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Photochemical Preparation of Methyl-terminated Si(111) Surface Using a Grignard Reagent

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Methyl-terminated Si(111) surface was successfully fabricated using a photochemical grafting technique. This methylated surface was formed by illuminating visible light onto a hydrogen-terminated Si(111) surface that was immersed in a Grignard–tetrahydrofuran solution. It had an oxide-inhibiting property and atomically flat surface. In addition, the water contact angle improved with grafting parameters such as illumination time and light intensity and went as high as (89.0 ± 0.80)°. This improvement was associated with the increase in the fraction of the silicon surface grafted with methyl groups.

Organic molecules on semiconductor surfaces[1–16] have promising applications in the construction of future electronic devices. The establishment of covalent bonding between the silicon surface and a carbon atom of the organic compound (Si–C bond) is crucial in this system. However, it is physically impossible for some organic molecules (e.g., vinylferrocene) to have a one-on-one attachment with each topmost atom of silicon due to the mismatch between their size and the spacing of the Si atoms on the surface. The absence of these attachments could lead to partial oxidation of the silicon substrate surface, which in turn, introduces surface states that are detrimental to the intended usage of the grafted surface. The filling-in of small and inert molecules between the grafted organic molecules is a strategy to minimize this oxidation. The small size and stability of methyl group on a silicon surface make it a very promising material for this purpose.

Methyl ($-CH_3$) is the simplest among the alkyl groups (C_nH_{2n+1}). It has the capability to completely cover the silicon surface[16–19] because its van der Waals radius is small enough to fit in between the Si atom spacing in the Si(111) surface. Furthermore, the bonding of carbon with the silicon surface has superior stability compared to the bonding of other elements that may also fit in between the Si(111) spacing (e.g., hydrogen and halogens). To note, halogen-terminated silicon surfaces have high chemical reactivity that make them unsuitable for stabilizing the silicon surface.

Conventional techniques of producing a methyl-terminated Si(111) surface include (1) the chlorination–alkylation method[7,8,14,16,20–22] and (2) electrochemical method.[6,9,10,17] The chlorination–alkylation method uses a Cl-terminated Si(111) as an intermediate state between the H-terminated and the CH_3-terminated states. Chlorination is done either by using PCl_5 in chlorobenzene at an elevated temperature[7,8,14,21,22] or by using Cl_2 gas diluted in argon.[16,20] The electrochemical preparation uses anodic potential to trigger the methyl-grafting process.[6,9,10,17] However, for advanced applications that would require design patterns to create circuits on the Si(111) surface, a light-based technique is advantageous because it can be adaptable with photopatterning technique. In this technique, the designing of organic-molecule-based spatial patterns on the silicon surface can be done using a simple optical apparatus. This letter will report on a photochemical grafting process for methyl-termination of Si(111) surface that employs this advantage. As opposed to the chlorination–alkylation process, photochemical preparation uses a hydrogen-terminated surface directly as the grafting substrate instead of using a chlorine-terminated surface. This avoids the use of either a hazardous thermal chlorination process or a gas-based chlorination process in an inert atmosphere. In contrast to the electrochemical preparation, the photochemical preparation uses no external power supply. Thus, photochemical grafting can avoid some complications such as ohmic contact with the Si substrate or electrical connection from an external power supply in a hazardous liquid bath. The creation of an ohmic contact also introduces fixtures on the silicon surface that are permanent or difficult to remove.

A single-sided mirror-polished phosphorus-doped n-type Si(111) wafer with a resistivity of around 1–10 Ω cm was used as the substrate in this study. The photochemical preparation was done by illuminating visible light onto the H-terminated Si(111) surface immersed in a 12% (ca. $1\,\mathrm{mol\,L^{-1}}$) Grignard–tetrahydrofuran (CH_3MgBr–THF) solution, purchased from Kanto Chemicals Co., Inc., at room temperature. The method for preparing the hydrogen-terminated Si(111) surface is presented elsewhere.[23] A xenon lamp (Asahi Spectra Co., Ltd., Max 1000) was used as the visible light source with controllable light intensity. The spectrum of light emitted from the optical fiber is shown in the work of Sano et al.[24] The solution was placed inside an optical cell and was purged with a stream of nitrogen gas prior to and during the photochemical grafting process. Because the Grignard reagent is water-sensitive, the grafting process was done inside a moisture-controlled chamber and all the materials used were ensured to be dry (Caution: CH_3MgBr without solvents burns spontaneously and reacts vigorously with acids, alcohol, and amines). In addition, because THF is volatile, a reservoir bottle filled with THF was attached along with the nitrogen gas line to compensate for the THF that was lost during the bubbling process. Importantly, to ensure the safe disposal of the waste Grignard–THF solution, this waste was made to react with acetone, and the pH of the by-products was monitored and ensured to be near neutral before placing it in a chemical waste container.

The photochemically treated sample was subjected to postcleaning procedures. It was rinsed with THF, followed by cleaning in an ultrasonic bath using ethanol and ultrapure water for 10 min each. After each step, the sample was dried using streams of nitrogen gas. The static water contact angle of the samples was measured using a water contact angle meter (Kyowa Interface Science Co., Ltd., DM 500). Water droplets 1.8 µL in volume were used for the measurements. Meanwhile, X-ray photoelectron spectroscopy was performed using an XPS system (Kratos Analytical Ltd., ESCA-3400). The X-ray source

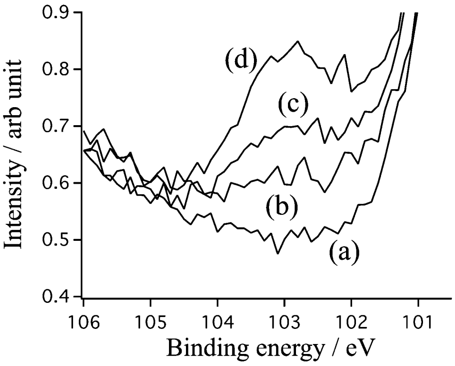


Figure 1. Si 2p spectra (focus on the region associated with silicon oxide) of the different samples. (a) H-Terminated Si(111) sample irradiated with visible light for 2 h in the CH_3MgBr–THF solution, (b) H-terminated Si(111) sample, (c) H-terminated Si(111) sample that was immersed in the Grignard–THF solution for 2 h in the dark, and (d) H-terminated Si(111) sample irradiated with visible light for 2 h in THF without Grignard reagent.

was Mg Kα operated at an acceleration voltage of 10 kV and an emission current of 10 mA. The C 1s and Si 2p regions were scanned with a step size of 0.1 eV for 298.5 ms. These scans were repeated 10 times. Surface topographic images were acquired using an atomic force microscope (Asylum Research, MFP-3D-SA AFM) with an aluminum back-coated Si probe (SII NanoTechnology Inc., SI-DF20) in AC mode.

The sample that underwent the photochemical preparation in Grignard–THF solution exhibited an oxide-inhibiting property. Figure 1 shows that this sample (Figure 1a) had no distinct peak corresponding to silicon oxide, unlike the other samples that are presented (Figures 1b–1d). Note that Figure 1 shows only the portion of the Si 2p spectra associated with silicon oxide, while the other portions of the Si 2p spectra are not shown in the graph. In addition, the peak values of the Si 2p spectra (at around 99.4 eV) were set to equal magnitudes to normalize them for analysis. The hydrogen-terminated Si(111) sample (Figure 1b) exhibited peaks corresponding to silicon oxide. The oxide might have developed during the postcleaning treatment. Likewise, the sample that was immersed in the Grignard–THF solution for 2 h in the dark (Figure 1c) also exhibited peaks corresponding to silicon oxide, but its level was higher compared with the hydrogen-terminated Si(111) sample shown in Figure 1b. In this case, the absence of light would retard the methyl grafting that could protect the surface from oxidation. The immersion of the sample for 2 h in the Grignard–THF solution and the postcleaning procedure promoted oxidation that destroyed the hydrogenated surface. The sample irradiated with visible light for 2 h in THF without the Grignard reagent (Figure 1d) showed the largest fraction of silicon oxide. In this case, there was no source of methyl that could be grafted on the silicon surface. Instead of grafting, the presence of light triggered extensive oxidation due to the photogenerated holes on the silicon surface. In summary, the methyl-termination certainly protected the silicon surface from oxidation more powerfully than the hydrogen-termination.

The oxide-inhibiting property of the sample that underwent the photochemical treatment is attributed to attachment of methyl onto the silicon surface via the formation of Si–C bonds. This sample (Figure 2) had a C 1s spectrum that showed peak asymmetry (or "shoulder") toward higher binding energy. The peak asymmetry can be due to contaminations[6] (e.g., THF and ethanol) that adhered onto the surface and were not completely removed during the postcleaning procedure. The holes that were generated on the silicon surface during the illumination of the n-type silicon triggered the oxidative decomposition of CH_3MgBr that in turn liberated the methyl radicals that are needed in the successive steps of the grafting process. The following is our proposed photochemical reaction scheme based on the reaction scheme proposed by Fellah et al.:[5,6]

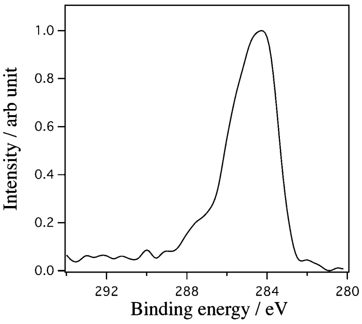


Figure 2. C 1s spectra of the H-terminated Si(111) sample irradiated with visible light for 2 h in the CH_3MgBr–THF solution.

$$CH_3MgBr + p^+ \rightarrow CH_3\bullet + MgBr^+ \tag{1}$$

$$\equiv Si{-}H + CH_3\bullet \rightarrow \equiv Si\bullet + CH_4 \tag{2}$$

$$\equiv Si\bullet + CH_3\bullet \rightarrow \equiv Si{-}CH_3 \tag{3}$$

The methyl-terminated Si(111) possesses an atomically flat surface. Figure 3 shows an AFM topographical image of this sample. The image shows a stair-like structure with monoatomic steps. This stair-like structure was also a feature of the hydrogen-terminated sample resulting from the HF and NH_4F treatments.[23] Figure 3 demonstrates that the structure of the hydrogen-terminated Si(111) surface has been preserved during the photochemical preparation. This preservation would be possible if the grafted molecules form a film with an atomically flat structure. The covalently bonded carbon is oriented perpendicular to the Si(111) surface[14] with a bond length of 1.85 Å.[25] This orientation suggests that a methyl layer can formed as a film on Si(111) surface with an atomically flat structure.

Figure 4a shows the water contact angles of the sample as a function of the grafting time (at a light intensity of 35 mW cm^{-2}). The sample with zero grafting time was identical to that of the H-terminated Si(111) presented in Figure 1b. Its water contact angle was 78.8°, which is lower than the water contact angle of the H-terminated Si(111) that does not undergo the postcleaning treatment, i.e., 85.4°. This drop can be attributed to the destruction of hydrogenated surface during the postcleaning procedure; this hypothesis is in agreement with the result observed in Figure 1b. In another aspect of the graph, the grafting process progresses with time. At a shorter grafting time (1 h), only a few methyl groups were grafted onto the silicon surface. The attached hydrogen atoms that were not substituted by methyl were destroyed either in the Grignard–THF solution or by the postcleaning treatment, and thus, the

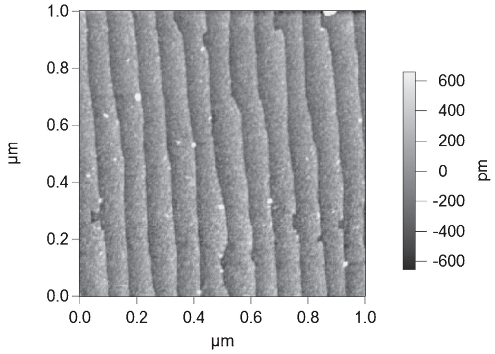
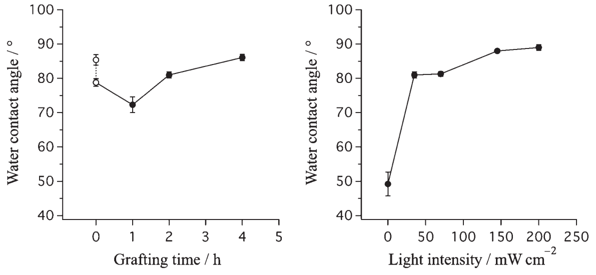


Figure 3. AFM topographical image of a CH_3-terminated Si(111).



(a)

(b)

Figure 4. Graph of water contact angle with (a) grafting time at 35 mW cm^{-2} light intensity and (b) light intensity for 2 h. The open circle in Figure 4a denotes the value of the water contact angle of a hydrogen-terminated Si(111).

water contact angle was lower than that of the H-terminated samples. As grafting time progressed, the silicon surface became more methylated, and thus, the water contact angle increased.

Figure 4b shows the water contact angles of the sample as a function of the light intensity grafted for 2 h. The increase in the water contact angle with the light intensity (Figure 4b) was attributed to the faster grafting process. The sample with zero light intensity was the same as that of the sample presented in Figure 1c, i.e., the sample that was immersed in the Grignard–THF solution for 2 h in the dark. Its water contact angle was 49.2°. This low value was expected because the sample underwent soaking for 2 h in the Grignard–THF solution without developing CH_3 passivation. The hydrogenated surface oxidized during this process. This argument is in agreement with the results shown in Figure 1c. In addition, the highest water contact angle that we achieved was $(89.0 \pm 0.80)°$. This value was obtained from the sample that was illuminated for 2 h at a light intensity of 200 mW cm^{-2}. The value was higher than the previously reported value for methyl-terminated silicon, i.e., $(78 \pm 2)°$.[20]

This report presented a new method for fabricating methyl-terminated Si(111) surface. This method showed the possibility of utilizing photogenerated holes to trigger the methyl grafting process instead of using positive charges from anodic potential[6] or electrons captured (or positive charges generated) from the reduction of alkyl halides.[5] In addition, this technique offers a safer and simpler procedure of producing methyl-terminated Si(111) compared with the conventional methods.

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