Thin Solid Films 518 (2009) 591–595

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Photoswitching of electron transfer property of diarylethene–viologen linked molecular layer constructed on a hydrogen-terminated Si(111) Surface

Takuya Masuda [a,b], Masahiro Irie [c,1], Kohei Uosaki [a,b,d,*]

[a] Physical Chemistry Laboratory, Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan
[b] Network Center for Molecular and System Life Sciences, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan
[c] Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Hakozaki 6-10-1, Higashi-ku, Fukuoka 812-8581, Japan
[d] International Center for Materials Nanoarchitectonics Satellite (MANA), National Institute of Material Science (NIMS), Sapporo 060-0810, Japan

ARTICLE INFO

Available online 10 July 2009

Keywords:
Hydrogen terminated Si(111)
Photoswitching
Electron Transfer
Diarylethene
Viologen
Molecular layer

ABSTRACT

An organic monolayer with diarylethene and viologen moieties as a photochromic and an electroactive group, respectively, was constructed on a hydrogen-terminated Si(111) surface by sequential surface reactions. Photoswitching behaviour of electron transfer from the Si electrode to viologen moiety, larger and smaller current after UV and visible irradiation, respectively, was observed. This photoswitching behaviour can be explained by a change in molecular conductivity of diarylethene moiety, which separates Si surface and viologen moiety, as a result of ring closing and opening induced by UV and visible irradiation, respectively.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Controlling optical and electrical properties has attracted much attention because of its potential applications for molecular electronic devices such as memories and switches. One possible way to construct such devices is incorporation of molecular layers with a photochromic unit on solid surfaces.

Diarylethene is considered to be one of the most promising photochromic units because of its thermally irreversibility and extremely high fatigue durability [1]. Diarylethene has two isomers as shown in Scheme 1. One is an open-ring isomer (**1a**) formed by visible irradiation and the other is a closed-ring isomer (**1b**) formed by UV irradiation. Photoswitching of optical, electrical and electrochemical properties of the diarylethenes has been demonstrated in single crystalline phase [2,3], polymer [4], solution [5] and molecular thin films [6,7]. Recently, molecular conductivities of diarylethenes were measured in single molecular level using break junctions and huge difference in conductivities between the two isomers was reported [8–10].

Although surface immobilization of diarylethene moiety is essential for useful application, only a few groups have reported the introduction of diarylethene derivatives into surface molecular layers via covalent bond because of difficulty in synthesis of molecule with surface attachment, linker and diarylethene moieties [11–21].

Recently, we reported a construction of mono- and multi-viologen layers on Si(111) surface, by sequential surface reactions, i.e., layer-by-layer growth, without losing their electron mediation capability [22,23]. This method can be utilized for constructing other tailor-made organic molecular layers with multiple functional components by building up various molecules as building blocks. Moreover, as far as the practical applications are concerned, functional molecular layers constructed on a Si surface via Si–C covalent bond have a distinct advantage over those formed on other solid surfaces because of their extremely high stability and potential hybridization with the advanced silicon technology.

Here, we constructed an organic molecular layer with viologen and diarylethene moieties as an electron acceptor and a photochromic unit, respectively, on a H-Si(111) electrode by sequential chemical reactions and demonstrated photoswitching of electron transfer from the Si electrode to viologen moiety by utilizing photoinduced ring opening/closing of diarylethene moiety, which is present between the Si electrode and viologen moiety.

2. Experimental details

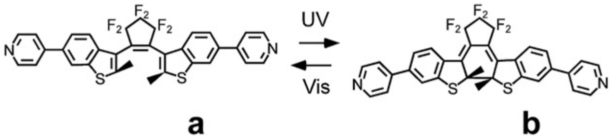
Ultrapure nitrogen (99.9995%) and argon (99.999%) were purchased from Air–Water. Ultrapure-grade sulfuric acid and potassium chloride and reagent-grade sodium sulfate, hydrochloric acid, hydrofluoric acid, hydrogen peroxide, benzene, ethanol, potassium tetrachloroplatinate (II), 1-bromobutane, 1, 4-dibromobutane, 4-vinylbenzylchloride (4VBC), 4-methylstyrene (4MS) and 4, 4′-bipyridine from Aldrich, ultrapure-grade methylene chloride (dichloromethane) and DMF from Dojin Laboratory and special grade (for semiconductor industries) ammonium fluoride from Morita Chemical were used as received except for 4VBC and 4MS, which were purified by vacuum distillation before use. Water was purified using a Milli-Q system (Yamato, WQ-500). The Ag and Pt wires used as the reference electrodes and counter electrodes were purchased from Nilaco.

---

[*] Corresponding author. Physical Chemistry Laboratory, Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan. Tel.: +81 11 706 3812; fax: +81 11 706 3440.
E-mail address: uosaki@pcl.sci.hokudai.ac.jp (K. Uosaki).

[1] Present address: Department of Chemistry, Rikkyo University, Nishi-Ikebukuro, Toshima-ku, Tokyo 171-8501, Japan.

0040-6090/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2009.07.035



Scheme 1. Schematic illustration of photochromic reaction of the diarylethene.

Si(111) substrate (n-type; P-doped, 1–10 Ω cm), which was obtained from Shin-Etsu Semiconductor, was treated by sequential immersion of the sample in freshly prepared sulfuric acid and hydrogen peroxide (2:1 by volume) at 60 °C for 20 min, in aqueous solution of 0.5% hydrofluoric acid at room temperature (RT) for 5 min and in freshly prepared RCA solution (water/hydrogen peroxide/hydrochloric acid, 4:1:1 by volume) at 80 °C for 20 min. After these treatments, the sample was immersed in deaerated aqueous solution of 40% ammonium fluoride for 5 min to obtain a monohydride-terminated surface, that is, H-Si(111) [24,25].

X-ray photoelectron spectra (XP spectra) were obtained using a Rigakudenki model XPS-7000 X-ray photoelectron spectrometer with monochromic Mg–Kα radiation at 25–300 W [26]. Photoelectron was collected at 0° from the surface normal, i.e., take-off angle of 90°.

Electrochemical measurements were performed in a three electrode electrochemical cell equipped with a quartz window in front of the working electrode [22,23,27]. A Ag/AgCl electrode, a Pt wire, and the Si(111) substrates were used as a reference, a counter, and a working electrode, respectively. A potentiostat (Hokuto Denko, HA-501G) was used to control the potential of working electrode and a function generator (Hokuto Denko, HB-111) was used to provide an external potential. Cyclic voltammograms (CVs) were recorded on an X–Y recorder (Graphtec, WX-1200). 0.1 M Na_2SO_4 aqueous solution prepared by Milli-Q water and sodium sulfate was used as an electrolyte solution was. UV and visible light were provided by a Hg lamp (Ushio, USH-250D) through a band path filter (Melles Griot, Center Wavelength: 340.3 nm, Bandwidth: 8.7 nm) and a 500 W Xenon lamp (Ushio, UXL-500-D) through an IR cut filter (Toshiba, IRA-20) and a UV cut filter (Sigma Koki), respectively. Intensities of UV and visible light measured by an optical power meter (Melles Griot) were 150 μW cm^{-2} and 50 mW cm^{-2}, respectively.

3. Results and discussion

3.1. Constriction and characterization of molecular layers

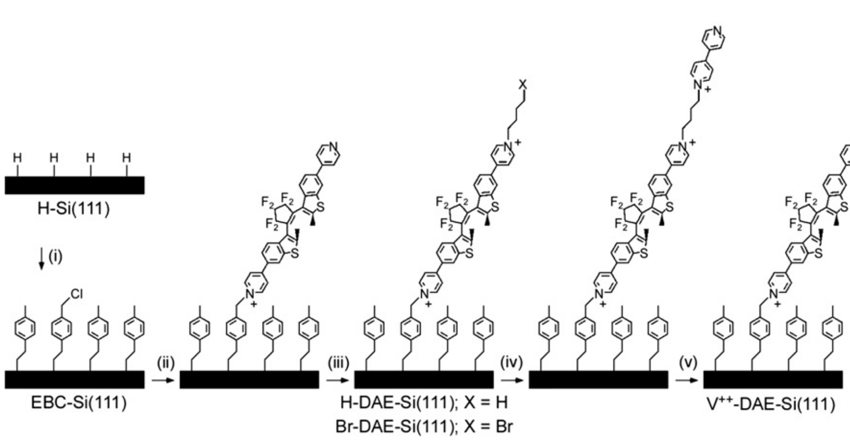
Freshly prepared H-Si(111) surfaces were sequentially reacted with various molecules as shown in Scheme 2. After each modification step, the surface composition was characterized by XPS. The H-Si(111) surface was illuminated with 254 nm light (≈3.2 mW cm^{-2}) for 8 h in deaerated solution containing 4VBC and 4MS (mole fraction of 1:20) (Step (i) in Scheme 2) to form a mixed monolayer of 4-ethylbenzylchloride (EBC) and 1-ethyl-4-methyl-benzene (EMB). We denote the monolayer terminated Si as EBC-Si, although majority of the monolayer is of EMB group. Fig. 1(a) shows XP spectrum of the EBC-Si(111)surface. In a wide scan spectrum (Fig. 1a (a)), peaks corresponding to Si 2p, Si 2s, C 1s, and O 1s peaks were observed around 100 eV, 150 eV, 285 eV, and 530 eV, respectively [26]. A narrow scan spectrum in the Si 2p region (Fig. 1b (a)) showed only a peak of Si(0) at 99.4 eV and no peak due to oxidized Si around 103 eV [26], confirming the formation of a densely-packed mixed molecular layer of 4VBC and 4MS on the Si(111) surface via Si–C covalent bonds without formation of silicon oxide. No peak was observed in N 1s and F 1s regions (Fig. 1c and d (a)).

The EBC-Si(111) surface was reacted with diarylethene (**1a**) in an acetonitrile solution containing 10 mM diarylethene under Ar atmosphere at reflux temperature for 12 h (step (ii) in Scheme 2) and then reacted with either 1, 4-dibromobutane or 1-bromobutane in neat liquid at 80 °C for 12 h (step (iii) in Scheme 2) to yield Br-DAE- or H-DAE-Si (111) surface, respectively. At the H-DAE-Si(111) surface (Fig. 1a, c and d (b)), N 1s and F 1s peaks appeared around 400 eV and 688 eV corresponding to quaternary nitrogen and fluorine species of diarylethene, respectively [26], showing attachment of the DAE moieties. The absence of a peak due to Si(IV) around 103 eV shows that oxide formation was inhibited by the organic monolayer (Fig. 1b (b)).

The Br-DAE-Si(111) surface was further reacted with 4, 4′-bipyridine (BPY) in a BPY saturated benzene solution at 80 °C for 12 h (Step (iv) in Scheme 2). Finally, the substrate was reacted with 1-bromobutane in a neat liquid at 80 °C for 12 h (Step (v) in Scheme 2) to yield a V^{++}-DAE-Si (111) surface, which has viologen and diarylethene moieties. N 1s increased by attachment of the viologen moiety, whereas F 1s decreased due to attenuation of emitted photoelectron, by formation of upper layer (Fig. 1c and d (c)). Appearance of a small peak due to Si(IV) around 103 eV and growth of O 1s peak at 532 eV implies that the Si surface is slightly oxidized during this step (Fig. 1a and b (c)). Thus, a viologen–diarylethene linked molecule was synthesized at a H-Si(111) surface.

3.2. Electrochemical characteristics of V^{++}-DAE- Si(111) surface

Fig. 2(a) shows CVs of the n-type V^{++}-DAE-Si(111) surfaces in a 0.1 M Na_2SO_4 aqueous solution at a scan rate of 50 mV s^{-1} after UV (blue line) and visible (red line) irradiations. A cathodic peak corresponding to the reduction of viologen moieties to viologen radical cation ($V^{++}/V^{+•}$)



Scheme 2. Schematic illustration of sequential surface modification steps. Step (i): Irradiation of UV (254 nm, 3.2 mW cm^{-2}) in a mixed solution of 4VBC and 4MS (1:10, 1:20 and 1:50 by mole fraction) under Ar atmosphere at room temperature for 6 h. Step (ii): Refluxing in an acetonitrile solution of 10 mM diarylethene (1a) for 12 h, and then immersion into neat 1, 4-dibromobutane at 80 °C for 12 h. Step (iii): Refluxing in a benzene solution saturated with 4, 4′-bipyridine for 12 h, and then immersion into neat 1-bromobutane at 80 °C for 12 h.

Download English Version:

https://daneshyari.com/en/article/1672172

Download Persian Version:

https://daneshyari.com/article/1672172

Daneshyari.com