

Surface Characterization and Electrochemical Properties of Methyl Monolayers on Si (111)

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Organic monolayers offer a powerful way to modify the chemical and physical properties of silicon surfaces. The modification of silicon surfaces by covalent attachment of organic molecules has been the subject of much interest in recent years [1-4]. The monolayer modified silicon surface has possibility for creating a new functional interface having semiconductor properties; hence, the surface has the high potential for utility in the fields of micro/nano electronics and biological assays. In the present work, we attempt to form covalently attached organic monolayers on Si (111) wafer surfaces by using a Grignard reaction. The characteristics of these modified surfaces are investigated by X-ray photoelectron spectroscopy (XPS), scanning tunneling microscope (STM), and electrochemical measurements.

N-type Si(111) wafers (3-8 Ω cm) were used for the present work. The wafers were treated with SPM ($\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 = 4 : 1$) followed by rinsing with 18 M Ω cm deionized (DI) water. The wafers were immersed in 1.0 wt% HF to prepare clean, hydrogen-terminated surface. Then the H at the surface was replaced with Cl by exposing the surface to chlorine gas under ultraviolet irradiation. Subsequently the Cl-terminated surfaces were treated with Grignard reagent (RMgBr / tetrahydrofuran (THF) solvent, R = Methyl-, Butyl-, Decyl-, and Allyl- group), followed by rinsing with CF_3COOH / THF and dichloromethane.

Chemical structures of the monolayer modified surfaces were investigated by XPS. The surface after modification of molecules was observed by using STM under the condition of the argon purged atmosphere. Cyclic voltammetry was performed in deoxygenated aqueous solution of potassium ferricyanide, potassium ferrocyanide, and potassium chloride. The silicon surface was used as a working electrode. An ohmic contact was obtained using a layer of Ga-In on the back side of the silicon sample. The platinum was used as a counter and reference electrodes.

Figure 1 shows XPS carbon 1s narrow spectra of Si (111) surface after the Grignard reaction in CH_3MgBr / THF. A single peak at 284.0 eV assigned to C-Si bonds is observed. The coverage of modified surface is calculated by using the integrated peak area of carbon (1s) and silicon (2p) XPS narrow scans. The effective coverage, that is the areal density of absolute to maximum areal density [1], was estimated to be 0.94. From the result, it is indicated that the modified surface is constituted with well ordered, single moiety. In addition, the coverage of butyl- or decyl- modified surfaces were estimated to be 1.01 and 0.64, respectively. The methyl-modified surface is observed by STM under the condition of argon-purged atmosphere. The lattice image is

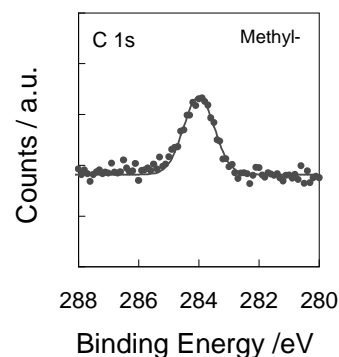


Figure 1 Carbon 1s XP narrow spectra of Si(111) surface after immersion in CH_3MgBr / THF.

acquired, indicating that the Si bonds at surface are terminated by methyl moiety.

In order to investigate the electrochemical properties and stability in aqueous solution, cyclic voltammetry was performed in the dark, under an argon atmosphere at ambient temperature. Cyclic voltammograms for methyl-modified Si (111) shows a strong cathodic current peak depended on $\text{Fe}^{3+} / \text{Fe}^{2+}$ redox couple at an overpotential of about -0.5 V at first cycle compared with that of H-Si (111) [peak ; overpotential of around -0.7 V]. Next, successive cyclic voltammograms are measured from 0 min to 120 min. The values of the peak currents for H-Si (111) are rapidly decreased with an increase in the immersion time. On the other hand, the peak currents of methyl- modified Si (111) kept almost constant values at each measurement time. From these results, it is considered the methyl- modified Si (111) surface has good electric conductivity and stability in aqueous solution.

This methyl modified surface shows very unique property in solution compared with H-Si (111). The difference in electrochemical properties between for methyl- modified and for other alkyl- modified surface will be also discussed.

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