Methyl termination and ATR-FTIR evaluation of n-Si (111) electrode towards photoelectrochemical cell fabrication

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We confirmed methyl termination on n-Si(111) surface by ATR-FTIR measurement, which was fabricated by a photo chloro-reaction and its methylation. The coverage of the methylation was about 63.7 %, and the surface was not re-terminated by hydrogen. Photoelectrochemical properties of the n-Si(111) was measured as an electrode for a photoelectrochemical cell, and an onset potential obtaining photocurrent for the methyl terminated n-Si(111) electrode was observed as negative shift at 70 mV comparing with that of the hydrogen terminated n-Si(111) electrode. Therefore, the negative shift would be expected for improving open circuit voltage towards solar cell.

Keywords: Methyl termination, ATR-FTIR, semiconductor electrode, Si, photoelectrochemical cell

Introduction
Recently, we have remarked photovoltaic power generation, and have produced higher efficiency solar cells by proceeding to the influential investigation. However, those includes great problem which is high costs to produce them by semiconductor fabrication processes as p-n junction and use of transparent conductive indium oxide etc. The low costs and energy conversion efficiency are very important to spread of the solar cell utilization.1,2 Previously, higher open circuit voltage was discovered with n-Si photoelectrochemical cells (PEC) comparing with familiar p-n junction solar cell, and is able to fabricate them with the low costs and easily. But, the cell has a point that the n-Si surface is gradually oxidized by exposing an electrolyte solution, and then SiO₂ is slowly formed as an insulation layer on the surface. Researches have been carried out to solve the problem by immobilizing the surface with alkyl base etc.3-8. For example, the alkyl termination on the Si surface is investigated toward developments of bio sensors for DNA and protein detection by giving functionalize on the surface9, furthermore the termination is known to make the surface stable for the oxidation in the solution4,10,11. Therefore, we designed the functional n-Si surface toward PEC in this study. We investigated alkyl terminated n-Si surface by ATR-FTIR, which was known hardly to oxidate the surface in electrolyte solution, and we selected methyl base as the alkyl species most simply, and then n-Si was measured about photoelectrochemical properties electrochemically as a working electrode by Pt electrodeposition onto the surface. Especially, an onset potential (U_OC) for obtaining photocurrent was examined to know the termination effects, and estimated the photovoltage properties toward PEC.

Experimental Section
We carried out the methyl termination with a method reported by Bansal et al, which was immobilized on the surface by two steps alkyl termination via a chlorination in scheme 1.5,12. The n-Si(111) surface was exposed by so-called RCA washing process as HF, H₂O, NH₃ + H₂O₂ solution, H₂O, HCl + H₂O₂ solution and H₂O₂ and then the surface was terminated hydrogen. After the surface was washed by diethyl ether, the chloride termination

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Scheme 1—Termination process of hydrogen, chlorine and alkyl base
was performed by immersing the Si(111) to sat. PCl₅/chlorobenzene solution under heating at 100 °C for 1 h irradiating UV light in flowing Ar gas. Next, by immersing them in CH₃Li/diethyl ether in Ar, and refluxing at 50 °C for 3 h, the methyl termination was completed on the surface. Before the surface was measured by ART-FTIR, they are washed by diethyl ether, 2-propanol and pure water. Furthermore, the surface was not re-terminated by hydrogen for parts of non-methyl termination, which was immersed in HF solution for 15 min. In Fig. 1, an electrode was fabricated by using the n-Si(111) as a working electrode to be in contact with In-Ga alloy, and electrochemical measurements was performed with a Pt counter electrode and a Ag/AgCl (sat. KCl) reference electrode under 100 mW/cm² irradiation by a solar simulator at AM 1.5. The n-Si(111) working electrode was carried out at Pt electrodeposition to induce electron transfer easily in 5 mM K₂PtCl₆ + 0.1 M LiClO₄ solution at 83 mC/cm² imposing at -1.0 V, before properties of the electrode were measured.

**Results and discussion**

ATR-FTIR spectrum is shown about the hydrogen and methyl terminated n-Si(111) surface in Fig. 2. Since we were able to observe peaks of C-H stretching vibrations based on the methyl base at 2975 cm⁻¹ (asymmetry) at line (b) in Fig. 2 (A) and (B), the methyl termination would be performed. Other peaks were also obtained by detecting the methylene base identified C-H stretching vibration at 2930 cm⁻¹ (asymmetry) and 2855 cm⁻¹ (symmetry) in Fig. 2 (B). Furthermore, try of hydrogen re-termination results in not obtaining the spectra based on hydrogen termination on the n-Si(111) surface. These results would show that the surface was covered sufficiently with the methyl bases by this processes, hence the re-termination by hydrogen will not happen. The rough coverage of the methyl termination was calculated from the area based on the Fig. 2 (A). The result gave ca. 63.7 % by table 1, and it would suppose that the methyl termination was completed adequately. A coverage have been reported at about 50 % by alkene (1-octene, 1-octadecene, 1-octyne and styrene etc.) on the n-Si(111) surface¹³, hence in this study the coverage of methyl termination will be enough. The n-Si(111) was measured as an electrode for photocurrent-potential curves in 1 M KI solution. In Fig. 3, onset potential (U₀c) for photocurrent indicated -0.25 V at the hydrogen terminated electrode, and -0.32 V at the methyl terminated electrode. The methyl termination gave the electrode effect of the negative shift of the onset potential about 70 mV, which is concretely not so clear yet, but
the methyl termination can raise the electrode potential by the negative shift. This shift would be expected for improving open circuit voltage \(U_{oc}\) as photoelectrochemical cell (PEC).

Conclusions

By measuring the Si(111) surface by ART-FTIR, we confirmed the methyl termination on the surface by the UV irradiation in PCl₅/chlorobenzene solution and immersing them in CH₃Li/diethyle ether in Ar, and refluxing at 50 °C for 3 h. Furthermore the coverage was estimated at about 63.7 %, and the re-termination of hydrogen by NH₄F solution was not obtained. Photocatalysis properties showed the negative shift of \(U_{oc}\) in 1\(^{-}\text{I}^-/\text{I}_3^+\) solution, hence improvement of open circuit voltage would be expected by the use of photoelectrochemical cell.

References