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Preparation of amino-terminated monolayers via hydrolysis of phthalimide anchored to Si(1 1 1)

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Abstract

Phthalimide monolayers were prepared on silicon (1 1 1) by the reaction of hydrogen–terminated silicon surfaces with vinylphthalimide. The hydrolysis reaction of phthalimide on silicon surfaces was performed in a methylamine solution to prepare amino-terminated monolayers. A series of reactions to prepare amino-terminated monolayers was investigated with attenuated total reflectance infrared spectroscopy and atomic force microscopy. This work provides a simple method to prepare amino-terminated organic monolayers act as anchor layers to immobilize functional molecules such as dyes, DNA and proteins.

Keywords: Atomic force microscopy; Silicon–carbon bond; Infrared absorption spectroscopy; Surface chemical reaction; Silicon; Organo-functionalization of surfaces; Attenuated total reflectance infrared spectroscopy

1. Introduction

Recently, organic monolayers anchored to silicon surfaces via silicon–carbon (Si–C) covalent bonds have attracted a growing interest as one of the promising ways to assemble organic molecules. Organic monolayers anchored to silicon surfaces covalently have been performed via the reaction of hydrogen–terminated silicon (H–Si) surfaces with alkenes [1–5], aryldiazonium ions [6], or Grignard reagents [7]. Allongue et al. demonstrated the preparation of bromophenyl anchored to Si(1 1 1) with well-defined interfaces and achieved the visualization of molecules in atomic resolution [6]. For applications, alkyl monolayers are available as resist films for lithography because of the stability under a variety of conditions [1,2]. The surface modification of alkyl monolayers on Si(1 1 1) on the nanometer scale was demonstrated using an atomic force microscope (AFM) [8]. As the following step, the immobilization of a variety of molecules such as organic dyes, DNA, and proteins onto patterned surfaces is expected. Milder reaction is desirable for the modification of silicon surfaces with functional molecules to avoid the decomposition. One of the promising ways is to use amino-terminated monolayers as anchor layers to immobilize functional molecules [9–13]. Allylamine is one of the candidates for the preparation of amino-terminated organic monolayers on silicon surfaces since it has both a terminal C=C bond and an amino group. However, it is necessary to deactivate the amino group with a protecting group [12] to avoid the undesirable reaction of the amino group of allylamine with H–Si surfaces [14,15]. In the previous work, we synthesized 1-allyl-2,2,5,5-tetramethyl-[1,2,5] azadisilolidine and prepared the monolayers on Si. Then, fluorescein isothiocyanate (FITC) was immobilized on silicon via the reaction shown in Fig. 1 [12]. In the present study, we studied more simple method to prepare amino-terminated monolayers on silicon. We used vinylphthalimide as a precursor and prepared amino-terminated organic

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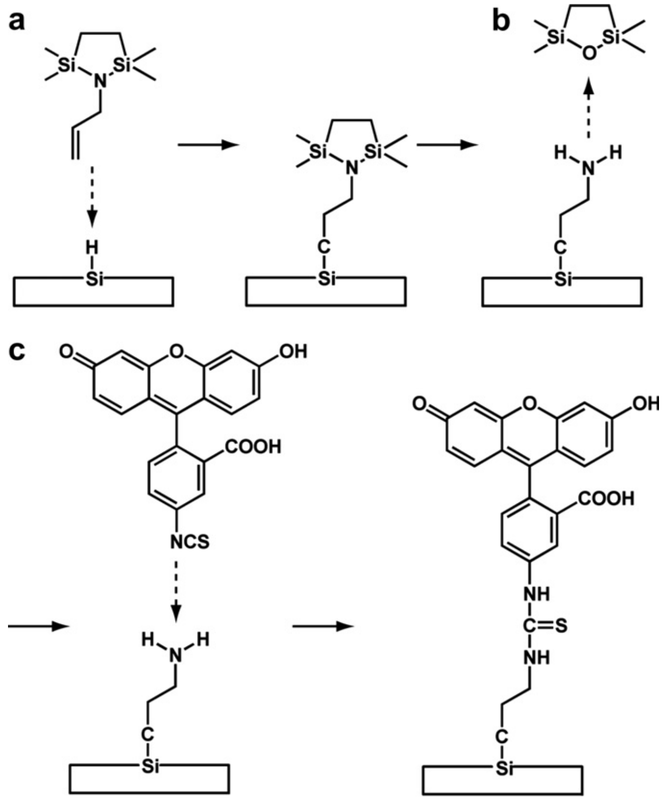

Fig. 1. Schematic view of immobilization of FITC on an aminopropyl monolayer: (a) thermal reaction between protected-allylamine and H–Si, (b) hydrolysis of the protecting group in an acidic solution, and (c) anchoring of FITC to the aminopropyl monolayer.

monolayers via the hydrolysis of phthalimide monolayers as shown in Fig. 2. Vinylphthalimide is commercially available and stable in air. In addition, the method and yield of the hydrolysis reaction of phthalimide in the liquid phase are well known [16,17]. Characterization of organic monolayers was performed with attenuated total reflectance infrared spectroscopy (ATR-IR) and AFM.

2. Experimental

Double-sided polished n-type Si(111) wafers (1–10 Ω cm) were cut with a dimension of 20 × 50 × 0.5 mm^3 and used as silicon ATR substrates. The short sides of the silicon substrate were polished to give a trapezoidal shape with 45° bevels.

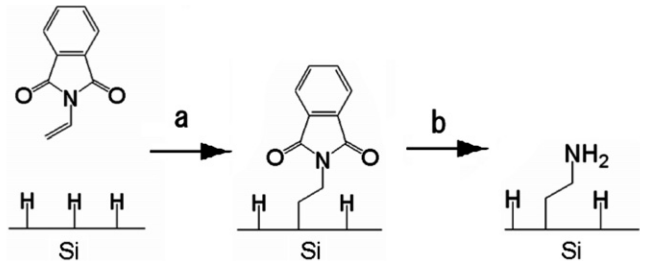

Fig. 2. Preparation of an amino-terminated monolayer through the hydrolysis of phthalimide: (a) reaction between vinylphthalimide and H–Si to form a phthalimide monolayer and (b) hydrolysis of phthalimide to form an amino-terminated monolayer.

Hydrogen termination of Si(111) surfaces was carried out according to the literature by Wade and Chidsey [18]. The H–Si(111) substrates were transferred into a vinylphthalimide/mesitylene solution with a concentration of 1.17 g/30 ml, which was deoxygenated by argon bubbling for at least 1 h prior to the reaction. The solution was heated at 423 K for 3 h under the continuous argon bubbling and then it was cooled down to room temperature. The substrates were taken out of the solution and rinsed with petroleum ether, ethanol and dichloromethane.

The hydrolysis of phthalimide anchored to Si surfaces was performed by immersing the substrates in a 48 mM $NaBH_4$ solution [16] or a toluene solution of methylamine (33 vol%) [17] at room temperature. Subsequently, amino-terminated monolayers prepared were rinsed in triethylamine.

ATR-IR spectra were obtained with a Fourier transform infrared spectrometer (JASCO, FT/IR-670 Plus) equipped with an ATR unit (SPECAC, P/N11.000). The sample chamber was kept under vacuum (ca. 10 Pa) with an oil rotary pump with a liquid nitrogen trap. The spectral resolution was 1 cm^{-1}. Silicon (111) surfaces oxidized chemically in 3:1 H_2SO_4:30% H_2O_2, by volume, were used as references.

Tapping-mode AFM measurements were performed using an AFM (Jeol, JSPM-1300) under ambient conditions with Si_3N_4 cantilevers (MikroMasch, Force constant 4.5 N/m, Resonant frequency 150 kHz).

3. Results and discussion

Fig. 3a and b shows ATR-IR spectra of a phthalimide monolayer around 3000 cm^{-1} and 1700 cm^{-1}, respectively. Peaks corresponding to C–H stretching vibrations of methylene were observed around 2800–3000 cm^{-1}. The C=O stretch characteristic of the phthalimide monolayer was clearly observed at 1715 cm^{-1} and 1775 cm^{-1}. Fig. 4 shows ATR-IR spectra of a H–Si surface and phthalimide monolayer in the Si–H region. In the spectrum of the H–Si surface, a band assigned to a silicon monohydride stretching mode appeared at 2083.9 cm^{-1}, close to the peak position (2083.7 cm^{-1}) of the silicon monohydride stretch on an ideally hydrogen–terminated Si(111) surface [19]. The full width at half maximum value of this band (1.51 cm^{-1}) is broader than the value (0.95 cm^{-1}) reported by Higashi et al. with a spectral resolution of 0.25 cm^{-1} [19]. The insufficient spectral resolution (1 cm^{-1}) of our measurement might be responsible for broadening the width of the band. On the other hand, significant bands for silicon dihydride (2111 cm^{-1}) and trihydride (2137 cm^{-1}) [20] stretching did not appeared. Therefore, we concluded that the silicon (111) surface was covered with silicon monohydride. After the reaction of H–Si surfaces with vinylphthalimide, silicon monohydride characteristic completely disappeared. These