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Author(s)	Shin, Dae-Hyun; Yoo, Byung-Gak; Yoon, Cheol Min et al.
Citation	Bulletin of the Korean Chemical Society, 28(2), 177-178
Issue Date	2007-02-20
Doc URL	https://hdl.handle.net/2115/50219
Type	journal article
File Information	BKCS28-2_177-178.pdf



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

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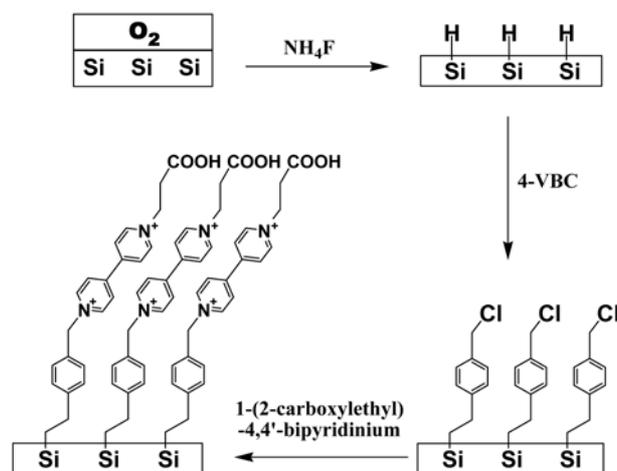
Received October 27, 2006

Key Words : Si(111), Viologen, Electrochemistry, ATR-FTIR, Oxygen

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 surfaces^{9,10} 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% NH_4F 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



Scheme 1. The synthetic sequence of Si(111)-4-vinylbenzyl-1-(2-carboxylethyl)-4,4'-bipyridium.

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 CH_2 stretching, respectively.^{1,2,14} The CH_2 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* Si-C covalent bond. When Si(111)-4-VBC 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,¹ no similar spectral features were

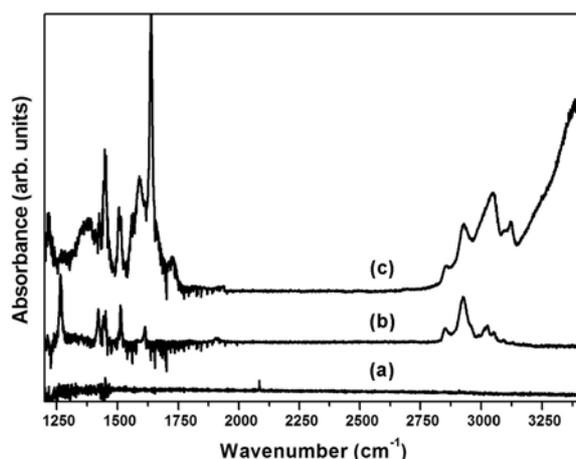


Figure 1. ATR-FTIR spectra of (a) H-Si(111), (b) 4-VBC-Si(111), and (c) Si-4-VB-VCOOH substrates.

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),¹ the formation of OH or oxide at silicon surface may occur depending on the degree of packing of monolayer formed. We note that it was recently reported that the initial electronic properties and structure of the interface were found to be long-lasting only when the monolayer surface coverage was greater than 0.42, leaving intermolecular channels narrower than 2.82 Å, the diameter of water.⁴ We believe that we formed such a high-quality 4-VBC monolayer that OH stretching was not seen in Figure 1B.

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 electrode was completely covered with the well-packed organic monolayer having little holes for possibility of water or electrolyte penetration. When viologen remained to be covalently bonded at the well-packed 4-VBC-Si(111) surface, the silicon electrode showed the prominent reduction and corresponding oxidation peaks at -0.54 V and -0.40 V, respectively, for the redox probe at the scan rate of 10 mV/s. The peak separation became larger as the scan rate was increased, indicating that charge transfer kinetics was involved with the surface electrochemical process. Much larger cathodic current without any corresponding oxidation peak flowed when the identical experiment was performed in the presence of molecular oxygen, suggesting that the reduced viologen catalyzed reduction of molecular oxygen at the silicon surface. We note that the catalytic activation current of molecular oxygen was observed at silicon surface, which is known uncontrollably reactive toward oxygen, and that the peak potential in the presence of oxygen was close to that of the cathodic peak potential of viologen in the absence

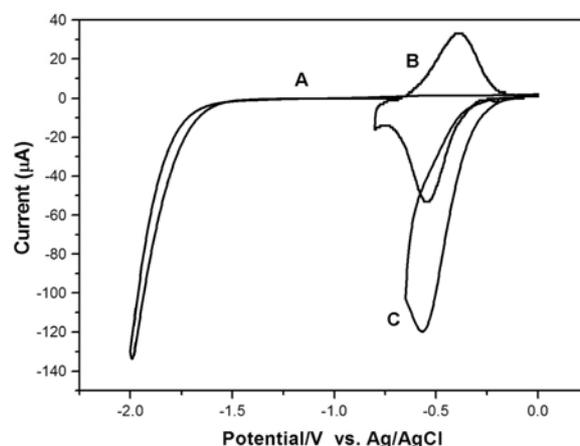


Figure 2. Cyclic voltammograms of 4-VBC-Si(111) electrode under argon atmosphere (a), and the first redox process of viologen (2+/+) at Si-4-VB-VCOOH in the absence (b) and presence (c) of molecular oxygen in 0.1 M potassium chloride electrolyte solution. Scan rate; 10 mV/S.

of oxygen. These would not be possible unless the bimolecular reaction rate between the reduced viologen bound at the silicon surface and oxygen in solution was extremely fast as was the case with other electrodes.⁹ The chemically modified 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.

Acknowledgement. This work was financially supported by Korea Science and Engineering Foundation (F01-2005-000-10127-0) and BK21 Material Chemistry in 2006.

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