

Annual Review of Analytical Chemistry Functionalized Silicon Electrodes in Electrochemistry

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Abstract

Avoiding the growth of SiO_x has been an enduring task for the use of silicon as an electrode material in dynamic electrochemistry. This is because electrochemical assays become unstable when the SiO_x levels change during measurements. Moreover, the silicon electrode can be completely passivated for electron transfer if a thick layer of insulating SiO_x grows on the surface. As such, the field of silicon electrochemistry was mainly developed by electron-transfer studies in nonaqueous electrolytes and by applications employing SiO_x-passivated silicon-electrodes where no DC currents are required to cross the electrode/electrolyte interface. A solution to this challenge began by functionalizing Si-H electrodes with monolayers based on Si-O-Si linkages. These monolayers have proven very efficient to avoid SiO_x formation but are not stable for a long-term operation in aqueous electrolytes due to hydrolysis. It was only with the development of self-assembled monolayers based on Si-C linkages that a reliable protection against SiO_x formation was achieved, particularly with monolayers based on α,ω -dialkynes. This review discusses in detail how this surface chemistry achieves such protection, the electron-transfer behavior of these monolayer-modified silicon surfaces, and the new opportunities for electrochemical applications in aqueous solution.

INTRODUCTION AND SCOPE

Recent decades have seen major advances in the functionalization of silicon electrodes with selfassembled monolayers (SAMs). The impact has been important for several areas of electrochemistry, including memory devices (1–3), optical energy conversion (4), electrochemical sensors (5, 6), biologically active interfaces (7, 8), photoelectrochemical patterning (9), molecular electronics (10), and electrostatic catalysis (11, 12). Surface-modification strategies afford opportunities to control electronic (13) and chemical properties of silicon devices (14, 15), tune the photoelectronic characteristics beyond the dopant type (6, 16), and build molecular-scale devices on silicon surfaces (17).

A persistent challenge has been the functionalization and application of silicon electrodes without the formation of significant levels of SiO_x , which can adversely affect the electronic properties of the silicon electrode, particularly if the oxide levels change during a measurement. For instance, a silicon/SAM interface without the presence of SiO_x is an almost defect-free electrical interface, with a direct electronic coupling between the surface and the organic functionality (14, 18, 19). The maintenance of this condition is key to stabilizing faradaic electrochemistry performed on silicon. As suggested in a recent study (20), even the presence of interfacial SiO_x at low levels that are not detected by X-ray spectroscopy (XPS) measurements may influence the electron transfer characteristic of redox-SAM-functionalized silicon substrates.

The scope of this review is to discuss how progress on functionalized silicon electrodes is closely associated with our ability to stabilize the silicon surfaces against oxidation during electrochemical measurements. Our focus is mostly dedicated to electrochemical assays performed in aqueous electrolytes, where minimizing SiO_x formation has proven very challenging. As shown in **Figure 1**, the most common method for producing functionalized SAMs covalently bound to silicon involves the reaction of bifunctional molecules. One end possesses functionality to conjugate to the silicon surface. The other end can be either the desired functionality or a reactive group that can be used to couple the desired functionality to the surface (18). These strategies allow molecular monolayers to be directly attached to the silicon surface through Si–O–Si or Si–C bonds. In this context, the next section starts with the oil crisis of 1973, which stimulated the development of photoelectrochemistry in semiconductors (21). As we illustrate, monolayers based on Si–O–Si bonds allowed Wrighton and coworkers to report the first significant achievements on minimizing silicon degradation during electrochemical measurements (22, 23).

PIONEERING STUDIES ON FUNCTIONALIZED SILICON ELECTRODES FOR PHOTOELECTROCHEMICAL APPLICATIONS

In the 1970s, the development of photodevices based on silicon/electrolyte junctions was focused on the conversion of light to electricity and for the photogeneration of storable chemical fuels in the form of electrolytic products (24). Considerable effort was directed toward maintaining the integrity of the silicon surface, as degradation of silicon had severe effects on the loss of performance of such photodevices. To understand the reasons, a basic description about the silicon/electrolyte junction characteristics is necessary (**Figure 2a**) (14, 25, 26). Mainly, immersion of a silicon electrode into a liquid electrolyte containing a redox couple results in a charge-transfer equilibration between the two phases. That is, the Fermi level (E_F) of the silicon electrode becomes poised to the redox potential of the solution (E_{redox}). This electrostatic equilibrium generates a space-charge layer (SCL) located in the silicon adjacent to the interface exposed to the liquid. Because the concentration of majority charge carriers near the junction becomes diminished, the SCL is also called the depletion region. The thickness of the depletion region increases with diminishing



The most common strategies for functionalizing silicon electrodes.

doping level. Therefore, the observation of photoeffects generally requires the use of a lowly doped semiconductor. In the dark, depleted silicon electrodes have insufficient carriers available near the surface for redox reactions to proceed, and charge transfer across the silicon/electrolyte junction is kinetically limited. On lowly doped n-type silicon, the depletion regime is sustained for potentials positive of the device flat band potential ($E_{\rm FB}$, the applied potential at which there is no SCL). At potentials negative of $E_{\rm FB}$, majority charge carriers start to accumulate on the surface, and the silicon electrode acquires a metallic behavior where photoeffects are no longer observed. On lowly doped p-type silicon, the situation is the reverse, with the depletion and accumulation regimes located at potentials more negative and positive of $E_{\rm FB}$, respectively. When a silicon electrode in the depletion regime is illuminated with suprabandgap light, electron-hole pairs are generated, and the direction of the electrical field into the space-charge layer makes the minority charge carriers gather on the silicon/electrolyte junction. Because holes and electrons are the minority charge carriers on n-type and p-type semiconductors, respectively, lowly doped n-type silicon can be used as a photoelectrode for anodic reactions (with an oxidizing power no greater than the energy of the valence band, E_{VB} , while lowly doped p-type silicon can be employed as a photoelectrode for cathodic reactions (with a reducing power equal to the energy of the conduction band, $E_{\rm CB}$). The problem with keeping silicon photoelectrodes stable is that, on n-type silicon, photooxidation of the electrode itself is a hole-dependent process that directly competes with the photooxidation of solution species. On p-type silicon, degradation also may happen as the holes available in the dark provide a mechanism for surface oxidation (27-29).

In 1977, Wrighton and coworkers (30) reported results on the sustained conversion of light to electricity by using a lowly doped n-type silicon-based photoelectrochemical cell operating



(*a*) A diagram showing the working principles of photoelectrochemistry on n-type and p-type silicon electrodes. The silicon electrode is biased into depletion, and the formation of space-charge layer (SCL) impedes electron transfer across the dark interface due to insufficient charge carriers in this region. Suprabandgap illumination of the silicon increases the minority charge carrier density and allows photooxidation and photoreduction to occur on n-type and p-type silicon electrodes, respectively. (*b*) Stabilization of n-type silicon in aqueous solution by derivatization. Plots of an n-type silicon electrode (4–5 Ω cm) illuminated with light at 632.8 nm. The silicon photoelectrode was held at +0.2 V versus a saturated calomel reference electrode in stirred solutions. The supporting electrolyte is 0.1 M NaClO₄ in doubly distilled deionized H₂O. Run 1 (*triangles*) involved an HF-etched naked electrode in supporting electrolyte plus 4 × 10⁻³ M Fe(CN)₆⁴⁻; and run 3 (*filled circles*) an electrode derivatized with (1,1'-ferrocenediyl)dichlorosilane, in the same solution as run 2 (22). Adapted with permission from Reference 22. Copyright 1979, American Chemical Society.

in an ethanolic electrolyte solution of ferricenium/ferrocene. The significant finding was that ferrocene could suppress the appearance of SiO_x on silicon. It was hypothesized that ferrocene was capturing photogenerated holes at a rate that prohibited SiO_x to grow. This discovery encouraged Wrighton and coworkers to chemically attach ferrocene onto the silicon surface to protect silicon from destructive photoreactions (**Figure 2b**). In these early studies, silicon derivatization was performed using organosilane molecules with ferrocene moieties attached (23, 31, 32). Other important findings of these studies were that (*a*) on functionalized lowly doped n-type silicon, ferrocene could be oxidized at more negative potentials (~0.5 V) than on a functionalized electrode of metallic behavior. Such a phenomenon was later associated by Lewis and coworkers to the presence of an open circuit photovoltage (33). (*b*) The photogenerated ferricenium would then be capable of oxidizing solution species, such as $[Fe(CN)_6]^{4-}$ ions (22). Lastly, (*c*) the durability of a ferrocene-silane-functionalized silicon photoanode could be improved in comparison to a naked silicon electrode, even in aqueous-based electrolytes, due to the inhibition of photogenerated hole processes associated with the SiO_x formation.

An alternative approach used by Tsubomura and coworkers (34) and Bard and coworkers (35) to stabilize silicon electrodes from photodegradation involved the replacement of a SAM by a thin noble metal coating layer. For instance, it was demonstrated that noble metal silicide-coated n-type silicon electrodes could be applied to the photogeneration of highly oxidizing species, such as chlorine and oxygen, with durable photoelectrochemical performance in aqueous solution (36). Later, it was shown that the electrochemical performance of the noble metal silicide-coated n-type silicon electrodes depended strongly upon the metal, the charge transfer kinetics at the silicide/ electrolyte interface, and the doping level of the silicon substrate (37).

The work of Wrighton's (30) and Bard's (35) groups emphasizes that stabilizing a silicon/ electrolyte interface is an important requirement for silicon electrodes. For monolayerfunctionalized silicon, the pioneering studies on photodevices made significant progress by using an organosilane-based surface chemistry strategy. Despite these early successes, it is evident that silane-derived monolayers bound to silicon are susceptible to hydrolysis, and thus the long-term applicability of these surfaces cannot sustain a SiO_x-free silicon/SAM interface. As we show later in this review, this challenge started to be addressed in 1990s with the use of SAMs that are based on the formation of Si–C linkages, rather than the Si–O–Si bonds of organosilanes. Meanwhile, the next section shows how the enduring challenge of avoiding SiO_x growth has initially led to the development of silicon electrochemical sensors based on field-effect transistors (FETs). In such devices, a thick SiO₂ layer is typically present to stabilize the surface, and no DC currents are required to cross the silicon/electrolyte interface.

FIELD-EFFECT TRANSISTOR SENSORS BASED ON ELECTROLYTE-INSULATOR-SILICON

FETs have been widely utilized in chemical and biological applications. Typically, these devices use high-input impedance measurements to not affect the dynamic equilibrium of chemical species. During the 1970s, different forms of FETs applied to sensing were developed, such as the chemically sensitive field-effect transistor (CHEMFET) (38), ion-sensitive field-effect transistor (ISFET) (39), and electrolyte insulator semiconductor field-effect transistor (EISFET) (40). In FET sensors, the gate electrode is sensitive to the chemical species adsorbed on the surface and detects the changes in surface potential. In 1988, Hafeman and coworkers (41) introduced the light-addressable potentiometric sensors (LAPS). Though based on the same technology as CHEMFET, the advantage of LAPS was in using light to allow spatial addressability of the surface by illuminating discrete regions of the silicon electrode (42).

Generally, FET sensors have been based on both functionalized and nonfunctionalized silicon. The unmodified FET sensors have a passivation layer of either SiO₂ or Si₃N₄ where silanol groups are at majority in either case. The charge of these functional groups is dependent on the concentration of protons in the solution (43), which alters the surface chemical potential and triggers the detectable redistribution of charge carriers in the semiconductor layer. As a result, the pH of the solution can be directly measured without further functionalization. By exploiting this technique, Bustillo and coworkers (44) performed DNA sequencing of genomes by fabricating 1.2 million arrays of FET sensors, with each well consisting of reagents for DNA extension. Each extended nucleotide produced H⁺ ions that altered pH of the solution and was detectable by the sensor. Similarly, Zhang and coworkers (45) developed an integrated chip to amplify and detect target DNA sequences with direct measurement of pH change during DNA polymerization. Additionally, unmodified FET sensors were also used for temporally monitoring neural activity (46, 47). Similarly, FET sensors have also been functionalized with antibodies (48), enzymes (49), ionophores (50), peptides (51), aptamers (52), and small molecules (53) for the consecutive detection of viruses (54), proteins (55, 56), DNA (45, 57), bacteria (58), and pH (46). Compared to sensors with unmodified silicon relying simply on surface charge, functionalization provides selectivity, as well as versatility, thus broadening the scope of sensor such that multiple analytes can be detected.

The great power of LAPS in sensing, as recently reviewed by Yoshinobu et al. (42), is that arrays of sensors can be formed with only one connecting wire. This is because a silicon-based surface illuminated by modulated light at discrete regions generates electron-hole pairs and, hence, an AC photocurrent is measured, only at the illuminated region (42). Because the capacitance at the space charge layer changes with the binding of (bio)chemical species to the interface, LAPS can detect changes in the surface Nernstian potential. This confers LAPS with the capability of sensing the spatial distribution of pH or the concentration of a specific chemical species (Figure 3). Because measurements occur only at the illuminated spot, LAPS allows the collection of electrochemical data with spatial resolution in a serial (single scanning-focused modulated light beam) (59) or parallel fashion (multiple sources of modulated light at the same surface) (60). LAPS remains, however, as a potentiometric sensing technique with no DC currents crossing the interface. This is an inevitability of the thick insulating SiO₂/Si₃N₄ layer that is necessary to stabilize the measuring interface, as hydrogenated silicon is not stable in aqueous media. Stabilizing silicon in aqueous media without an intervening silicon oxide layer has proven to be an enduring challenge in combining the light addressability of LAPS with the opportunities of amperometric measurements. As discussed in the next section, addressing this challenge is closely associated with alternatives to organosilane chemistry for the modification of the silicon and its protection against oxidation.

PROTECTING SILICON FROM OXIDATION WITH ORGANIC MONOLAYERS BASED ON SILICON-CARBON LINKAGES

To overcome the challenge of protecting oxide-free silicon substrates from oxidation, the use of organic monolayers covalently bound to silicon via the Si–C bond is an appealing direction (62). A strong interfacial bond (447 kJ mol⁻¹) and the low polarity of the Si–C bond mean it is less likely to hydrolyze than the Si–O–Si bonds exhibited by interfacial siloxanes. Nevertheless, SAMs based on Si–C bonds need to be sufficiently ordered to provide the density of the organic functionality to prevent the ingress of water and oxygen into the monolayer and hence from interacting with the silicon substrate (63). In addition, in order to allow amperometric measurements, the SAM needs to be thin enough for electron transfer to occur.

Pioneered by Linford & Chidsey (64) in the 1990s, the first organic monolayer directly bonded to an apparently oxide-free silicon surface was prepared by reacting a hydrogen-terminated silicon



(*a*) Representation of a typical light-addressable potentiometric sensor (LAPS) configuration. A bias voltage is applied to form a space-charge layer into the semiconducting electrode. Then, a modulated focused light beam is used to address discrete regions of the surface while an amplifier is used to record local-induced photocurrents. (*b*) Example of photocurrent versus bias voltage curves obtained with LAPS for different concentrations of a target analyte. For instance, at a constant photocurrent value, the shift in bias voltage is proportional to the change of analyte concentration. Adapted from Reference 61 under the terms of the Creative Commons Attribution Non-Commercial (CC BY-NC-ND) License, https://creativecommons.org/licenses/by-nc-nd/4.0/.

surface with deoxygenated diacyl peroxides $[RC(O)O]_2$ at 90–100°C. Under such conditions, the diacyl peroxides were decomposed, liberating CO₂ molecules and giving alkyl radicals R•. The radical species extract the H from the silicon surface, resulting in Si•, which then interacted with another alkyl radical R• or coupled directly with a diacyl peroxide molecule to yield an alkyl or acyloxy covalently linked silicon surface Si–R or Si–OC(O)–R' (64, 65). It was shown that 70% of the resultant monolayer was coupled to the silicon via an Si–C linkage. The Si–C coupled parts of the monolayer were resistant to degradation while the remaining 30% coupled via Si–OC(O) linkage was less stable and would be removed under hydrolytic condition. Subsequently, it was found that the treatment of H–Si(111) and a mixture of 90% 1-alkene and 10% diacyl peroxide eventually yielded a monolayer with identical thickness and density to the one prepared from 100% diacyl peroxide. Isotope labeling experiments showed that the majority of the alkyl chains in the monolayer were from 1-alkene and connected by an Si–C linkage even though the diacyl peroxide was required to generate free radicals to initiate the coupling reaction (65).

During the intervening 25 years since the seminal discovery by Chidsey and coworkers (64, 65), several methods for preparing an organic monolayer directly bonded to oxide-free silicon have been reported (**Figure 1**). The most common methods include radical-mediated hydrosilylation, thermal- and UV-initiated hydrosilylation (20, 65–71), alkylation of a halide-terminated surface (72–74), Grignard reaction (75), and electrochemical grafting (76, 77). To achieve oxide-free silicon, the modification usually involves a step to remove the native oxide layer on the silicon

substrate with NH₄F or HF solution, and the reaction environment needs to be oxygen and moisture free. The quality of the monolayer formed using different methods may vary. Any variation in the monolayers will result in variance in the electrical property of the silicon electrodes (63). These modification methods have been well summarized in several reviews that readers could refer to for details (62, 63, 78).

With a view to protecting the silicon substrate from oxidation, it is noteworthy that Si–C-linked SAMs on silicon have been subjected to a wide range of extreme conditions to test their stability. Negligible changes in monolayer thickness and water contact angle have been found after being treated in boiling water, boiling acid/base, and boiling chloroform (65). The fact that the Si–C bond is more stable than Si–O bond is attributed to the similar electronegativity between Si and C and hence less likely to be cleaved by nucleophilic substitution (78). The thermal stability of the Si–C-linked SAM has also been tested using high-resolution electron energy loss spectroscopy. Excellent stability was again observed with the alkyl monolayer withstanding heat treatment up to approximately 342°C (79).

The capability to prepare defect-free alkyl monolayers was first explored in depth on Si(111) surfaces. The outcome was that the carbon adjacent to the silicon surface, the distal carbon moieties, and the alkyl chain length are all factors affecting the quality of the monolayer and its capability to protect the underlying silicon from oxidation. For instance, Haick and coworkers (72, 73) compared the stability of the monolayers with Si–C–C, Si–C=C, and Si–C≡C linkages that had the same carbon back bond but differed in the types of C-C bond nearest to the Si(111) surface. They found that the Si–CH=CH–R surface showed the best stability against oxidation over 65 days in air or 24 h in water. Some degree of oxide was detected for Si-C-C-R and Si-C≡C-R (R = alkyl). The poorer stability of Si-C-C-R could be explained by a low surface coverage of the monolayer in which XPS showed that only \sim 50% of the Si-H bonds were converted to an Si-C linkage. This 50% modification of the Si atoms is attributed to the footprint of the aliphatic hydrocarbon chain of 20 $Å^2$ being greater than the spacing of the Si atoms in Si(111). For both Si-CH=CH-R and Si-C=C-R surfaces, the coverages were estimated to be near 100% because the footprint of the alkyl chain was less. It was suggested that in Si-C=C-R linkage the intermolecular $\pi - \pi$ interactions between the neighboring molecules played an important role in stabilizing the system. However, the extra lone electron pair in Si–C \equiv C, was thought to be transferred to the Si-C bond, making it more susceptible to oxidizing agents such as O_2 and H_2O (72, 73) (Figure 4a).

The stability of monolayers formed using thermal hydrosilylation, with different carbon functionalities adjacent to the Si surface on Si(111), was also explored by Zuilhof and coworkers (67, 68). In thermal hydrosilylation, heat initiates the reaction by creating a surface radical that attacks the unsaturated bond to link the alkyl chains to the substrate by a Si-C bond. Monolayers grafted in this way are not subject to multilayer formation or hydrolysis. Si-C-C and Si-C=C linkage surfaces were prepared from 1-alkene and 1-alkyne derivatives. The proposed reasons for the higher stability of the Si-C=C-R surfaces were the following: (a) From the thermodynamic point of view, the 1-alkyne moiety is more reactive toward H-Si than 1-alkene, and there is more energy gained when forming Si-C=C (67, 68); (b) the Si-C=C linkage has a smaller van der Waals radius, resulting in less steric hindrance between neighboring molecules than the Si-C-C linkage; and (c) the Si-C=C is more rigid, which aids in defining the conformation of the entire molecule, the result of which is a more ordered monolayer (67, 68). As a result, the monolayer formed by Si-C=C linkage is more densely packed and of higher quality to protect the underlying silicon from oxidation. As discussed below, this is absolutely crucial for the ability of monolayer-modified silicon electrodes to perform amperometric electrochemistry in aqueous solution.



(*a*) Comparison between the capability of Si–CH=CH–CH₃ and Si–C≡C–CH₃ monolayers to prevent oxygenated species from reacting on Si(111) surfaces. Adapted with permission from Reference 73. Copyright 2008, American Chemical Society. (*b*) X-ray spectroscopy (XPS) narrow scans for the Si 2p region of acetylenyl- and methyl-terminated Si(100) surfaces. (*b,i*) Organic monolayer prepared by thermal hydrosilylation of 1,8-nonadyine at 170°C (3 h) showing no evidence of SiO_x formation (*inset*). (*b,ii*) Alkyl-passivated Si(100) surfaces prepared by thermal grafting of alkyne at 95°C (7 h) and characterized by the presence of a SiO_x peak at ca. 103 eV. (*b,iii*) XPS data for an acetylenyl monolayer prepared from 1,8-nondiyne at a lower hydrosilylation temperature (95°C, 7 h) showing detectable levels of SiO_x (*inset*). These results suggest that the distal acetylene moiety of 1,8-nonadiyne is important for obtaining Si(100) surfaces on which SiO_x levels are below the detection limit of XPS. The quality of the organic monolayer is affected by the reaction temperature. Adapted with permission from Reference 70. Copyright 2009, American Chemical Society.

It is worth mentioning that Si(111) has a higher atomic density of exposed atoms in this face orientation when compared to Si(100), which allows the formation of high-density and well-packed SAMs compared to Si(100). This confers an important level of protection against silicon oxidation. Nevertheless, this crystal orientation is not often used in industry. The industrially relevant crystal orientation is the Si(100) face, but it has a lower atomic density of exposed atoms, which makes preparing dense monolayers on this crystal structure very challenging. In this context, Ciampi et al. (70) used thermal hydrosilylation to show that acetylene groups positioned at both the proximal and distal ends of the monolayer improve the quality and stability of the monolayer compared with a monolayer formed from an alkene or a molecule with a single alkyne. For an Si(100) surface that was functionalized with 1,8-nonadiyne, it was shown to be apparently SiO_x -free with only negligible electrochemical deterioration after being subjected to hundreds of cycles from -0.1 V to +0.8 V versus Ag/AgCl in aqueous perchloric acid solution. Note that SiOx-free means that there is no detectable oxide using XPS, which of course does not preclude there being a tiny amount of oxide present. To highlight the importance of the π binding at the distal acetylene group, 1-heptyne and 1,8-nonadyne were grafted to H-Si(100) at the same temperature (Figure 4b). A significantly lower level of SiO_x was detected for the 1,8-nonadiyne-grafted surface than for the 1-heptyne-grafted surface. By diluting the 1,8-nonadiyne with 1-heptyne, which reduced the density of the distal alkyne moieties, the electrochemical behavior of the modified silicon electrode deviated from ideal (70).

ELECTRON-TRANSFER STUDIES ON SILICON SURFACES PROTECTED BY ORGANIC MONOLAYERS

As discussed so far, the growth of an SiO_x layer is thermodynamically spontaneous on a silicon surface. Ohwada and coworkers (80) have shown in detail that native SiO_x forms on silicon surfaces exposed to air in a layer-by-layer growth mechanism. They also showed that growth of SiO_x in ultrapure water is accompanied by the dissolution of the silicon substrate. This process degrades the atomic flatness of silicon and produces a rough oxide surface. From an electrochemical perspective, Shapter and coworkers (81) showed that the rate of growth of SiO_x is drastically increased when a hydrogen-terminated silicon surface is biased to +0.7 V versus Ag/AgCl in aqueous electrolyte. With increasing time, the insulating SiO_x film gets thicker, and the electrode becomes electrochemically passivated.

A consequence of the degradation in electrochemical performance in aqueous solution is that, for studies that explore electron-transfer processes at a silicon/electrolyte interface, nonaqueous electrolytes are typically employed. The poorer solvating properties of these solvents typically lead to greater electrode stability (82, 83). Consequently, nonaqueous electrolytes have allowed a systematic understanding of the silicon/electrolyte junction under a wide variety of experimental conditions.

Significant progress in nonaqueous solvents was achieved with ferrocene self-assembled monolayers. The surface-modification methods and the electrochemical findings were well summarized in reviews that readers could refer to for details (14, 18). Particularly for ferrocene monolayers based on benzyl alcohol linkers, an impressive 10^8 cycles were reported in propylene carbonate containing 1 M Bu₄NPF₆ (3) without electrode failure. Such a result really highlights how nonaqueous solvents can contribute to the electrochemical stability of monolayer-functionalized silicon electrodes. In terms of photoeffects, Hapiot, Fabre, and coworkers (16) showed that no oxidation of ferrocene was observed for a depleted n-type silicon in the dark (**Figure 5**). In this case, the electroactivity of ferrocene was observed in CH₃CN containing 0.1 M Bu₄NClO₄ only under illumination because photogenerated holes were required to promote oxidation of ferrocene. As a result of the photovoltage, the $E_{1/2}$ of ferrocene bounded on a depleted n-type silicon was



Figure 5

Cyclic voltammograms recorded on a Si(111) electrode functionalized with a ferrocene-terminated monolayer. Electrochemical activity was recorded in CH₃CN containing 0.1 M Bu₄NClO₄ (*dasbed line*) in the dark and (*solid line*) under illumination. Adapted with permission from Reference 16. Copyright 2008, American Chemical Society. Abbreviation: SCE, saturated calomel electrode.

approximately 0.2–0.3 V more negative than that observed for ferrocene bound to p-type silicon under the accumulation regime.

Avoiding oxidation of the underlying silicon during the preparation and characterization of the redox monolayer is always a crucial issue to be addressed. This is particularly so because even traces of water or oxygen that may penetrate through the molecular layer or pinholes can cause SiO_x formation that will influence the electron transfer properties of the electrode. As shown by Allongue et al. (84), SiO_x formation that starts from defects of a SAM, or even from the step edges of the silicon electrode, can laterally expand through the substrate and under the organic layer if oxygen and water are available. Although such issues can be minimized for electrochemical studies performed in organic solvents, it is a major challenge for electrochemical studies and applications that require an aqueous-based electrolyte. In this scenario, the stability and effectiveness (85) of monolayers based on α,ω -dialkynes in minimizing the oxidation of silicon have opened interesting opportunities for electron-transfer studies in aqueous electrolytes. For that, the α,ω -dialkyne molecules provide an extra advantage: They allow the surface to be further functionalized with azido-substituted redox species by using the "click" Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition reaction (**Figure 6a**) (86).

Recently, Ahmad et al. (69) clicked azidomethylferrocene molecules on highly doped Si(100) electrodes functionalized with α,ω -dialkynes of different alkyl chain lengths. The motivation was to evaluate the effect of the tunneling distance on processes of electron transfer happening on an Si(100) electrode operating in aqueous electrolytes. In molecular tunneling junctions, the apparent electron-transfer rate constant (k_{app}) for different alkyl chain lengths exhibits an exponential distance dependence according to $k_{app} \approx \exp[-\beta d]$, where d relates to the electron tunneling distance (controlled by the SAM thickness), and β is the tunneling decay coefficient. The conclusion from the study was that, although a thicker SAM expectedly led to the observation of a slower electron-tunneling rate, the k_{app} values were found to increase with the surface coverage of ferrocene. In addition, β was found to be smaller than the 1.2 per CH₂ value observed on ferrocene-terminated alkanethiol monolayers on gold (87). The dependence of k_{app} on the surface coverage was attributed to electrons hopping between ferrocene molecules across the redox film (88). This observation was previously noted by Chidsey et al. (89), mathematically described by Blauch & Saveant (90), and explored by Riveros et al. (91) on silicon to explain kinetic anomalies for redox SAMs. The smaller than expected β value was linked to the presence of hotspots that act as a preferential path of lower resistivity over the well-ordered SAM. It was hypothesized by Cahen and coworkers (20) that these hotspots are tiny amounts of SiO_x (below the XPS detection limit) at the underlying SAM that decrease the Schottky barrier for electron transfer across the organic monolayer. This is an intriguing hypothesis, as it suggests that hopping of electrons and the presence of SiO_x levels below the XPS detection limit may influence fundamental information on electron-transfer rates recorded on silicon.

From a thermodynamic perspective, Yang et al. (92) showed that when the same azidomethylferrocene molecules are clicked on dialkyne-protected lowly doped n-type Si(100) electrodes, light can be used to modulate the potential required for electron transfer. They observed that an increase in the intensity of illumination drove $E_{1/2}$ toward more negative potentials. The observation that light can be used to change $E_{1/2}$ values of redox species (33, 93, 94) agrees with results from ferrocenylsilane-based redox SAMs (22). Overall, more electron-hole pairs are generated with the increase of light intensity and, as such, the quasi-Fermi level of silicon moves to higher energy due to the progressive occupancy of the conduction band. The novel finding was that an increase in k_{app} occurred with the thermodynamic shift. At fixed conditions of SAM thickness and ferrocene surface coverage, Yang et al. found that k_{app} progressively changed from 690 s⁻¹ to 2,470 s⁻¹ by modulating the illumination intensity from 3 to 94 mW cm⁻² (92). This observation



(*a*) Cu(I)-catalyzed Huisgen 1,3-dipolar "click" reaction of azidomethylferrocene on an acetylenyl monolayer-protected silicon surface. (*b*) Cyclic voltammograms (100 mV s⁻¹, 1.0 M HClO₄) for lowly doped n-type Si(111) surfaces modified according to protocol shown in panel *a*. Simulated traces (*light blue line*) for as-prepared samples (*light blue symbols*) indicate that repulsive forces dominate the electrostatic balance of the system. However, when a potential step of +0.3 V was applied for 140 s, the electrostatic balance shifted to attractive interactions (*dark blue line and symbols*). Averaged values from cathodic and anodic peaks of experimental full-width at half maximum (FWHM) values, and refined Frumkin *G* values appear as labels. (*c*) Band diagrams showing the distortion of the semiconductor side of the barrier due to the presence of an electrochemically induced dipole layer of surface charges due to ferricenium moieties. (*d*) Inverted voltammograms obtained at 25 mV s⁻¹ where $E_{p,c}$ was noted at potentials more positive than $E_{p,a}$. Adapted from Reference 95. Copyright 2017, Springer Nature.

was made possible due to the stability of the dialkyne-based chemistry construct during several electrochemical assays in aqueous electrolyte. Two main reasons were proposed for k_{app} varying with light intensity: (*a*) With increasing light intensity, the concentration of holes available on lowly doped n-type Si(100) to receive electrons from ferrocene increases; (*b*) with increasing light intensity, the driving force for electrons to be transferred from ferrocene to silicon increases. This driving force can be expressed in terms of the difference between $E_{\rm V}$ and $E_{\rm redox}$, which is expected to increase with photon flux according to the light-induced thermodynamic shift.

In electrochemistry, significant knowledge about charge-transfer processes is generated from the analysis of voltammograms. Recently, Vogel et al. (95) showed that nonideal electrochemical activity can be systematically reproduced for redox probes confined at silicon electrodes. The topic is discussed here with support from **Figure 6**. As shown in **Figure 6***b*, fresh prepared ferrocene-functionalized lowly doped Si(111) electrodes at a surface coverage of 2.9×10^{-10} mol cm⁻² display a full-width at half maximum (FWHM) value of 142 mV. Such an increase over the ideal 90.6 mV is attributed to the predominance of repulsive interactions between the ferrocene moieties (95). The interesting finding was that, when an anodic bias is deliberately applied to drop the surface coverage of ferrocene below 1.7×10^{-10} mol cm⁻², the FWHM values unexpectedly dropped to 75-55 mV. This is a diagnostic of attractive forces dominating the surface tethers. Such an effect is not observed on a metal or highly doped silicon. The diagnostic is corroborated by the fitted Frumkin interaction parameter (G), which changed from negative (predominance of repulsive forces) to positive (predominance of attractive forces). The conclusion was that the increase in G is due to redistribution of electrons over the silicon side of the barrier. This electrostatic effect is shown in Figure 6c. Overall, the static positive charges of the electrochemical-generated ferricenium moieties lift the electronic bands of the silicon and distort the magnitude of the band bending at the silicon/electrolyte interface. As shown in Figure 6d, the direct consequence is an inversion of peak positions on voltammograms, with the potential of the cathodic peak shifting anodically of the anodic maxima ($E_{p,c} > E_{p,a}$). The narrowing of the peaks below 90.6 mV and inversion of the peak potentials are attributed to the manifestation of the same electrostatic process. From a practical perspective, the extent of this electrostatic effect can be explored to control electroactivity of redox species that take part in catalytic reactions (11, 12).

Finally, for appreciable electron transfer to occur on redox SAMs on silicon, there must be a sufficient electronic coupling between the redox species and underlying electrode through the organic monolayer. Although this is possible with physisorbed species (96), electronic coupling is strongest to weakest when going from covalent bonds to ionic to hydrogen bonds to van der Waals interactions (97, 98). The limitation of having surface-bound redox species is that, for addressing redox species in solution, the redox potential of the attached mediator must be matched to the soluble redox species. To avoid that, the attachment of nanoparticles or carbon nanotubes on monolayer protected silicon is an interesting strategy (99-103). This is possible because such nanomaterials can restore efficient electron transfer across an otherwise passivated surface (104, 105). Gold nanoparticles (AuNPs) are usually the nanomaterial of choice (106-110), but the mediation of electrons fails for very small nanoparticles or thick SAMs (104, 105). On dialkyne-protected lowly doped n-type Si(100), azidopropylamine molecules were clicked to allow the attachment of AuNPs (111). With this system, electrochemical reactions of solubilized $Ru(NH_3)_6^{3+}$, Co(phen)₃²⁺, FcMeOH, and Fe(CN₆)³⁻ were addressed in aqueous electrolyte. However, as the surface construct has a net positive charge owing to the terminated amine groups, the passivating ability and nonspecific resistance of the SAM showed dependence on the charge of the soluble redox species. For the positively charged $Co(phen)_3^{2+}$, 650 redox cycles were mediated by AuNPs and with nonsignificant growth of SiO_x . This study shows that nanoparticles can be used to mediate electron transfer on silicon across a passivating SAM with redox species in solution.

APPLICATIONS OF MONOLAYER-PROTECTED SILICON ELECTRODES

Sensing is one of the main applications of silicon electrodes if they can be rendered stable in aqueous solution. A key area of focus in sensing is the development of DNA biosensors (112). Within this regard, light addressability could be used on silicon-based electrodes for patterning complex features via electrodeposition (9, 113) or by producing chemically active species that triggered DNA patterning on the electrode (114). For instance, Jacobson and coworkers (114) reported a photoelectrochemical procedure to synthesize an array of DNA. They used an amorphous silicon surface coated with 100 nm of a Ti/Pt layer as protection pads. Light

illumination was controlled by a digital micromirror device to form local virtual electrodes and photoelectrochemically generate protons. The protons were responsible for the local cleavage of acid-labile protection groups of DNA phosphoramidite synthesis reagents. The combination of light-induced chemistry and lithography was discussed by Hughes and coworkers (115) as a pathway for nucleic acid-based storage systems. Besides patterning, light addressability could also be used to retrieve electrochemical information from a Si(100) surface and quantify DNA hybridization. The proof-of-concept was shown in 2015 by Choudhury et al. (6). In that study, a monolayer-protected lowly doped Si(100) electrode was functionalized with an array of DNA probes (Figure 7*a*). A single-stranded DNA analyte was added to the electrolyte, and whether DNA duplexes were formed at each spot in the array was determined electrochemically by scanning the light source across the array. This DNA detection scheme requires the presence of a redox-active intercalator in solution, such that an enhanced current is observed when the light passes over a spot containing duplexes (Figure 7b). The surface engineering requires bovine serum albumin (BSA) to be employed as an antifouling layer to prevent nonspecific adsorption of target DNA. A subsequent study found that the use of hexa(ethylene glycol) moiety for antifouling could retain the electrochemical property of the surface better than using BSA (116), as the protein adsorption to the silicon electrode accelerated its oxidation (117).

The work discussed on DNA illustrates well how light-induced electron transfer can be used to write or read chemical information onto/from a surface. In terms of patterning, the technique allows modification of a surface with metals, polymers, or (bio)molecular assemblies by the combination of light and potential. It is a fast approach that does not require physical masks, templates, or inks (26). Noteworthy work on silicon was done by Yoneyama and coworkers (118, 119), which reported the photoelectrochemical deposition of conductive polymer patterns. Particular attention has been given recently to light-induced patterning because the use of spatial-light modulators, which can spatiotemporally control the illumination of a silicon surface with complex features at a microscale accuracy (120). Perhaps the most exciting and highest-throughput modulator consists of a ferroelectric liquid crystal on silicon (FLCoS), which is made of 3 million arrays of discrete components individually manipulable to alter polarization of incident light. Therefore, it provides a nonsequential methodology that allows light-induced electron transfer of patterns onto large electrode areas. On monolayer-protected amorphous silicon photoelectrodes, Vogel et al. (9) used this approach to electrodeposit a "Mona-Lisa" pattern made of Cu₂O nanocrystals with precise control of shape, size, interparticle spacing, and crystallographic orientation. These parameters could be regulated via changing the potential, intensity of illumination, and concentration of anions in the bath plating. Another example of using spatial light modulators for photoelectrochemical patterning was reported by Li and coworkers. In their approach, an amorphous silicon layer was deposited on an ITO-coated glass slide and acted as the photoelectrode for the printing of AgNPs (113, 121) and AuNPs (122). The parameters that affect the spatial resolution of the technique, currently at the few microscale range, were recently discussed both for reviews focused on LAPS (42) and for light-addressable faradaic electrochemistry (26).

Monolayer-protected Si(100) surfaces were used to fabricate switchable platforms for cell biology applications (see **Figure 8***a*). Ng et al. (7) modified a silicon surface with a mixed monolayer of 1,8-nonadiyne and 10-undecenoic acid. The carboxylic acid group was used to attach the cell-binding tripeptide sequence arginine-glycine-aspartate (RGD) to the electrode surface. Hexa(ethylene glycol) molecules bearing either negatively charged sulfonate or positively charged ammonium groups were coupled to the acetylene moiety to render the silicon surface with resistance to nonspecific adsorption of cells. The surface was patterned such that the negatively charged sulfonate-terminated hexa(ethylene glycol) molecules were in defined locations with the concomitant ammonium species in other locations. When the surface was biased to +300 mV,



A light pointer is scanned across a lowly doped modified p-type Si(100) surface to amperometrically monitor hybridization on DNA arrays. (*a*) If a duplex is formed, the redox species anthraquinone-2-sulfonic (AQMS) acid intercalates into the duplex and long-range charge transfer can occur. (*b*) Amperometric response of the modified silicon electrode as a function of the position of the light beam across a four-element array. At each position, a surface-attached ssDNA probe sequence was exposed to target DNA that is complementary, single C–A base-pair mismatch, noncomplementary and complementary again to the surface probe. Adapted with permission from Reference 6. Copyright 2015, Royal Society of Chemistry.

the negatively charged sulfonate group was attracted to bend toward the silicon to expose RGD peptides, while the negatively charged ammonium group was electrostatically repelled to as far from the surface as possible, which concealed the RGD peptides. As a result, the cells selectively bind to the sulfonate terminated region. On the other hand, when the surface was biased to -300 mV, the RGD peptides were concealed by the molecules bearing the sulfonate groups projecting away from the surface, while in the ammonium-terminated region, the RGD peptides



(*a*) The operation principle of a molecular "switchable" surface designed to electrically control cell adhesion on a functionalized Si(100) surface. Adapted with permission from Reference 7. Copyright 2012, Wiley. (*b*) Rare cells (*green*) can be preconcentrated on an electrochemically cleavable antibody-modified lowly doped p-type Si(100) surface from a mixture of cells. The platform enables analysis of surface-attached cells, for example, with fluorescence microscopy, before a unique single cell is selected with a focused light beam and photoelectrochemically released from the platform. Adapted with permission from Reference 8. Copyright 2018, Springer Nature.

were now exposed due to the bending of the ammonium group. As such, the cells were more attracted to the ammonium-terminated area. That is, by switching the applied potential from +300 mV to -300 mV, the ammonium-terminated region could be switched from antifouling to cell adhesive, with cell binding being observed (7).

Another strategy for tuning the bioactivity of a silicon electrode surface involved the use of an electrochemically switchable moiety in the monolayer. The electrochemically switchable unit is a benzoquinone-based moiety conjugating with an oligo (ethylene glycol) fragment so the surface was antifouling. At the time when a reducing bias was applied, an intramolecular lactonization reaction occurred to cleave off the oligo (ethylene glycol) fragment, so the silicon surface became amenable for cell adhesion (123). In this way, a photoelectrochemical platform was designed to capture and electrochemically release rare circulating tumor cells (CTCs). As shown in **Figure 8***b*, the platform was composed of a monolithic semiconductor surface modified with antibody-conjugated electrochemically cleavable molecules to capture CTCs that could be specifically selected with optical microscope, was released electrochemically by cleaving the antibody-binding molecule, and was retrieved later for downstream genetic analysis to study cell heterogeneity (8).

Hydrosilylation using 1,8-nonadiyne has recently been extended to passivate a transparent semiconducting electrode composed of a very thin amorphous silicon film on an indium tin oxide coated glass coverslip (124). The motivation of preparing such an electrode was to satisfy the need of performing photoswitchable electrochemistry and simultaneous high-resolution optical imaging in the field of biology. The modified surface showed near perfect electrochemical behavior in aqueous media under illumination and was compatible with a high-resolution confocal microscope to obtain a detailed fluorescent image of cells (124). Also motivated by cell biology applications, Yang et al. (125) reported a light-addressable potassium (K⁺) sensor. In this Si(100)-based device, a beam of light was focused on the surface and used to promote oxidation of surface-attached ferrocene groups. Owing to charge-balance considerations, K⁺ transfer was triggered from an overlaid K⁺-selective film to the solution phase. As a consequence, the ferrocene $E_{1/2}$ position was a direct function of K⁺ activity at the electrode surface. This capability was used to measure extracellular K⁺ concentration changes by stimulating single living breast cancer cells. Different from LAPS, the approach relied on dynamic electrochemistry and may be performed with other electrochemical analysis when studying biological events.

SUMMARY AND OUTLOOK

The functionalization of silicon surfaces with molecular constructs based on Si–C linkages has made incredible advances in the last 25 years or so. The level of protection achieved against anodic degradation of the silicon electrode in aqueous electrolyte is impressive. Particularly for silicon surfaces functionalized with α,ω -dialkynes, a long-term electrochemical stability is possible. Moreover, the further functionalization of monolayer-protected silicon allows the electrode to serve different purposes, such as the coupling of model redox probes for electron-transfer studies or the attachment of biomolecules required for biointerfaces that must operate in aqueous environments. Such control at the molecular level in addition to the electrochemical stability has provided not only access to better-performing silicon surfaces but a new approach for developing electrochemical devices.

From a fundamental perspective, many of the electron-transfer studies usually performed in nonaqueous electrolytes can now be conducted in aqueous environments with functionalized silicon electrodes. Such studies have contributed to a systematic understanding of the effect of surface coverage, light intensity, and electrostatic interactions on the thermodynamics and kinetics of processes of electron transfer. Nevertheless, our capability to discern fundamental electron-transfer information from the influence of SiO_x levels that are nondetectable by XPS is an aspect to be flagged. From a practical perspective, functionalized silicon electrodes can today join the knowledge built over the years from studies on photoeffects, the light addressability developed for LAPS, and the reliability of monolayers based on α,ω -dialkynes to generate a platform on which dynamic electrochemistry can be performed with microscale spatial resolution and without geometric restrictions. This has presented several opportunities for the nonsequential patterning of chemical and biochemical features on silicon electrodes, with positive implications for the development of electrocatalytic and bioactive devices. From a sensing perspective, monolayer-protected silicon electrodes can now combine the advantages of LAPS with the benefits of amperometric measurements, as exemplified with the DNA sensor shown in **Figure 7**. This may be a promising pathway to join the selectivity of electrochemical sensors with the high throughput-out that is typical of optical sensing arrays. Many other applications are facilitated by light-addressable electrochemistry, and of special interest is its use in cell biology research. As shown in **Figure 8***b*, cells can be simultaneously analyzed in a nonpreorganized silicon electrode before a unique single cell is selected and photoelectrochemically released from the surface. This allows selection of individual cells based on their response to drugs, morphology, or surface expression. Although still in its early stage, the field of light-addressable dynamic electrochemistry appears to be an attractive way to expand the scope of silicon electrodes in electrochemistry and complement the use of related techniques, such as scanning photoelectrochemical microscopy.

DISCLOSURE STATEMENT

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