Surface Grafting of Ferrocene-Containing Triazene Derivatives on Si(100)

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Ferrocene-containing molecules have been grafted to Si(100) surfaces to form monolayers and multilayers via a triazene derivative and its subsequent diazonium chemistry. The growth of the ferrocene-containing films was controlled by molecular concentrations and reaction times. Results from ellipsometry showed that the film thicknesses were in the range of subnanometer to several nanometers. X-ray photoelectron spectroscopy has confirmed the structural integrity of ferrocene in the films. Electrochemical studies of the ferrocene-containing multilayer have shown a reversible one-electron wave of the ferrocene/ferrocenium couple. The multilayer coverage was found to be 2.8×10^{-9} mol cm^{-2}. The calculated electron transfer rate constant was 164 s^{-1}.

Introduction

Because of the attractive electrochemical properties of ferrocene-containing molecules, such as fast electron-transfer rates, reversible redox activities, and favorable redox potentials, we show here that ferrocene derivatives can be grafted onto oxide-free Si surfaces to form self-assembled layers. These redox-active ferrocene-containing layers on a Si surface, because of their ability to store and release charges reversibly, have the potential to be used as hybrid molecular/semiconductor memory devices.[1,2]

One of the most widely used methods for the formation of ferrocene-containing monolayers atop oxide-free Si substrates uses the hydrosilyation reaction of H-passivated Si(100) or Si(111) surfaces with ferrocene-containing alkenes or alkynes. These reactions are promoted by UV or visible irradiation, and/or by the application of heat.[3−8] Another highly investigated grafting method is to tether the ferrocene moieties through Si−O−C or Si−S−C linkages by the thermal reaction of alcohols, aldehydes or thiols with H-passivated Si.[1,2,7−10] Ferrocene-containing monolayers have also been formed by reaction with functional groups on preassembled linker layers. For example, ferrocene-containing monolayers on Si(111) were prepared from the attachment of an amine-substituted ferrocene derivative to a preassembled acid-terminated alkyl monolayer using carbodiimide coupling.[11] Heath's group also reported the formation of ferrocene monolayers on Si(111) through "click" chemistry with a preformed monolayer of acetylene.[12] However, all of above methods were used mostly for the formation of monolayers on Si surfaces; the preparation of multilayers of ferrocene derivatives with controllable thicknesses on Si surface was rarely reported. Ferrocene-containing multilayers are expected to afford higher charge capacity than the monolayers in solid-state memory devices.

Recently, we have developed a new method for directly covalent grafting of molecules onto semiconductor or metal surfaces (Si, GaAs, or Pd) through diazonium chemistry. This method offered an attractive route to highly passivating, robust monolayers and multilayers atop Si(100) or Si(111) surfaces using organic diazonium salts[13] or triazenes.[14] Organic molecules such as oligo(phenylene ethylene)s (OPEs)[15] and oligoanilines[16] have been grafted onto Si surfaces using this method. Metalloporphyrins were also

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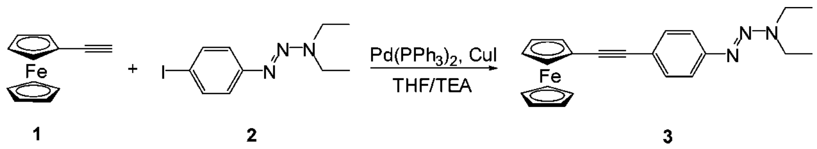
Scheme 1. Synthesis of Ferrocene-Containing Triazene 3



attached to Si(100) surfaces with controllable thicknesses ranging from a few nanometers to a few hundred nanometers.[17] Here, we report the surface grafting of ferrocene on Si(100) using its phenyltriazene derivative. As shown in Scheme 1, phenyltriazene-derived ferrocene **3** was prepared from the ethynylferrocene (**1**) and 4-iodo-*N*,*N*-diethylphenyltriazene (**2**) using a Pd-catalyzed coupling reaction. Compound **3** has high solubility in acetonitrile so that it can be used directly in the in situ film grafting method in aqueous HF/CH_3CN. The monolayer and multilayers of ferrocene-containing molecules on Si(100) thereby formed were examined using ellipsometry and X-ray photoelectron spectroscopy (XPS). The electrochemical characteristics were obtained by cyclic voltammetry (CV). Collectively, this work introduces a novel approach for preparing Si surface-bound monolayers and multilayers of ferrocene derivatives for applications such as molecular/semiconductor hybrid memory devices.[18]

Table 1. Film Thicknesses Resulting from Grafting of 3 on Hydrogen Passivated Si(100) Using Aqueous HF/CH_3CN Conditions

entry	concentration (mM)	time (min)	measured thickness (nm)[a]
1	0.1	60	0.8 ± 0.1
2	0.2	20	1.2 ± 0.1
3	0.2	40	2.0 ± 0.1
4	0.2	60	3.2 ± 0.1
5	0.5	10	1.9 ± 0.1
6	0.5	20	4.8 ± 0.2
7	0.5	40	6.6 ± 0.1
8	0.5	60	7.2 ± 0.2
9	0.5	120	7.4 ± 0.2

[a] The measured values are the average of four different spots on the same film with the ± values indicating the range of measurements.

Experimental Section

General. Unless noted otherwise, reactions were performed under a N_2 atmosphere. Triethylamine was distilled from CaH_2. Trimethylsilylacetylene (TMSA) was donated by FAR Research, Inc. or Petra Research, Inc. All other commercially available reagents were used as received unless noted otherwise. Reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) using E. Merck silica gel 60 F_{254} precoated plates (0.25 mm) unless stated otherwise. Flash column chromatography was performed with the indicated solvent systems using silica gel grade 60 (230−400 mesh). ^1H NMR spectra (400 MHz) and ^{13}C NMR (100 MHz) were collected in $CDCl_3$.

1-(*N*,*N*-Diethyl-phenyltriazene)ferrocene (3). To an oven-dried round-bottom flask containing a magnetic stir bar were added 1-ethynylferrocene (0.67 g, 3.2 mmol), 4-iodo-*N*,*N*-diethylphenyltriazene (**2**)[17] (0.97 g, 3.2 mmol), $Pd(PPh_3)_2Cl_2$ (42 mg, 0.06 mmol), and CuI (23 mg, 0.12 mmol). The flask was then sealed with a rubber septum, evacuated, and backfilled with N_2 (3×). THF (30 mL) and triethylamine (2 mL) were then added. The reaction was stirred at room temperature for 18 h. The reaction mixture was concentrated, and purified by flash chromatography (silica gel, hexanes/ethyl acetate, 5:1) to obtain **3** as a orange solid (650 mg, 53%). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.33 (d, $J = 8.8$, Ar−H, 2H), 7.37 (d, $J = 8.8$, Ar−H, 2H), 4.50 (t, $J = 8.5$, C_5H_4, 2H), 4.25 (s, C_5H_4, 5H), 4.23 (t, $J = 8.5$, C_5H_4, 2H), 3.77 (q, NCH_2, 4H), 1.27 (b, NCH_2CH_3, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.54, 132.06, 120.32, 120.13, 87.77, 86.27, 71.33, 69.97, 68.71, 65.81. HRMS: for $C_{22}H_{23}FeN_3$ 385.1235, Calcd 385.1241.

Ellipsometric Measurements. Measurements of surface optical constants and molecular layer thicknesses were taken with a single wavelength (632.8 nm) laser Gaertner Stokes ellipsometer. The n value for the H-passivated Si(100) surface was 3.83 and k was −0.02. The surface thickness was modeled as a single absorbing layer atop an infinitely thick substrate (fixed n_s). The observed range in repeated measurements of the same spot was typically less than 0.2 nm, and the typical experimental error is ±5%.

XPS Measurements. A Quantera XPS scanning microprobe was used in collecting the XPS data. The takeoff angle was 45°, and a 114.8 W monochromatic Al X-ray source was applied for all the measurements. All XPS peaks were referenced to the C_{1s} major peak at 284.5 eV.

Surface Grafting. Caution: *Piranha solution and hydrofluoric acid are hazardous materials that should only be handled by trained personnel using appropriate personal protective measures. Wastes from these procedures should only be disposed of by approved procedures.*[19] p-Type Si(100) wafers (prime grade, boron doped, 3−6 Ω cm) were cleaned in piranha solution (2:1 H_2SO_4:H_2O_2) followed by rinsing with water (resistivity >18 MΩ cm^{-1}). The wafers were then immersed in the etching solution, a mixture of 2% aqueous HF and CH_3CN (v:v, 1:1; 1% HF overall) for 5 min. Ferrocene **3** was dissolved in 1 mL of CH_3CN at various concentrations and added to the etching solution containing the Si wafer. The reaction container was then covered with a fitted lid and agitated on a platform shaker at 100 rpm for the indicated reaction time (Table 1). After the reaction, the substrates were rinsed with copious amounts of deionized water and CH_3CN and then dried with a stream of N_2.

Electrochemical Characterization. The CV was performed with a Bioanalytical Systems (BAS CV-50W) analyzer in a self-designed three-electrode cell. The working electrode, porphyrin grafted Si(100), was sealed against an opening in the cell bottom by epoxy resin. An ohmic contact was made on the previously scratched rear side of the sample by applying an In−Ga eutectic. The counter electrode was a platinum wire and the system 1×10^{-2} M Ag^+/Ag in acetonitrile was used as the reference electrode (+0.29 V vs aqueous SCE). 0.1 M Tetra-*n*-butylammonium perchlorate (Bu_4NClO_4) in acetonitrile was used as the electrolytic medium. All electrochemical measurements were carried out at room temperature under a constant flow of nitrogen.

Results and Discussion

Surface Grafting. Following our previously reported procedure for in situ surface grafting of organic triazenes on Si(100),[14] ferrocene derivative **3** was readily grafted to

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form near-monolayers or multilayers depending on conditions on H-passivated Si(100) surfaces. Different film thicknesses could be achieved by varying the concentrations of **3** and/or reaction times, and a film thickness of a few nanometers could be easily achieved.

All the grafting was done in a 1% aqueous HF solution (1:1 2% HF:CH_3CN). The thicknesses of these films were characterized by ellipsometry and the results are summarized in Table 1. A thin film of **3** with a thickness of 0.8 nm was obtained at low concentration (0.1 mM) (entry 1 in Table 1). This thickness is close to that of a monolayer considering the calculated molecular length (0.99 nm) of molecule **3** after grafting with the tilt angle of the Si−C bond on the Si(100) surface being 60°.[20] At higher concentrations, multilayers of **3** could be readily formed within a short period of time. For example, at 0.5 mM, a multilayer ~ 7 nm thick was grown on Si(100) within 1 h (entry 8). Extended reaction times increased the thickness of the ferrocene films on Si(100). However, there was no significant increase of film thicknesses after 1 h as shown in entries 8 and 9. As indicated in Table 1, the variation of thicknesses for each sample was small, indicating that the ferrocene films were quite homogeneous.

XPS Studies. In the XPS spectra of the ferrocene films on Si(100), both Fe and C signal were found (Figure 1). A very weak Si_{2p} signal from silicon oxide (~102 eV) was observed due to the extended handling. The relatively weak O_{1s} signal in the survey was from the contaminants on the surface. By curve fitting of Fe_{2p} spectrum, both of the Fe species in the II and III oxidant states were found, with binding energies of 708.4 and 712.1 eV, respectively, and the Fe(II) species predominated over the Fe(III) species with a ratio of about 15:1. These bonding energies represent pure and surface-bonded ferrocene and ferricenium salts, respectively.[3,21] The appearance of Fe(III) in the XPS spectra is quite common for surface grafted ferrocenes.[3,7] Because the potential of the O_2/H_2O redox couple is more positive than that of the ferricenium/ferrocene, the oxygen in the aqueous HF solutions we used for the in situ surface grafting at ambient conditions would oxidize the ferrocenyl groups to the ferricenium state.

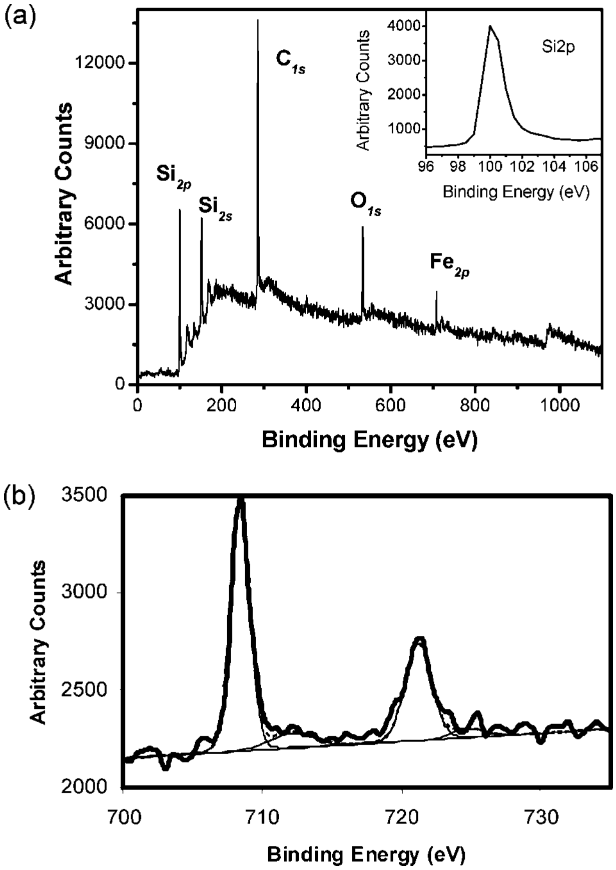

Figure 1. XPS spectra of a multilayer film (3.2 nm thickness, entry 4 in Table 1) of ferrocene **3** on Si(100): (a) survey and (b) Fe_{2p} spectra. Inset in (a) shows the Si_{2p} spectrum.

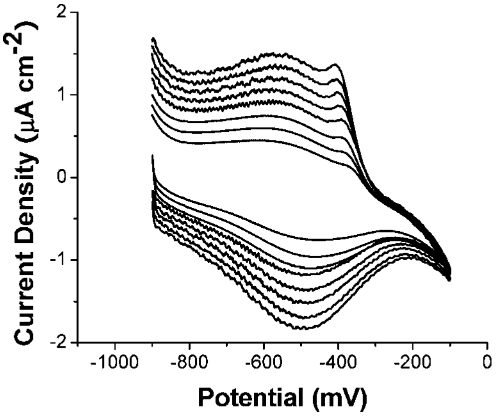

Figure 2. Representative cyclic voltammograms of a ferrocene film (thickness of 1.8 nm) on p-type Si(100) in 0.1 M NBu_4ClO_4/CH_3CN. The scan rates are from 0.3 to 1.0 V s^{-1}, from the smallest to the largest amplitude in increments of 0.1 V s^{-1}. The geometrical area of the electrode is 0.2 cm^2.

Electrochemical Studies. Representative cyclic voltammograms for a multilayer film of ferrocene with a thickness of 1.8 nm on a p-type Si(100) in NBu_4ClO_4/CH_3CN (0.1 M) are shown in Figure 2. The potential was swept from the lower to higher limit and back at eight different rates ranging from 0.3 to 1.0 V s^{-1}. A pair of anodic and cathodic waves was observed with peak potentials located from −0.59 to −0.61 and from −0.47 to −0.49 V versus Ag^+/Ag (in 0.1 M NBu_4ClO_4). According to the peak potentials, the formal potential for ferrocenyl moieties on the Si substrate was estimated to be −0.54 V versus Ag^+/Ag. The full width at half-maximum (fwhm) of the waves are very similar to the literature values at the same scanning rate.[3,4,11] The broad characteristic of the peak might be caused by the lateral and/or intermolecular interactions between the ferrocene molecules[4] as well as the heterogeneous nature of the electrochemical reaction. A small cathodic peak located in the range of −0.37 to −0.41 V also appeared for every scan. And this small peak we found comes from the Si substrates. As shown in Figure 3, the cathodic peak current exhibits linear dependence on the scan rate, indicating a surface confined

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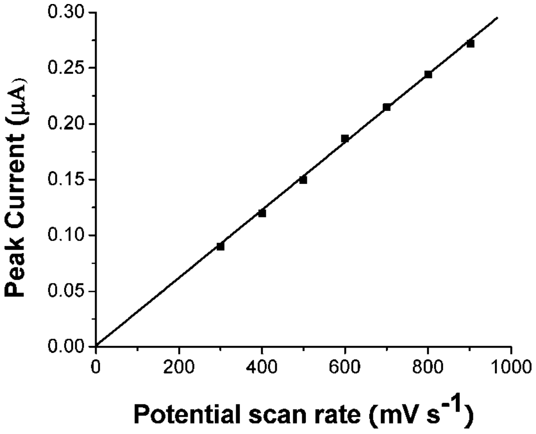

Figure 3. Cathodic peak current as a function of potential scan rate of the ferrocene redox peaks derived from the cyclic voltammograms in Figure 2.

redox process. By integrating the anodic waves of the voltammograms, the surface coverage Γ was estimated to be 2.8×10^{-9} mol cm^{-2}. Given the surface density of H-terminated silicon atoms at the Si(100) surface is 1.13×10^{-9} mol cm^{-2},[21] and the larger molecular size of ferrocene than hydrogen atoms, the surface coverage Γ obtained can only be attributed to a multilayer on Si(100) surface, which is in agreement with the ellipsometric thickness of 1.8 nm of the ferrocene film, considering a molecular length of 0.99 nm after grafting on the surface. The apparent rate constant of electron transfer, k_{app}, was calculated according to Laviron's approach based on the classical Butler−Volmer theory (eq 1)[23]

$$k_{\mathrm{app}} = (nF/RT)(v/m) \qquad (1)$$

where v is the scanning rate. $1/m$ can be determined according to its relation to the peak-to-peak separation ΔE_{p} using 1 for the electron transfer number n and 0.5 for the charge-transfer coefficient.[3,4,23] ΔE_{p} and $1/m$ was 102 mV and 4.2 at 1 V s^{-1}, respectively. Thus the k_{app} was calculated to be 164 s^{-1}, which is similar to the previously reported values for ferrocene films on Si surfaces calculated using the same method.[3,4] This value is not very accurate because of the deviation of the charge-transfer coefficient from 0.5 and the uncertainty of determination of the peak value due to its broad character. There is also a spread in its value due to the heterogeneous nature of the electrode reaction. In addition, the value is a little lower at a slower scanning rate, for which the error is increased, partly because of the weak signal, and thus is not reported. This electron transfer rate is relatively slow, which might be due to the tunneling barrier between the ferrocene moiety and the silicon surface, the value of which is closely related to the nature and length of the linker as well as to the nature of the silicon substrate and the packing of the molecules. For a molecular monolayer, the redox peak is small because of the very weak nature of the signal. These results from the electrochemical studies indicate that these ferrocene-containing multilayers have higher charge densities than monolayers, and the ferrocenyl groups in the multilayers grafted on Si(100) are electrochemically accessible with fast electron transfer rates.

Conclusion

A triazene-derived ferrocene was synthesized for surface grafting to Si(100) via diazonium chemistry through a convenient in situ method using aqueous HF. Using this method, we could easily prepare monolayer and multilayer films of ferrocene-containing molecules. The thicknesses of the films could be controlled in the range from subnanometers to several nanometers by varying the concentrations and reaction times. These ferrocene-containing films were electrochemically active. Electrochemical studies showed very good surface coverage for the multilayers and a relatively fast electron transfer rate of 164 s^{-1}. Collectively, the surface grafting of triazene-derived ferrocene on Si(100) might be useful in future generation molecule/semiconductor memory devices.[18]

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