Electrochemical Behavior of Methyl- and Butyl- Terminated Si(111) in Aqueous Solution

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Formation of the methyl- and *n*-butyl monolayer on (Cl)–Si(111) surfaces by using the Grignard reaction and their electrochemical behavior was investigated. The modified Si(111) surfaces were indicated to be closely packed with a single moiety species. The methyl-modified Si(111) surface was composed of (1 × 1) adlattice structure. The methyl-modified surface was stable in aqueous solution, and showed essentially good electrical conductive property with p-n junction like behavior.

Organic monolayers offer a powerful way to modify the chemical and physical properties of Si surfaces, and the modification of the Si surfaces by covalent attachment of organic molecules has been the subject of much interest in recent years.[1–6] The monolayer-modified Si surface has possibility for creating a new functional interface having semiconductor properties; hence, the surface has the high potential for the fields of micro/nano electronics and biological assays. Despite those beneficial properties for application, the formation of hydrocarbon moieties bonded on well-defined Si surfaces has not been widely studied until recently.

In this study, we investigate the formation of well-ordered covalently bonded organic monolayers on Si(111) wafer surfaces by using the Grignard reaction. The characteristics of methyl- and *n*-butyl-modified surfaces are performed by X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM). The electrochemical behavior of each modified Si(111) surface in aqueous solution is investigated using electrochemical measurement.

N-type Si(111) wafers (3–8 Ω cm) were used for the present work. The wafers were treated with SPM (H_2SO_4:H_2O_2 = 4:1) followed by rinsing with deionized water. The wafers were immersed in 40% NH_4F solution to obtain a clean, H-terminated surface.[7,8] Then the hydrogen at the surface was replaced with chlorine by exposing the surface to Cl–Ar mixture gas (1:100) under ultraviolet light (λ = 350 nm) irradiation for 5 min. Subsequently the Cl-terminated surfaces were treated with the Grignard reagent (1.0 M RMgBr/tetrahydrofuran (THF) solvent, R = Methyl (Me), *n*-Butyl (Bu)) at 65 °C for 18 h. In order to terminate the reaction, the specimen was transported into air and rinsed successively in THF containing 3% CF_3COOH, water, and trichloroethylene. Chemical structures of the modified surfaces were investigated using X-ray photoelectron spectrometer equipped with an Al Kα source. The modified surface was observed by using STM in Ar atmosphere at 25 °C. Cyclic voltammetry was performed in deoxygenated aqueous solution of 3 mM $K_3Fe(CN)_6$, 3 mM $K_4Fe(CN)_6$, and 1 M KCl under the dark condition at 25 °C. The Si surface was used as a working electrode. The Pt wires were used as a counter and reference electrodes.

Chemical structure of the monolayer-modified surfaces was characterized by XPS. Figure 1 shows the C 1s narrow spectra of

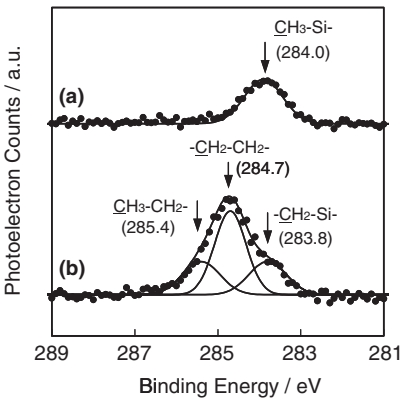

Figure 1. X-ray photoelectron spectra in the C 1s region of the modified Si(111) surface. (a) Me-modified surface, (b) Bu-modified surface.

Si(111) surface after the Grignard reaction in RMgBr/THF (R = Me, Bu). A single peak was observed in the spectrum for the Me-modified surface. In addition, these ratios of C 1s peak in the Bu-modified surface showed reasonable correlation to those of each fragment of the moiety. The coverage of modified surface was estimated by using the integrated peak areas of the C 1s and Si 2p XPS narrow scans. The effective coverage, which takes the cross-sectional size of the molecules into account, was calculated using the method by Chidsey et al.;[1,3] The cross-sectional area of each molecule was $(8.06\,\text{Å}^2)^{-1}$ (Me-), and $(18.3\,\text{Å}^2)^{-1}$ (Bu-), respectively. The areal density of surface Si atoms was $(12.7\,\text{Å}^2)^{-1}$. The value of the effective coverage of Me- and Bu-modified surface was estimated to be 0.94 and 1.01, respectively. From the result of these XPS characterizations, it is considered that each monolayer-modified surface is closely packed with a single moiety species. Furthermore, the Me-modified Si(111) surface is expected to form (1 × 1) adlattice structure since the areal density of methyl moiety is smaller than that of the surface Si atoms.

Figure 2 shows STM images of Me-modified surface. The step-terrace structure and (1 × 1) adlattice of methyl moieties were clearly discerned (Figure 2a). By magnifying the flat and small areas, the lattice constants of these adlattices were estimated to be 0.38 nm (Figure 2b), which corresponds to that of H–Si(111). Therefore, it is indicated that the modified Si(111) surface is terminated by methyl moiety with (1 × 1) adlattice structures.

Figure 3 show two successive cyclic voltammograms of a bare H–Si(111) surface (a), Bu–Si(111) (b), and Me–Si(111) surface (c). The cyclic voltammogram for the H–Si(111) was measured as a reference. Cathodic current peak depended on Fe^{3+}/Fe^{2+} redox couple was observed in all profiles at a first scan.

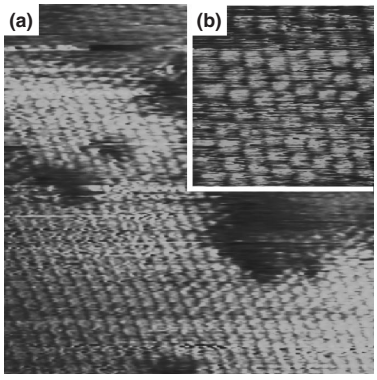

Figure 2. STM images of Me-modified Si(111) surface. The tip-and-sample bias voltage was fixed at −1.5 V (tip negative). (a) 15 nm × 15 nm, height span $\Delta h = 2$ nm, $I_t = 7$ nA, (b) 3 nm × 3 nm, height span $\Delta h = 1$ nm, $I_t = 2$ nA.

For the bare H–Si(111) surface in the electrolyte, the current decreased between successive cyclic voltammograms (Figure 3a). It is considered that such a degradation is due to the formation of SiO_2 at the Si surface.[1] In contrast, for the Bu– and Me–Si(111), the peak potentials and currents kept almost constant values up to 120 min (Figures 3b and 3c). From these results, each monolayer-modified Si(111) surface is indicated to be stable in the aqueous solution without any corrosion. Comparison of the curves at the first scan for the Me-modified and the bare H–Si(111) electrodes, the Me–Si(111) electrode shows a large current peak at lower applied bias voltage. The difference in the potential-current profiles between the Me–Si(111) and the Bu–Si(111) could be caused by the difference in a level of tunneling barrier and capacitance of an adlayer.[9] The level of the barrier and the capacitance increases in accordance with the thickness of the adlayer. The rise in these levels involves an increase in the applied bias voltage and a decrease in the current. On the other hand, the peak current of the Bu–Si(111) electrode was slightly larger than that of the bare H–Si(111) besides the influence of decrease in the tunneling barrier and the capacitance induced by the existence of the monolayer. Therefore, it is suggested that the Me–Si(111) has essentially good electrochemical property in the aqueous solution compared with the bare H–Si(111). As the origin of this property, it is assumed that the methyl adlayer is induced by the applied bias voltage, and may act as a conductive layer. Indeed, it seems that the Me–Si(111) substrate shows the p-n junction like behavior. It is known that a hydrogen-terminated single crystal diamond surface acts as thin p-type semi-conductive layer without any doping inpurity.[10] Therefore, it was thought that the Me–Si(111) surface consisting of H–C bond structure could have a similar property to hydrogen-terminated single crystal diamond surface.

In conclusion, we achieved the formation of well-ordered short-chained monolayer on Si(111). The Me–Si(111) was indicated to be composed of (1 × 1) adlattice structure. This surface had durability toward the electrolyte and showed good electrical conductive property essentially compared with the bare H–Si(111). This surface is expected to be applied to various functional devices such as electric, molecular, and sensing devices and systems.

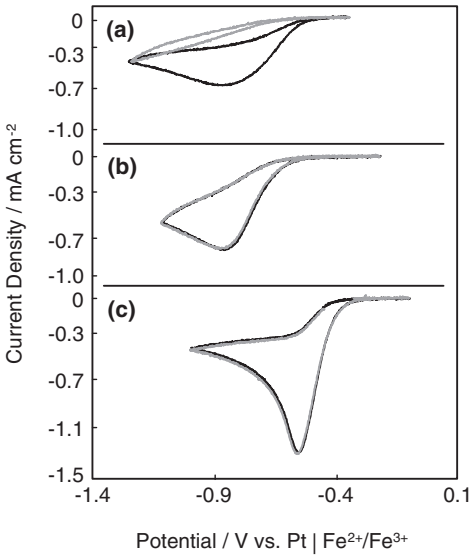

Figure 3. Two successive cyclic voltammograms of (a) the H–Si(111) electrode, (b) the Bu–Si(111) electrode, and (c) the Me–Si(111) electrode. Scan rate : 100 mV/s. Black line : at 0 min, gray line : at 120 min.

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