

## Construction of Organic Monolayers with Electron Transfer Function on a Hydrogen Terminated Si(111) Surface via Silicon–Carbon Bond and Their Electrochemical Characteristics in Dark and Under Illumination

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An organic monolayer with a functional group of electron mediation capability, viologen, was constructed on a hydrogen-terminated Si(111) surface via Si–C bond by photochemical attachment of 4-vinylbenzyl chloride followed by a surface quaternization reaction with 1-methyl-4-(4-pyridyl)pyridinium iodide. Furthermore, Pt particles were deposited on the monolayer by ion exchange reaction with  $\text{PtCl}_4^{2-}$  followed by reduction by hydrogen gas. The mediation of electron transfer by viologen moieties was proved and electrochemical hydrogen evolution reaction rates were enhanced after the Pt deposition.

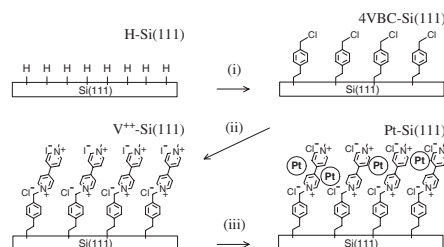
Construction of molecular layers on solid surfaces is one of the most important subjects not only for fundamental science but also for a wide range of applications such as wetting control, corrosion inhibition, and molecular- and bio-electronic devices and is one of the key techniques for the development of nanotechnology and nanoscience. A self-assembly (SA) technique has been extensively employed to construct organic layers because a molecularly ordered structure can be prepared very easily without special equipment.<sup>1</sup> Although the most studied system is self-assembled monolayers (SAMs) of alkanethiols on various metals especially on gold,<sup>2,3</sup> ordered molecular layers with various functionalities on semiconductor surfaces should be more important for technological applications. In particular, the monolayer with electron transfer function is very important in view of the application for molecular devices.<sup>4</sup> Although several attempts have been made to use GaAs<sup>5</sup> and InP<sup>6</sup> as a substrate, Si should be the most important substrate in view of the advanced silicon technology.

Recently monolayer formation via direct Si–C bond using thermal,<sup>7–11</sup> photochemical,<sup>12</sup> and electrochemical<sup>13</sup> reactions attracts much attention. We have investigated the formation process and structure of organic monolayers on a hydrogen-terminated Si(111) by using attenuated total reflectance Fourier transform infrared and sum frequency generation spectroscopy and found that the organic monolayers formed on Si(111) surfaces via Si–C bonds are in a relatively high conformational order as do alkanethiol SAMs on Au(111).<sup>7–9</sup>

Here, we constructed an organic molecular layer with a functional group of electron mediation capability, i.e., viologen, on a hydrogen-terminated Si(111) surface via direct Si–C bond. Surface composition and electron transfer characteristics after each construction step were studied by X-ray photoelectron spectroscopy (XPS) and electrochemical characterization, respectively. Furthermore, effects of platinum deposition on the monolayer modified surface on the electrochemical hydrogen evolution reaction (HER) in dark and under illumination were also investigated.

Surface modification was carried out as shown in Scheme 1.

(i) A freshly prepared hydrogen terminated (H–)Si(111) substrates (Shin-Etsu Semiconductor: B-doped p-type with resistivity of 1–10  $\Omega$  cm and P-doped n-type with resistivity of 1–10  $\Omega$  cm)<sup>14,15</sup> were illuminated with 254-nm light ( $\approx 1$  mW  $\text{cm}^{-2}$ ) for 24 h in deaerated 4-vinylbenzyl chloride (4VBC, Aldrich) to yield 4VBC modified (4VBC–) Si(111) surface. (ii) After the 4VBC–Si(111) substrate was rinsed with deaerated dichloromethane followed by sonication twice in dichloromethane for 10 min, it was kept in DMF solution containing saturated amount of 1-methyl-4-(4-pyridyl)pyridinium iodide, which was synthesized by refluxing 4,4'-bipyridine with methyl iodide in benzene, at 100 °C under Ar atmosphere for 20 h to yield a viologen-modified ( $\text{V}^{++}$ –) Si(111) surface. (iii) The  $\text{V}^{++}$ –Si(111) substrate was rinsed with DMF, ethanol, and dichloromethane sequentially and then halide ions were replaced by  $\text{PtCl}_4^{2-}$  by ion exchange reaction by keeping the  $\text{V}^{++}$ –Si(111) substrate in an aqueous solution of 10 mM  $\text{K}_2\text{PtCl}_4$  (Wako) for 10 min. After being rinsed with Milli-Q water (resistivity  $> 18$  M $\Omega$  cm), the substrate was placed in water saturated under  $\text{H}_2$  stream for 20 min so that  $\text{PtCl}_4^{2-}$  was reduced to Pt particle (Pt–Si(111) surface). Because there is a possibility that  $\text{V}^{++}$  was reduced to  $\text{V}^{+}$  during the reduction of  $\text{PtCl}_4^{2-}$ , the substrate was immersed in aqueous solution of 0.1 M HCl for 30 s to re-oxidize  $\text{V}^{+}$  to  $\text{V}^{++}$ <sup>16</sup> and then rinsed with water.



Scheme 1. Surface modification steps.

XPS measurements were carried out using an X-ray photoelectron spectrometer (Rigaku XPS-7000) with monochromic Mg  $K\alpha$  radiation at 25–300 W.

Electrochemical measurements were performed in a three electrode photoelectrochemical cell. A Ag/AgCl electrode, a Pt wire, and the Si(111) substrates were used as a reference, a counter, and a working electrode, respectively. The electrolyte solution was 0.1 M  $\text{Na}_2\text{SO}_4$  aqueous solution prepared by Milli-Q water and sodium sulfate (Wako Pure Chemicals). A 500-W Xenon lamp (Ushio, UXL-500-D) through an IR cut filter (Toshiba, IRA-20) and a UV cut filter (Sigma Koki) was used for photocurrent measurements.

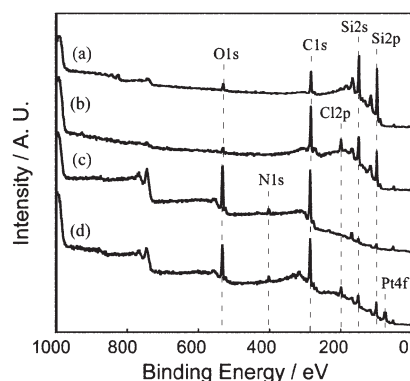
Figure 1 shows the wide scan XPS spectra of the (a) H–Si(111), (b) 4VBC–Si(111), (c)  $\text{V}^{++}$ –Si(111), and (d) Pt–Si(111) substrate. At the H–Si(111) surface (Figure 1a), peaks

corresponding to Si 2p, Si 2s, C 1s, and O 1s were observed around 100, 150, 285, and 530 eV, respectively,<sup>17</sup> and no other elements such as fluorine was detected. Narrow scan spectrum in the Si 2p region (95–110 eV) showed only a peak of Si<sup>0</sup> and no peak due to oxidized Si. These results confirmed that the Si(111) surface was ideally hydrogen-terminated. The C 1s peak ( $\approx 285$  eV) and O 1s peak ( $\approx 530$  eV) are probably the result of the surface contamination during the sample transfer to XPS apparatus.

The appearance of the strong C 1s peak and Cl 2p peak in the spectrum of the 4VBC–Si(111) (Figure 1b) and the absence of oxidized Si 2p peak in the narrow scan spectrum in the Si 2p region suggest the formation of the densely packed 4VBC layer on the Si(111) surface via Si–C covalent bond.

The appearance of the N 1s peak at 400 eV corresponding to quarternized nitrogen species of bipyridine<sup>17</sup> and the significant decrease of Si 2s and Si 2p peaks after step (ii) (Figure 1c) show the attachment of the viologen group to 4VBC–Si(111) surface. The growth of O 1s peak at 532 eV and the observation of a small amount of oxidized Si peak in the Si 2p region spectrum imply the formation of thin Si oxide layer during this step.

The deposition of Pt particles on the V<sup>++</sup>–Si(111) surface after the step (iii) was confirmed by the appearance of a Pt 4f peak near 70 eV in Figure 1d.<sup>17</sup>

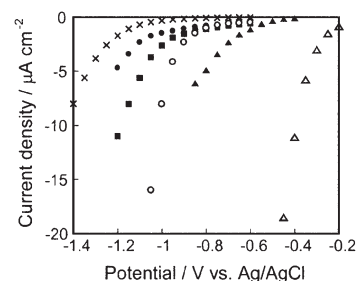


**Figure 1.** XPS wide scan of the substrate after each modification step. (a) H–Si(111), (b) 4VBC–Si(111), (c) V<sup>++</sup>–Si(111), and (d) Pt–Si(111).

Figure 2 shows steady state current–voltage (I–V) curves in 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution of n–Si(111) in dark and of p–Si(111) under illumination obtained after each modification process. At the H–Si(111) electrode, cathodic current started to flow from around –0.6 V. Since steady current was observed, the current should be due to HER. At the 4VBC–Si(111) electrode, the HER current started to flow at more negative potential than at the H–Si(111) electrode and the I–V curve shifted negatively by about 0.1 V, showing that the 4VBC layer acts as a barrier layer for HER at the Si surface.

At the V<sup>++</sup>–Si(111) electrode the HER current started flow at more positive potential than at the H–Si(111) electrode and the I–V curve shifted positively by 0.1 and 0.2 V from the ones at the H–Si(111) and 4VBC–Si(111) electrodes, respectively, suggesting that the electron transfer reaction was mediated by the viologen moiety in the organic monolayer.

HER rate was further enhanced by the deposition of Pt on the monolayer. The I–V curve shifted positively by 0.2 V from the one at the V<sup>++</sup>–Si(111) electrode, proving that the Pt particles on the V<sup>++</sup>–Si(111) served as a catalyst for HER.



**Figure 2.** Steady-state current–potential curves of Si(111) substrates in aqueous solution of 0.1 M Na<sub>2</sub>SO<sub>4</sub>. In dark, n-type, ● H–Si(111), × 4VBC–Si(111), ■ V<sup>++</sup>–Si(111), ▲ Pt–Si(111). Under illumination, p-type, ○ H–Si(111), △ Pt–Si(111). Scan rate; 1 mV s<sup>–1</sup>.

Photoelectrochemical HER was also enhanced by the same modification procedure. The HER current at the p-type H–Si(111) under illumination started to flow at around –0.8 V and the I–V curve at the p-type Pt–Si(111) electrode shifted positively by 0.55 V from that at the p-type H–Si(111).

In conclusion, we have constructed an organic monolayer with viologen moiety on an H–terminated n- and p–Si(111) surfaces via Si–C bond. Electron mediation capability of viologen moiety was demonstrated as the current due to HER at the viologen-modified Si(111) electrode started to flow at more positive potential than at the H–terminated and 4VBC–modified Si(111) electrodes. Electrochemical HER rates at the n–Si(111) electrode in dark and at the p–Si(111) electrode under illumination were significantly enhanced by the Pt deposition on the monolayer modified surface, showing the effective catalytic function of the Pt particles.

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