A mild and efficient Si (111) surface modification *via* hydrosilylation of activated alkynes[†]

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Received 8th August 2005, Accepted 20th September 2005 First published as an Advance Article on the web 5th October 2005 DOI: 10.1039/b511535c

A new Si surface modification with organic groups *via* hydrosilylation at room temperature is reported. A hydrogen-terminated Si (111) surface was reacted with activated alkynes such as propiolate esters, propiolic acid, but-3-yne-2-one, propiolonitrile and phenylacetylene at room temperature for 24–40 h to give modified surfaces. The coverage ratio was estimated to be 31–56% by XPS analysis. This surface modification method is mild, highly efficient and procedurally simple. The novel surfaces modified with various organic functional groups are expected to have interesting utilities.

Introduction

Modification of silicon surfaces by organic groups has been attracting much attention.¹ For example, modified surfaces are expected to have improved stability and properties as electronic devices compared to hydrogen-terminated Si surfaces.² They are also expected to have potential use in biosensors.³ Several methods for surface modification have been reported, using thermal conditions⁴ and light irradiation^{5,3c} or use of organometallic reagents such as Grignard or organolithium reagents.^{2,6} We are interested in exploring more mild and efficient modification methods of single-crystal silicon surfaces by organic monolayers in order to introduce sensitive functional groups and discover novel properties.

Recently, we have found and reported the regioselective hydrosilylation of activated alkynes such as propiolate esters with tris(trimethylsilyl)silane (2).⁷ The hydrosilylation is highly selective, clean, and requires only a simple procedure to succeed. Tris(trimethylsilyl)silane (2) has Si-Si bonds and can be considered to be a molecular model for silicon surfaces.⁸ The Si-H bond dissociation energy of 2 (experimental value 84 kcal mol⁻¹,⁹ 80 kcal mol⁻¹ calculated here by B3LYP/6-31G*//HF/STO-3G*) is relatively small. It would be difficult to obtain a precise Si-H bond energy on hydrogenterminated Si (111) surfaces experimentally. Thus, in order to compare Si-H bond dissociation energies of 2 and Si (111) surfaces, the Si-H bond energy for Si₆₂H₅₆, a Si (111) model, was calculated here as 82 kcal mol⁻¹ by B3LYP/6-31G*//HF/ STO-3 G^{*10} and is found to be similar to that of 2. Therefore, use of the hydrosilylation reaction of 2 as a surface model has been justified. The neat conditions using reactive alkynes to form a C–Si bond may be also suitable for modification of silicon surfaces. In this study, we have examined hydrosilylation of activated alkynes on Si (111) surfaces and modified surfaces with various organic functional groups have been obtained.

Results and discussion

In addition to our previous results,⁷ various activated alkynes **1** reacted with a silicon surface model compound tris(trimethylsilyl)silane (**2**) smoothly without solvent at room temperature (eqn (1) and Table 1). The reaction of substrates with ester, free carboxyl, ketone, cyano and aryl groups **1a–n** gave Z-alkenes **3a–n** stereoselectively in high yields. This result shows high chemoselectivity of Si–H with activated alkynes compared to free COOH and OH groups under the reaction conditions.

$$H \xrightarrow{\qquad } X + (Me_{3}Si)_{3}Si \xrightarrow{\qquad } H \xrightarrow{\qquad neat} \xrightarrow{\qquad } H \xrightarrow{\qquad } H \xrightarrow{\qquad } X$$
(1)

The substrates 1 were used for surface hydrosilylation (eqn (2)). Si-H surface was prepared by treatment of an Si

Table 1 Hydrosilylation of alkynes 1 with 2^a

Entry	Substrate	Х	Product (Yield (%))
1^b	1a	CO ₂ Me	3a (89)
2^b	1b	CO ₂ Et	3b (92)
3^b	1c	$CO_2CH_2CF_3$	3c (91)
4	1d	CO ₂ CH ₂ CH ₂ CN	3d (94)
5	1e	$CO_2(CH_2)_{17}CH_3$	3e (63)
6	1f	$CO_2CH_2C_6H_4-p-CF_3$	3f (78)
7	1g	CO ₂ CH ₂ CH ₂ OH	3 g (75)
8	1ĥ	CO ₂ ^t Bu	3h (91)
9^b	1i	CO ₂ H	3i (90)
10^{b}	1j	COMe	3j (83)
11	1k	CN	3k (85)
12	11	Ph	3l (89)
13	1m	$C_6H_4-p-CF_3$	3m (83)
14	1n	C_6H_4-p-F	3n (77)

^{*a*} The reaction was carried out using 1 (1.0 mmol) and 2 (1.05 mmol) at room temperature overnight. ^{*b*} Reference 7.

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 $[\]dagger$ Electronic supplementary information (ESI) available: XPS spectra and the STO-3G*-optimized structures of Si_{62}H_{56} and 'Si_{62}H_{55}. See DOI: 10.1039/b511535c

(111) wafer by the RCA cleaning method¹¹ followed by etching with 5% aq. HF and 40% aq. NH_4F .¹² The freshly prepared Si–H surfaces were immersed in the neat alkynes 1.¹³ The vessel was gently rotated at room temperature for 24–40 hours to give functionalized alkenyl silicon surfaces 4 with ester, free carboxyl, ketone, cyano and aryl groups.¹⁴ Analysis of the functionalized silicon surfaces 4b–d, 4f, 4k, and 4m–n was carried out by XPS spectroscopy (Figs. 1–3 and Figs. S1–4 in the ESI†). Si 2p peaks at 103 eV assignable to Si–O by surface oxidation were very small.¹⁵ The C 1s peaks of 4c, 4f and 4m show typical CF₃ high binding energies at 293–294 eV (Fig. 2 and ESI Figs. S1, S3†).^{16,5b,3a} Carbonyl (C=O) binding energies for 4b–d and 4f appear in the 289.5–290 eV region.



The F 1s peaks for 4c, 4f, and 4m–n and the N 1s peaks for 4d and 4k are shown in Figs. 2–3 and ESI† Figs. S1–4. The

relative intensities of F 1s and N 1s peaks with respect to the Si 2p peaks were used to estimate the coverage ratio, $^{17-20}$ because the C 1s peaks often contain contaminated carbon peaks. The XPS spectra were recorded at different take-off angles, and data taken at each take-off angle were used to calculate the coverage ratios (Table 2). Thus, the coverage ratios for **4** at take-off angle 0° were estimated as 31–56%. For **4c**, the relationship between coverage ratio and reaction time for several measurements is shown in Fig. 4. In spite of the experimental errors, the coverage ratios increase with time (until *ca.* 40 h).

Recently, hydrosilylation of alkenes and alkynes with nanocrystalline silicon assisted by white light,^{5b} and modification of hydrogen terminated Si (100) and Si (111) surfaces by visible light irradiation^{5c,d} have been reported. This hydrosilylation of activated alkynes with Si (111)–H surface was carried out under room light (fluorescent lamp) partially during the total reaction time. Therefore, in order to examine the effect of room light, the reaction under dark conditions was also carried out. The estimated coverage ratios under room light and in the dark did not show a clear difference (Fig. 4).²¹ The reaction rates of a surface model, tris(trimethylsilyl)silane (2), with 1a under room light and in the dark did not show any differences both using neat conditions and in CD₂Cl₂ solution. The precise light effect on the surface reaction is currently under investigation.

Using the same conditions (room light, room temperature, 40 h), a low coverage ratio (14%) estimated by F 1s and Si 2p peaks of XPS was obtained by the reaction of Si–H surface with a 1-alkene, 2,2,2-trifluoroethyl 5-hexenoate



Fig. 1 XPS spectra of functionalized Si (111) surface 4b.



Fig. 2 XPS spectra of functionalized Si (111) surface 4c.



Fig. 3 XPS spectra of functionalized Si (111) surface 4d.

Table 2Estimated coverage ratio of organic monolayer coupled onSi (111) surface

Entry	Sample	Reaction conditions	Coverage ratio (%) ^a		
			0°	30°	60°
1	$4c^b$	rt, 40 h	56	54	55
2	4d	rt, 24 h	31	31	24
3	4 f	rt, 40 h	56	60	55
4	4k	rt, 24 h	51	48	50
5	4m	rt, 40 h	42	67	
6	4n	rt, 40 h	46	50	

^{*a*} Calculated from the relative intensities of F 1s/N 1s peaks to the Si 2p peaks by XPS taken at different take-off angles. ^{*b*} Several measurements for 4c are shown in Fig. 4.



Fig. 4 Coverage ratios of Si surface 4c as function of reaction time. **\blacksquare** is under room light and \blacktriangle is in the dark.

 $(H_2C=CH(CH_2)_3CO_2CH_2CF_3)$. This result indicates these reaction conditions are very mild compared to the reported thermal or light-induced conditions^{4,5,3c} and selective to activated alkynes.

A functionalized Si prism was prepared and examined by attenuated total internal reflection (ATR)-IR equipped with a MCT detector. Absorbance peaks for C–H stretching vibrations at 2925 and 2855 cm⁻¹ were observed for octadecyl propenoate modifed Si surface **4e** (Fig. 5). The position of the methylene stretch is within the region of the reported values of the functionalized silicon surfaces.^{14a} However, long carbon



Fig. 5 ATR-IR spectrum of Si surface 4e. Reaction times are indicated.

Table 3 Static water contact angles of the silicon surfaces

Entry	Sample	Contact angle/deg	Standard error/deg				
1	Si–H	83	1.6				
2	4a (Si-CH=CH-CO ₂ Me)	62	2.4				
3	4b (Si–CH=CH– CO_2Et)	63	0.8				
4	4c (Si-CH=CH-CO ₂ CH ₂ CF ₃)	75	1.3				
5	4d (Si-CH=CH-CO ₂ CH ₂ CH ₂ CN)	77	3.5				
6	4e (Si–CH=CH–CO ₂ (CH ₂) ₁₇ CH ₃)	85	0.8				
7	4f (Si–CH=CH– $CO_2CH_2C_6H_4$ – p -CF ₃)	72	0.9				
8	4g (Si–CH=CHCO ₂ CH ₂ CH ₂ OH)	67	2.4				
9	4h (Si–CH=CH–CO ₂ ^t Bu)	68	0.7				
10	4i (Si–CH=CH–COOH)	31	2.5				
11	4i (Si–CH=CH–COOH) ^a	38	1.5				
12	4j (Si–CH=CH–COMe)	53	1.1				
13	4k (Si–CH=CH–CN)	72	1.1				
14	4l (Si–CH=CHPh)	66	0.5				
15	4m (Si–CH=CHC ₆ H ₄ – p -CF ₃)	73	1.2				
16	4n (Si–CH=CHC ₆ H ₄ – p -F)	64	0.7				
^{<i>a</i>} Prepared by treatment of 4h with trifluoroacetic acid in CH_2Cl_2 (TFA : $CH_2Cl_2 = 1 : 4$, v/v).							

chains may not be well-ordered, because of possible conformational mixtures of ester moieties on the surface. Reaction time dependence for these peaks is also indicated.

Static water contact angles of Si-H and the functionalized silicon surfaces were measured and are shown in Table 3. The contact angle for the Si-H surface (83°) is in agreement with the reported data.²² The contact angle for the silicon surface with a longer alkyl (C_{18}) ester group (4e) is 85°. The somewhat lower value for long alkyl chain functionalized 4e compared to the value (*ca.* $108-110^{\circ}$) for hydrophobic long alkyl chains^{5c,d} probably arises from the polar ester functionality. The contact angles reported for ester functionalized surfaces are also less than 90° and depend on the substituents.^{3a,5d,14a} The silicon surface with CO₂H group has a small contact angle (31°) and shows the hydrophilic property. For reference, the contact angle for fully oxidized (by 98% $H_2SO_4 + 30\% H_2O_2$) silicon surface was examined but the contact angle is too small and could not be determined because of the high wetting property of the surface.

Polar silicon oxidized surface sites formed by adventitious oxygen may also reduce the contact angles to some extent, although surface oxidation observed by XPS is small.^{23,24} The relationship between water contact angle, polarity of functional groups and coverage ratio is under investigation.

The mechanism of this very mild surface modification can be deduced as a radical chain mechanism as follows. Chatgilialoglu *et al.* reported the spontaneous formation of silyl radical by the reaction of tris(trimethylsilyl)silane (**2**) and oxygen.²⁵ We have also reported the reactions of **2** and activated alkynes **1** without an explicit radical initiator and it was suggested that the radical initiating step was caused by the contaminated molecular oxygen.⁷ The radical initiating step in this surface modification can be also speculated to be caused by contaminated molecular oxygen similar to the mechanism suggested for the reactions of **2** and activated alkynes **1**.^{7,26} In the reaction of **2** and **1**, no significant quantities of oxidized by-products were obtained. This is probably because molecular oxygen mainly reacts as an initiator. The relatively small Si–H bond energy of Si (111) surfaces, estimated as



Scheme 1

82 kcal mol⁻¹ for the Si₆₅H₅₆ model above described, ¹⁰ which is similar to Si–H for **2**, could allow an autoxidation-induced initiating step and also the subsequent radical chain reactions. The resulting surface silyl radical **A** would react with alkynes **1** to lead to carbon radical **B**. **B** would abstract a hydrogen from an adjacent Si–H and regenerate a silyl radical on the surface (see Scheme 1).^{4a,27}

Although the stereochemistry of the C=C double bond was determined as *cis* for the model hydrosilylated products 3, in the silicon surface hydrosilylation, the C=C stereochemistry is not determined. From consideration of the surface steric requirements and the presumed radical mechanism, the *trans* form could be preferred.

In summary, we have developed a very mild, efficient and simple process for silicon surface organic group modification. The use of activated alkynes takes advantage of silicon–carbon bond formation on the surface. Further study on the utility of the surfaces with various organic functional groups is under investigation.

Experimental

1. Model reactions

General methods for eqn (1). Melting points are uncorrected. IR spectra were recorded in the FT mode. ¹H NMR spectra were recorded at 400 MHz. ¹³C NMR spectra were recorded at 100.6 MHz. ¹H Chemical shifts are reported in ppm relative to Me₄Si. ¹³C Chemical shifts are reported in ppm relative to CDCl₃ (77.1 ppm). Chemical shifts (¹⁹F) are reported relative to CFCl₃. ¹³C Assignments were determined by DEPT and HSQC. Mass spectra were recorded at an ionizing voltage of 70 eV by EI or FAB. All reactions were carried out under a nitrogen atmosphere.

Substrates **1d,e,f,g** were prepared by the reaction of propiolic acid and the corresponding alcohols with BF₃-etherate according to the literature method.²⁸ **1k** was prepared according to the literature.²⁸

2-Cyanoethyl propiolate (1d). (Yield 68%) ($R_f = 0.4$, hexaneether = 1 : 2): Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 2.76 (t, 2H, J = 6.3 Hz), 2.99 (s, 1H), 4.39 (t, 2H, J = 6.3 Hz). ¹³C NMR (100.6 MHz, CDCl₃) δ 17.81 (-CH₂-CN), 60.20 $(-CH_2-O-C(O)-)$, 73.77 (HC=C-), 76.48 (HC=C-), 116.22 (-CN), 151.91 (-COO-); IR (neat) 3269, 2973, 2255, 2121, 1724, 1467, 1415, 1335, 1239, 1001, 754 cm⁻¹.

Octadecyl propiolate (1e). (Yield 31%) ($R_f = 0.45$, hexaneether = 10 : 1): Colorless crystals; mp 46–47 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.88 (t, 3H, J = 6.9 Hz), 1.25 (broad, 30H), 1.67 (m, 2H), 2.86 (s, 1H), 4.19 (t, 2H, J = 6.8 Hz). ¹³C NMR (100.6 MHz, CDCl₃) δ 14.20, 22.78, 25.84, 28.40, 29.25, 29.45, 29.54, 29.63, 29.71, 29.74, 29.78, 32.02, 66.60, 74.44 (HC=*C*-), 74.90 (H*C*=*C*-), 152.93 (–COO–); IR (KBr) 3225, 2921, 2848, 2116, 1697, 1467, 1256 cm⁻¹; MS (EI) *m/z* 322 (M⁺); exact mass M⁺ 322.2863 (Calcd for C₂₁H₃₈O₂, 322.2872). Anal. Calcd for C₂₁H₃₈O₂: C, 78.20; H, 11.88. Found: C, 78.22; H, 11.88%.

4-(Trifluoromethyl)benzyl propiolate (1f). (Yield 66%) ($R_{\rm f} = 0.30$, hexane–ether = 10 : 1): Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 2.94 (s, 1H), 5.27 (s, 2H), 7.50 (d, 2H, J = 8.0 Hz), 7.64 (d, 2H, J = 8.0 Hz); ¹³C NMR (100.6 MHz, CDCl₃) δ 66.86 (ArCH₂–), 74.29 (HC=*C*–), 75.68 (H*C*=C–), 123.98 (q, CF₃, $J_{\rm C-F} = 272.4$ Hz), 125.74 (q, $J_{\rm C-F} = 3.8$ Hz), 128.55, 130.90 (q, $J_{\rm C-F} = 32.8$ Hz), 138.53, 152.37 (–COO–); IR (neat) 3299, 2124, 1722, 1326, 1223, 1167, 1126, 1067, 1020, 838, 822, 754 cm⁻¹. MS (EI) *m*/*z* 228 (M⁺); exact mass M⁺ 228.0402 (Calcd for C₁₁H₇F₃O₂, 228.0398).

2-Hydroxyethyl propiolate (1g). (Yield 26%) ($R_{\rm f} = 0.15$, hexane–ether = 1 : 1): Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 2.30 (s, 1H), 2.95 (s, 1H), 3.85 (m, 2H), 4.30 (m, 2H). ¹³C NMR (100.6 MHz, CDCl₃) δ 60.50, 67.63, 74.40 (HC=C–), 75.57 (HC=C–), 152.81 (–COO–). IR (neat) 3269, 2960, 2884, 2119, 1713, 1453, 1370, 1242, 1079, 1010, 944, 883, 754 cm⁻¹.

2,2,2-Trifluoroethyl 5-hexenoate. To a mixture of 5-hexenoic acid (580 mg, 5.0 mmol) and 2,2,2-trifluoroethanol (600 mg, 6.0 mmol) in dichloromethane (5.0 mL) was added 4-(dimethylamino)pyridine (122 mg, 1.0 mmol) and 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (1.15 g, 6.0 mmol). After stirring at room temperature overnight, the reaction mixture was diluted with dichloromethane and washed with water. The organic phase was dried (MgSO₄), 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 (600 mg, 61%) ($R_{\rm f}$ = 0.4). Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 1.77 (m, 2H), 2.12 (m, 2H), 2.43 (t, J = 7.4 Hz, 2H), 4.46 (q, J = 8.4 Hz, 2H), 4.99 ~ 5.06 (m, 2H), 5.77 (m, 1H); ¹³C NMR (100.6 MHz, CDCl₃) δ 23.8 (–CH₂CH₂CH₂–), 32.9 (–CH₂CH₂CH₂–), 60.4 (q, –CH₂–CF₃, $J_{\rm C-F}$ = 36.6 Hz), 115.8 (CH₂=CH–), 123.1 (q, –CH₂–CF₃, $J_{\rm C-F}$ = 277.0 Hz), 137.3 (CH₂=CH–), 172.0 (–CO₂–); IR (neat) 3082, 2979, 2941, 2872, 1761, 1643, 1415, 1282, 1169, 977, 917, 840 cm⁻¹. MS (EI) *m*/*z* 196 (M⁺), 97 (M⁺ – OCH₂CF₃), 83 (CH₂CF₃); exact mass M⁺ 196.0711 (calcd for C₈H₁₁O₂F₃, 196.0711).

Hydrosilylation of tris(trimethylsilyl)silane (2) with alkynes 1 in neat condition was performed by the reported procedure.⁷

(*Z*)-2-Cyanoethyl 3-[tris(trimethylsilyl)silyl]propenoate (3d). (Yield 94%) ($R_{\rm f} = 0.15$, hexane–ethyl acetate = 10 : 1): Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 0.18 (s, 27H), 2.72 (t, 2H, J = 6.4 Hz), 4.32 (t, 2H, J = 6.4 Hz), 6.61 (d, 1H, J = 13.7 Hz), 6.87 (d, 1H, J = 13.7 Hz). ¹³C NMR (100.6 MHz, CDCl₃) δ 1.38 (–SiCH₃), 18.17 (–CH₂–CN), 58.30 (–CH₂–O– C(O)–), 116.90 (–CN), 133.23 (–SiCH=CH–C(O)–), 152.00 (–SiCH=CH–C(O)–), 165.89 (–COO–); IR (neat) 2949, 2893, 2256, 1725, 1581, 1357, 1244, 1200, 1168, 1036, 837, 688, 621 cm⁻¹. MS (EI) *m*/*z* 371 (M⁺); exact mass M⁺ 371.1595 (calcd for C₁₅H₃₃NO₂Si₄, 371.1588).

(Z)-Octadecyl 3-[tris(trimethylsily])silyl]propenoate (3e). (Yield 63%) ($R_{\rm f} = 0.5$, hexane): Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 0.18 (s, 27H), 0.88 (t, 3H, J = 6.9 Hz), 1.26 (broad, 30H), 1.63 (m, 2H), 4.09 (t, 2H, J = 6.8 Hz), 6.58 (d, 1H, J = 13.7 Hz), 6.72 (d, 1H, J = 13.7 Hz). ¹³C NMR (100.6 MHz, CDCl₃) δ 1.41 (–SiCH₃), 14.22, 22.79, 26.03, 28.89, 29.38, 29.46, 29.61, 29.68, 29.76, 29.77, 29.80, 32.03, 64.12, 134.80 (–SiCH=CH–C(O)–), 148.38 (–SiCH=CH–C(O)–), 166.69 (–COO–); IR (neat) 2925, 2854, 1717, 1243, 1205, 1175, 836, 621 cm⁻¹; MS (EI) *m*/*z* 570 (M⁺); exact mass M⁺ 570.4147 (calcd for C₃₀H₆₆O₂Si₄, 570.4140); Anal. Calcd for C₃₀H₆₆O₂Si₄: C, 63.08; H, 11.65. Found: C, 63.15; H, 11.71%.

(*Z*)-4-(Trifluoromethyl)benzyl 3-[tris(trimethylsilyl)silyl]propenoate (3f). (Yield 78%) ($R_{\rm f} = 0.55$ (hexane–ether = 50 : 1)): Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 0.16 (s, 27H), 5.19 (s, 2H), 6.65 (d, 1H, J = 13.7 Hz), 6.84 (d, 2H, J = 13.7 Hz), 7.49 (d, 1H, J = 7.9 Hz), 7.61 (d, 1H, J = 7.9 Hz). ¹³C NMR (100.6 MHz, CDCl₃) δ 1.37 (–SiCH₃), 64.91 (Ar–CH₂–), 124.13 (q, CF₃, $J_{\rm C-F} = 272.6$ Hz), 125.50 (q, $J_{\rm C-F} = 3.8$ Hz), 128.40, 130.33 (q, $J_{\rm C-F} = 32.8$ Hz), 133.80 (–SiCH=CH–C(O)–), 140.47, 150.90 (–SiCH=CH–C(O)–), 166.15 (–COO–); IR (neat) 2950, 2894, 1723, 1623, 1580, 1326, 1244, 1167, 1132, 1068, 838 cm⁻¹. MS (EI) *m/z* 476 (M⁺); exact Mass M⁺ 476.1672 (Calcd for C₂₀H₃₅F₃O₂Si₄, 476.1666).

(*Z*)-*tert*-Butyl 3-[tris(trimethylsilyl)silyl]propenoate (3h). (Yield 91%) ($R_{\rm f} = 0.65$, hexane): Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 0.17 (s, 27H), 1.46 (s, 9H), 6.49 (d, 1H, J = 13.4 Hz), 6.66 (d, 1H, J = 13.4 Hz); ¹³C NMR (100.6 MHz, CDCl₃) δ 1.4 (–SiCH₃), 28.3 (–C(CH₃)₃), 79.7 (-*C*(CH₃)₃), 136.0 (Si-*C*H=CH-C(O)-), 147.8 (Si-CH=*C*H-C(O)-), 166.0 (-*C*OO-); IR (neat) 2978, 2948, 2894, 1708, 1365, 1243, 1229, 1154, 836, 687, 620 cm⁻¹. MS (EI) *m*/*z* 374 (M⁺); exact mass M⁺ 374.1935 (calcd for C₁₆H₃₈O₂Si₄; 374.1949). Anal. Calcd for C₁₆H₃₈O₂Si₄: C, 51.27; H, 10.22. Found: C, 51.20; H, 10.32%.

(Z)-2-Hydroxyethyl 3-[tris(trimethylsilyl)silyl]propenoate (3g). (Yield 75%) ($R_f = 0.2$, hexane–ether = 2 : 1): Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 0.17 (s, 27H), 3.83 (m, 2H), 4.24 (m, 2H), 6.63 (d, 1H, J = 13.7 Hz), 6.82 (d, 1H, J =13.7 Hz); ¹³C NMR (100.6 MHz, CDCl₃) δ 1.4 (–Si*C*H₃), 61.6, 65.9, 133.9 (Si–CH=CH–C(O)–), 150.5 (Si–CH=*C*H–C(O)–), 167.0 (–*C*OO–); IR (neat) 3336, 2949, 2894, 1720, 1244, 1204, 1175, 836, 687, 621 cm⁻¹. MS (FAB) *m*/*z* 363 ((M + H)⁺); exact mass (M + H)⁺ 363.1658 (calcd for C₁₄H₃₅O₃Si₄, 363.1663).

(*Z*)-3-[Tris(trimethylsilyl)silyl]acrylonitrile (3k). (Yield 85%) ($R_{\rm f} = 0.1$, hexane–ether = 50 : 1): Colorless wax; ¹H NMR (400 MHz, CDCl₃) δ 0.26 (s, 27H), 6.09 (d, 1H, *J* = 15.1 Hz), 6.94 (d, 1H, *J* = 15.1 Hz). ¹³C NMR (100.6 MHz, CDCl₃) δ 1.19 (-SiCH₃), 113.71 (-CN), 119.25 (-SiCH=CH–CN), 155.77 (-SiCH=CH–CN); IR (neat) 2951, 2895, 2214, 1400, 1246, 836, 721, 689, 622 cm⁻¹; MS (EI) *m*/*z* 299 (M⁺); exact mass M⁺ 299.1376 (calcd for C₁₂H₂₉NSi₄, 299.1377).

NMR spectra of (Z)-2-phenyl-1-[tris(trimethylsilyl)silyl]ethene (31) were in accord with the reported data.²⁹

(*Z*)-2-(4-Trifluoromethyl)phenyl-1-[tris(trimethylsilyl)silyl]ethene (3m). (Yield 83%) ($R_{\rm f} = 0.7$, hexane): Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 0.14 (s, 27H), 6.07 (d, 1H, *J* = 14.6 Hz), 7.42 (d, 1H, *J* = 14.6 Hz), 7.45 (d, 2H, *J* = 8.2 Hz), 7.57 (d, 2H, *J* = 8.2 Hz); ¹³C NMR (100.6 MHz, CDCl₃) δ 1.3 (-SiCH₃), 124.3 (q, $J_{\rm C-F} = 271.6$ Hz), 125.3 (q, $J_{\rm C-F} = 3.8$ Hz), 128.1 (Si–CH=CH–), 128.3, 129.2 (q, $J_{\rm C-F} = 32.8$ Hz), 144.2, 144.9 (Si–CH=CH–); ¹⁹F NMR (376.3 MHz, CDCl₃) δ –67.9; IR (neat) 2951, 2895, 1618, 1327, 1246, 1167, 1130, 1109, 1167, 836, 688, 623 cm⁻¹. MS (EI) *m*/*z* 418 (M⁺); exact mass M⁺ 418.1623 (calcd for C₁₈H₃₃F₃Si₄, 418.1611).

(*Z*)-2-(4-Fluorophenyl)-1-[tris(trimethylsilyl)silyl]ethene (3n). (Yield 77%) ($R_{\rm f} = 0.7$, hexane): Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 0.13 (s, 27H), 5.88 (d, 1H, J = 14.6 Hz), 7.00 (m, 2H), 7.31 (m, 2H), 7.36 (d, 1H, J = 14.6 Hz); ¹³C NMR (100.6 MHz, CDCl₃) δ 1.3 (-SiCH₃), 115.2 (d, $J_{\rm C-F} = 21.4$ Hz), 124.5 (Si–CH=CH–), 129.7 (d, $J_{\rm C-F} = 7.6$ Hz), 136.8 (d, $J_{\rm C-F} = 3.1$ Hz), 145.3 (Si–CH=CH–), 162.1 (d, $J_{\rm C-F} =$ 246.4 Hz); ¹⁹F NMR (376.3 MHz, CDCl₃) δ –115.3; IR (neat) 2950, 2894, 1603, 1505, 1245, 1155, 836, 746, 687, 617 cm⁻¹. MS (EI) *m*/*z* 368 (M⁺); exact mass M⁺ 368.1645 (calcd for C₁₇H₃₃FSi₄, 368.1643).

2. Si (111) surface modification

For XPS spectra measurements, single-crystal n-Si (111) wafers (resistivity of 1–5 Ω cm and thickness of 825 \pm 25 μ m), polished on one side, were used. They were cut into pieces of about 10 \times 10 mm² in area. For ATR-IR measurements, single-crystal n-Si (111) wafers, polished on both sides



Si(111) Surface.

Scheme 2

and cut into the shape of a prism with dimensions of 30 \times $10 \times 0.8 \text{ mm}^3$, were used. The Si (111) wafers were cleaned by the RCA method¹¹ [successive immersion in a mixture of 95%] H_2SO_4 and 30% H_2O_2 (4 : 1 in volume) for 15 min at 100 °C, 5% HF for 5 min at room temperature, a mixture of 25% aqueous NH₃, 30% H_2O_2 , and water (1 : 1 : 5 in volume) for 10 min at 80 °C, and a mixture of 35% HCl, 30% H_2O_2 , and water (1 : 1 : 6 in volume) for 10 min at 80 $^{\circ}$ C]. They were then etched with 5% aq. HF for 5 min and with 40% aq. NH_4F for 15 min. Pure (Milli-Q) water was used for preparation of water solutions and rinsing the Si wafer between each step. The freshly prepared Si-H surfaces were then immersed in the neat alkynes 1. In the case of 1e, the reaction was carried out in 0.4 M CH₂Cl₂ solution. The vessel was gently rotated at room temperature under room light (fluorescent lamp 40 W, Toshiba, FLR40S·W/M, 2 m from the reaction vessel) for 24-40 hours. The immersed wafers were successively rinsed with dichloromethane, sonicated in dichloromethane, and dried under vacuum.

XPS spectra were obtained with a KRATOS-AXIS-165 spectrometer, with a Mg Ka line (1253.6 eV) or a monochromated Al Ka 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. Total scan times for XPS fine scans were ca. 2 h. All modified sample wafers were sufficiently electrically conductive at room temperature so that no charging compensation was required. ATR-IR were obtained with a JASCO FT/IR-460 spectrometer equipped with a MCT detector. Light was focused onto one of the 45° bevels of the ATR plate. The sample enclosure was purged with nitrogen gas. Background spectra were obtained using a freshly prepared oxidized silicon surface (by 98% H₂SO₄ + 30% H₂O₂). All measured spectra were processed by a linear baseline correction and no other correction was applied.

Contact angles of water were measured using a microscope equipped with a digital camera at ambient temperature and humidity. A drop of water ($\sim 1 \mu L$) was put on the surface using a microsyringe. Five measurements were made at different spots for each surface.

Acknowledgements

We are grateful to Professor K. Kakiuchi and Mr Y. Okajima (Nara Institute of Science and Technology) for measurement of XPS spectra. We thank Dr A. Imanishi (Osaka University) for useful advice on the surface analysis.

References

- 1 (a) J. M. Buriak, Chem. Rev., 2002, 102, 1271; (b) D. D. Wayner and R. A. Wolkow, J. Chem. Soc., Perkin Trans. 2, 2002, 23.
- 2 (a) A. Bansal and N. S. Lewis, J. Phys. Chem. B, 1998, 102, 1067;
 (b) K. Nakato, S. Takabayashi, A. Imanishi, K. Murakoshi and Y. Nakato, Sol. Energy Mater. Sol. Cells, 2004, 83, 323; (c)
 S. Takabayashi, R. Nakamura and Y. Nakato, J. Photochem. Photobiol., A, 2004, 166, 107.
- 3 (a) T. Strother, W. Cai, X. Zhao, R. Hamers and L. M. Smith, J. Am. Chem. Soc., 2000, **122**, 1205; (b) L. C. P. M. de Smet, G. A. Stork, G. H. F. Hurenkamp, Q.-Y. Sun, H. Topal, P. J. E. Vronen, A. B. Sieval, A. Wright, G. M. Visser, H. Zuihof and E. J. R. Sudhölter, J. Am. Chem. Soc., 2003, **125**, 13916; (c) T. L. Lasseter, B. Clare, N. L. Abbott and R. J. Hamers, J. Am. Chem. Soc., 2004, **126**, 10220.
- 4 (a) M. R. Linford, P. Fenter, P. M. Eisenberger and C. E. D. Chidsey, J. Am. Chem. Soc., 1995, 117, 3145; (b)
 A. B. Sieval, V. Vleeming, H. Zuihof and E. J. R. Sudhölter, Langmuir, 1999, 15, 8288.
- 5 (a) R. L. Cicero, M. R. Linford and C. E. D. Chidsey, Langmuir, 2000, 16, 5688; (b) M. P. Stewart and J. M. Buriak, J. Am. Chem. Soc., 2001, 123, 7821; (c) Q.-Y. Sun, L. C. P. M. de Smet, B. van Lagen, A. Wright, H. Zuilhof and E. J. R. Sudhölter, Angew. Chem., Int. Ed., 2004, 43, 1352; (d) Q. Y. Sun, L. C. P. M. de Smet, B. van Lagen, M. Giesbers, P. C. Thüne, J. van Engelenburg, F. A. de Wolf, H. Zuilhof and E. J. R. Sudhölter, J. Am. Chem. Soc., 2005, 127, 2514.
- 6 (a) L. J. Webb and N. S. Lewis, J. Phys. Chem. B, 2003, 107, 5404; (b) N. Y. Kim and P. E. Laibinis, J. Am. Chem. Soc., 1999, 121, 7162.
- 7 Y. Liu, S. Yamazaki and S. Yamabe, J. Org. Chem., 2005, 70, 556.
 8 J. M. Buriak, M. P. Stewart, T. W. Geders, M. J. Allen, H. C. Choi, J. Smith, D. Raftery and L. T. Canham, J. Am. Chem. Soc., 1999, 121, 11491.
- 9 (a) C. Chatgilialoglu and M. Newcomb, Adv. Organomet. Chem., 1999, 44, 67; (b) C. Chatgilialoglu, Chem. Rev., 1995, 95, 1229.
- 10 Bond dissociation energies were calculated by B3LYP/6-31G*//HF/ STO-3G* according to the following equation:

 $D(\text{Si-H}) = H^{298}(\text{Si'}) + H^{298}(\text{H'}) - H^{298}(\text{Si-H})$

 $H^{298} = E(B3LYP/6-31G^*//HF/STO3G^*) + H(thermal correction to enthalpy)$

The calculation method B3LYP/6-31G*//HF/STO-3G* was selected due to the large size of Si₆₂H₅₆, Si (111) model. The bond energy of **2** calculated by B3LYP/6-31G* was 81 kcal mol⁻¹. The STO-3G*-optimized structures of Si₆₂H₅₆ and 'Si₆₂H₅₅ are shown in Fig. S5–6 in the ESI⁺.

- 11 W. Kern and D. A. Puotinen, RCA Rev., 1970, 31, 187.
- 12 G. S. Higashi, Y. J. Chabal, G. W. Trucks and K. Raghavachari, *Appl. Phys. Lett.*, 1990, 56, 656.
- 13 In the case of 1e, the reaction was carried out in 0.4 M CH_2Cl_2 solution.
- 14 For precedent for functionalized silicon surfaces by thermal reaction and transformation, see, (a) A. B. Sieval, A. L. Demirel, J. W. M. Nissink, M. R. Linford, J. H. van der Maas, W. H. de Jeu, H. Zuilhof and E. J. R. Sudhölter, *Langmuir*, 1998, 14, 1759; (b) H. Zuilhof and E. J. R. Sudhölter, *Adv. Mater.*, 2000, 12, 1457.
- 15 The Si 2p1/2 and Si 2p3/2 peaks were not resolved.
- 16 (a) K. Siegbahn, C. Nordling, C. Jahansson, J. Hedman, P. F. Heden, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne and Y. Baer, "ESCA: Applied to Free Molecules, American Elsevier, North-Holland, 1969; (b) J. Zhang, C. Q. Cui, T. B. Lim, E.-T. Kang, K. G. Neoh, S. L. Lim and K. L. Tan, Chem. Mater., 1999, 11, 1061; (c) T. Strother, W. Cai, X. Zhao, R. Hamers and L. M. Smith, J. Am. Chem. Soc., 2000, 122, 1205.
- 17 F. J. Himpsel, F. R. McFeely, A. Taleb-Ibrahimi and J. A. Yarmoff, *Phys. Rev. B*, 1988, **38**, 6084.
- 18 M. P. Seah and W. A. Dench, Surf. Interface Anal., 1979, 1, 2.
- 19 P. J. Cumpson, Surf. Interface Anal., 2001, 31, 23.

20 Coverage ratio was calculated according to the following equations as an example for a CF_3 -functionalized sample (Scheme 2).

Coverage ratio =
$$\left(\frac{I_{F1s}}{3RSF_{F1s}}\right) / \left(\frac{I_{Si2p} \cdot \text{Intensity ratio}_{Si(111) \text{ surface}}}{AF_{ml} \cdot RSF_{Si2p}}\right)$$

 $AF_{ml}(Attenuation factor_{monolayer}) = e^{-d_{ml}/(\lambda_{ml} \cdot \cos \theta)}$

Intensity ratio_{Si(111)} surface
$$= \frac{e^{-d_{ml}/(\lambda_{ml} \cdot \cos \theta)} \cdot \int_{0}^{d_{111}} e^{-z/(\lambda_{Si} \cdot \cos \theta)} d(z)}{e^{-d_{ml}/(\lambda_{ml} \cdot \cos \theta)} \cdot \int_{0}^{\infty} e^{-z/(\lambda_{Si} \cdot \cos \theta)} d(z)}$$
$$= 1 - e^{-d_{111}/(\lambda_{Si} \cdot \cos \theta)}$$

Average layer spacing $d'_{111} = 2d_{111} = 1.568 \text{ Å}^{17}$ was used. Relative sensitivity factors (RSF_{F1s} = 1.000, RSF_{N1s} = 0.505, RSF_{Si2p} = 0.371 for Mg K α X-rays; RSF_{N1s} = 0.477, RSF_{Si2p} = 0.328 for monochromated Al K α X-rays) in KRATOS-AXIS-165 data library and the inelastic mean free path (IMFP) λ_{Si} (21.88 Å for Si photoelectrons of kinetic energy = 1154 eV for Mg K α X-rays; 25.0 Å for kinetic energy = 1387 eV for monochromated Al K α X-rays) were used.¹⁸ θ represents the takeoff angle in XPS measurement. d_{ml} was calculated by PM3 calculations of distances of monolayers using model compounds (for example, (Me₃Si)₃Si-CH=CH-C₆H₄-*p*-CF₃). IMFP of organic monolayer was calculated according to the literature.¹⁹.

- 21 In a few cases, low coverage ratios (20–25%) at 40 h were obtained both under light and in the dark. We believe the low coverage may arise from contamination at some stage, including possibly the etching process.
- 22 T. Okubo, H. Tsuchiya, M. Sadakata, T. Yasuda and K. Tanaka, *Appl. Surf. Chem.*, 2001, **171**, 252.
- 23 The silicon oxidation was estimated using the following equation by XPS. Peak area of SiOx/total peak area of Si 2p ratios (χ_{SiOx}) are 0.014–0.038 for **4b–d**, **4f**, **4k**, and **4m–n** and the equivalent fractional monolayer coverage (*Equiv.*_{ml}) of SiO_x were estimated as 0.20–0.62.²⁴ *Equiv.*_{ml} = χ_{SiOx} /Intensity ratio_{Si(111)} surface²⁰.
- 24 L. J. Webb and N. S. Lewis, J. Phys. Chem. B, 2003, 107, 5404.
- 25 (a) A. B. Zaborovskiy, D. S. Lutsyk, R. E. Prystansky, V. I. Kopylets, V. I. Timokhin and C. Chatgilialoglu, J. Organomet. Chem., 2004, 689, 2912; (b) C. Chatgilialoglu, C. Ferreri and T. Gimisi, Tris(timethylsilyl)silane in Organic Synthesis, in The Chemistry of Organosilicon Compounds, ed. S. Rappoport and Y. Apeloig, Wiley, New York, 1998, vol. 2, p. 1539.
- 26 L. C. P. M. de Smet, H. Zuilhöf, E. J. R. Sudhölter, L. H. Lie, A. Houlton and B. R. Horrocks, J. Phys. Chem. B, 2005, 109, 12020.
- 27 R. Boukherroub, S. Morin, F. Bensebaa and D. D. Wayner, Langmuir, 1999, 15, 3831.
- 28 M. E. Jung and K. R. Buszek, J. Am. Chem. Soc., 1988, 110, 3965.
- 29 B. Kopping, C. Chatgilialoglu, M. Zehnder and B. Giese, J. Org. Chem., 1992, 57, 3994.