Formation of Viologen-containing Organic Monolayer on Si(111) Surface

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Since Linford and Chidsey demonstrated that pyrolysis of neat diacyl peroxides in the presence of hydrogen-terminated single crystalline silicon led to the formation of a densely-packed organic monolayer covalently bonded to the silicon surface,1,2 studies on the construction of organic monolayers on silicon surfaces has expanded to develop chemical protection strategies for Si surfaces3-5 and to form metal-organic layer-Si junctions for device applications in nanoelectronics.6-8 In this work, we wish to report that silicon surface was functionalized by an organic monolayer with viologen, which was effective for the reduction of molecular oxygen at the silicon surface. We have previously reported electrochemistry of viologens physically as well as chemically self-assembled on electrode surfaces9,10 and chemical modification of light-emitting silicon materials.11 Masuda and Uosaki’s recent letter12 prompted the present work but a more versatile functional viologen with carboxyl group was immobilized via direct C-Si bond formation at the silicon surface in our case and we present the experimental evidences of viologen-containing organic monolayer formed covalently at Si(111) surfaces by ATR-FTIR and voltammetry.

The parallelogram ATR prism was prepared from phosphorous doped n-type Si(111) wafers (1.0-10 Ω cm), which were polished on both sides for the ATR-FTIR measurements as before.13 Acetone and DI water were used for rinsing Si(111) samples in sonication and piranha solution was used for making oxide layer on silicon surfaces. To obtain a hydrogen-terminated Si(111) surface, the ATR prism was immersed in a 40% NH4F solution and dried in a flowing nitrogen gas. The sample was then thermally treated with 4-vinylbenzyl chloride (4-VBC) and 4-propylcarboxylic-4'-bipyridine, which was prepared from 4,4'-bipyridine and bromopropionic acid, to produce Si-4-vinylbenzyl-1-(2-carboxylethyl)-4,4'-bipyridium (Si-4-VB-VCOOH).

ATR-FTIR measurements were performed using a Bio-Rad Excaliber™ spectrometer equipped with HgCdTe (MCT) detector and home-made sample holder. Ar gas was continuously introduced into the FTIR chamber. The ATR-FTIR spectra were recorded with p- and s-polarization for an oxidized Si(111) surface as a background. Electrochemical experiments were carried out using an EG&G 283A potentiostat in a three electrode electrochemical 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 used was 0.1 M KCl aqueous solution. All the potential was quoted against Ag/AgCl. The preparation sequence of the viologen-containing organic monolayer is shown in Scheme 1.

Figure 1 compares the FTIR spectra of the (a) H-Si(111), (b) 4-VBC-Si(111), and (c) Si-4-VB-VCOOH substrates. Two peaks commonly seen around 2920 cm⁻¹ and 2850 cm⁻¹ in both (b) and (c) were assigned to the asymmetric and the symmetric CH₂ stretching, respectively.1,2,14 The CH₂ bending scissors were found around 1470 cm⁻¹ as the C=O stretching around 1650 cm⁻¹. A broad peak above 3200 cm⁻¹ was assigned to OH stretching. The peaks of CH stretching vibrations of the benzene ring were observed between 3000 cm⁻¹ and 3100 cm⁻¹. As the hydrogen-terminated Si(111) was reacted with 4-vinylbenzyl chloride, a sharp Si-H peak at 2108 cm⁻¹ disappeared and new peaks were found around 3040 cm⁻¹, 2920 cm⁻¹, 2850 cm⁻¹ and 1470 cm⁻¹, indicating that 4-VBC was successfully immobilized at Si(111) surface via direct C-Si bond formation at the silicon surface. When Si(111)-4-VB-substrate was further treated with 4-propylcarboxylic-4'-bipyridine, additional peaks were observed around 1650 cm⁻¹ for C=O stretching and above 3200 cm⁻¹ for O-H stretching, suggesting that covalent binding of 4-propylcarboxylic-4'-bipyridine was achieved at the Cl position of 4-VBC-Si(111). Although it has been previously noted that the O-H stretch, which had disappeared in the hydrogen-terminated Si surface, largely returns when straight alkyl monolayer was formed at Si(111) surface,3 no similar spectral features were
seen in the present work. Although the OH or oxide was
discussed to be formed based on the difference in the
nearest-neighbor distance between silicon atoms on the
Si(111) surface (3.84 Å) and alkyl chains (diameter 4.6 Å),
the formation of OH or oxide at silicon surface may occur
depending on the degree of packing of monolayer formed.
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Figure 2 shows cyclic voltammograms of 4-VBC-Si(111)
electrode (a), and the first redox process of viologen (2+/+)
at Si-4-VB-VCOOH in the absence (b) and presence (c) of
molecular oxygen in 0.1 M potassium chloride electrolyte
solution. The small background current as well as ideal
polarizable behavior in the wide potential range from 0 to
−1.6 V versus silver-silver chloride reference electrode
observed at Si(111)-4-VBC indicates that the silicon elec-
trode was completely covered with the well-packed organic
monolayer having little holes for possibility of water or
electrolyte penetration. When viologen remained to be coava-
ently bonded at the well-packed 4-VBC-Si(111) surface, the
carbonate electrode showed the prominent reduction and corre-
ponding oxidation peaks at −0.54 V and −0.40 V, respec-
tively, for the redox probe at the scan rate of 10 mV/s. The
peak separation became larger as the scan rate was increas-
ing, indicating that charge transfer kinetics was involved with
the surface electrochemical process. Much larger cathodic
current without any corresponding oxidation peak flowed
at the silicon surface and oxygen in solution was extremely fast
as was the case with other electrodes. The chemically modi-
ified silicon electrode may be profitably usable for oxygen
sensing. In addition, the carboxyl group at the end of the
functionalized viologen on silicon surface can be further
derivatized with −NH2 group, for example, in biological
molecular system. Work is in progress toward this direction.

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