

Photochemical Bonding of Ferrocenyl Monolayers on Si(111) Surface

Hiroyuki Sugimura, Daiji Kasahara, Mingxiu Zhao, Hikaru Sano, Takashi Ichii, Kuniaki Murase
Department of Materials Science and Engineering, Kyoto University, Kyoto 606-8501, Japan

The study on organic/silicon(Si) interfaces is of primary importance for the integration of molecular electronics and semiconductor microdevices. From this viewpoint, self-assembled monolayers (SAMs) covalently attached to Si surface without an interfacial oxide layer have been attracted much attention. Redox-active molecules have an ability to store and release electric charges reversibly so that SAMs consisting of such types of molecules are expected to work as key elements in novel solid-state memory devices. Ferrocene and its derivatives are typical redox activities and, accordingly, considered to be a favorable model for studies on charge transfer at organic/Si interfaces.

Here we report on the immobilization of three different ferrocene derivatives, vinylferrocene (Fc-CH=CH₂, VFc), ethynylferrocene (Fc-C≡CH, EFc), and ferrocenecarboxaldehyde (Fc-CHO, FcA) on Si substrates through chemical reactions of hydrogen-terminated Si(111) [Si(111)-H] surface [Fc = ferrocenyl group]. Figure 1a shows an AFM image of a Si(111)-H surface consisting of atomically flat terraces separated with a monoatomic step. On to this Si(111)-H surface, VFc molecules were immobilized by a thermal activation method. A Si(111)-H sample was immersed for 2 hours in a hot solution (150 °C) of 1 mM VFc in mesitylene. As shown in Fig. 1b, there are many particulate deposits on the sample surface. These deposits are most likely to be polymerized VFc molecules. From electrochemical studies on this sample, we assume that a VFc monolayer is present under the deposits. On the other hand, we could obtain a VFc modified Si with a higher quality as shown in Fig. 1c by a photochemical method. This sample was prepared by immersing a Si(111)-H substrate in 2 mM VFc solution in mesitylene kept at room temperature and then illuminating with a Xe lamp (a white visible light ranging 400 - 800 nm) for 4 hours. Although a small number of particulate deposits are still remaining, the step and terrace structure of Si(111)-H is preserved. Finally, we employed n-decane as an alternative solvent. Figure 1d shows a sample prepared by the visible excitation method in 10 mM VFc/n-decane with a 4-hour illumination. We successfully obtained a high quality VFc monolayer almost without particulate deposits. In n-decane, polymerization of VFc is found to be suppressed. In addition, XPS analysis revealed that VFc molecules were certainly present on the sample surface. This process, that is, visible excitation in n-decane, was effective for the monolayer formation from EFc and FcA as well. The charge transfer behavior of well-prepared VFc/Si, EFc/Si and FcA/Si will be presented.

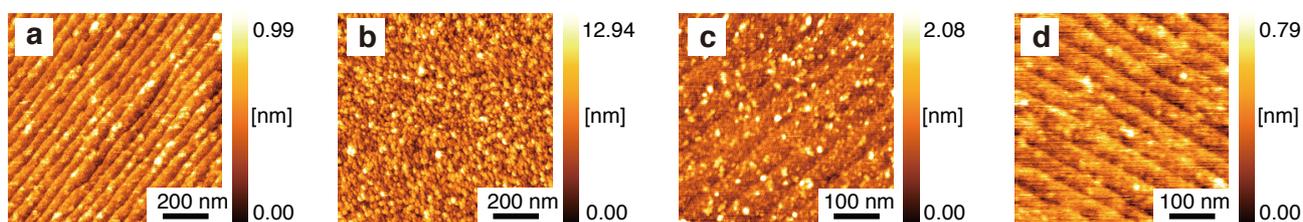


Figure 1 AFM images of Si(111)-H surfaces modified with VFc. a) Si(111)-H surface without VFc, b) Si substrate after the thermal activation in VFc/mesitylene solution, c) Si substrate after the visible light excitation in VFc/mesitylene solution and d) Si substrate after the visible light excitation in VFc/n-decane solution.

1. N. Tajimi, H. Sano, K. Murase, K.-H. Lee, and H. Sugimura, *Langmuir* **34** (2007) 3193-3198.