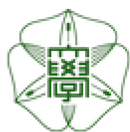
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Photoanodic Formation of an Organic Monolayer on a Hydrogen-terminated Si(111) Surface via Si-C Covalent Bond Using a Grignard Reagent and its Application for One-step Monolayer-patterning

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(Received:)

Abstract

Alkyl monolayer (octadecyl) was formed on a hydrogen-terminated Si(111) (H-Si(111)) electrode via Si-C covalent bond by photoanodic reaction with $C_{18}H_{37}MgCl$ in THF solution. The formation of the organic monolayer was confirmed by attenuated total reflection (ATR) FT-IR spectroscopy. This process was applied to a one-step patterning of an organic monolayer on a H-Si(111) by illuminating the H-Si(111) electrode through photomask in a $C_{18}H_{37}MgCl$/THF solution at positive potential. The formation of the pattern reflecting the shape of the photomask was confirmed by SEM observations.

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Introduction

Construction of ordered molecular layers on silicon surface and their patterning techniques at nano ~ micron dimension have received recent attention for potential use of a wide range of applications, such as molecular electronic and bio-sensing semiconductor devices.[1-5] The formation of a well-defined pattern of organic molecules requires the construction of a highly ordered organic layer on the silicon surface. Organic monolayers formed on hydrogen-terminated silicon surfaces via Si-C covalent bond are one of the promising systems because a highly structural order of the monolayer is expected due to its direct Si-C bonding compared with that via the more classical Si-O-C bridging.[6, 7] It has been reported that this monolayer system shows high thermal and chemical stabilities.[1-3] There have been a number of reports on the direct preparation of organic monolayers on Si surface via Si-C linkages by wet processes such as thermally induced hydrosilylation,[8-10] hydrosilylation involving a radical initiator[3, 11] or a catalyst,[12, 13] and photochemical hydrosilylation using UV[14-17] or white light.[18, 19] Electrochemical routes, such as anodic oxidation of Grignard compounds[20-25] and cathodic reduction of diazo[26-28] and halogenoalkane[29] compounds have also been developed. Electrochemical activation of the reactants in the above reactions results in an efficient formation of reactive radicals only near the electrode surface and, therefore, the electrochemical routes are expected to provide very fast process for the organic modification process.

Several approaches based on beam lithography have been proposed for the patterning of organic monolayers formed on Si surfaces via Si-C covalent bond. In lithographic techniques, patterning process usually consists of two- or more steps. Two representative methods of the two-step processes using the hydrogen-terminated Si surface as a starting material are illustrated in Figure 1. In the upper route (Figure 1 (a)), the H-Si substrate is first illuminated by UV through a photomask to convert the illuminated region to

oxide-covered surface, followed by the monolayer modification of the hydrogen terminated region.[30, 31] In the lower route (Figure 1 (b)), the monolayer is formed first and then patterning is carried out by decomposing the monolayer under UV or electron beam irradiation through a mask.[32-34] Although these two-step methods have been used as good and reproducible patterning methods, they sometimes require much time to obtain final patterned samples and expensive equipments for beam lithography.

Here we propose a novel photoelectrochemical route for the formation of an organic monolayer on a hydrogen terminated n-type Si(111) electrode surface via Si-C covalent bond using a Grignard reagent. Octadecyl monolayer is formed on an atomically flat hydrogen terminated n-type Si(111) electrode surface by illuminating the electrode in $C_{18}H_{37}MgCl$/THF solution with Xenon lamp or Nd-YAG laser at positive potentials. The potential required for the monolayer formation in this case is less positive than that at p-type Si(111) electrode in dark. The formation of an octadecyl monolayer was confirmed by attenuated total reflection (ATR) FT-IR spectroscopy and ellipsometry. We also demonstrated that this process can be used as a one-step patterning method of an organic monolayer on a Si(111) surface based on the fact that the monolayer formation takes place only under illumination.

Experimental

Substrate preparation[7, 35]

A double-sided polished Si(111) single-crystal wafer (phosphorus or boron-doped, resistively of 1-10 Ωcm for both) was cut into 10 x 10 x 0.5 mm^2 and treated by sequential immersion in sulfuric acid and hydrogen peroxide (2:1 by volume) at 60 °C for 20 min, in a 0.5% HF aqueous solution at room temperature (RT) for 5 min, and in a freshly prepared RCA solution ($H_2O/H_2O_2/HCl$, 4:1:1 v/v) at 80 °C for 20 min. After these treatments, the sample was immersed in a 40% deaerated aqueous NH_4F solution for 5 min to obtain a

monohydride-terminated surface (H-Si(111)). The sample was then rinsed with Millipore water (18.2 MΩcm) and dried under N_2 stream. For the preparation of ATR prisms, the Si wafer was cut to be 30 x 30 x 0.5 mm^3 and the two opposite edges of the prisms were mechanically polished with 45° bevels to allow for multiple internal reflection.

Photoelectrochemical formation and patterning of an octadecyl monolayer

Preparation of an octadecyl monolayer and its patterning were performed in a closed three-electrode electrochemical cell, which was placed in Ar atmosphere (Figure 2). Pt wire and Ag wire were served as counter electrode (CE) and quasi-reference electrode (QRE), respectively. Grignard electrolyte (0.5 M $C_{18}H_{37}MgCl$/THF solution) was purchased from Aldrich and used as supplied. The Grignard solution was conductive enough to be used as an electrolyte solution without extra supporting salt. Xenon lamp (Ushio UXL-500-D, ~200 mW/cm^2) with 400 nm cut-off filter or Nd-YAG laser (532 nm, 10 Hz, ~30 mJ/ pulse /cm^2) was used as a light source. After preparation of the n-type H-Si(111) sample, an ohmic contact was made to the back side of the sample by scratching the Si surface and rubbing it with In-Ga eutectic. The H-Si(111) sample was mounted in an electrochemical cell with an O-ring seal and the exposed surface was contacted with the electrolyte solution by keeping the potential at 0 V (vs. Ag QRE) where the current does not flow. The electrode surface was then irradiated with the light and the electrode potential was scanned or stepped anodically under illumination. For the patterning of a monolayer, photomask was placed between the sample and the light source as shown in Figure 2 with the distance between the photomask and the sample as 5 mm. The photomask was a Cu grid (Oken Shoji), which is usually used as a sample support for transmission electron microscope (TEM) observations. After the photoelectrochemical treatment, the Si samples were rinsed thoroughly with THF, acetonitrile and methanol and then sonicated in methanol and in dichloromethane. They were stored in

dichloromethane and sonicated in dichloromethane again just before characterizations.

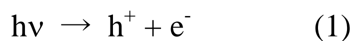
ATR FT- IR, Ellipsometry and SEM characterizations

ATR FT-IR spectra were obtained using a Bio-RAD FTS-30 spectrometer equipped with an HgCdTe (mercury cadmium telluride) detector cooled with liquid nitrogen. All the spectra were measured in p polarization with respect to a spectrum of an oxidized Si(111) surface and were recorded by integrating 256 interferrograms with a resolution of 2 cm^{-1}. Spectroscopic ellipsometry measurements were carried out by a SOPRA GESP-5 spectrometer using a 30 W Xenon lamp. The incident angle was set to 75° and the Δ and Ψ were acquired between 300 and 800 nm. SEM observations were performed using a JEOL JSM-T330A.

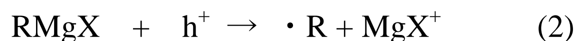
Results and Discussion

Photoelectrochemical measurements and characterization of the monolayer modified Si(111)

Figure 3 shows current voltage curves of n-type H-Si(111) electrode in a $C_{18}H_{37}MgCl$ / THF solution (a) under illumination and (b) in dark. Anodic current started to flow at 1.3 V and then increased as the electrode potential became more positive under the illumination, while almost no current flowed up to1.9 V in dark. For a comparison, a current voltage curve of a p-type H-Si(111) in the same solution in dark is shown in Figure 3 (c). The current at a given potential is higher at the n-type electrode under illumination than that at the p-type electrode in dark. The formation of organic monolayer on a hydrogen terminated p-type Si(111) by anodic oxidation of Grignard reagents have been investigated.[21-25] The anodic photocurrent observed in Figure 3 (a) should be mainly due to the electrochemical oxidation of the Grignard reagent by the photo-generated holes to form a reactive alkyl radical as shown below.



$$h\nu \rightarrow h^+ + e^- \qquad (1)$$



$$RMgX \;+\; h^+ \rightarrow \cdot R + MgX^+ \qquad (2)$$

By illuminating a semiconductor by photons, the energy of which is larger than the energy gap of the semiconductor, electron-hole pairs are formed.[36] In general, photo-generated holes in an n-type semiconductor electrode have stronger oxidation power than those in a p-type semiconductor electrode at a given potential as the Fermi level former is near the conduction band while that of the latter is near the valence band. Schematic energy diagram to describe this situation is shown in Figure 4. Thus, to obtain the same current density a more positive potential should be applied at a p-type Si electrode in dark than at the n-type Si electrode under illumination.

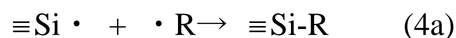
Figure 5 shows ATR FT-IR spectra of H-Si(111) surfaces in 2000 – 2200 cm^{-1} and 2800 – 3000 cm^{-1} regions (a) before and (b) after the photoelectrochemical reaction at 1.7 V for 195 s in 0.5 M $C_{18}H_{37}MgCl$/THF solution under illumination with the Xenon lamp. The total accumulated charge was 3700 $\mu C/cm^2$. Only a sharp peak corresponding to Si-H monohydride stretching was observed at 2084 cm^{-1} before the reaction (Figure 5 (a)), confirming the formation of an atomically flat H-Si(111) surface. After the photoelectrochemical reaction, the Si-H peak completely disappeared and the C-H stretching bands were detected in the region of 2850 – 2970 cm^{-1}, showing the formation of an organic layer on Si(111) surface. The total integrated intensity of the C-H stretching bands was only ca. 50% of that of the octadecyl monolayer on H-Si(111) surface prepared by thermal hydrosilylation in neat octadecene at 200 °C, which is known to have a high conformational order,[6, 7, 37] showing that the conformational order of the monolayer was not as high as that of the octadecyl monolayer on a H-Si(111) surface prepared by thermal hydrosilylation in neat octadecene at 200 °C. The peak position of the asymmetric CH_2 stretching (the main peak in Figure 5 (b)) was 2927 cm^{-1}, which was much higher than that of the thermally prepared

monolayer (2920 cm^{-1}),[7, 37] indicating the existence of conformational disorder of the alkyl chains.[38-40] The film thickness determined by spectroscopic ellipsometry was 1.30 ± 0.12 nm, which is smaller than the observed film thickness of ca. 2.1 nm of thermally prepared monolayer.[7] These results showed that the coverage of the monolayer was not very high and the monolayer was not highly ordered. XPS measurements showed no clear peak at 103.2 eV corresponding to Si^{4+},[41, 42] indicating that the oxidation of the underlying silicon surface did not take place.

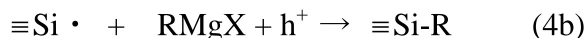
As discussed for the electrochemical formation of alkyl monolayer on a p-type H-Si(111) in dark,[21-23] the alkyl radical may abstract a hydrogen atom from the hydrogen-terminated silicon surface

$$\equiv\text{Si-H} + \cdot\text{R} \rightarrow \equiv\text{Si}\cdot + \text{RH} \qquad (3)$$

The dangling bond created at the silicon surface may then react with another alkyl radical or the Grignard to form a Si-C bond.



$$\equiv\text{Si}\cdot + \cdot\text{R} \rightarrow \equiv\text{Si-R} \qquad (4a)$$



$$\equiv\text{Si}\cdot + \text{RMgX} + h^{+} \rightarrow \equiv\text{Si-R} \qquad (4b)$$

According to the reaction steps of (1) - (4) as shown above, two elementary charges per one attached alkyl group are required. If all the hydrogen atoms of H-Si(111) surface are converted to alkyl groups, ca. 240 μC/cm^2 is needed to obtain the full coverage. The maximum coverage of this system is, however, reported to be ca. 50 % substitution of the hydrogen atoms due to the steric hindrance of octadecene molecules in the monolayer and, therefore, only ca. 120 μC/cm^2 is necessary for the saturation. The present results showed that saturated coverage was not reached even after 3700 μC/cm^2 of anodic charge, which is more than 30 times of the expected value, flowed. Thus, the reaction efficiency of this photoelectrochemical route seems to be rather low as is the case of electrochemical route in dark. Most probable reason for this low efficiency is due to the other reactions of radicals

such as dimerization of alkyl radicals and abstraction of a hydrogen atom from the solvent by alkyl and Si radicals.[21-23] We are now investigating the effect of various reaction conditions such as potential and light intensity to obtain the higher coverage and improve the efficiency.[43] It should be noted that although the reaction efficiency was low, it took less than 5 minutes to complete the reaction under the present experimental conditions because of the efficient photo-generation of holes.

Photoelectrochemical patterning of an octadecyl monolayer

Figure 6 shows an SEM image of the Si(111) surface after photoelectrochemical reaction under illumination with Nd-YAG laser through a Cu grid with periodic pattern consisting of square holes and bars. The grid pattern was transferred with clear contrast. The bright square areas were the photo-irradiated regions where the monolayer was expected to be formed and non-irradiated region should be still hydrogen-terminated. Thus, we were able to prepare the micro-pattern consisting of monolayer-covered regions and hydrogen-terminated regions on an atomically flat Si(111) surface very quickly just in one-step. In this particular case, it took less than ten minutes after preparation of H-Si(111) substrate. A careful inspection of the SEM image revealed a characteristic internal structure within the square region, which is probably due to the interference effect of the laser light by the periodic pattern of the photomask. It is expected, therefore, that diffracted and real images of a photomask can be transferred with any magnification by controlling the distance between the sample and the photomask and by placing an appropriate optical lens in the laser path.

Conclusion

Octadecyl monolayer was prepared on a H-Si(111) by photoelectrochemical anodic

oxidation of $C_{18}H_{37}MgCl$ in THF solution. The formation of octadecyl_monolayer was confirmed by ATR FT-IR spectroscopy and ellipsometry, although the coverage and conformational order of the monolayer were not high. The reaction efficiency was rather low but the reaction time was less than 5 min. A fast and direct photo-patterning of the monolayer on Si surface was presented based on the photoelectrochemical method by using a photomask. The pattern reflecting the shape of the photomask was clearly transferred, which was confirmed by SEM observations, indicating the formation of the micro-pattern consisting of the monolayer-covered and hydrogen-terminated regions. This approach is simple and convenient for fabricating microstructures of molecules derived from Grignard reagents and can be applied to various molecular-patterned microdevices.

Acknowledgments

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Figure captions

Figure 1

Conventional two-step patterning techniques using lithography to obtain a patterned monolayer on a hydrogen- terminated Si surface. Patterned monolayer can be obtained either by (a) formation of patterned hydrogen-terminated regions followed by monolayer formation at the hydrogen-terminated regions or (b) formation of monolayer followed by decomposition of the monolayer by irradiation of the surface by electron beam or UV light thorough photomask.

Figure 2

Experimental set-up for electrochemical measurement and photoelectrochemical monolayer-patterning. A Cu gird pattern, which is used as a photomask, consists of square holes (450 μm x 450 μm) and bars (50 μm in width) with 500 μm pitch. CE:counter electrode, RE: reference electrode.

Figure 3

Current-voltage relations of n-type H-Si(111) electrode (a) under illumination and (b) in dark, and (c) of p-type H-Si(111) electrode in dark in 0.5 M $C_{18}H_{37}MgCl$/THF solution. H-Si(111) electrode was first immersed in the solution at 0 V and scanned in the positive direction to 2.1 V, and then scanned back to 0 V. Scan rate: 10 mV/s. A 500 W Xenon lamp was used as a light source.

Figure 4

Schematic band diagrams for the alkyl radical generation by (a) photoelectrochemical (b) electrochemical anodic oxidation of Grignard reagent at n- and p-type Si electrodes,

respectively. CB, VB and E_F are conduction band, valence band and Fermi level of Si substrate.

Figure 5

ATR FT-IR spectra of n-type H-Si(111) surface (a) before and (b) after photoelectrochemical reaction in 0.5 M $C_{18}H_{37}MgCl$/THF solution. The electrode potential was stepped from 0 V to 1.7 V after immersing the electrode in the solution at 0 V, and held at 1.7 V for 195 s. Total accumulated charge was 3700 $\mu C/cm^2$. A 500 W Xenon lamp was used as a light source.

Figure 6

Scanning electron micrograph of the monolayer-patterned n-type H-Si(111) surface. The potential of the H-Si(111) electrode was stepped from 0 V to 2.0 V after immersing the electrode in 0.5 M $C_{18}H_{37}MgCl$/THF solution at 0 V, and held at 2.0 V for 300 s. The total accumulated charge was 9214 $\mu C/cm^2$. A Nd-YAG laser was used as a light source.

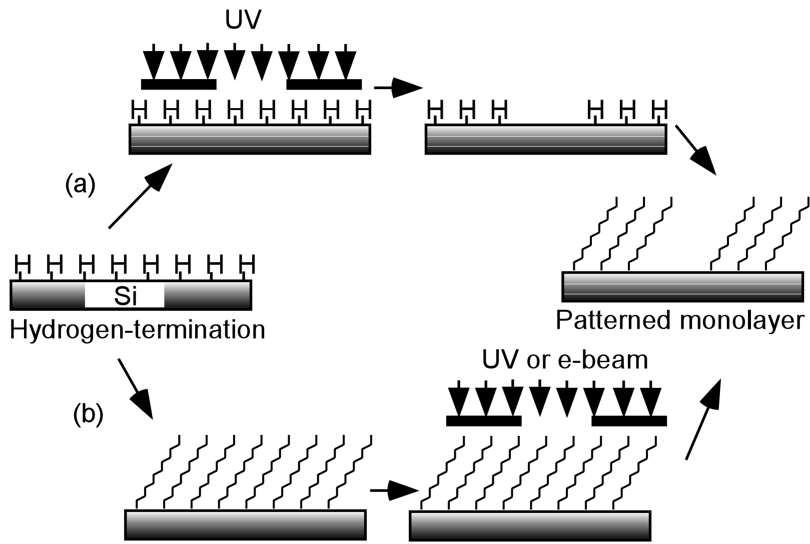


Figure 1 S. Takakusagi, T. Miyasaka and K. Uosaki.....

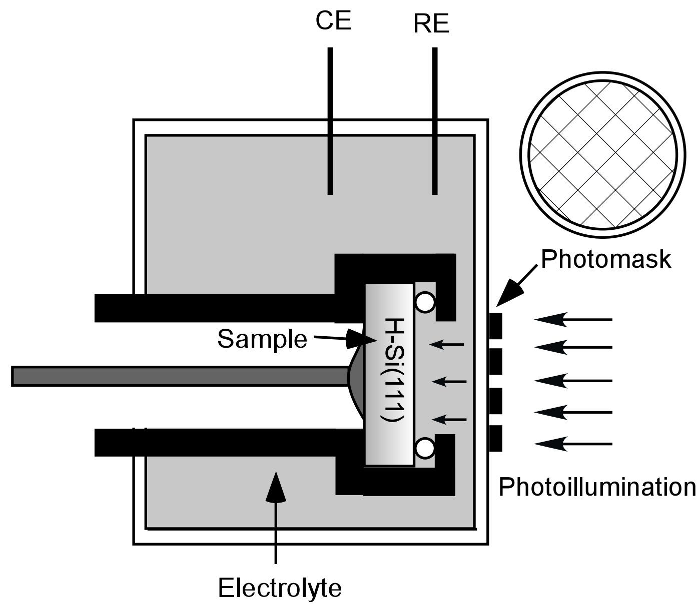
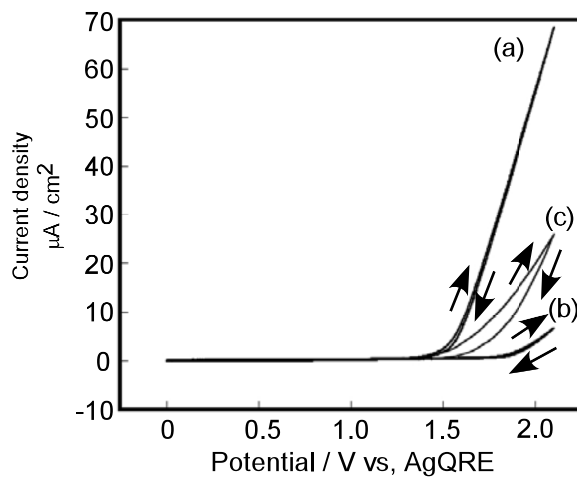


Figure 2 S. Takakusagi, T. Miyasaka and K. Uosaki.....



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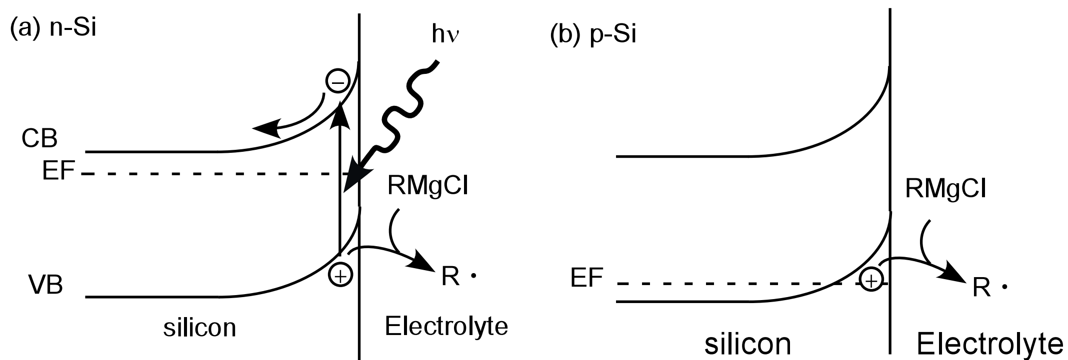

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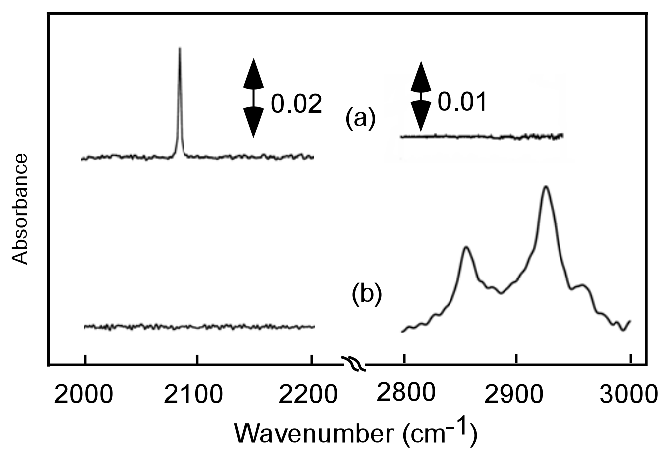

Figure 5 S. Takakusagi, T. Miyasaka and K. Uosaki.....

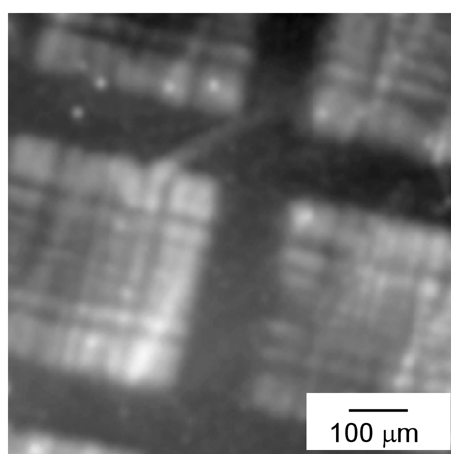

Figure 6 S. Takakusagi, T. Miyasaka and K. Uosaki.....