Electrical Conduction Property of Covalently Attached Methyl Monolayer on Si(111)

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Self-assembled monolayers offer a powerful way to modify 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 previous work, we have investigated the formation of covalently attached organic monolayers on Si (111) wafer surfaces by using the Grignard reaction. The butyl- and methyl- modified surfaces were indicated to be closely packed with single moiety species. Especially, the methyl-modified surface was composed of (1x1) adlattice structure. In addition, the methyl-modified surface was stable in an aqueous solution, and showed higher conductivity compared with the bare H-Si(111) surface by a cyclic voltammetry [5].

In this study, an electrical conduction property of the methyl monolayer on Si(111) is evaluated from electrical profiles of a thin film transistor-based device fabricated by using the methyl-modified Si substrate.

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 18 MΩ cm deionized water. The wafers were immersed in deoxygenated 40 % NH_4F solution to prepare a 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 the Grignard reagent (CH_3MgBr / tetrahydrofuran (THF)), followed by rinsing with CF_3COOH / THF and dichloromethane. The Al was then evaporated on the modified surface and the backside of Si to form source, drain, and back-gate electrode contacts in order to evaluate a conductivity of the methyl monolayer from the transistor profile.

In our previous work, cyclic voltammograms of bare H-Si and methyl-modified Si surface was measured in deoxygenated aqueous solution containing $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$. Cathodic current peak depending on Fe^{3+} / Fe^{2+} redox couple was observed in both profiles at a first scan. Comparing the voltammograms for the methyl-modified and the bare H-Si(111) electrodes, the methyl-modified Si(111) electrode showed a large current peak at lower applied bias voltage [5]. Therefore, the methyl-modified Si has an essentially good electrochemical property in the aqueous solution compared with the bare H-Si. It is expected the methyl adlayer is induced by the applied bias voltage to act as a conductive layer. Indeed, it seems that the methyl-modified Si(111) substrate shows the p-n junction like behavior.

In order to clarify the conduction property of the methyl monolayer on Si(111) under the existence of water on the surface or moisture condition, a thin film transistor-based device in which the methyl monolayer was used as a conductive layer was fabricated, as schematically shown in Fig. 1(a). Figure 1 (b) shows I_{sd}-V_{sd} profiles of the fabricated device. The profiles indicated typical response of a transistor having a p-channel conductive layer. In addition, when the back-gate voltage was applied to over 0.8 V, the source-drain current rose rapidly. From these results, the methyl monolayer on Si(111) was considered to act as a p-type semi-conductive layer. The difference in the characteristics of the methyl monolayer-based thin film transistor under moisture or dry condition and the results of another electrical measurements will be discussed.

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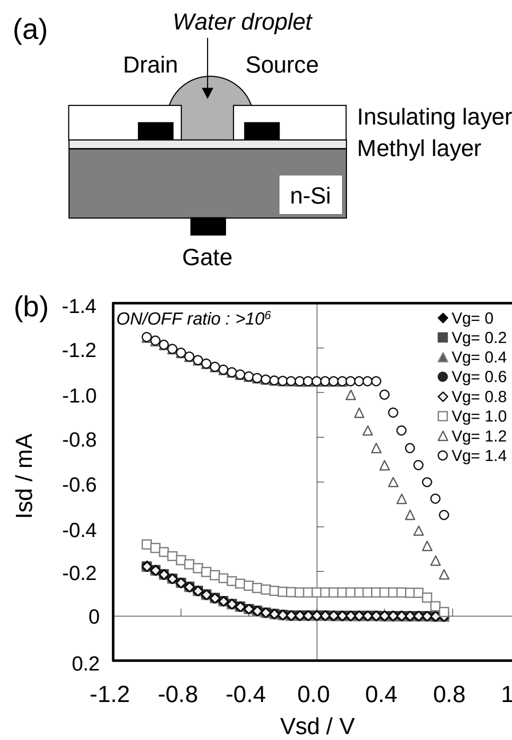

Figure 1. (a) Schematic illustration of a thin film transistor for which the methyl monolayer was used as a conductive layer. (b) I_{sd}-V_{sd} profiles of the thin film transistor-based device.

References
[1] C. J. Barrelet et al., *Langmuir*, **17** (2001) 3460.
[2] J. Cheng et al., *J. Phys. Chem. B*, **105** (2001) 10900.
[3] J. Terry et al., *J. Appl. Phys.*, **85** (1999) 213.
[4] T. Yamada et al. *J. Am. Chem. Soc.* **125**, (2003) 8039.
[5] D. Niwa et al., *Chem. Lett.*, **33** (2004) 284.