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Ferrocene-Terminated Monolayers Covalently Bound to Hydrogen-Terminated Silicon Surfaces. Toward the Development of Charge Storage and Communication Devices

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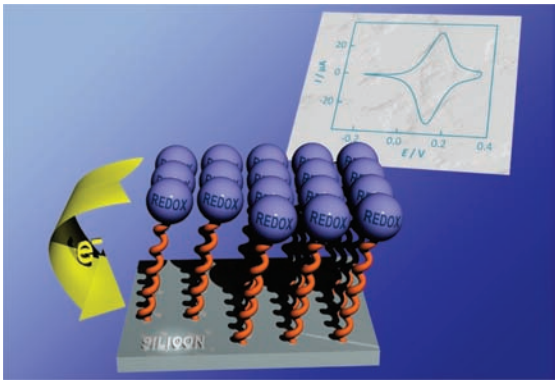
CONSPECTUS

The combination of monocrystalline silicon's well-defined structure and the ability to prepare hydrogen-terminated surfaces (Si—H) easily and reproducibly has made this material a very attractive substrate for immobilizing functional molecules. The functionalization of Si—H using the covalent attachment of organic monolayers has received intense attention due to the numerous potential applications of controlled and robust organic/Si interfaces. Researchers have investigated these materials in diverse fields such as molecular electronics, chemistry, and bioanalytical chemistry. Applications include the preparation of surface insulators, the incorporation of chemical or biochemical functionality at interfaces for use in photovoltaic conversion, and the development of new chemical and biological sensing devices.



Unlike those of gold, silicon's electronic properties are tunable, and researchers can directly integrate silicon-based devices within electronic circuitry. Moreover, the technological processes used for the micro- and nanopatterning of silicon are numerous and mature enough for producing highly miniaturized functional electronic components. In this Account, we describe a powerful approach that integrates redox-active molecules, such as ferrocene, onto silicon toward electrically addressable systems devoted to information storage or transfer.

Ferrocene exhibits attractive electrochemical characteristics: fast electron-transfer rate, low oxidation potential, and two stable redox states (neutral ferrocene and oxidized ferrocenium). Accordingly, ferrocene-modified silicon surfaces could be used as charge storage components with the bound ferrocene center as the memory element. Upon application of a positive potential to silicon, ferrocene is oxidized to its corresponding ferrocenium form. This redox change is equivalent to the change of a bit of information from the "0" to "1" state. To erase the stored charge and return the device to its initial state, a low potential must be applied to reduce the whole generated ferrocenium. In this type of application, the electron is transferred from the ferrocene headgroups to the underlying conducting silicon surface by a tunneling process across the monolayer. To produce a stable and reproducible electrical response, this process must be efficient, fast, and reversible. The stability, charge density, and capacitance performances of high-quality ferrocene-terminated monolayers could compete with those of the existing semiconductor-based memory devices, such as dynamic random access memories, DRAMs. Moreover, we provide experimental evidence that a series of immobilized ferrocene centers can efficiently communicate via a lateral electron hopping process. Using these modified interfaces, we demonstrate that the thin redox-active monolayer can behave as a purely conducting material, highlighting an unprecedented very fast electron communication between immobilized redox groups. Perhaps more importantly, the surface coverage of ferrocene allows us to precisely control the rate of this process. Such characteristics are relevant not only for electrocatalytic reactions but also for widening the potential applications of these assemblies to novel molecular electronic devices (e.g. chemiresistors, chemically sensitive field-effect transistors (CHEMFETs)) and redox chemistry on insulating surfaces.

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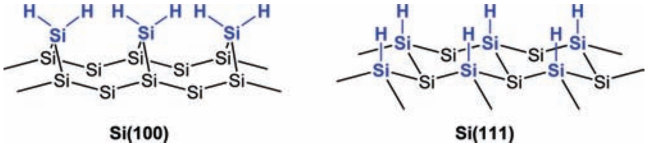
Introduction

Silicon is the Earth's second most abundant chemical element, and today high-purity silicon crystals are mass-produced. The most common surface orientations of commercially available silicon are (100) and (111). Upon exposure to air and water, both types become rapidly coated with a self-limiting, thin native oxide film that can be removed thermally under ultrahigh-vacuum conditions or wet-chemically by immersion in aqueous fluoride-containing solutions. Generally, the Si(100) surfaces treated with diluted HF (typically, 2−5%) are terminated by hydrogen predominantly in the form of dihydride and the Si(111) surfaces treated with NH_4F 40% are completely terminated with monohydride bonds normal to the surface (Scheme 1).[1,2] One great interest of the hydrogenated, oxide-free silicon surface (henceforth referred to as Si−H) is its very low density of electrically active surface defects (the so-called surface states),[3,4] which renders it particularly attractive for electrical applications. Furthermore, the Si−H surface can be handled in air under ambient conditions and rinsed in water or organic solvents for brief periods without any significant degradation of its ideal electronic properties. Despite the extensive use of Si(100) in semiconductor technology, Si(111) substrates are often preferred for further covalent grafting of organic monolayers because (i) monohydride-terminated Si(111) is atomically flat while hydrogenated Si(100) prepared under wet conditions is rough and (ii) the organic functionalization of such surfaces yields usually both more densely packed and ordered monolayers, with a higher surface coverage.[5−7] Since the seminal reports of Linford and Chidsey,[8,9] there has been a considerable body of work devoted to the covalent attachment of Si−C linked organic monolayers onto hydrogen-terminated, oxide-free silicon surfaces using linear 1-alkenes and 1-alkynes.[5−7] Such monolayers are thermally and chemically very robust owing to the nonpolar character of the strong interfacial Si−C bond. Moreover, the absence of a SiO_2 layer results in a almost defect-free electrical interface with a direct electronic coupling between the surface and the organic functionality. This situation is somewhat opposite to that of alkylsilane-derived monolayers bound to oxidized silicon,[10] which are often unstable because interfacial siloxane bonds, Si−O−Si, are susceptible to hydrolysis, and thus the long-term applicability of these surfaces remains lower than that of covalently modified unoxidized silicon.

SCHEME 1. Hydrogen-Terminated Silicon Surfaces



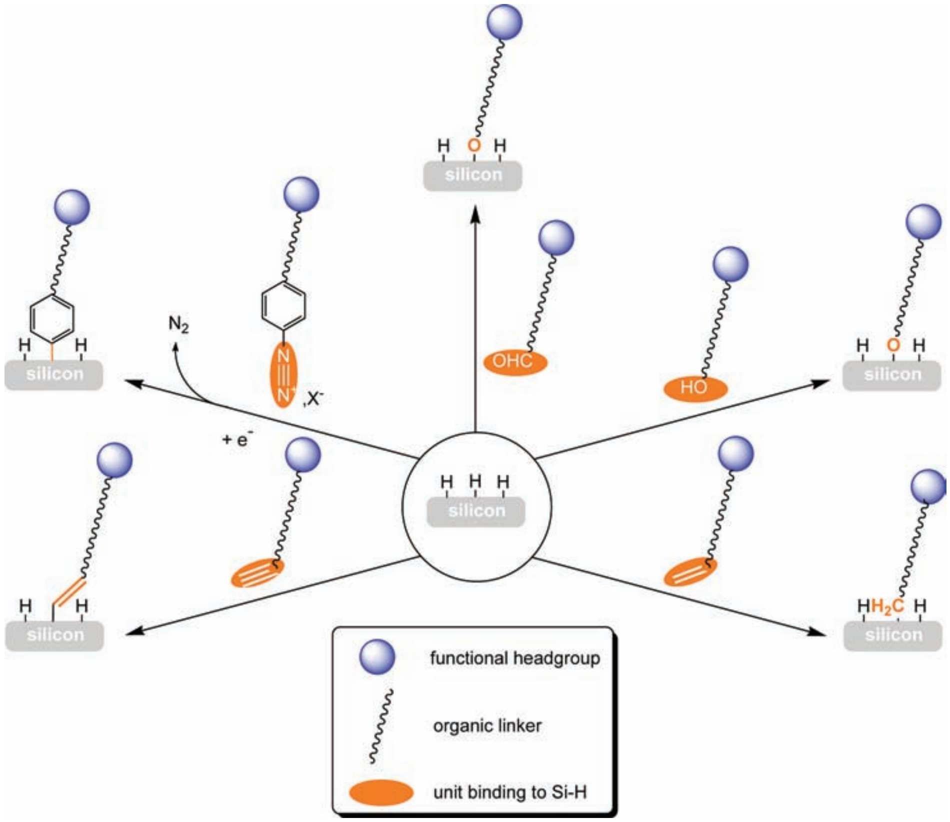
Owing to stimulating properties exhibited by linear *n*-alkyl monolayer-modified silicon surfaces, the hydrosilylation reaction has been extended to the attachment of ω-functionalized monolayers for incorporating diverse specific chemical or biochemical headgroups to silicon. Such surfaces have great potential in the field of molecular electronics, photovoltaic devices, and chemical and biological sensing.[7] In this context, the derivatization of Si−H surfaces with redox-active molecules constitutes a powerful approach to the fabrication of electrically addressable devices, particularly when the goal is integrated systems devoted to information storage or transfer. Seminal works on ferrocene self-assembled monolayers on gold[11] have demonstrated that these electroactive structures can serve as excellent model systems for studying electron transfer at surfaces, the properties of the electrical double-layer, and microenvironment effects on long-range interfacial electron transfer kinetics. Owing to attractive electrochemical characteristics exhibited by ferrocene, namely, fast electron-transfer rate, low oxidation potential, and stability of its two redox states (neutral ferrocene and oxidized ferrocenium), its introduction in organic monolayers can also be of interest for electrocatalysis, electroanalysis, and biosensing devices and for the wiring of enzymes to electrodes.[12]

This Account is intended to provide a compendium of recent advances in redox-active ferrocene-terminated monolayers covalently bound to Si−H surfaces, focusing on the attachment procedures, the electrochemical characteristics, and the charge storage capabilities of these functional surfaces. In addition, we also highlight that the electronic communication between the redox headgroups can be fine-tuned from an extremely slow to an unprecedented very fast process similar to that observed in a purely conducting material.

Attachment Procedures

ω-Functionalized Monolayers Bound to Si−H. The most common method for producing functionalized monolayers covalently bound to silicon involves the reaction of bifunctional molecules with Si−H. One end is the unit binding to the surface, and the other end is either the desired functionality or a reactive group subsequently converted to the desired functionality in high yield (Scheme 2). In the latter case, protection of the ω-substituent (e.g., amine) is often necessary in order to avoid its reaction with the Si−H surface or the formation of monolayers with mixed termination. A typical reaction for producing ω-functionalized monolayers is the photochemically, thermally, or catalytically activated hydrosi-

SCHEME 2. Direct Covalent Attachment of α,ω-Disubstituted Bifunctional Molecules to Si−H

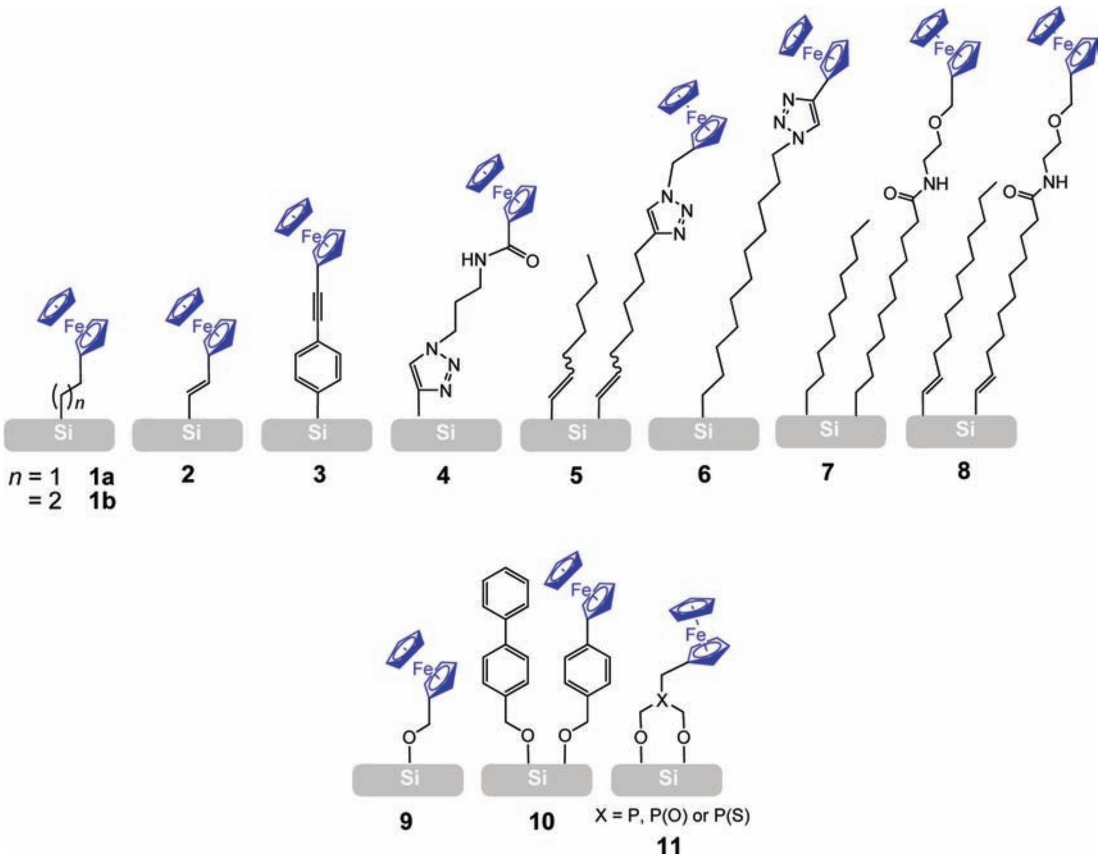


lylation with ω-substituted 1-alkenes. Another reaction of interest is the electrochemical grafting of aryldiazonium salts onto Si−H.[13,14] Molecular monolayers prepared from such reactions are attached to the silicon surface through Si−C interfacial bonds. However, it has been also demonstrated that Si−O-linked monolayers could be also prepared from the reaction of alcohols[15] and aldehydes[15,16] with Si−H. Contrariwise, disordered monolayers with Si−C and Si−O mixed termination are produced from the thermal grafting of ω-alkenoic acids and ω-alkenyl alcohols at elevated temperatures (above ca. 150 °C).

A crucial issue that must be addressed by surface scientists working in this field is to minimize the oxidation of underlying silicon during the preparation of the molecular monolayer in order to maintain a low density of surface states as close as that of the initial Si−H surface. It must be kept in mind that the maximum surface coverages of alkene- and alkyne-derived monolayers bound to Si(111) are 50−55%[9,17,18] and 60−65%[19] respectively, which means that 45−50% and 35−40% of Si−H sites remain after completion of the monolayer. These sites are susceptible to oxidation if water or oxygen can penetrate through the molecular layer via defects or pinholes. Therefore, the densest possible packing of the monolayer is sought in order to provide an efficient hydrophobic environment that is not readily penetrated by water or oxygen molecules. While this challenging prospect can be easily reached for monolayers produced from linear 1-alkenes or 1-alkynes, provided that the conditions of surface chemistry are optimized, serious efforts are required for ω-functionalized monolayers and, in particular, for redox-active monolayers essentially owing to the steric hindrance of the electroactive unit. One successful strategy to minimize the oxidation of silicon is the dilution of the redox-center-terminated chains with inert organic chains. This enables control of the surface coverage of the redox center and improvement of both the quality and the packing density of the resulting redox-active monolayer. Importantly, the presence of interfacial oxide even at low levels that are not detected by contact angle and X-ray photoelectron spectroscopy (XPS) measurements may influence the electron transfer characteristics of redox-active modified silicon surfaces.[20]

Ferrocene-Terminated Monolayers Bound to Si−H. Direct and multistep synthetic approaches have been used to functionalize Si−H surfaces with ferrocene-terminated monolayers. Following the first approach, ferrocene substituted by vinyl (**1a**),[21−25] ethynyl (**2**),[26,27] and OH-containing (methanol,[28] carboxaldehyde (**9**),[23,25] benzyl alcohol (**10**),[29−31] and phosphine (**11**)[32]) linkers have been grafted in a one-step pro-

SCHEME 3. Si–C (top) and Si–O (bottom) Linked Ferrocenyl Monolayers on Si–H[a]



[a] For some surfaces (**5**, **7**, **8**, and **10**), the dilution of ferrocene-terminated chains by inert nonredox chains enables the control of the surface coverage of the electroactive units.

cedure to Si(100) and Si(111) surfaces via the formation of interfacial Si–C or Si–O bonds (Scheme 3). A ferrocene-modified Si(100) surface (**3**) was also prepared in one-step through aryldiazonium chemistry using a phenyltriazene-derived ferrocene.[33] However, as commonly reported,[34] the aryldiazonium procedure fails to produce monomolecular films in a reproducible and controllable manner. Ferrocene monolayers on silicon have also been prepared in several steps from reactive preassembled monolayers through organolithium (surface **1b**[35]), "click" (**4**,[36] **5**[37,38] and **6**[27,39]), and carbodiimide (**7**[40,41] and **8**[42]) chemistries. Compared with the one-step grafting method, the multistep procedure often involves milder conditions (e.g., reaction in aqueous medium at room temperature). Moreover, another advantage is that the functionalization step takes place on usually densely packed, well-ordered long-chain monolayers, while the one-step attachment of substituted ferrocenes onto Si–H can produce both less ordered and less passivating monolayers. For some surfaces (**5**,[37] **7**,[40] **8**,[42] and **10**[29]), the dilution of ferrocene-terminated chains with nonredox organic chains has proved to be a useful strategy for controlling the concentration of bound ferrocene while maintaining the molecular orientation and ordering of the monolayer. Interestingly, in these mixed monolayers, the diluting chains keep the ferrocene groups well-separated from one another.

Electrochemical Characteristics of Ferrocene-Terminated Silicon Surfaces

The electrochemical characteristics of ferrocenyl monolayers prepared following the one- and multistep procedures are summarized in Table 1, and representative cyclic voltammograms for three different ferrocene-terminated Si(111) surfaces are shown in Figure 1. Cyclic voltammetry is a convenient method to determine some key electrochemical parameters, such as the formal potential, $E°'$ (average of anodic and cathodic peak potentials), the surface coverage of ferrocene units, Γ_{Fc} (from the charge integrated under the voltammetric peak), and the apparent rate constant of electron transfer, k_{app}, for the ferrocenium/ferrocene system (from the variation of cyclic voltammograms with the potential scan rate). From data in Table 1, it can be stated that silicon orientation has no significant effect on both Γ_{Fc} and the redox activity of bound ferrocene. Considering the ferrocene molecules as spheres with a diameter of 6.6 Å,[43] the theoretical maxi-

TABLE 1. Electrochemical Data of Ferrocene Monolayers Covalently Bound to Si—H

surface	silicon type and orientation	surface coverage of ferrocene (mol cm^{-2})	$E°'$ (V vs SCE)[a]	k_{app} (s^{-1})[b]	refs
1a	*p*-(100)	$(0.8-2.4) \times 10^{-10}$	0.38	130	23, 24
	n-(100)	[c]	0.24[e]	[c]	23
	n-(111)	7.5×10^{-10}	0.36	[c]	25
1b	*p*-(100)	$(3.7-4.8) \times 10^{-11}$	0.40	[c]	35
2	*p*-(100)	3.1×10^{-11}	0.61	160	26
3	*p*-(100)	2.8×10^{-9}[d]	−0.24	160	33
4	*n*-(111)	6.5×10^{-12}	0.11	[c]	36
5	*p*-(100)	3.4×10^{-10}	0.32	5.5	37
6	*p*-(100)	1.0×10^{-10}	0.47	30	39
7	*p*-(111)	3.5×10^{-10}	0.50	50	40
	n-(111)	3.5×10^{-10}	0.25[e]	[c]	41
8	*n*-(111)	5.0×10^{-10}	0.13[e]	[c]	42
9	*p*-(100)	5.0×10^{-10}	0.50	10	23
	n-(100)	[c]	0.05[e]	[c]	23
	n-(111)	2.1×10^{-10}	0.33	[c]	25
10	*p*-(100)	4.2×10^{-10}	0.62−0.77[f]	10^3-10^5[f]	29
11	*p*-(100)	1.2×10^{-10}	0.34−0.40[g]	[c]	32

[a] Saturated calomel electrode. [b] Apparent charge transfer rate constant for the bound ferrocenium/ferrocene couple. [c] Not reported. [d] Formation of multilayers occurred. [e] Under illumination; no redox response was observed in the dark. [f] Depending on the surface coverage. [g] Depending on the substituent on the phosphorus atom.

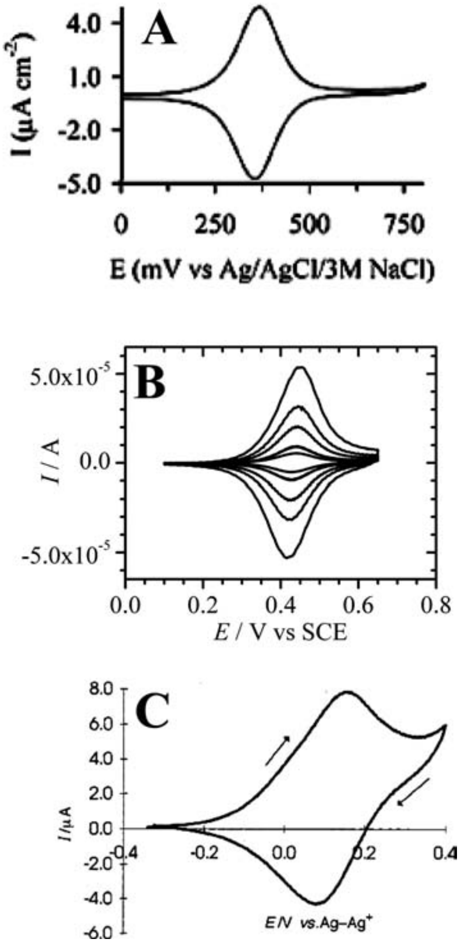


FIGURE 1. Representative cyclic voltammograms of the ferrocene-modified *p*-type silicon surfaces: (A) **5** in aqueous 1.0 M $HClO_4$ at 0.02 V s^{-1}, $\Gamma_{Fc} = 3.4 \times 10^{-10}$ mol cm^{-2}. Adapted with permission from ref 37. Copyright 2009 American Chemical Society. (B) **7** in CH_3CN + 10^{-1} M Bu_4NClO_4, $\Gamma_{Fc} = 3.0 \times 10^{-10}$ mol cm^{-2}. The scan rates are 0.1, 0.2, 0.4, 0.6, and 1 V s^{-1}. Reprinted with permission from ref 40. Copyright 2006 American Chemical Society. (C) **11** (X = P) in CH_3CN + 10^{-1} M Bu_4NPF_6 at 0.1 V s^{-1}, $\Gamma_{Fc} = 1.2 \times 10^{-10}$ mol cm^{-2}. Adapted with permission from ref 32. Copyright 1998 Royal Society of Chemistry.

mum Γ_{Fc} can be estimated at 4.8×10^{-10} mol cm^{-2}. Therefore, values measured for the surfaces **1a**, **5**, **7**, **8**, **9**, and **10** indicate a highly dense packing of ferrocene-terminated chains. Additionally, the electrochemical characteristics of such modified surfaces show features close to the ideal case for surface-confined reversible redox species, namely a small separation between the anodic and cathodic peak potentials at low scan rates (some tens of millivolts), an equality of anodic and cathodic peak currents and a full-width at half-height of the voltammetric peak close to 100 mV indicating the presence of weak lateral interactions between the ferrocene centers (Figure 1).[44] These monolayers were stable over repeated cycling through a large number of scans, from 10^3 up to an impressive number of 10^8 scans for surface **10**. In contrast, single-component monolayers with $\Gamma_{Fc} < 5 \times 10^{-11}$ mol cm^{-2} showed clearly nonideal surface electrochemistry, characterized by a splitting of the anodic and cathodic peaks and a poor reversibility of the redox process. Their electrochemical stability was also poor owing to the large number of remaining Si—H sites prone to oxidation during the electrochemical measurements. Unlike single-component monolayers, it must be underlined that the mixed monolayers with such low Γ_{Fc} values retain their ideal electrochemical characteristics and stability because the total surface coverage (ferrocene-terminated chains plus nonredox chains) is high and approximately constant in all the mixed monolayers.

There are two other noteworthy features of the electrochemical behavior of the ferrocenyl monolayers bound to silicon. Both k_{app} and $E°'$ for bound ferrocene are found to be highly dependent on the length and the chemical composition of the organic linker and the doping type of the underlying semiconductor. Expectedly, a decrease in k_{app} is observed upon increasing the distance between the redox center and the underlying silicon surface (compare **1a**[23] and **2**[26] with **5**,[37] **6**,[39] and **7**[40]), consistent with tunneling electron transfer. However, larger effects are obtained as a function of the organic linker, as evidenced with surface **10**. Despite a longer ferrocene—silicon distance, the k_{app} values reported for **10** (ranging from 10^3 to 10^5 s^{-1} upon decreasing Γ_{Fc})[29] are considerably higher than those measured for **1a** and **9**, that is, 130 and 10 s^{-1}, respectively.[23] Such observations are consistent with a strong electronic coupling mediated by the short aromatic linker in **10**.

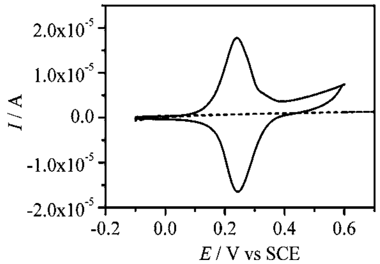


FIGURE 2. Effect of light on the electrochemical response of the *n*-type surface **7** in CH_3CN + 0.1 M Bu_4NClO_4 (−−−) in the dark and (—) under illumination. Reprinted with permission from ref 41. Copyright 2008 American Chemical Society.

For some monolayers bound to *p*-type surfaces (**2**, **7**, **9**, and **10**), the $E°'$ of bound ferrocene was 100−250 mV positively shifted relative to values measured for the molecules in solution ($E°'$ of the ferrocenium/ferrocene couple is ca. 0.40 V vs SCE when studied in a common organic solvent). In the case of densely packed ferrocenyl monolayers, this behavior can be explained by space−charge and counteranions/solvent exclusion effects at the monolayer−solution interface.[29] Moreover, the voltammetric characteristics of modified *p*-type surfaces are found not to be sensitive to illumination, which demonstrates that electron transfer is not limited by the number of charge carriers in the semiconductor.[45] This behavior is consistent with electrochemistry of a *p*-type semiconductor in accumulation conditions, that is, accumulation of valence band holes in the space charge region of silicon. Under these conditions, the *p*-type electrode behaves as a metal. In contrast, no oxidation current was observed for modified *n*-type surfaces in the dark as expected for a semiconductor under depletion conditions, that is, when few majority carriers are available for charge transfer.[45] The electroactivity of ferrocene-modified *n*-type surfaces was observed only under illumination because photogenerated electron−hole pairs are required to promote electrooxidation of ferrocene (Figure 2). As a result of the activation of the redox process, the redox potential of ferrocene bound to *n*-type silicon under various illumination intensities is around 200−300 mV lower than that observed for ferrocene bound to *p*-type silicon.

Charge Storage in the Ferrocene Headgroups

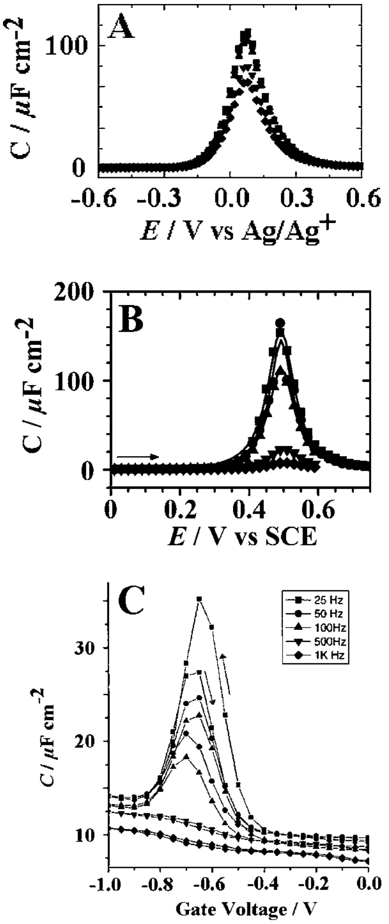


FIGURE 3. Capacitance−potential curves of ferrocene-modified *p*-type silicon surfaces measured at (■) 25, (●) 50, (▲) 100, (▼) 500, and (◆) 1000 Hz: (A) Si(100)-**1a** in $CH_3CN + 10^{-1}$ M Et_4NClO_4, $\Gamma_{Fc} = 2.4 \times 10^{-10}$ mol cm^{-2}. Adapted from ref 23 with permission from Elsevier. (B) **7** in $CH_3CN + 10^{-1}$ M Bu_4NClO_4, $\Gamma_{Fc} = 3.5 \times 10^{-10}$ mol cm^{-2}. Adapted with permission from ref 40. Copyright 2006 American Chemical Society. (C) **10** in propylene carbonate containing 1.0 M Bu_4NPF_6, Γ_{Fc} not reported, area 1×10^{-4} cm^2. Reprinted with permission from ref 30. Copyright 2002, American Institute of Physics.

Capacitance and Charge Retention Characteristics. Globally, the cyclic voltammetry measurements have enabled demonstration that surfaces **1a**, **5**, **7**, **8**, **9**, and **10** exhibited stable and ideal electrochemical characteristics, with particular emphasis on **10** showing the most remarkable electrochemical stability (10^8 cycles). Such data must be supplemented by capacitance and charge-retention measurements to determine whether molecular memories could result from such hybrid junctions. However, to avoid photoinduced charge transfer processes, only modified *p*-type surfaces have been characterized. First of all, the capacitance characterization of these functional surfaces showed capacitance peaks at potentials relatively close to the formal potential of bound ferrocene (Figure 3). These peaks were not observed for nonredox organic monolayers and were clearly attributed to the charging/discharging currents associated with the oxidation/reduction of bound ferrocene. Micrometer-sized electrolyte−molecule−silicon (EMS) capacitor structures with **10** yielded a maximum capacitance of 20−30 μF cm^{-2} at 100 Hz,[29,30,46] while values higher than 100 μF cm^{-2} were obtained at the same frequency for millimeter-sized **1a**[23] or **7**[40] studied in traditional electrochemical cells. Even though the values measured for **1a** and **7** are particularly encouraging, it remains to be demonstrated whether the charge storage capacity of these surfaces is retained as the cell size shrinks. Indeed, this constitutes a crucial issue for existing memory cells. The charge retention characteristics of these ferrocenyl monolayers were determined rigorously by the Bocian and Lindsey groups for the surface **10** using a chronoamperometry-derived electrochemical technique.[47] Charge retention was expressed in terms of half-life times ($t_{1/2}$), that is, the time required for reducing half of the total electrogenerated ferrocenium species to ferrocene after the electrical disconnection of the modified surface. The $t_{1/2}$ values obtained for **10** were in the 150−200 s range for $\Gamma_{Fc} > 2 \times 10^{-11}$ mol cm^{-2} and were found to decrease dramatically upon decreasing Γ_{Fc} at lower coverages.[29] For example, a value of only 25 s was determined at $\Gamma_{Fc} = 1.0 \times 10^{-11}$ mol cm^{-2}. Based on the fact that the charge-retention time can be increased by increasing the insulating linker length, Fabre et al. have also examined the charge retention capabilities of the surface **7**. A maximum $t_{1/2}$ of 200 s was obtained at $\Gamma_{Fc} = 3.5 \times 10^{-10}$ mol cm^{-2} with a similar surface coverage dependence.

Comparison with Existing Memory Devices. Among the existing charge storage devices of modern computers, the dynamic random access memory (DRAM) is the prime candidate for which there is the most interesting opportunity of integrating ferrocene-functionalized silicon surfaces. DRAM is a volatile memory because the information can be stored only when powered. Unlike DRAM, FLASH memory is nonvolatile because no power is needed to maintain the information stored in the cell. The capacitance of today's DRAM storage cell is on the order of 30 fF with benchmark cell-size of ca. 1 μm × 1 μm, which corresponds to a capacitance density of 3 μF cm^{-2}.[48] Furthermore, this device operates at a minimum voltage of 1.0 V, and the leakage current of the DRAM access transistor is on the order of 1 fA. With such characteristics, a typical DRAM cell can retain the state of the stored data for ca. 100 ms because the dielectric between the two electrodes of the DRAM capacitor is not able to stabilize the charged state. The major challenge for DRAM manufacturers is therefore the requirement of high cell capacitance and low leakage currents in order to preserve adequate retention time. Consequently, ferrocenyl monolayer-functionalized silicon surfaces could provide some benefits in the current memory devices, in terms of redox stability, charge-retention time, and capacitance. Moreover, because the potential required to oxidize ferrocene is much lower than 1.0 V, the charge could be stored with lower power consumption. Higher charge densities are also expected because the surface coverages reached for high-quality ferrocenyl monolayers are in the range $(1.0{-}4.0) \times 10^{-10}$ mol cm^{-2}, which corresponds to charge densities in the range 10−40 μC cm^{-2}, these values being much higher than those measured for Si/SiO$_2$ capacitors currently used in DRAM memories. A major issue that must be addressed deals with the thermal stability of ferrocene-functionalized silicon surfaces. High-temperature conditions (>400 °C) are commonly used during the fabrication of charge storage devices. Even though unsubstituted ferrocene was reported to be decomposed only above ca. 450 °C,[49] evidence must be provided that the ferrocene-terminated organic chains exhibit a comparable or higher thermal stability and that the redox activity of the resulting assemblies remains unchanged after high-temperature treatment. Moreover, the use of solid electrolytes, such as high-κ dielectric materials (e.g., aluminum nitride, AlN), instead of liquid electrolytes would be required in order to satisfy such thermal requirements.

Lateral Charge Transport between Ferrocene Headgroups

Another important issue with ferrocene-terminated monolayers concerns the elucidation of the charge transport mechanism in these assemblies, and in particular, a central question is the control of mass-transport and charge-transfer processes occurring at monolayer-modified interfaces. In this connection, common investigations are based on transient electrochemical methods, such as the simple examination of the response of a reversible redox couple by cyclic voltammetry at the modified surface used as an electrode. When the redox centers are immobilized on the surface, similar procedures could be used and are especially powerful when combined with the use of ultramicroelectrodes (UME). However, these studies provide a global view of the modified surface and are, in principle, limited to the investigations made on conducting (or semiconducting) substrates. In these experimental conditions, the control of the electron transfer may have several origins and may involve different pathways, typically tunneling through space or through the organic layer to the substrate, direct electron transfer between the surface and the redox molecules in solution, and charge exchange between redox-active species attached to the surface. This complexity typically hampers an accurate estimation of the individual contributions of each pathway. An elegant approach to solve this issue has been proposed by Fabre, Hapiot, Zuilhof, and co-workers,[41,42] using high-quality ferrocenyl monolayers on silicon (**7** and **8**) in combination with scanning electrochemical microscopy (SECM). SECM has been shown to be a powerful tool to analyze redox-active monolayer or polymer-

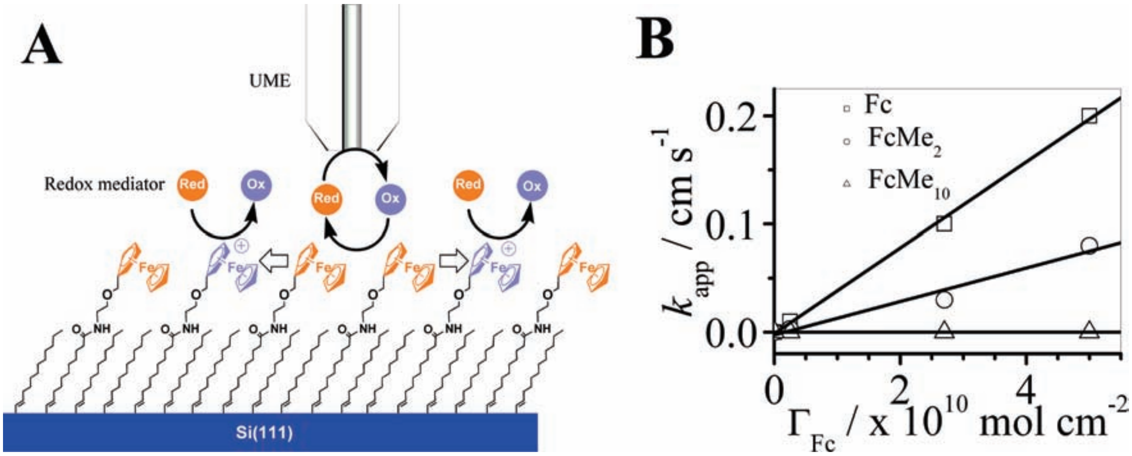


FIGURE 4. (A) Electron transfer at a mixed dodecenyl/ferrocene-terminated monolayer-modified *n*-type Si(111) surface (**8**) probed by SECM in the presence of a dissolved redox mediator and in the dark. (B) Plots of k_{app} vs Γ_{Fc} for three ferrocene-based redox mediators: ferrocene (Fc, □), dimethylferrocene ($FcMe_2$, ○), and decamethylferrocene ($FcMe_{10}$, Δ) at 1 mM in DMF + 0.1 M Bu_4NClO_4. $FcMe_2$ and Fc display a more positive formal potential, $E°'$ (0.32 and 0.40 V vs SCE, respectively), than that of the grafted Fc and consequently can oxidize the bound Fc centers. $FcMe_{10}$ has a less positive $E°'$ (0.0 V vs SCE) and consequently cannot oxidize the bound Fc centers. Reprinted with permission from ref 42. Copyright 2010 Wiley-VCH.

modified surfaces.[50] The major difference from many other electrochemical methods is that, in SECM, the surface is locally probed from the solution side with an UME and a dissolved redox mediator. Such a configuration thus permits the characterization of electroactive layers on insulating surfaces. Therefore the contribution of the substrate in the charge transport mechanism can be eliminated, and this subsequently allows an accurate determination of the bimolecular electron transfer kinetics between attached and dissolved redox species.[51] Considering the insulating properties of *n*-type silicon in the dark with respect to oxidation, a preliminary SECM study under these conditions of the single-component ferrocenyl monolayer has demonstrated that the charge hopping between the ferrocene headgroups was so fast that the time resolution of the SECM setup only allowed a lower limit for this rate,[41] similar to ultrafast charge hopping in redox polymers.[52] These authors have then demonstrated that the 2D charge propagation rate between bound redox centers could be simply and efficiently controlled via the surface coverage of the electroactive units and the nature of the dissolved mediator. A straightforward linear relationship between k_{app} and Γ_{Fc} was observed, which reflected the variations in the electron-transfer kinetics at the layer, switching from an extremely slow to a very fast process (Figure 4). In addition to its contribution to fundamental electrochemistry, this study opens up a promising platform for the design of novel electrochemical sensors and other electrochemically switchable systems based on insulating substrates.

Conclusions and Outlook

Ferrocene-terminated monolayers covalently bound to Si–H showed stability, electron-transfer, and charge retention characteristics essentially determined by the composition and the length of the organic linker but also by the surface coverage of ferrocene. Ferrocene-modified *p*-type Si(100) and Si(111) surfaces with Γ_{Fc} in the range (1.0–4.0) × 10^{-10} mol cm^{-2} exhibited a stable (between 10^3 and 10^8 redox cycles without significant degradation) and perfectly reversible one-electron system attributed to the bound ferrocenium/ferrocene couple. Unlike modified *n*-type surfaces, which required illumination to promote the oxidation of ferrocene, their characteristics were not dependent on the intensity of the illumination. High charge storage capacities (>10 μF cm^{-2}) and charge retention times (>100 s) have also been reported. Taken together, such properties demonstrate the potential of these redox assemblies for molecular memory devices.

In order to improve the performances of the molecular-based memory devices but also to widen the scope of this research toward current rectifying diodes and electroswitchable optical systems, modified silicon surfaces incorporating other electroactive molecules, such as metalloporphyrins,[27,29,53] polyoxometallates,[54,55] and organometallics,[56] have been also considered. For example, the integration of metal-complexed porphyrins to silicon could provide a real breakthrough in the field of molecular-based information storage. Indeed, metalloporphyrins show very exciting electrochemical characteristics, such as multiple electron transfer steps at relatively low potentials, chemical stability of the different redox forms under ambient conditions, and a versatility of their redox properties depending on the nature of the complexed metal. Metalloporphyrin-modified silicon surfaces could be used as multibit information storage media with high charge density in which electrical charge is stored in multiple redox states of the bound molecules. However, the use of polyoxometallates as multiredox centers in monolayers would be more compatible with the fabrication techniques of molecular-based information storage devices using high temperatures. Indeed, the polyoxometallates have been often considered as inorganic analogues of metalloporphyrins with the advantage of being more resistant toward an oxidizing environment and more thermally stable.

BIOGRAPHICAL INFORMATION

Bruno Fabre, 43, received his Ph.D. in 1994 at Grenoble University, France, under the supervision of Prof. Gérard Bidan. In 1995, he joined the Centre National de la Recherche Scientifique (CNRS) as a full time researcher in the Laboratory of Molecular and Macromolecular Electrochemistry at the University of Rennes. In 2002, he was awarded a NATO advanced fellowship to perform his research in the Steacie Institute for Molecular Sciences (National Research Council, Ottawa, Canada) under the guidance of Prof. D. D. M. Wayner. He is currently Directeur de Recherche at CNRS working in the laboratory Sciences Chimiques de Rennes. His research interests focus on chemically modified electrodes, the functionalization and micro- or nanopatterning of silicon surfaces.

FOOTNOTES

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