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

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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 ($\equiv$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%.

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

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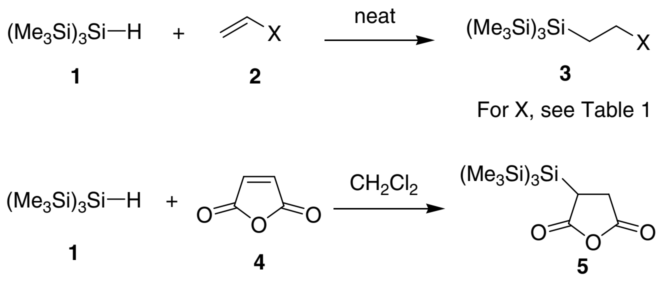
spectroscopy (IR) [6,9] and X-ray photoelectron spectroscopy (XPS) [5,10] characterization are most often used to estimate the monolayer coverage of modified surfaces. However, the accuracy of XPS analysis in estimation of coverage of an organic monolayer is usually decreased by surface contaminated 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

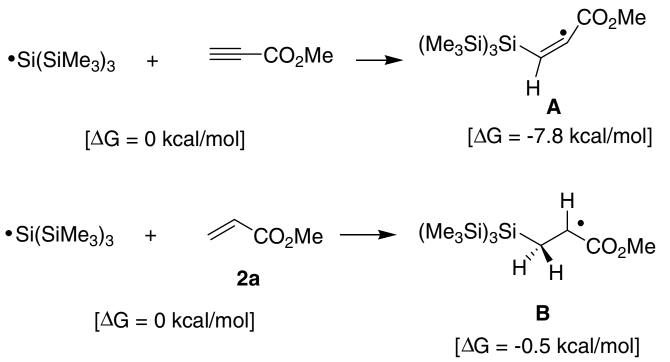
We have reported that a hydrogen-terminated Si(1 1 1) surface was easily modified by activated alkynes such as propiolate esters and propionitrile. This surface modification was directed by model reactions of activated alkynes and tris(trimethylsilyl)silane (**1**), a molecular model of the Si–H group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