3** was immersed in dichloromethane solution of $CBr_4$ and $PPh_3$ at room temperature for 20 h (the concentration of $CBr_4$ and $PPh_3$ is 0.25 mol/L, respectively). The obtained surface was successively washed with Milli-Q water, rinsed with ethanol and dichloromethane, sonicated in dichloromethane, and dried under vacuum to give **S4**.

#### 3.2.4. Ester and amide formation on surface

A freshly prepared hydroxy- or carboxy-terminated surface was immersed in dichloromethane solution of

Boc-glycine or 11 (1 equiv.), EDCI (1.2 equiv.) and DMAP (0.2 equiv. for ester formation) or HOBT (1.0 equiv. for amide formation) at room temperature for 20 h (the concentration of Boc-glycine or 11 is 0.5 mol/L). The obtained surface was successively washed with Milli-Q water, rinsed with ethanol and dichloromethane, sonicated in dichloromethane, and dried under vacuum.

### 3.2.5. Estimation of monolayer coverage by XPS

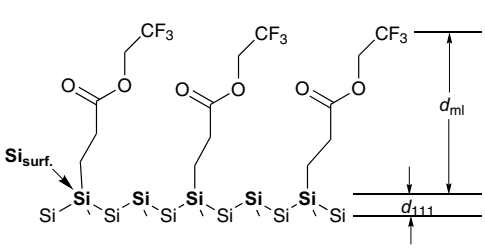
Coverage ratio was calculated according to the following equations as an example for a $CF_3$-functionalized sample **S1c** shown below [8]

$$\text{Coverage_Ratio} = \left(\frac{I_{\text{F1s}}}{3\text{RSF}_{\text{F1s}}}\right) \Big/ \left(\frac{I_{\text{Si2p}} \cdot \text{Intensity_Ratio}_{\text{Si(1 1 1)_surface}}}{\text{AF}_{\text{ml}} \cdot \text{RSF}_{\text{Si2p}}}\right) \quad (1)$$

$$\text{AF}_{\text{ml}}(\text{Attenuation_Factor}_{\text{monolayer}}) = \text{e}^{-d_{\text{ml}}/(\lambda_{\text{ml}} \cdot \cos\theta)} \quad (2)$$

$$\text{Intensity_Ratio}_{\text{Si(1 1 1)_surface}} = \frac{\text{e}^{-d_{\text{ml}}/(\lambda_{\text{ml}} \cdot \cos\theta)} \cdot \int_0^{d'_{1\,1\,1}} \text{e}^{-z/(\lambda_{\text{Si}} \cdot \cos\theta)} d(z)}{\text{e}^{-d_{\text{ml}}/(\lambda_{\text{ml}} \cdot \cos\theta)} \cdot \int_0^{\infty} \text{e}^{-z/(\lambda_{\text{Si}} \cdot \cos\theta)} d(z)} = 1 - \text{e}^{-d'_{1\,1\,1}/(\lambda_{\text{Si}} \cdot \cos\theta)} \quad (3)$$

Average layer spacing $d'_{1\,1\,1} = 2d_{1\,1\,1} = 1.568$ Å [24a] were used. Relative sensitivity factors ($\text{RSF}_{\text{F1s}} = 1.000$, $\text{RSF}_{\text{N1s}} = 0.505$, $\text{RSF}_{\text{Si2p}} = 0.371$ for Mg Kα X-rays; $\text{RSF}_{\text{N1s}} = 0.477$, $\text{RSF}_{\text{Si2p}} = 0.328$ for monochromated Al Kα X-rays) in KRATOS-AXIS-165 data library and the inelastic mean free path (IMFP) $\lambda_{\text{Si}}$ (21.88 Å for Si photoelectrons of kinetic energy = 1154 eV for Mg Kα X-rays; 25.0 Å for kinetic energy = 1387 eV for monochromated Al Kα X-rays) were used [24b]. $\theta$ represents takeoff angle in XPS measurement. $d_{\text{ml}}$ was calculated by PM3 calculations of distances of monolayer using model compounds (for example, $(Me_3Si)_3Si$–$CH_2$–$CH_2$–$CO_2$–$CH_2$–$CF_3$). IMFP of organic monolayer was calculated according to the literature [24c]. In the coverage estimation, total peak area for Si 2p (including oxidized Si) was used.




Si(111) Surface **S1c**

### 3.2.6. Estimation of monolayer coverage by ester reduction and GC analysis

n-Si(1 1 1) wafers polished on both sides were used. They were cut to several pieces with a same size ($1.5 \times 1.5$ cm$^2$). These wafers were put into a reaction tube, and between every two-piece wafers a clean Teflon O'ring in a proper size was inserted to keep an interval and enable the surface contacting with the reaction solution. Modification of these Si wafers by propiolate or acrylate esters and followed reduction by $LiAlH_4$ were performed by the procedure described above. After surface reduction, the reaction mixture was treated with 1 N HCl solution and extracted with diethyl ether. The extract was concentrated and transferred to 500 μl vessel. Ether was evaporated and 200 μl of *n*-propanol was added to the vessel. The obtained propanol solution was analyzed by GC to estimate the concentration of liberated alcohol.

*GC calibration*: Six *n*-propanol solutions of octadecyl alcohol and 4-(trifluoromethyl)benzyl alcohol were prepared, respectively. The concentration of each solution were different within a range of $4.0 \times 10^{-5}$–$5.0 \times 10^{-4}$ mol/L. Each solution was analyzed by GC for five times. The mean intensities (peak integral) of the alcohol peak were used to draw the intensity vs. concentration (*I*–*C*) plot. A linear fitting of the plot gave a simple linear relationship between the GC intensity and the solution concentration of each alcohol compound. The linear relationship is presented as: $I = k \cdot C$. For octadecyl alcohol, $k = 1.652 \times 10^7$; for 4-trifluoromethylbenzyl alcohol, $k = 2.704 \times 10^7$.

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[19] For the reaction of Si(1 1 1)–H with **2b**, formation of the surface **S1b** was assumed from the model reaction result. The reaction of **1** and **2b** gave **3b** as major product and no *O*-silylated product was identified. However, because of the reported results of competing reactions of Si(1 1 1)–H with C=C and OH groups [4c] and formation of Si–OR by thermal reaction of Si(1 1 1)–H and alcohols, [41] a close analysis of the surface will be needed to rule out the reaction of the OH groups with the Si–H bonds.

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[26] The surface reaction does not require an explicit radical initiator or high reaction temperature, similar to the reaction of Si(1 1 1) with propiolate esters or tris(trimethylsilyl)silane with propiolate esters [12,8]. According to the proposed mechanism for the reaction of tris(trimethylsilyl)silane with propiolate esters [8] autoxidation of surface Si–H group by contaminated molecular oxygen to generate a silicon radical on the surface may be the speculative initial step of the total radical chain reaction.

[27] In order to examine the role of charge carriers and obtain some insight into the reaction mechanisms, the reaction of p-type Si(1 1 1)–H with trifluoroethyl propiolate was carried out. The reaction gave a 46% coverage ratio by F1s XPS spectra. We believe the value is similar to that of n-Si(1 1 1) within the experimental error and the effect of charge carriers may be small [42].

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[35] The possibility to increase the surface quality after chemical transformation was examined. Retreatment of Si(1 1 1)–CH=CH$CO_2CH_2CF_3$ surface (22% coverage) with 5% HF (1 min) and subsequent reaction with alkyne HC≡C$CO_2CH_2CF_3$ gave the surface with 38% coverage by XPS. Further study on application to various surfaces is planned in due course.

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[38] A serial of propanol solution of octadecyl alcohol in the concentration range of about $4.0 \times 10^{-5} \sim 5.0 \times 10^{-4}$ mol/L was prepared and measured by GC to draw the calibration plots. A linear relationship between the GC intensity (peak integral) and the solution concentration was obtained.

[39] Surface **S11** ($\equiv$Si–CH=CH–$CO_2CH_2$–$C_6H_4$-*p*-$CF_3$) was also prepared from reaction of Si(1 1 1)–H surface with 4-trifluoromethylbenzyl propiolate [8] and subsequent reduction and GC analysis were performed. Coverage of surface **S11** was estimated to be 24%, which is quite lower than that of 56% previously reported by XPS [8]. The possible loss of more volatile trifluoromethylbenzyl alcohol (b.p. 78–80 °C/4 mmHg) than 1-octadecanol (b.p. 170–171 °C/2 mmHg) during the concentration of the solution might cause the decrease of the coverage ratio. Investigation of other methods to preconcentrate other than evaporation (e.g. solid phase extraction) is required for volatile alcohols.

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