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Wet chemical routes to the assembly of organic monolayers on silicon surfaces via the formation of Si-C bonds: Surface preparation, passivation and functionalization

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Abstract

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Keywords

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Wet chemical routes to the assembly of organic monolayers on silicon surfaces *via* the formation of Si–C bonds: surface preparation, passivation and functionalization

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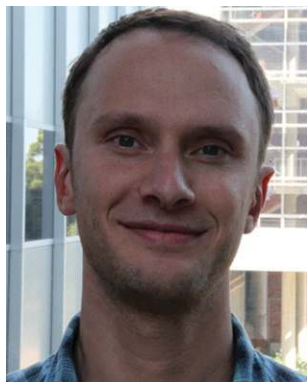
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1. Introduction

As micro-devices are reduced down to the nanoscale, surface properties gain more and more importance. As a consequence, molecular layers attached onto either crystalline, nanowire or nanoporous material surfaces, arguably, become more than a mere passivating coating. The notion that chemically

well-defined organic films could impart precise functionalities to a bulk inorganic material, and hence open the door to new technologies, has prompted a vast research effort in the area of self-assembled monolayers (SAMs).^{1–4} In 1980, Sagiv published a seminal paper reporting the reaction of chloro- and alkoxy-silanes (RSiCl_3 and RSi(OH)_3 with $\text{R} = \text{C}_{18}\text{H}_{37}$) with hydroxyl-terminated surfaces of oxidized substrates (glass, poly(vinyl alcohol), oxidized polyethylene and aluminium) to afford a covalent molecular layer.² This work represents the first report of SAMs ('ordered molecular assemblies formed by the adsorption of an active surfactants on a solid surface'¹). The 'oleophobic'

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structure that Sagiv reported suffered from limitations dictated by both the glass-like nature of the substrate and by the silane chemistry used. Namely, there was an inhomogeneous in-plane distribution of surface active sites and poorly defined polymerised material among the reaction products.⁵ Further, the silicon–oxygen bonds that are formed tend to be prone to hydrolysis, especially under basic conditions, and thermal degradation of the structure has been reported.⁶ Despite their intrinsic limitations, silane layers (Si–O–SiR) gave researchers a novel tool to modify surfaces with unprecedented control.^{7,8}

It was not until almost a decade later that reports of alkanethiols forming well-ordered and dense SAMs on gold^{4,9–12} opened the possibility of easily accessible model systems to study fundamental physical-chemistry phenomena (*e.g.* heterogeneous electron transfer, double-layer effects).^{13–17} Despite the gold–thiolate bond being thermally unstable in heated solvents,¹ and prone to oxidation in air,¹⁸ monolayers of alkanethiols on gold are sufficiently stable for a range of applications. Further, because of the simplicity in preparing and handling thiol SAMs on gold, thiol and disulfide tagged biomolecules have frequently been used in biosensing studies.^{19–21} A notable exception are multi-step fabrication procedures, where the experimental complications encountered have been associated with the SAM oxidation.²² Further, severe limitations exist that need to be considered if the SAMs are intended for electrochemical applications, since stability is limited to a relatively narrow potential window.^{23–25} As comprehensively reviewed elsewhere,^{26–30} and as discussed to an introductory level in a following section of this review (Section 2), formation of molecular layers on crystalline silicon surfaces without an intervening oxide layer is an extremely appealing approach toward robust layers on a surface.^{31–34} Silicon–carbon linked monolayers on silicon substrates are expected to complement and/or extend the applications of the currently most relevant technological material³⁵ toward the development of atomic scale devices,^{36–38} diverse molecular devices,^{39–48} and well-defined sensing interfaces.^{49–53}

The following sections are intended as an up-to-date presentation of the topic of molecular layers on non-oxidized silicon surfaces. Particular emphasis is put on outlining the strategies toward the goal of chemically well-defined structures. An outline of this review is as follows. Concepts relevant to the understanding of the silicon surface passivation using simple monatomic reagents (*e.g.* hydrogen) are introduced in Section 2. Subsequently, an overview of the available repertoire of chemical strategies toward organic–silicon devices is presented, with a discussion on the current understanding of the mechanism for the monolayer formation onto Si(111) and Si(100), the most common crystal orientations. The major motivations for the development of synthetic schemes to passivate, and controllably functionalize, crystalline silicon surfaces are then the subject of Section 3. Explored approaches toward functional monolayers, where sequential reactions are used to address chemical, physical, and electrical properties of the organic–silicon architecture, are expanded in detail. The last section of this article (Section 4), before an outlook on future challenges and opportunities is presented, introduces the current state of silicon–organic devices for biological sensing.

Four notable and broad areas of research in the organic/silicon field are either not treated here or considered only briefly, since they are either discussed or reviewed in detail elsewhere. Those are: (a) the expanding literature on porous silicon chemistry and porous silicon biosensing applications;^{54–62} (b) metal–insulator–semiconductor (MIS) studies on organic modified silicon surfaces;^{39,43,48,63–67} (c) chemomechanical functionalisation approaches (*i.e.* ‘wetting and scribe’ methods);^{68,69} and (d) ultra-high vacuum reactions (UHV, 10^{-10} mbar or lower) of unsaturated molecules on reconstructed semiconductor surfaces.^{42,70,71}

2. Silicon–carbon-bound monolayers

2.1 Surface preparation

Organic monolayer formation *via* solution methods unequivocally starts with the chemical etching of the silicon oxide layer and the saturation of exposed surface bonds. Ensuring that the coordination requirements of surface atoms are satisfied reduces the reactivity of the etched surface and allows for temporary handling of the sample under ambient conditions which are not stringent in terms of the presence of moisture and oxygen. Hydrogen is the most commonly used passivating agent for surface preparation,⁷² but strategies relying on halogens such as iodine⁷³ and chlorine⁷⁴ have been also reported. Hydride-terminated silicon surfaces are typically prepared by chemical etching in fluoride-containing solutions, with dilute (<10%) hydrofluoric acid used to passivate the Si(100) orientation and *ca.* 40% ammonium fluoride solutions used for the (111) face (Fig. 1).^{75–78} Hydrogenated silicon surfaces are attractive to work with because of their ease of preparation,⁷⁸ their relative stability in air,^{79,80} and during brief water ring procedures,^{31,76} and their lack of appreciable reactivity toward a range of common solvents (including acetonitrile,⁸¹ diethyl ether,⁴⁶ chlorobenzene,⁸² hexane,⁸³ toluene⁸⁴ and mesitylene^{85,86}). These features allow for the experimentally straightforward



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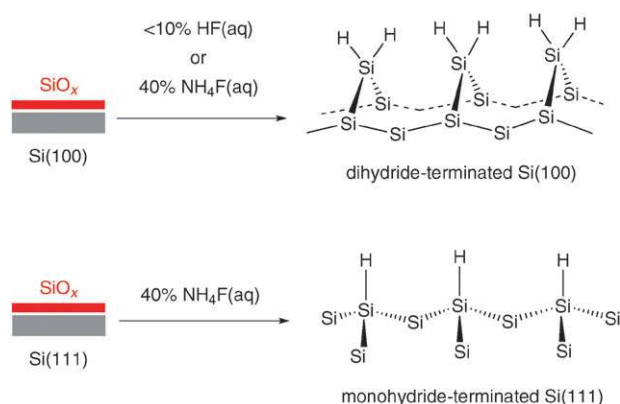


Fig. 1 Preparation of hydride-terminated Si(100) and Si(111) surfaces by chemical etching in fluoride-containing solutions (ref. 75–78, 90 and 105). Alternative etchants (*e.g.* KOH, NaOH) have also been reported and a comprehensive discussion on the available wet-chemical routes to Si(*hkl*)–H surfaces is found in ref. 95.

preparation of covalent organic layers by wet chemical methods.⁸⁷

Notable exceptions to the typically straightforward conditions are [2 + 2] and [4 + 2] cycloaddition reactions under ‘dry’ UHV conditions. Under UHV, the surface oxide layer is thermally removed (*i.e.* sublimed at temperatures above 1100 °C) and the surface can undergo numerous types of reconstruction under appropriate annealing conditions.⁴² Cycloaddition reactions have been reported on the 2×1 reconstructed Si(100) surfaces for alkenes and alkynes^{27,28,70} and UHV reactions of Si(111)–H with olefins are also documented.⁸⁸

Unreconstructed monohydride,⁷⁸ atomically flat,^{76,89} Si(111) can be prepared by wet chemical etching in ammonium

fluoride, and the mechanism has been studied in detail.⁹⁰ Further, both the doping-level and the miscut angle are reported to influence the quality of the etched substrate.⁹¹ It is worth noting that what is generally referred to as a *chemical* etch is better explained as a competition between a purely chemical and an electrochemical process (Fig. 2), even at open circuit potentials (OCP) in a modest accumulation regime (n-type, OCP < flat-band potential).⁹⁰ Alternative etchants, such as aqueous hydrofluoric acid^{76,92} and sodium hydroxide^{93,94} can also be used and mechanisms for the silicon dissolution have been proposed for both systems.^{75,94} However, both hydrofluoric acid and sodium hydroxide mediated etchings are generally found to yield microscopically rough surfaces showing a mixture of mono-, di- and tri-hydrides.⁹²

For Si(100), the material that is currently used in the majority of semiconductor devices largely because of a fortunate matching of the interatomic spacing of silicon atoms with the lattice constant of silicon dioxide,⁹⁵ the preparation of mono- and di-hydrogen terminated and atomically flat surfaces can only be achieved with UHV techniques. This is most commonly achieved by exposing either a reconstructed Si(100)–(2×1)⁹⁶ (pairing of dangling bonds on adjacent atoms⁹⁷) or (un)reconstructed Si(100)–(1×1),^{98–100} to molecular hydrogen at high temperatures. If prepared outside of the UHV chamber, as in device-quality surfaces,⁹⁹ the hydrofluoric acid-etched hydrogen-terminated Si(100) surface is best described as having a complex¹⁰¹ mono-, di- and tri-hydride configuration^{75,77,102} with minor oxygenated defect sites. Because of the anisotropic nature of the ammonium fluoride etching, and in agreement with early spectroscopic data,¹⁰³ this etching procedure has been generally limited to the (111) orientation since it is generally believed to lead to roughening of the (100) surface.¹⁰⁴

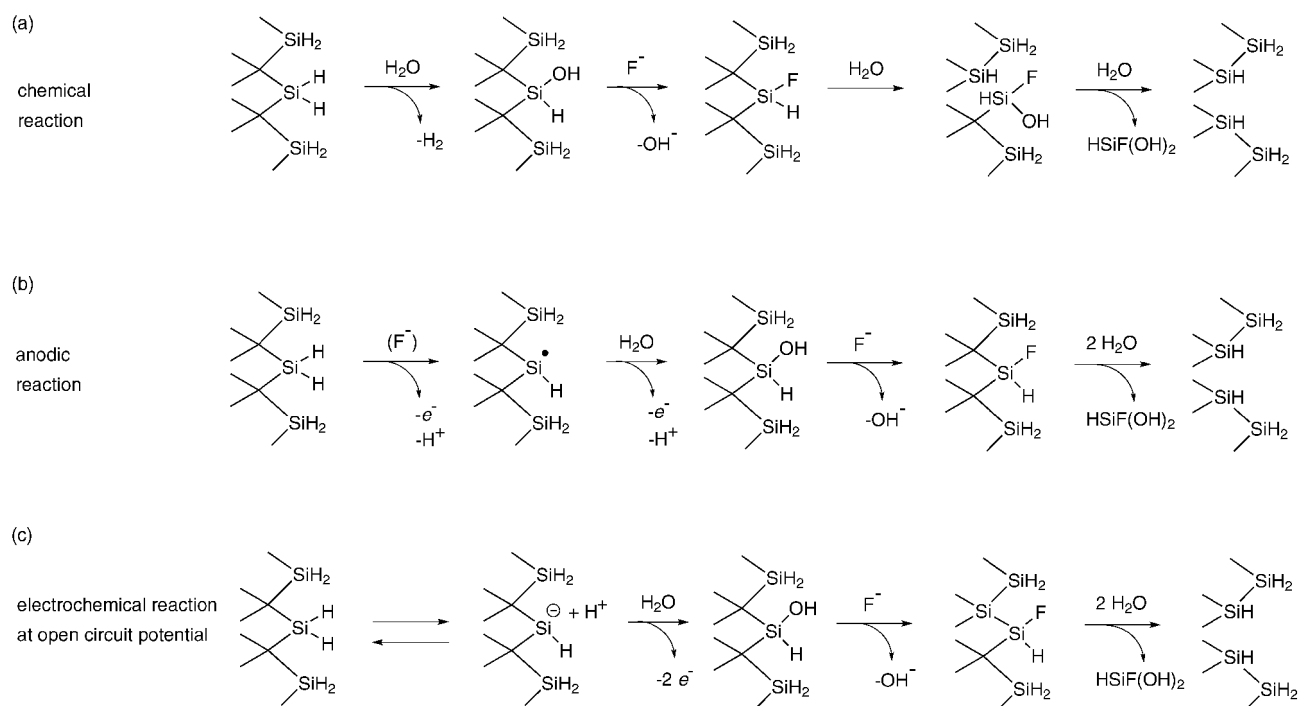


Fig. 2 Reaction models for the etching mechanism of silicon surfaces in ammonium fluoride aqueous solutions. The dissolution of silicon is believed to comprise both a chemical and an electrochemical component (ref. 89 and 90).

However, Hines and co-workers have very recently disproved previous assignments of the FTIR spectrum of ammonium fluoride-etched Si(100) surfaces and argued in favour of a mainly dihydride-terminated and a near-atomically smooth surface.¹⁰⁵ This finding is in sharp contrast with the general consensus, and is very likely to stimulate new work in the area. Note that due to steric reasons, further reaction of a R-Si(Si_x)H_n termination (with $n = 1$ or 2 , $x = 4 - (n + 1)$, R = alkyl/alkenyl chain) is greatly hampered. Therefore the complete chemical reaction of all Si-H surface sites is not expected for the chemically etched Si(100) surface.¹⁰² Further, the presence of oxygen-containing defect sites at the Si(100)-H surface introduces a relevant practical complication in that traces of oxygen and water contaminants⁷⁹ (even as low as 10^{-9} mole in the reaction chamber during a thermal promoted reaction) might react with olefins and acetylenes. The resulting products of such reactions will eventually condense with defect surface sites, to yield Si-O-C-bridged species.⁹⁸

The superior chemical homogeneity of the fluoride⁷⁸ etched Si(111) surface, relative to the Si(100) counterpart, is reflected in the high number of reports on non-oxidized (111) passivated surfaces,^{31,47,66,74,83,87,106–124} compared with Si(100).^{33,102,125–129}

2.2 Reactions of the hydride-terminated silicon surface

2.2.1 Thermal hydrosilylation of unsaturated molecules.

Prompted by a vast body of knowledge in analogous solution phase reactions for silicon compounds, Linford and Chidsey published in 1993 the first report of Si-C bound alkyl chain on non-oxidized Si(111)-H surfaces.⁸⁷ These monolayers were prepared *via* the pyrolysis of diacyl peroxides ([CH₃RC(O)O]₂, 100 °C, 1 h). In a later report,³¹ Chidsey and co-workers described how 1-alkenes (and 1-alkynes) could be grafted in a thermal reaction (100 °C, 1 h) to Si(111)-H surfaces in the presence of a varying concentration of a diacyl peroxide initiator.¹³⁰ According to the results of deuterium labelling experiments, and observing a preferential reaction of the 1-alkene species (CH₃(CH₂)₁₅CH=CH₂) compared with that of the diacylperoxide, even for the high peroxide/olefin ratios, the authors suggested a radical mechanism. The proposed mechanism involves initiation at a silyl radical site (after the homolytic cleavage of a Si-H by a peroxide-derived radical) with the addition to the α -carbon of a terminal olefin to give a carbon-centered radical on the grafted molecule.³¹ The secondary alkyl radical will, in turn, abstract a hydrogen atom at an adjacent Si-H¹³¹ site to give a new silicon radical (dangling bond) and therefore provide a new alkene addition site. This radical chain mechanism, as depicted in Fig. 3, was also supported by the knowledge of analogous reactions occurring in gas-phase organosilane chemistry.¹³² Importantly,

the secondary radical on the β -carbon, as shown in Fig. 3, would allow for a sterically favoured six-membered transition state after hydrogen abstraction from a Si-H site. The relative ease of the hydrogen abstraction step in the chain propagation was suggested to account for the apparent lack of side reactions, for example, the apparent absence of adventitious formation of polymeric multilayers.¹³³

Interestingly, high-quality films were also obtained for a 1-alkyne (1-hexadecyne),¹³⁴ as well as for a chlorine-terminated 1-alkene (11-chloro-1-undecene). This supports the versatility of the approach and the compatibility of chloro compounds with the hydrosilylation conditions.^{31,135} Quite controversial are the available results for the hydrosilylation of ω -bromo-1-alkenes (*e.g.* 11-bromo-1-undecene). Initial results from Linford *et al.* suggested the formation of poor-quality surfaces and the authors reasoned this as an incompatibility of bromine with the radical reaction.³¹ However, more recent reports by Bedzyk and co-workers and by Cahen and co-workers advocate for densely-packed, but chemically poorly-defined, Si(111) monolayers of undecylenic acid 2-bromo-ethyl ester and 11-bromo-1-undecene, respectively.^{136,137}

We note that Bedzyk and co-workers introduced the use of X-ray standing waves (XSW) to measure simultaneously chemical and physical properties of monolayers on a single-crystal surface. From the available XSW data on undecylenic acid 2-bromo-ethyl ester SAMs, and in good agreement with X-ray photoelectron spectroscopy (XPS), X-ray reflectometry (XRR) and X-ray fluorescence (XRF) measurements, the authors¹³⁶ concluded that abstraction of bromine at the silicon surface occurs during the SAM formation. This event generates silicon surface atoms bound to bromine and a terminal methylene radical that opens the possibility of alternate grafting routes not involving the terminal olefin in the molecule. The proposed binding configurations, and an estimated abundance of each grafted species as calculated from XSW, XPS and XRF data, are presented in Fig. 4.

While it is difficult to argue against the proposed alkene addition/hydrogen abstraction chain mechanism, crucial evidence in favour of the plausible surface chain reaction were afforded in 2000 and 2002 by Lopinski *et al.*⁷¹ and by Cicero *et al.*,⁸⁸ respectively, using UHV scanning tunnelling microscopy (STM) analysis. Since the hexagonal array of sites of the Si(111) surface⁸⁸ and the parallel alignment of dimers of the reconstructed Si(100) surface⁷¹ are expected to dictate the formation of differently shaped arrays of tethered organic molecules, the authors found evidence to support a propagating radical chain initiating at isolated sites defined by the STM tip.^{71,88} On Si(100) surfaces, molecular lines of styrene, up to 130 molecules long, grew until stopped by surface defects (*e.g.* missing dimers).⁷¹ In contrast, on the hexagonal Si(111) lattice

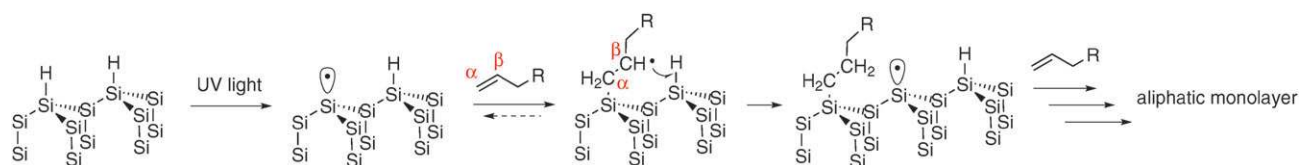


Fig. 3 Schematic depiction of the chain propagation mechanism for 1-alkenes reacting with Si(111) silyl radical as proposed by Linford and Chidsey (ref. 31).

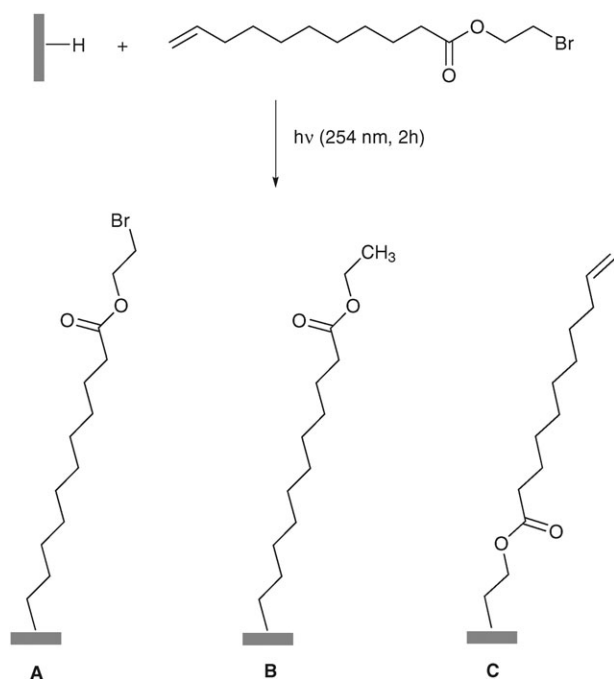


Fig. 4 Concurrent alternative binding modes in the UV-mediated attachment of undecylenic acid 2-bromo-ethyl esters onto Si(111)-H surfaces (ref. 136). The predominant structure is believed to be the hydrosilylated, but partially degraded, monolayer B (A \leq 0.10 monolayers (ML); B \geq 0.27 ML; C \leq 0.13 ML).

a *random walk*¹³³ of the radical chain leads to poorly defined island of grafted styrene.⁸⁸ While UHV studies suggest a radical chain mechanism they do not prove that the same mechanism is operating in wet chemical systems. However, the observation that monolayer growth is self-limiting and comes to a halt after a finite number of adsorption events, *e.g.* when adjacent hydrogen atoms are no longer available for abstraction,^{88,133} is a strong evidence of monolayer rather than multilayer formation.¹³⁸ Further, in contrast to layers grafted *via* siloxo (Si-O-Si) bridges,^{81,139,140} the silicon-to-carbon bond¹⁴¹ structure is relatively ordered and not prone to hydrolysis.³¹ That is, the silicon-carbon bond is highly stable under a range of conditions.^{31–33,87}

We note that a major departure from the prevailing theories on the hydrosilylation mechanism has recently emerged.

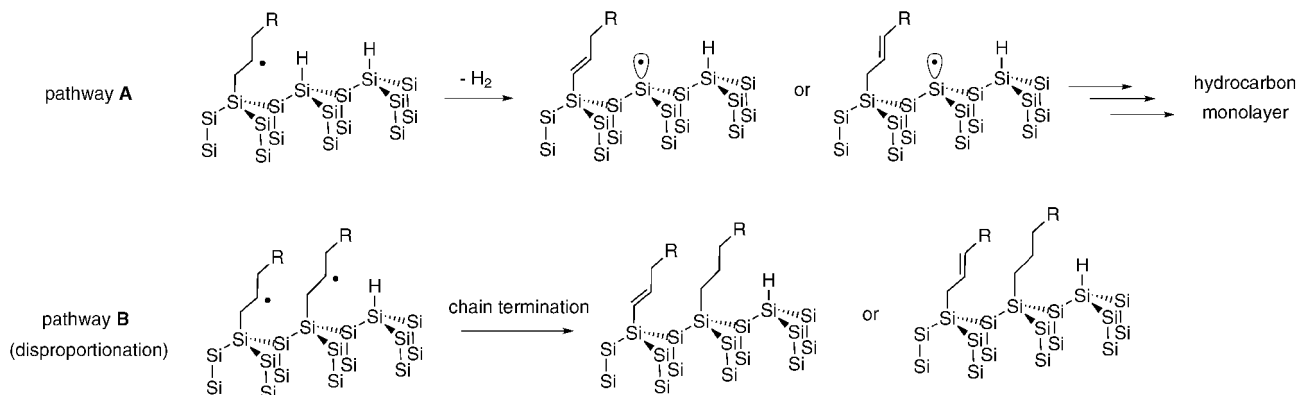


Fig. 5 Re-evaluation of the radical chain mechanism for the hydrosilylation of 1-alkenes (ref. 142).

Wiley and co-workers have observed a significant retention of unsaturation for the thermal and chemomechanical (*i.e.* scribing) hydrosilylation of 1-octene at both smooth and rough Si(100) surfaces.¹⁴² Most surprisingly, strong C=C spectral features, either due to Si-C=C or R-C=C-R functionalities in the monolayer, were observed in near-edge X-ray absorption fine structure (NEXAFS) spectra using synchrotron radiation. The authors estimated that the fraction of surface-bound molecules retaining a double bond is in the 0.13–0.21 range for the smooth substrates and between 0.28–0.40 for rough ones. Similar NEXAFS C=C features had also been observed by Cahen and co-workers, but dismissed as being due to irradiation-induced damage under the experimental conditions used.¹⁴³ In the recent report of Wiley and co-workers, precautions were taken to minimize exposure of the film while retaining a satisfactory signal-to-noise ratio. Most importantly the incident X-ray flux was kept at a level two orders of magnitude less than that required to induce damage in similar monolayers prepared on Si(111).¹⁴³ Mechanistic implications to account for the significant sp^2 character of monolayers prepared from 1-alkenes are striking. Further studies will help in elucidating these preliminary observations but it is likely that in order for the monolayer to retain a substantial level of unsaturation a pathway that simultaneously continues radical propagation and accounts for double bond formation must be operative during the hydrosilylation reaction. As the authors noted, unsaturation may be either retained by donation of a hydrogen atom to the surface (pathway A, Fig. 5) or by disproportionation of neighbouring β -radical intermediates (pathway B, Fig. 5).

2.2.2 Alkylation of halide-terminated surfaces. A two-step chlorination/alkylation sequence on hydride-terminated silicon surfaces, as initially reported by Bansal *et al.*,⁷⁴ has also been demonstrated on numerous occasions. This method generally results in ordered,¹⁴⁴ electrically and chemically well-passivated alkyl Si(111)^{82,109,114,124,144–150} and Si(100)¹⁰² surfaces (Fig. 6). A brief discussion is required to elucidate the unique features, and intrinsic limitations, of the chlorination/alkylation approach.

First, the displacement of a surface halogen atom by either an alkyl Grignard (RMgBr) or an alkyl lithium reagent (RLi) is the only reported method for single methyl groups to be reacted with unoxidized silicon surfaces. Most importantly,

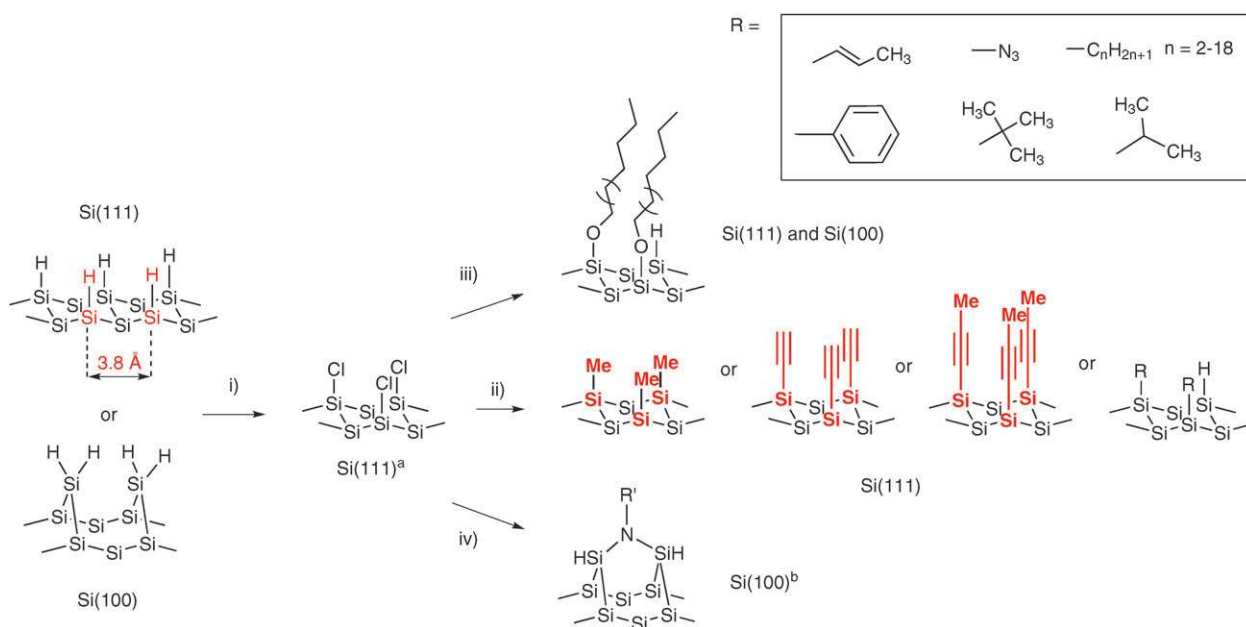


Fig. 6 Representative modification schemes for halogenated Si(111) and Si(100) surfaces. Chlorinated surfaces are a versatile substrate (i), and can be further reacted with a range of organic molecules (ii–iv). Selected examples include: (i) PCl_5 or Cl_2 (g); (ii) RLi ($\text{R} = -\text{CH}_3, -\text{C}_4\text{H}_9, -\text{C}_6\text{H}_{13}, -\text{C}_{10}\text{H}_{21}, -\text{Cl}_8\text{H}_{37}$), or RMgX ($\text{R} = -\text{C}_n\text{H}_{2n+1}$ ($n = 1-18$), $-t\text{-Bu}$, $-i\text{-Pr}$, $-\text{C}_6\text{H}_5$, $-\text{CH}=\text{CHCH}_3$; $\text{X} = \text{Br}$ or Cl), or NaN_3 , $\text{NaC}\equiv\text{CH}$, $\text{NaC}\equiv\text{CCH}_3$; (iii) ROH ($\text{R} = -\text{C}_n\text{H}_{2n+1}$ ($n = 12, 18$); and (iv) $\text{R}'\text{NH}_2$ ($\text{R}' = -\text{C}_4\text{H}_9, -\text{C}_8\text{H}_{17}, -\text{C}_6\text{H}_5$) (ref. 74, 102, 109, 110, 114, 124 and 153–158). The reaction of acetylates and methyl Grignard with chlorinated surfaces allows full Si–C atop site termination on the Si(111) surface (structures in bold). ^aWith the exception of the work by Nemanick *et al.* (ref. 102), alkylation of chlorinated surfaces has been generally reported for Si(111) substrates. ^bUHV reaction (ref. 156).

this method is claimed to allow for the complete passivation of Si surface sites of the unreconstructed Si(111)–H surface.^{74,144,145,150} As schematically depicted in Fig. 6 the distance between Si surface sites on the Si(111) surfaces is 3.8 Å,⁹⁵ while the van der Waals radius of a methyl group is *ca.* 2 Å.¹²⁴ It is thus possible to react every Si–H site (colored for clarity in Fig. 6), and fully-passivated Si(111)– CH_3 surfaces have been prepared.^{109,144,150} Somewhat larger (*ca.* 4.5–5.0 Å) is the van der Waals radius of the methylene units in longer alkyl chains (*i.e.* $\text{C}_n\text{H}_{2n+1}$, $n \geq 2$).³¹ As such, regardless of the chemical strategy used, complete passivation of the Si(111) surface cannot be achieved due to van der Waals interactions between methylene units of adjacent alkyl chains.^{31,150}

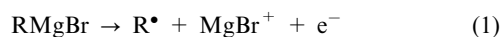
Second, alkylated and methylated Si(111) surfaces prepared *via* this route have a satisfactory stability in air¹⁵⁰ and show remarkable electrical properties,^{114,145} with the lowest surface recombination velocity ($<25 \text{ cm s}^{-1}$) reported to date for a passivated (non-hydride-terminated⁷²) silicon surface.¹⁵¹ The low recombination velocity of charge carriers is supporting evidence that there is a negligible number of surface defect sites (trap density $<3 \times 10^{-9} \text{ cm}^{-2}$).¹⁴⁵ Importantly, the high quality of the surfaces prepared in this two-step route, together with allowing access to *short* methyl films, made possible a systematic evaluation of the influence of the passivating layer thickness over the rate of native oxide growth.¹⁵⁰ Through a detailed high-resolution soft X-ray photoelectron spectroscopy (SXPS, synchrotron radiation between 10 and 300 eV) study, Webb *et al.*¹⁵⁰ showed how the protective role of the film had little or no dependence on both chain length and density of step edges. This was done by varying (i) the alkyl

chain length ($\text{CH}_3\text{--Si(111)}$ and $\text{C}_2\text{H}_5\text{--Si(111)}$) and (ii) the fractional number of silicon surface atoms localized along step edges (wafers with different nominal miscut angles were used, namely 0.5° and 7°). As the authors concluded,¹⁵⁰ their observations strongly support an oxidative protective mechanism largely due to Si–C bonds disrupting the native oxide growth mechanism⁸⁰ and not exclusively resulting from limited access of oxygenated species to the substrate.^{32,115,152}

Despite the vast literature now available on the tandem chlorination/alkyl Grignard route,^{74,102,109,114,124,145,148,150} and the general agreement over the high quality of the reaction product, the most obvious limitation of this methodology appears to be the complicated and inefficient (see Section 3.1) derivatization of films having a $\text{C}_n\text{H}_{2n+1}$ structure. Further, the need for stringent conditions (such as the exclusion of water and oxygen) for both the chlorination (generally phosphorus(v) chloride with radical initiators) and the Grignard reaction might discourage the routine use of this two-step strategy. The latter issue was partially addressed in an improved and simplified method for the preparation of halogenated silicon surfaces reported by Eves and Lopinski¹⁵³ that relied on gas phase reactions of Si(111)–H surfaces with molecular chlorine and bromine at room temperature (*e.g.* 2% chlorine in argon at *ca.* 760 Torr, 1 h). Chlorinated surfaces (but not the brominated versions) prepared under these conditions are remarkably stable toward oxidation in the presence of air and water, despite the expected polarization of Si–Si back bonds.⁹⁰ Analogous gas phase reactions have also been reported for Si(100)–H using an experimental protocol that is only slightly more demanding.¹⁵⁴

For completeness it should be noted that halogenated Si(111) surfaces have also been reacted with sodium acetylides (to generate Si–C≡CH and Si–C≡C–CH₃ linkages),^{110,155} primary amines (Si–N linkage),¹⁵⁶ primary alcohols (Si–O linkage)¹⁵⁷ and sodium azide (Si–N₃ surfaces) (Fig. 6).¹⁵⁸ The reaction of acetylides with chlorinated surfaces, in an analogous fashion to that discussed above for the Si(111)–CH₃ surfaces, allows full Si–C site termination on the Si(111) surface (see Fig. 6), and will be further detailed in Section 3.4.

2.2.3 Direct attachment of alkyl Grignard onto Si–H surfaces. In a study aimed to expand the number of available wet-chemical approaches toward Si–C bound layers Boukherroub *et al.*⁸³ described the direct thermal attachment of an alkyl Grignard reagent (decylmagnesium bromide) onto hydrogen-terminated Si(111) surface. The layers obtained showed only minor degradation upon immersion in both concentrated aqueous potassium hydroxide and 40% aqueous ammonium fluoride solutions, as judged from attenuation of the methylene stretch vibrations in the FTIR spectrum. While this direct approach surely represents a simplified protocol in regards to the two-step procedure of Bansal *et al.*,⁷⁴ conclusive evidence on its mechanism is still lacking. This lack of evidence is despite a suggestion of a role played by alkyl halide contaminants¹⁵⁹ from the Grignard solution proposed by Chazalviel and co-workers.¹⁶⁰ In brief, Chazalviel reasoned that on the grounds of higher reaction yields found in n-type substrates, as compared to p-type, an electrochemical,¹⁶¹ rather than merely chemical,¹⁶² mechanism was involved. This is in agreement with the more positive reduction potential for the alkyl halide (RBr), relative to the redox potential of the Grignard reagent (RMgBr). The oxidative decomposition of the Grignard reagent and the reduction of alkyl bromide are suggested to occur simultaneously at the surface. To account for the more efficient grafting process observed on the n-type, as compared to p-type surfaces, the alkyl halide reduction to afford an initial radical species is suggested by the authors¹⁶⁰ to be the rate-limiting step of the entire¹⁶³ reaction sequence



and



where electrons are exchanged with the silicon conduction band. This would require either holes to be injected into silicon valence band or electrons being captured from the conduction band. The energy level for a weak oxidizing agent is expected to be comparable to the energy levels in the conduction band and therefore lowered activation energies will favor an electron capture rather than a hole injection event. In the absence of appreciable photogenerated hole–electron pair formation, an event that would result in accumulation in a region close to the surface (*i.e.* space charge region) of electrons on a p-type material and holes in an n-type, the RBr reduction will proceed faster over n-type electrodes than in p-type (empty conduction band). This may account for a superior grafting efficiency.

2.2.4 Photochemical hydrosilylation reactions and mechanistic considerations. The discussion in the last section afforded insights into the energetics of the semiconductor–electrolyte interface, a topic that has been discussed in greater detail elsewhere,¹⁶⁴ but most importantly will serve to introduce an intriguing ongoing debate over the effect mediated by the doping level and type in light-mediated hydrosilylation reactions at the hydride-terminated silicon surface.^{165,166} Initially reported by Terry *et al.* in a study aimed to provide direct evidence of the silicon–carbon bond formation for the reaction of 1-pentene with Si(111)–H,¹⁴⁶ the UV-mediated hydrosilylation reaction of unsaturated hydrocarbons has since seen numerous applications.^{50–52,113,133,167–169} The process generally affords good hydrocarbon chain surface coverages,^{113,133} chemically stable surfaces,⁸³ and allows for a straightforward light-addressable surface patterning.^{51,52,168} For further details on the early body of work on the photochemical hydrosilylation, the reader should consult the comprehensive reviews of Buriak.^{27,28} Here we will mainly focus our discussion on more recent advances, while trying to bring to the attention of the reader the need for conclusive data to resolve the details of the surface hydrosilylation reaction mechanism, both under illumination and thermal conditions.

Interestingly, as discovered by Stewart and Buriak¹⁷⁰ for porous silicon and more recently reported by Sudhölter and co-workers for crystalline Si(100) and Si(111) substrates (Fig. 7),^{126,171} attachment of olefins (and acetylenes¹⁷²) can be successfully carried out under visible light irradiation (up to 658 nm^{126,166}). However, contact angle and FTIR spectral data for the hydrosilylation of 1-undecenylic acid (CH₂=CH(CH₂)₈COOH), under visible light (447 and 658 nm), suggest that the monolayers formed are not densely packed.¹⁶⁶ This mild approach (generally 477 nm light is used) promises to allow the immobilization of labile biomolecules and has been used to attach fully-acetylated olefin-bearing carbohydrates onto Si(100) surfaces.^{126,171}

From a mechanistic standpoint, however, visible light reactions have considerable implications with regards to the initiation of the radical chain reaction.^{88,119,133} As Chidsey and colleagues noted in their early work,¹³³ homolytic cleavage of the Si–H bond ($\geq 84 \text{ kcal mol}^{-1}$)^{173,174} requires *ca.* 350 nm (or lower) photons. Illumination at 450 nm of hydride-terminated substrates kept in air showed no appreciable effects in regard to surface photooxidation by radical reaction with dioxygen.¹⁷⁵ Analogously, homolytic dissociation of Si–Si bonds requires light of wavelengths shorter than 540 nm.¹²⁶ For these reasons, there is general agreement over the mechanism involved in the chain propagation,^{71,88,119,133} which is assumed to proceed through an identical radical chain to that described above for thermal method³¹ and UHV techniques^{71,88} (Fig. 3). However, less clear are the events leading to the formation of silyl radicals (silicon dangling bonds) under white light illumination as well as in uncatalyzed thermal reactions.¹⁷⁶

Using light at a wavelength of 447 nm with a controlled light intensity Eves *et al.* estimated,¹¹⁹ using STM analysis, changes in the number of nucleation sites with increasing exposure times, and hence presented evidence for a low efficiency process governing the initial stages of the hydrosilylation of

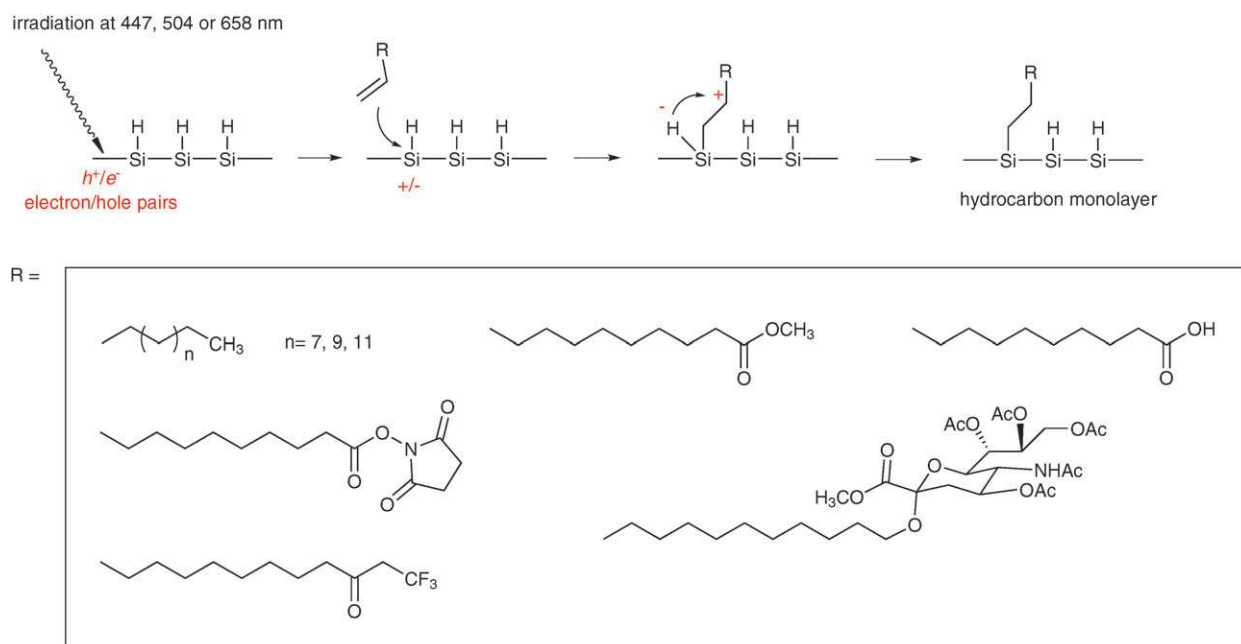


Fig. 7 White-light promoted hydrosilylation reaction (ref. 126, 166, 171 and 201). It has been proposed that surface-localized holes facilitate the nucleophilic attack of 1-alkene species ($\text{CH}_2=\text{CH}-\text{R}$, R is detailed in the figure inset).

1-decene. It was concluded that each photon had a remarkably low (*ca.* 10^{-7}) probability of forming a nucleation site. Since the homolytic dissociation of surface Si-H (and Si-Si) cannot be operative under white light illumination¹²⁶ and given the low efficiency of the initiation process, plausible alternative mechanisms include light-induced radical formation from impurities in solution¹¹⁹ and a hole-related mechanism (Fig. 7) favouring the reaction on illuminated n-type substrates, as compared to p-type, as proposed by Sun *et al.*¹²⁶

Alternatively, as in the case of 1-alkynes thermally reacted onto p-type H-Si(100)-(1 × 1) samples,¹⁷⁷ a concerted hydrosilylation mechanism has been argued for by Cerofolini and colleagues^{178–181} (Fig. 8). On the basis of detailed angle-resolved XPS analysis,¹⁸⁰ this group showed the formation of densely packed layers and suggested in the case of 1-alkynes (specifically 1-octyne),^{98,179} that a large fraction of surface attached vinyl moieties survive the thermal reaction (**a**, Fig. 8).¹⁸² In the opinion of Cerofolini *et al.* the remaining π bonds are available for subsequent insertion of either water or oxygen. These events account for a slow (negligible oxidation in the time scale of several months^{100,180}) formation of an oxo-bridge between carbonaceous material and the silicon substrate (**e**, Fig. 8). Note that the hydrosilylation reaction could, in principle, proceed *via* routes (iii) and (iv) shown in Fig. 8 to yield the bridged species **b** and **c**. The XPS evidence of Cerofolini and co-workers supporting an alkenyl layer on Si(100) are in good agreement with the *ca.* 1600 cm^{-1} FTIR vibration (Si-C=C stretch) for the 1-alkyne hydrosilylation on Si(111)-H of Linford and Chidsey.³¹

It is important to comment on the findings of Sieval *et al.*¹²⁵ on the thermal reaction of 1-alkynes onto a non-rigorous dihydride phase (*i.e.* hydrofluoric acid-etched and not otherwise treated Si(100) surface). These are highly significant with regards to the need for multiple tools in the chemical analysis

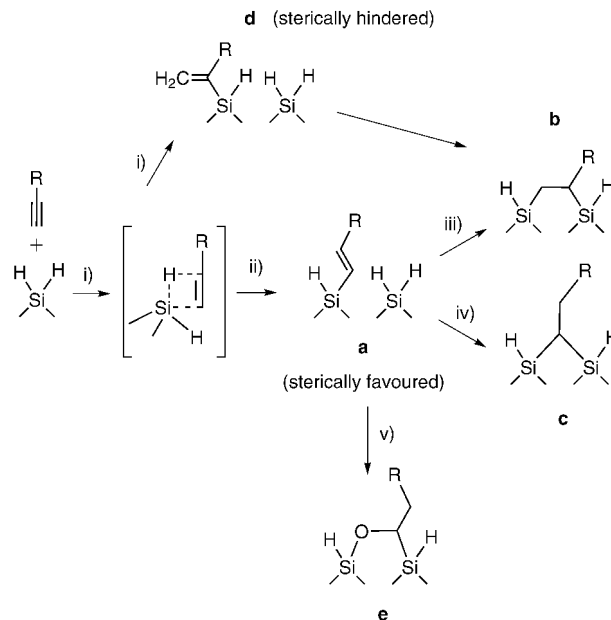


Fig. 8 Thermal hydrosilylation of 1-alkynes at the dihydride 1 × 1 Si(100) surface as proposed by Cerofolini and co-workers (ref. 178–181). A plausible concerted reaction mechanism (i), and the candidate surface products (**a–d**) are outlined. XPS evidence supports the sterically favoured alkenyl anti-Markovnikov (ii) surface as the major product (**a**) in the hydrosilylation of terminal alkynes. Steric reasons are believed to dictate the stereochemistry of the reaction, and prevent the formation (i) of the sterically hindered Markovnikov product (**d**). Possible oxidation products (*e.g.* **e**) are also shown.

of monolayers and to the pivotal role played by the substrate orientation and preparation. This group observed a total attenuation of the Si-C=C stretch which was considered as plausible evidence for complete cleavage of both alkyne π

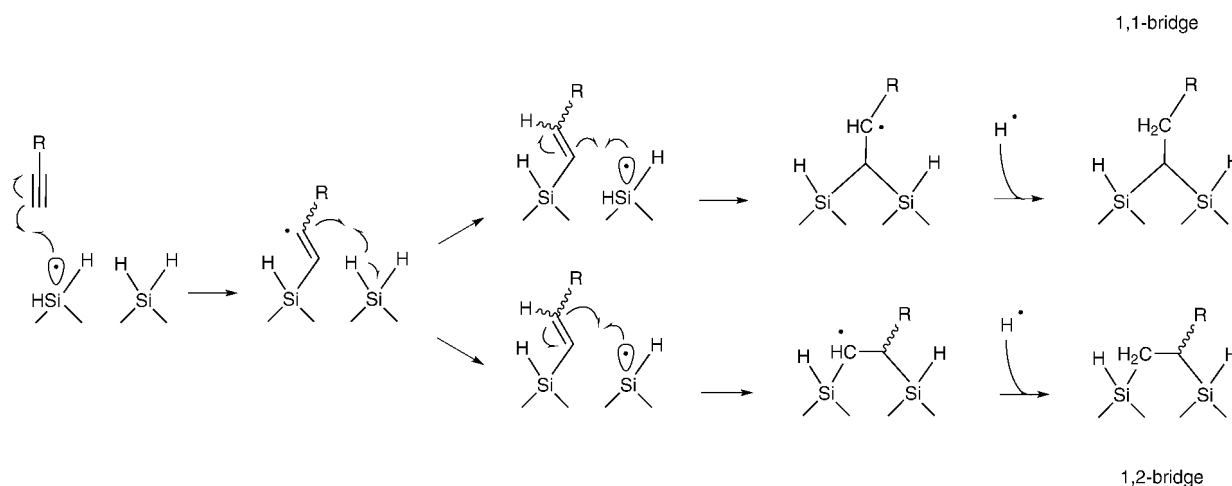


Fig. 9 Thermal hydrosilylation of 1-alkynes at the Si(100)-H surface as suggested by Sieval and co-workers (ref. 125). FTIR spectral evidence supported the complete reduction of π bonds, as for tethered molecules bound to two adjacent Si surface sites.

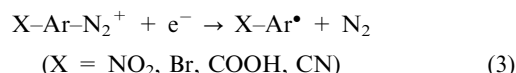
bonds (bis-silylation) through a radical mechanism (Fig. 9). Therefore, based on FTIR spectral data and quantum mechanical calculations, the formation of surface heterocycles (either 1,1- or 1,2-bridged products) involving bridged silicon surface atoms cannot be disregarded on Si(100)-H.¹²⁵ Interestingly, analogous discrepancies for the immobilization of 1-alkynes are found in the porous silicon literature.^{28,84,183} Whether the different conclusions of Sun *et al.*^{126,166} and Cerofolini and co-workers¹⁸⁰ with regards to the hydrosilylation mechanism are due to either the different unsaturated hydrocarbons used (*e.g.* different lengths), or due to differences in reaction conditions, surface preparation protocols or characterization techniques, is not clear at present and will require further work.

It also needs to be noted that covalent silicon-carbon linked layers may degrade after prolonged (*e.g.* *ca.* 2 h) exposure to UV radiation. XPS and FTIR spectral evidence support the UV-mediated cleavage of the Si-C bond of both Si(111) and Si(100) of alkyl layers, under either argon¹⁸⁴ or air.¹⁸⁵ These findings could lead to a novel surface patterning approach,¹⁸⁵ but most notably add serious implications in regards to the quality of monolayers prepared under UV irradiation.

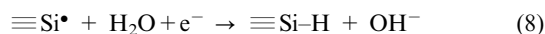
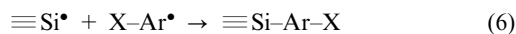
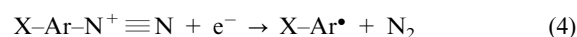
2.2.5 Lewis acid-catalyzed hydrosilylation reactions. A well-established functionalization approach for the derivatization of hydride-terminated porous silicon (PSi)^{186,187} is the Lewis acid-mediated (*e.g.* AlEtCl₂) attachment of olefins and acetylenes. This method has attracted little interest on crystalline surfaces⁸³ presumably due to the low surface coverage initially reported.¹⁸⁸ Further, in contrast to the data reported for PSi, this catalytic reaction requires heating and significantly longer reaction times when performed on Si(111)-H surfaces.^{83,186}

2.2.6 Electrochemical approaches to Si-C-bound hydrocarbon monolayers. Expanding to crystalline silicon surfaces a technique previously used only to graft aryl layers on carbon substrates,^{189,190} Allongue and co-workers^{107,191} showed the electrochemical formation of phenyl layers on n-type Si(111) by reduction of commercially available aryl diazonium salts.

These experiments were, in part, prompted by the findings of Chazalviel and co-workers for PSi systems. They showed that under anodic polarization, methoxy-terminated surfaces ($\equiv\text{Si}-\text{OCH}_3$ and $\equiv\text{Si}-(\text{OCH}_3)_2$) can be prepared.¹⁹² The aryl diazonium approach benefits from the low cathodic overpotentials necessary to generate aryl radicals



The prepared Si-C bound layers resist chemical etching in 40% hydrofluoric acid.¹⁹³ When the reduction was performed in aqueous electrolytes containing diluted sulfuric acid combined with 2% hydrofluoric acid, the reaction gave no detectable high-binding energy shifts in the Si 2p XPS spectra (even at low take off angles, 5–10°) indicating the absence of SiO_x species.¹⁰⁷ Allongue and co-workers, on the basis of Rutherford backscattering, STM imaging, angle resolved XPS, capacitance measurements, and from the measured charged passed during the grafting process,¹⁹⁴ concluded that no appreciable multilayer formation occurred^{107,117,191} under the cathodic conditions used. A reaction scheme for the electrochemical reduction of diazonium salts on hydride silicon was also proposed:¹⁹¹

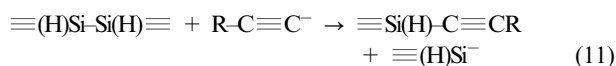
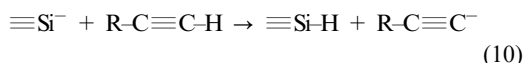


where X is either a bromine atom or a nitro group, and $\equiv\text{Si-H}$ depicts the monohydro phase of the ammonium fluoride etched Si(111) surface. Importantly the proposed mechanism accounts for the observed hydrogen evolution (7) *via* a Heyrovsky-type reaction.^{90,94} The silyl radical generated can either react with aryl groups (6) or abstract hydrogen from a water molecule to regenerate the hydride terminated species (8). As supported by FTIR spectral data,¹⁰⁷ reaction products

include hydride terminated species with lack of sizable SiO_x -related XPS emissions.^{107,191}

An important difference between the approach of the Allongue group and almost all of the available literature on un-oxidized silicon-carbon bound layers is that they use straightforward aqueous conditions used in handling etched Si(111) wafers. As the Si-C bond is completely inert towards 2% hydrofluoric acid, its presence in the electrolyte during the reduction of the diazonium salt allowed for any SiO_x species formed during the reaction to be dissolved without interfering with the organic layer formation. This approach to limit silicon oxidation in the final surface is in contrast to the entire body of work on non-oxidized passivated silicon surfaces, where the strategy has been to minimize oxidation of the substrate by thoroughly excluding oxygenated species from the reaction chamber.

An alternative electrochemical route to give silicon-carbon bound monolayers, adapted from anodic and cathodic galvanostatic procedures initially reported for PSi ,¹⁹⁵ is the cathodic electrografting of terminal alkynes onto highly-doped hydride-terminated Si(111) and Si(100) substrates.¹⁹⁶ The method uses a conducting (Pt-coated) atomic force microscope (AFM) tip acting as the anode in a electrografting reaction to produce well-defined and chemically resistant nanoscale (*ca.* 40 nm) features. The forward negative bias (−1.0 to −2.2 V)¹⁹⁷ applied to the SiH surface limits oxidative events at the substrate when the electrografting of various 1-alkynes is done in air. There is no evidence of hydrogen shifts from the substrate to a π bond since no consumption of $\nu(\text{C}\equiv\text{C})$ FTIR modes is found in porous silicon substrates after the galvanostatic attachment of various 1-alkynes.¹⁹⁵ The mechanism involved in the formation of a silylated alkyne ($\text{Si}-\text{C}\equiv\text{CR}$) product *via* the cathodic reaction of a generic 1-alkyne ($\text{R}-\text{C}\equiv\text{C}-\text{H}$) was proposed to be as below



where the initial formation of a silyl anion, after the reduction of a Si-H site (9), is followed by an acid/base reaction to give a carbanion (10) and subsequent nucleophilic attack of a Si-Si bond (11).¹⁹⁵ Importantly, the reaction is highly selective toward acetylenes, with no monolayers forming from 1-alkenes, and the highly conjugated alkynyl system produced might show interesting electronic properties.¹⁹⁶

3. ω -Functionalized monolayers on silicon surfaces

To introduce a pivotal concept to the discussion of the following paragraphs, where an overview will be given of the available derivatization routes toward functional silicon layers, it should be noted that the silicon hydride phase has indeed a broad reactivity and, beside reactions with unsaturated hydrocarbons and halogens, the immobilization of nitriles,³¹ alcohols,^{44,81} aldehydes,¹⁶⁸ and ketones¹⁹⁸ have all been documented.

3.1 Derivatization of methyl-terminated monolayers

As discussed in the previous section, a rapidly expanding area in the literature is on the chemical and electrical passivation of hydride-terminated silicon surfaces with common *hkl* orientations. This provides the surface chemist with an array of tools to access either carbon-silicon,^{31,87} nitrogen-silicon,¹⁵⁶ or oxygen-silicon^{81,139,168,199} bonded organic layers.^{27,29} A common feature of most of the early work in this area, and to some extent a limitation of most of the procedures reported in the literature, is a methyl termination at the distal end of the organic films. Chidsey and co-workers reported a brilliant chemical strategy to decorate octadecyl Si(111) monolayers with 4'-[3-trifluoromethyl-3*H*-diazirin-3-yl]-benzoic acid *N*-hydroxysuccinimide ester (TBDA-OSu, a singlet carbene), that allowed for the subsequent immobilization of amine-tagged DNA molecules (Fig. 10).¹⁶⁹ However, in general, covalent modification of a poorly reactive alkyl terminated surface suffers from low yields (*ca.* 10%) and has seen very limited use.³² Similarly, *in situ* modification of a methyl-terminated layer with primary amines ($\text{H}_2\text{NR}'$), *via* a sulfonyl chloride intermediate ($\text{Si}-\text{RCH}_2\text{SO}_2\text{Cl}$) to afford tethered sulfonamides ($\text{Si}-\text{RCH}_2\text{SO}_2\text{NHR}'$), was also among the first reports on the functionalization of covalent monolayers on non-oxidized silicon (111) surfaces.^{169,200} However, presumably as a result of the toxicity of chlorine and sulfur dioxide, this gas-phase procedure has not proven popular.

With regards to the further modification of chemically inert alkyl monolayers (*i.e.* methyl-terminated) two very recent reports by Zuilhof and co-workers have opened up novel chemical activation perspectives. In the first of the two papers the use of conducting atomic force microscopy (AFM) to oxidize hexadecyl monolayers, hereafter referred to as C_{16} film, on Si(111) substrates was reported.²⁰¹ Oxidative conditions were tuned and, for a narrow range of bias and reaction times, terminal methyl groups (and possibly outer methylene units in the monolayer) can be oxidized with negligible oxidative damage of the underlying substrate. Although electro-oxidative patterning is a well-established tool in nanoscience and numerous examples for the activation of *n*-octadecyltrichlorosilane (OTS) layers on SiO_x are available,^{202,203} a significant difference has now emerged with regards to the bias threshold required to promote the monolayer oxidation. Compared to OTS systems, the bias required to initiate oxidation of methyl groups is significantly lowered in non-oxidized Si-C-bound SAMs. A plausible explanation for this effect is an increase in the effective electric field between the AFM tip and the substrate, experienced by the C_{16} layer, due to the absence of an insulating SiO_x layer.²⁰¹ This finding is expected to allow for an improved chemical selectivity toward functionalities in the SAM of non-oxidized systems.

In the second of these two works, Zuilhof and co-workers showed that short plasma treatments could be used as a controlled and reproducible approach to the oxidation of C_{16} films on both Si(100) and Si(111) surfaces.²⁰⁴ Despite the chemical heterogeneity of the oxidized surface, described as containing a range of hydroxyl, carbonyl and carboxylic functionalities, spectroscopic data supported minimal disruption of the alkyl film. This is because experimental data suggest the oxidation process is limited to the top few Å of the

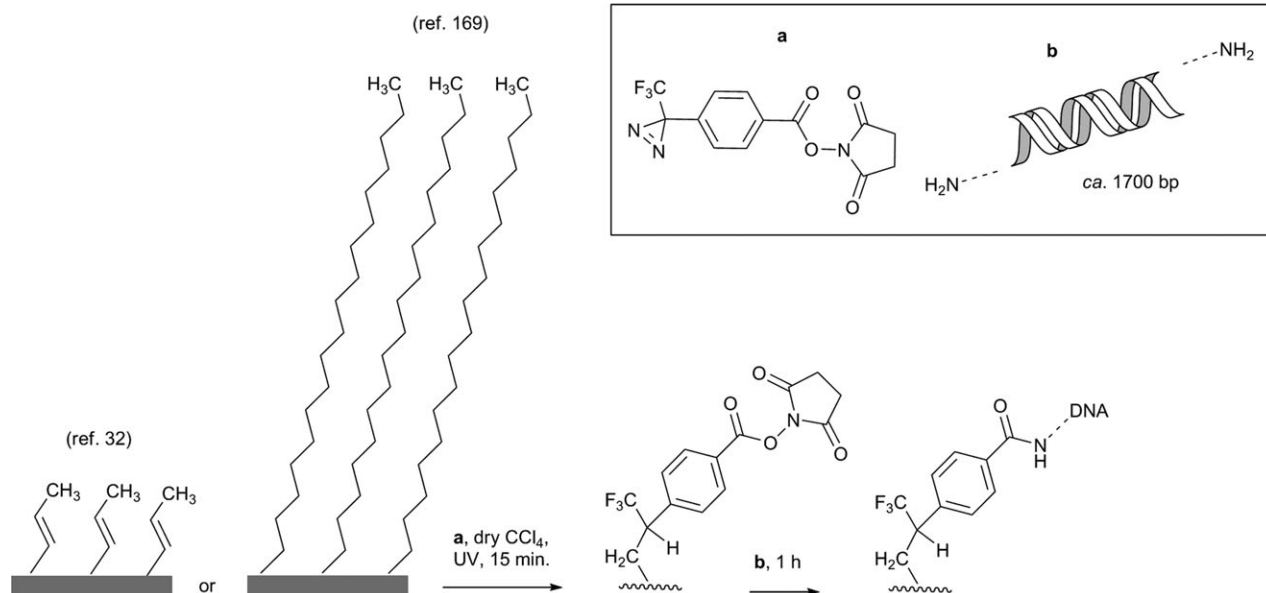


Fig. 10 Derivatization of methyl-terminated Si(111) layers with a photoactive aryldiaziridine cross-linker (a), TDBA-OSu (ref. 32 and 169). The activated octadecyl layer was further functionalized with dsDNA fragments amino-modified at both 5' ends (b).

hydrocarbon layer. Notably, the plasma-induced oxidation of the C₁₆ film was accompanied by minor to negligible substrate oxidation. Furthermore, (i) derivatization of the oxidized film by reaction of aldehyde functionalities with amine-derivatives (*m*-trifluoromethylbenzylamine TFBA and cysteamine, a and b in Fig. 11, respectively), (ii) the subsequent grafting of Au nanoparticles onto the cysteamine-modified SAM, and (iii) an example of plasma treatment combined with PDMS masking to produce micrometer-sized oxidized patterns, have demonstrated the vast scope of this novel route to high-quality functional layers readily prepared from simple 1-alkenes.

3.2 Formation and derivatization of amino-, hydroxyl- and thiol-terminated monolayers

In order to fully benefit from the organic/semiconductor approach—in other words being able to expand the bulk properties of the substrate in a controlled fashion—more convenient protocols for the attachment of further functionality onto passivated silicon surfaces relies on the grafting of bifunctional molecules. The difficulties encountered with the insertion of a molecule of interest in carbon–hydrogen bonds prompted the investigation of chemical routes involving the grafting of ω -functionalized 1-alkenes onto the Si–H substrate. Restrictions are nevertheless dictated by functional group incompatibilities with surface hydrides. For example, competition between olefins and amine functionalities for the reactive surface termination^{156,205,206} makes it necessary to introduce protection/deprotection procedures to prevent side-reactions of the amine moiety with the surface.

As initially demonstrated by Smith and colleagues,⁴⁹ and as shown in Fig. 12 and 13, attachment of thiol-modified DNA to the Si(100) surface could be achieved on *tert*-butoxycarbonyl-protected amine-terminated surfaces (*t*-BOC protected 1-aminodec-1-ene) after SAM deprotection, and by using a suitable (water soluble) heterobifunctional cross-linker

molecule (sulfosuccinimidyl 4-(*N*-maleimidomethyl) cyclohexane-1-carboxylate, SSMCC). Further applications of amino-decane-modified silicon surfaces,^{53,207} alternative protection/deprotection strategies^{86,208} and novel cross-linker molecules (*i.e.* *N*-succinimidyl 3-maleimidopropionate, SMP¹¹¹ and diluted glutaraldehyde/sodium cyanoborohydride solutions²⁰⁷) have been also reported (Fig. 13). Similarly, formation of disordered monolayers for ω -functionalized 1-alkenes³³ have been encountered in the preparation of oxygen- and thiol-terminated Si(111) monolayers, and cross-reaction events were prevented only by using dimethoxytriphenylmethyl (Si-RODMT),^{209,210} *tert*-butyl dimethylsilyl (Si-ROTBDMs)¹²⁰ and trifluoroacetyl (Si-RSC(O)CF₃)⁶⁶ protecting groups (Fig. 14) prior to attachment of DNA,^{209,210} amino acids (following activation with carbonyl diimidazole or disuccinimidyl carbonate),¹²⁰ or prior to the assembly of semiconductor-alkyl-S-metal junctions and nanoelectrodes arrays.^{66,211}

Note that standard solution phase deprotection procedures²¹² might be too harsh for organic–crystalline surface systems. As an example, conventional wet chemistry removal of the DMT group with aqueous ammonia resulted in a pitted Si(111) surface prompting the use of anhydrous methylamine.²⁰⁹ Further, removal of the TBDMS with diluted hydrochloric acid solutions caused minor oxidation of the silicon substrate¹²⁰ and alkaline hydrolysis of trifluoroacetyl-protected amine-terminated Si(100) surfaces caused significant corrosion of the substrate.⁴⁹

3.3 Formation and derivatization of carboxylic acid-based monolayers

If compared to the approaches detailed in the previous paragraph, the preparation of monolayers with 1-alkenes bearing terminal ester groups appears to be less demanding; the reaction with the H-terminated substrate is reported to occur preferentially at the C=C end of the molecule

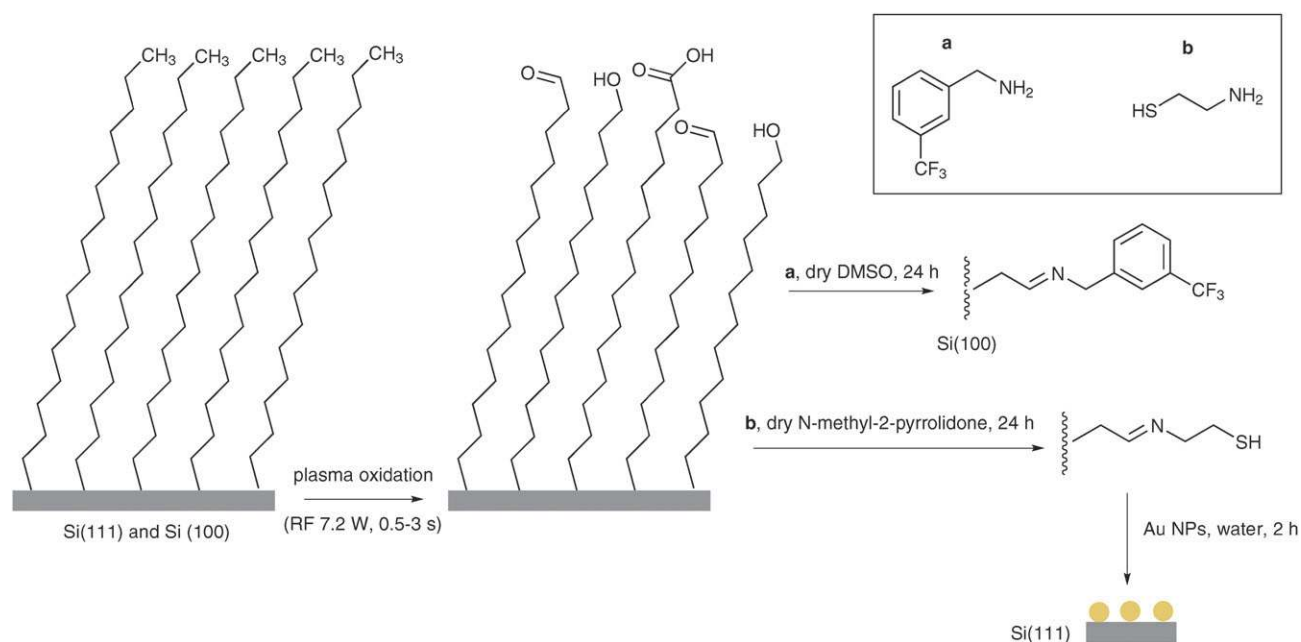


Fig. 11 Recent developments in the activation of chemically inert alkyl monolayers. Preparation of fluorine- and thiol-terminated surface-bound imines (ref. 204). Surface aldehydes formed upon the plasma-induced oxidation of alkyl chains were reacted with spectroscopic probes (a), TFBA and suitable thiol-terminated linker molecules (b), cysteamine for the subsequent attachment of Au nanoparticles.

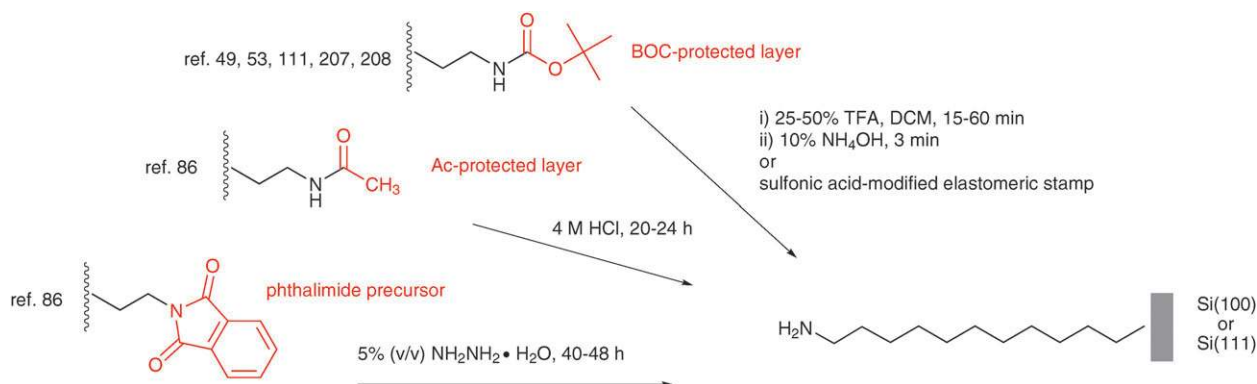


Fig. 12 Representative protection/deprotection schemes for the preparation of amino-terminated Si(100) and Si(111) layers. Note that the reaction of tethered phthalimide groups with hydrazine (NH_2NH_2), to yield the amino-terminated layer, required long reaction times to reach completion (*ca.* 2 days). The BOC and acetamide (AcNH-) protecting groups were removed under strongly acidic conditions or by soft lithographic printing techniques (ref. 208).

(Fig. 15).³³ Sieval *et al.*³³ conducted a systematic FTIR spectroscopy and XRR study on Si(100) monolayers prepared by thermal reaction of 1-alkenes bearing an ester moiety and reported high-quality films, with no appreciable SAM degradation, for methyl and propyl esters hydrolyzed *in situ* to the corresponding carboxylic acid surface (using concentrated hydrochloric acid/2-propanol). Milder reaction conditions for the chemical conversion of ethyl ester-terminated layers prepared on Si(111) were described by Boukherroub and Wayner,¹¹³ and are shown to be suitable for reaction with biological molecules. Largely based on FTIR spectral data, but also supported by XPS evidence, the authors reported (i) mild reduction conditions to the alcohol layer using NaBH_4 , (ii) reaction with alkyl Grignard reagent to alkylate tethered alkyl chains containing carbonyl groups and importantly,

(iii) an example of biomolecule immobilization on the 'free' carboxylic acid surface using conventional solid phase amide coupling protocols (Fig. 15).¹¹³ Wayner and co-workers further expanded the repertoire of available wet-chemical modifications for ester-terminated surfaces by showing a two-step manipulation of a passivated Si(111) electrode surface.¹⁶⁷ Conversion of the ester surface to a thiophene-terminated layer ($\text{Si-RCCOC}_2\text{H}_5$ to $\text{Si-RC(2-thienyl)}_2\text{OH}$) was followed by the photoelectrochemical oxidation of the confined thiophene moieties in a thiophene solution. Generated polythiophene films showed superior morphological and electrical properties, and are therefore reasoned to be covalently attached to the underlying functionalized layer.^{167,213}

Less conclusive, presumably as a result of diverse hydrosilylation conditions employed, are the results for layers

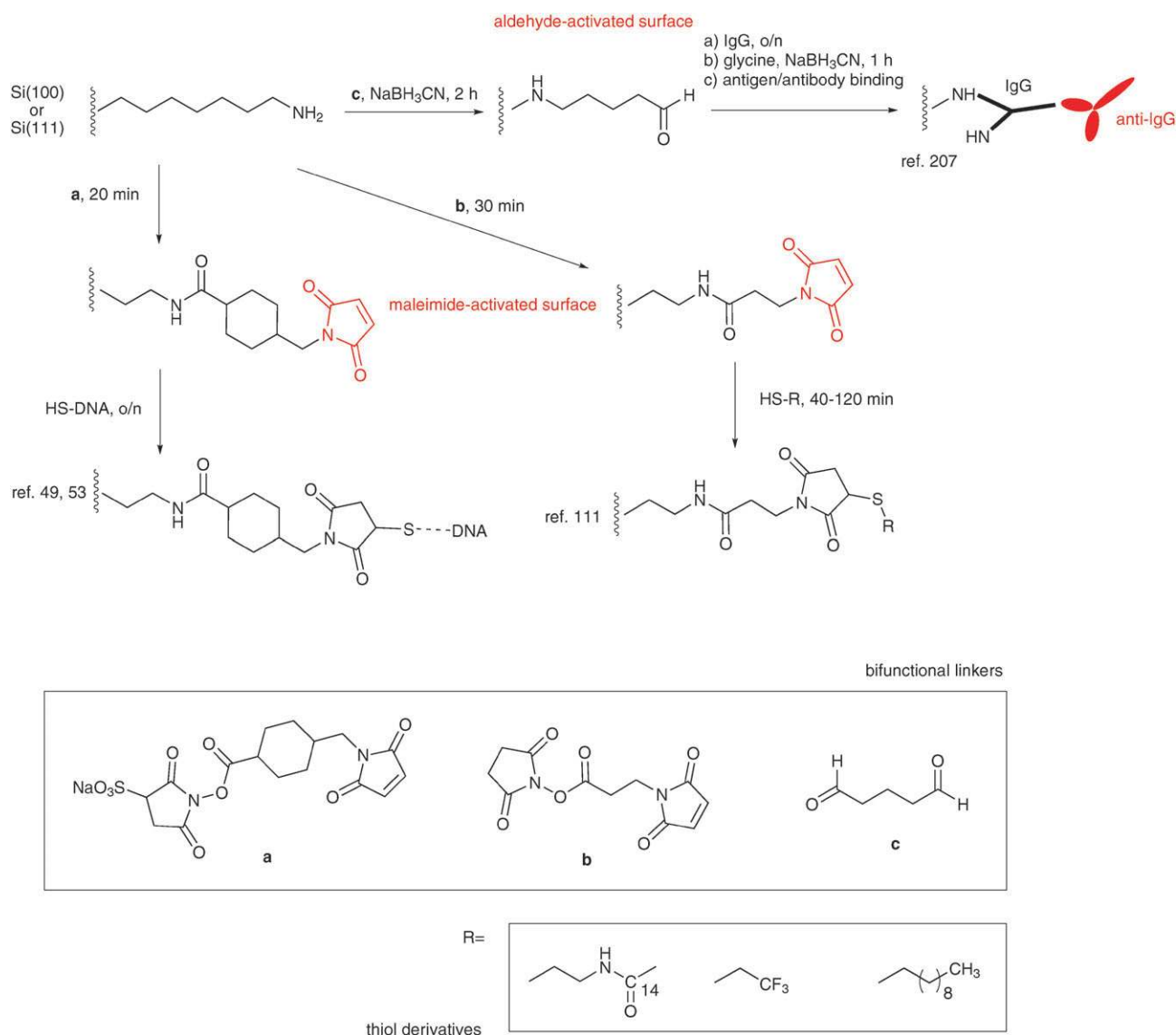


Fig. 13 Representative synthetic schemes for the modification of amino-terminated Si(100) and Si(111) layers. Si(100) arrays for DNA hybridization assays were prepared by reacting thiol-modified single-strand DNA oligomers with the thiol-reactive maleimide moiety in the SSMCC (a) linker. Immobilization of thiol-containing molecules (R-SH, with R detailed in the inset) was also investigated on SMP (b) functionalized Si(111) surfaces (ref. 111). Glutaraldehyde (c, 3%) in solutions of sodium cyanoborohydride was used to prepare biosensors for the detection of human IgG *via* electrochemical impedance spectroscopy.

prepared from 10-undecylenic acid. On the basis of FTIR data, where broadened antisymmetric and symmetry methylene stretching vibrations and shifts to higher frequencies were observed, Sieval and co-workers suggested the formation of disordered assemblies for the thermal reaction of the organic acid (200 °C, 2 h).³³ Opposite conclusions based on an XPS and FTIR analysis were drawn by Voicu *et al.* for films prepared on Si(111)-H through light-promoted (300 nm, 3 h) reactions with 10-undecylenic acid.⁵¹ Voicu and co-workers prepared high quality acid-terminated films that were further reacted with DNA molecules, affording a convenient and simplified protocol for the immobilization of a bifunctional molecule (*i.e.* 10-undecylenic acid) with no deprotection steps being necessary. Minor, but detectable reactivity toward the acid function of undecylenic acid was reported in porous

silicon (PSi).²¹⁴ Nevertheless, under the same reaction conditions used to graft the acid-terminated olefin (95 °C, 16 h) only minor attenuations for the Si-H_x stretchings (transmission mode FTIR spectroscopy) were found in control experiments with decanoic acid (CH₃(CH₂)₈COOH); this further supported a preferential reaction of silicon-hydrogen bonds at the C=C terminus.²¹⁴ The result was unexpected as freshly etched PSi surfaces display a Lewis acid character (Si-H), and hence reaction with Lewis bases might be expected to be favoured, and alcohols,^{81,139,140,215} ketones¹⁹⁸ and aldehydes^{123,168,216} have all been reported to react with the hydride-terminated silicon surface.

As presented in Fig. 16, Bowden *et al.*¹⁰⁸ assembled undecylenic acid and octadecyl²¹⁷ layers on Si(111)-H at room temperature (24 h), without UV irradiation, in the presence of

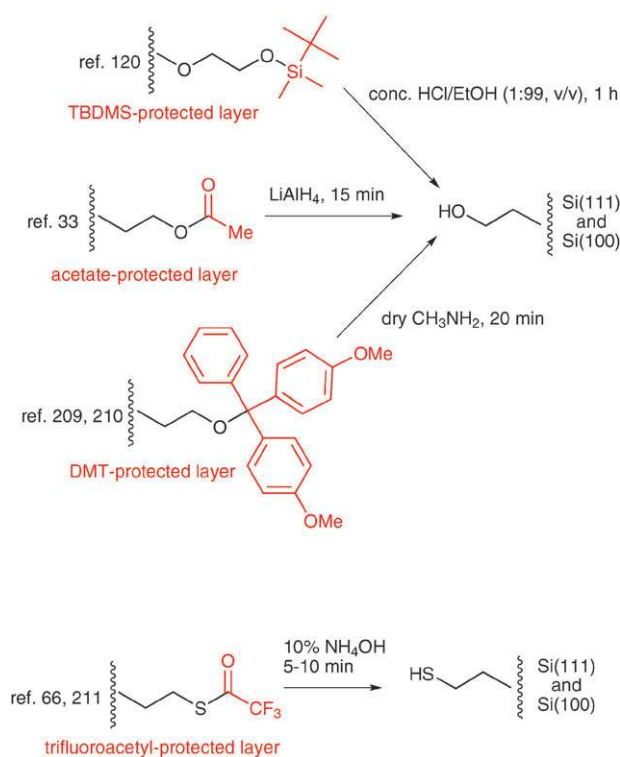


Fig. 14 Available protection/deprotection schemes for preparation of hydroxyl- and thiol-terminated Si(111) and Si(100) layers.

a derivative of TEMPO (4-(decanoate)-2,2,6,6-tetramethyl-1-piperidinyloxy, TEMPO- C_{10}).²¹⁷ XPS and FTIR spectral data supported the formation of well-ordered and stable structures, preferentially bonded to the silicon substrate through the olefin end of the SAM-forming molecule. Further, the authors performed an elegant control experiment with a mixed 1-octadecene/fluorine-tagged acid molecule system

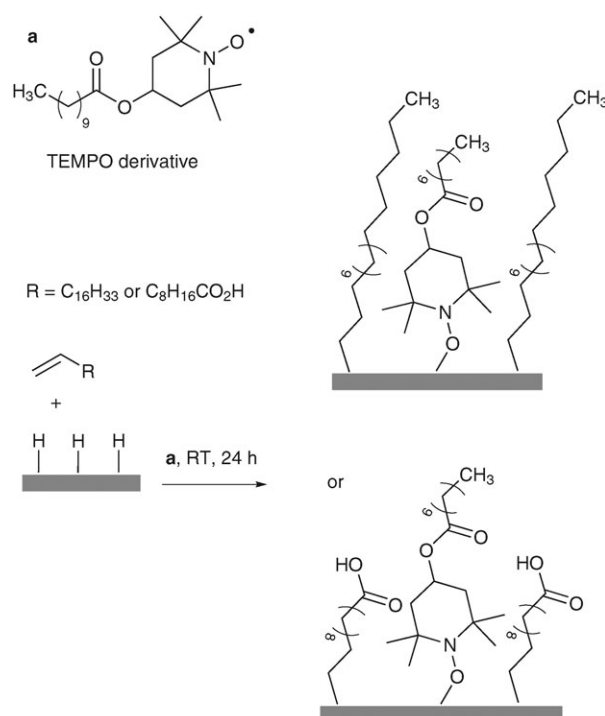


Fig. 16 Mild conditions for the assembly of methyl- and carboxylic acid-terminated layers on Si(111). In the presence of a TEMPO derivative (e.g. TEMPO- C_{10} , a), the hydrosilylation of 1-alkenes proceeded at room temperature. The presence of tethered TEMPO derivatives in the reaction product has been documented (ref. 108 and 217).

($\text{CH}_3(\text{CH}_2)_{15}\text{CH}=\text{CH}_2/\text{CF}_3\text{CF}_2\text{CF}_2\text{C}(\text{O})\text{O}(\text{CH}_2)_3\text{COOH}$) to study whether the acid and olefin moieties would bind to the Si(111)-H at competitive rates. The absence of a detectable fluorine-derived XPS emission demonstrated that olefins selectively bind to a Si(111)-H surface even when 1-alkenes

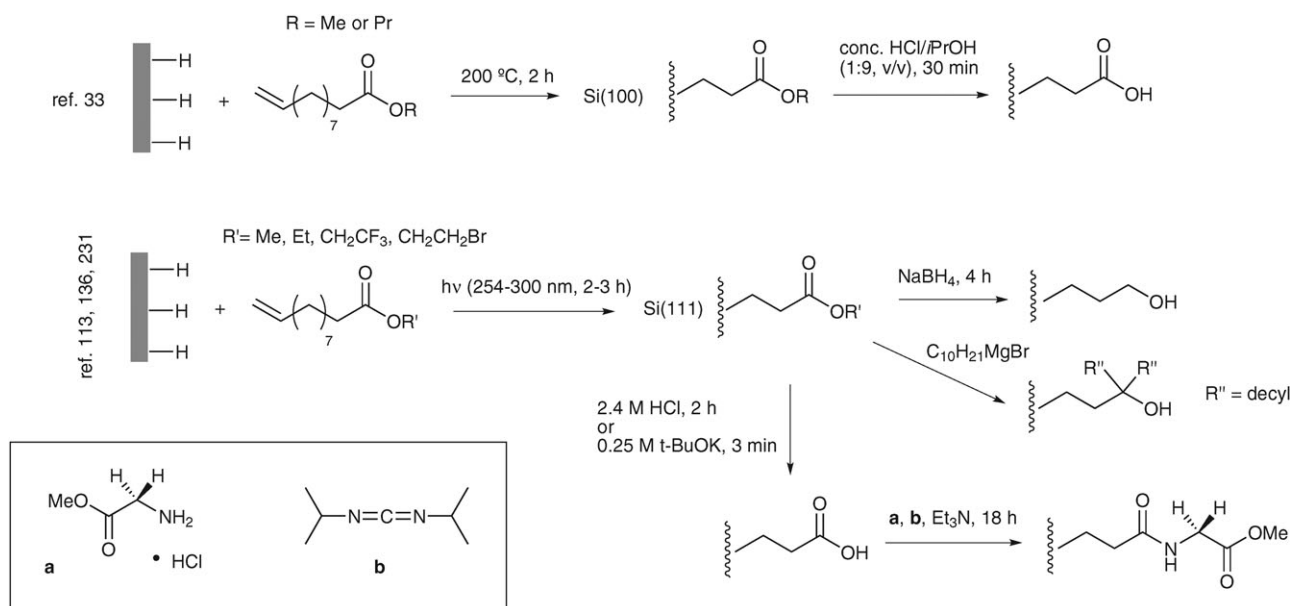


Fig. 15 Preparation and reactivity of 10-undecenoyl ester-derived monolayers on Si(100) and Si(111) substrates. An early example of biologically-relevant molecule immobilization is shown (ref. 113). Upon hydrolysis of the tethered ester molecule, the carboxylic acid terminated surface was coupled to glycine methyl ester (a) using a carbodiimide reagent, 1,3-diisopropylcarbodiimide, (b).

are present in solution, and helped in elucidating the mode of binding of undecylenic acid.¹⁰⁸

The knowledge of a negligible reactivity for carboxylic acid functionalities with surface hydrides has allowed for the preparation of more complex monolayers. Toward this end, Chazalviel and co-workers have demonstrated that well-defined mixed carboxyl-terminated alkyl monolayers (Si-(CH₂)₉CH₃/Si-(CH₂)₁₀COOH) can be prepared on Si(111) *via* photochemical reactions (312 nm).²¹⁸ The authors, on the basis of IR spectroscopy and AFM data, argue in favour of no reaction between the acid functionalities and the silicon substrate, and stress on the need of a final rinse with hot acetic acid to remove adventitious contaminants.²¹⁸ In the same report, they also propose a quantitative model, heavily reliant on a liquid-phase calibration procedure of the IR absorption intensity, to estimate the composition of the mixed monolayer, and reached the conclusion of SAMs richer in acid chains than the grafting solution.^{106,218}

Cathodic electrografting of ω -functionalized 1-alkynes has also been reported (Fig. 17).¹²⁷ This showed an improved surface coverage for 10-undecynoic acid (HC \equiv C(CH₂)₈COOH) and 6-heptynoic acid methyl ester (HC \equiv C(CH₂)₄COOCH₃) layers in Si(111) and Si(100) systems when compared to thermal and photochemical (HC \equiv (CH₂)₄COOCH₃ only) processes.¹²⁷ Both serving to introduce a convenient IR spectroscopic marker, and allowing for the subsequent attachment of amine-tagged molecules, an esterification protocol to activate an acid moiety (Si-RCOOH) with *N*-hydroxysuccinimide (Si-RC(O)NHS), relying on the use of conventional carbodiimide reagents (generally *N*-ethyl-*N'*-(3-(dimethylamino)propyl)carbodiimide (EDC)), was initially discussed for silicon substrates in a report by Boukherroub *et al.*²¹⁴ This method now represents a widely used platform toward diverse functional silicon surfaces.^{51,52,57,59,106,116,219–221} (Fig. 17, route A). A detailed quantitative IR spectroscopic study on the amidation reaction at monocrystalline Si(111) surfaces has been recently reported by Chazalviel and co-workers.¹⁰⁶ The method presents some limitations with regards to sterically hindered molecules (*e.g.* single-strand DNA oligomers tethered to a primary amine linker) and provided that small capping agents, such as ethanolamine, are employed to deactivate unreacted sites,^{50,51} NHS-activated films are open to the immobilization of primary amines (–CO–NH–R), as well as substituted hydrazine (–CO–NH–NH–R).²²¹ This two-step procedure (activation followed by nucleophilic displacement) does not require harsh hydrolysis steps as in the case of tethered acid esters.^{33,222} It was implemented by Wojtyk *et al.*²²³ and by Yin *et al.*⁵² through the direct thermal and photochemical (UV-mediated) attachment of *N*-succinimidyl undecenoate (ω -NHS-functionalized 1-alkene) onto porous silicon and Si(100)–H surfaces, respectively. Furthermore, irradiation with visible light (447 nm) at room temperature of n-type Si(111)–H substrates has been recently reported to afford good quality NHS-terminated layers in a one-pot procedure.²²⁴ On the contrary, under thermal hydrosilylation conditions, there are spectroscopic indications of partial degradation of this NHS-functionalized Si(111) assembly if prepared through the direct procedure.²²⁴ However, this one-pot approach toward the assembly of

succinimidyl ester-terminated surfaces requires significant synthetic effort as the relevant ω -functionalized 1-alkene molecule is not commercially available and has to be custom-synthesized.^{58,59,225} We reason this as the major cause behind the limited number of literature examples on this directive approach, while on the other hand the step-wise NHS/EDC activation scheme (Si-RCOOH to Si-RC(O)NHS) remain widespread in surface science.^{50,51,226,227}

It is also worth noting that an optimization study to evaluate the optimal range of NHS and EDC concentrations and molar ratios has only very recently been published for porous silicon substrates by Sam *et al.*²²⁸ The authors have systematically varied the concentrations of the two reagents and semiquantitatively evaluated *via* transmission FTIR spectroscopy the presence and relative abundance of by-products (*e.g.* *N*-acylurea) and unreacted *O*-acylurea and anhydride species among the desired reaction product (*i.e.* pSi-RC(O)NHS). Very high yields for the activation reaction were found for a restricted range of NHS and EDC concentrations and molar ratios (5 mM < [EDC] ~ [NHS]). This was explained in terms of kinetic competition between different reaction pathways. A similar report detailing reaction pathways and kinetic information for the activation reaction at flat silicon surfaces has yet to be published and is much needed. At present, experimental conditions for the preparation of succinimidyl esters of 10-undecylenic acid SAMs grafted onto crystalline silicon appear to be far from standardized, with a broad range of published reagent concentrations and molar ratios,^{50,51} as well as differences in reaction temperatures and pH values for the solutions.^{106,116,228}

Few alternative protocols to carbodiimide based strategies have been reported for the manipulation of carboxylic acid-terminated silicon surfaces. A notable exception is the procedure for the functionalization and patterning of acid layers on Si(111) surfaces reported by Perring *et al.*¹⁰⁸ This group used trifluoroacetic anhydride and triethylamine to yield a nucleophile-reactive anhydride-terminated layer (Fig. 17, route B). The activated surface was then used in a multi-step procedure, where immobilized allylamine moieties (Si-RC(O)NHCH₂CH=CH₂) were further reacted, in the presence of Grubbs' first generation catalyst, with norbornene molecules in a ring-opening polymerization procedure.¹⁰⁸

In the search for coupling alternatives to the amide chemistry-based approaches described above, procedures such as those involving Si(111) layers terminated with semicarbazide groups (Si-RNHC(O)NHNH₂) to attach peptides bearing a glyoxylyl group (Si-RNHC(O)NHN=CHC(O)R'),²²⁹ epoxide-functionalized Si(111) films to confine thiolated oligonucleotides,¹¹² as well as aryl molecules covalently grafted onto Si(111)–H and functionalized with fullerene molecules,²³⁰ have been the subject of recent research. However, these are still only selected examples from a rapidly expanding area.

Despite not being of major concern in most of the bio-sensing applications so far published,^{50–53,210,231} the outcome of a multi-step strategy, such as any of those discussed above, is potentially affected by one, or more, of the following shortcomings: (a) cross-reactivity of ω -functionalized 1-alkene (or 1-alkyne) molecules with the hydride-terminated silicon

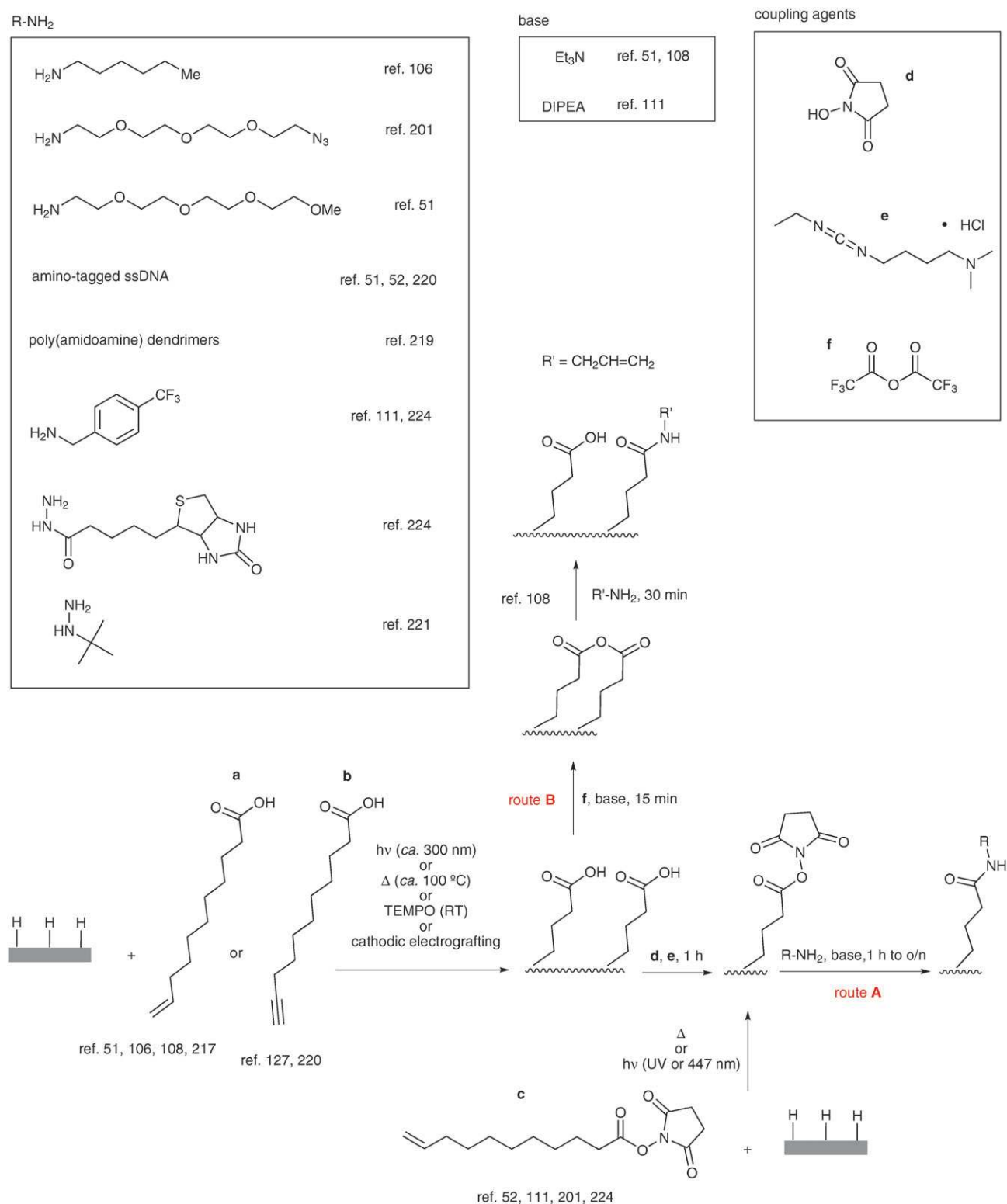


Fig. 17 Preparation and reactivity of *N*-hydroxysuccinimide(NHS)-ester-terminated Si(100) and Si(111) monolayers. Several protocols for the attachment of 10-undecylenic acid (**a**) and 10-undecynoic acid (**b**) onto hydride-terminated silicon surface are now available. Two schemes (routes **A** and **B**) for the reaction of the acid surface with primary amines (R-NH₂ and R'-NH₂) are shown. Route **A**. Chemical modification of the carboxylic acid function with *N*-hydroxysuccinimide (NHS, **d**) in the presence of the coupling agent *N*-ethyl-*N'*-(3-(dimethylamino)propyl)-carbodiimide hydrochloride (EDC, **e**) prior to the reaction with the amine nucleophile (R-NH₂). An alternative, direct, approach to the succinimide surface proceeds *via* the hydrosilylation of ω-NHS-functionalized 1-alkenes (**c**). Route **B**. Activation of the acid surface with trifluoroacetic anhydride (**f**) to yield an amine-reactive anhydride surface.

surface leading to ambiguous reaction products (*e.g.* silyl-ester formation^{33,214}); (b) use of poorly controlled activation procedures (*e.g.* capping agents required⁵¹); (c) harsh deprotection reactions required;^{33,49} (d) non-quantitative coupling yields;^{51,127} (e) surface segregation²³² of acid and alkyl chain in mixed decyl/10-carboxydecyl mixed layers;²³³ and (f) long term oxidation of the silicon substrate starting from defects sites in the monolayer.^{107,117} To address some or all of the above concerns is a precondition if both the structural^{78,89,119} and electronic⁹⁵ properties of the unoxidized crystalline silicon surface are to be retained upon the formation of an organic-passivated interface, that does not possess significant defect sites,^{66,114,117,124,234,235} but rather increases the chemical stability of the interface.^{32,115,147,152}

3.4 Reactivity of olefin- and acetylene-terminated monolayers

It is intuitive that issues on functional group incompatibilities with hydride terminations, as mentioned above, could be easily addressed by employing a symmetrical α,ω -bifunctional molecule in the hydrosilylation step. Further, selective and highly efficient coupling procedures, involving neither activation nor protection/deprotection steps, might be amenable to prepare high quality modified surfaces with reduced chemical ambiguity in the surface product.

A significant step forward in this direction was the report in 2006 by Dutta *et al.*,²³⁶ describing the grafting of a diene species ($\text{CH}_2=\text{CH}(\text{CH}_2)_9\text{O}(\text{CH}_2)_9\text{CH}=\text{CH}_2$, **a**, Fig. 18) onto Si(111)-H at room temperature, in the presence of trace amounts of TEMPO-C₁₀.^{108,217} The hydrosilylation product is an alkene-terminated layer, showing no signs of oxidation (XPS), and exposing a distal alkene moiety used in a subsequent cross-metathesis reaction. In diluted layers (1-octadecene **b** to **a**, 1/1 mole ratio), the tethered alkenes are exposed above surrounding methyl groups and thus accessible to the Grubbs' catalyst (**c**, Fig. 18). The subsequent reaction to confine substituted 1-alkene molecules (and release ethylene) was claimed to have reached *ca.* 50% conversion. However, the authors suggested possible side reactions between adjacent surface-bound olefins²³⁶ (Fig. 18). The alkene-terminated structure was demonstrated to be compatible with soft lithography patterning,²³⁶ and analogously functionalized surfaces ($\text{Si}-\text{RCH}=\text{CH}_2$) have seen further applications on scribed silicon surfaces to localize copper deposition,²³⁷ on Si(111) surfaces for the electrochemical deposition of platinum nanoparticles,²³⁸ and on Si(100) surfaces for the assembly of multilayer films using thiol-ene chemistry.²³⁹

Two general aspects of the surface cross-metathesis approach are worth a discussion and might be addressed in an improved derivatization protocol. First, despite the authors²³⁶ indicating the need for a mild method to assemble functional layers on silicon, the reported metathesis transformation required long reaction times (2 days), heat to be supplied (dichloromethane at reflux) and was carried out under a nitrogen atmosphere. Second, and perhaps not relevant in the case of commercially available alkenes, but surely of concern for less readily available molecules (*e.g.* requiring design and synthetic efforts), is the consumption of solution phase 1-alkenes to yield homodimers as byproducts of the

metathesis reaction. As discussed in a previous section of this review, one of the apparent limitations of the halogenation/alkylation route, *i.e.* the presence of poorly reactive methyl terminations in the monolayer, was elegantly circumvented by Lewis and co-workers in a recent report on the preparation of acetylene and methylacetylene terminated Si(111) surfaces ($\text{Si}-\text{C}\equiv\text{CH}$ and $\text{Si}-\text{C}\equiv\text{C}-\text{CH}_3$).¹⁵⁵ The surface protocol described still required the use of a nitrogen purged glove box and anhydrous conditions, but *via* reaction of Si(111)-Cl surfaces with solutions of sodium acetylides the authors have convincing evidence (from XPS, IR spectroscopy and charge-carrier recombination measurements) to argue for a complete passivation of silicon hydride sites followed by reaction of surface acetylenes. The reaction of 1-bromo-4-trifluoromethylbenzene in the presence of *n*-butyllithium was used to confine *p*-trifluoromethylbenzene groups ($\text{Si}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{CF}_3$) and was estimated to have proceeded in a satisfactory, *ca.* 35%, yield.

Prompted by the work of Lewis and co-workers,¹⁵⁵ Heath and co-workers¹¹⁰ reported the first copper-catalyzed Huisgen 1,3-dipolar cycloaddition of azides and terminal alkynes (CuAAC)^{240–242} applied to passivated silicon surfaces. CuAAC are the archetypal example of 'click' reactions,²⁴³ and have found numerous recent application in the field of surface chemistry.^{244,245} CuAAC reactions benefit from high selectivity, modularity, the absence of both activation and protection/deprotection steps, and are tolerant to a wide range of solvents and functional groups.^{246,247} The authors¹¹⁰ assembled a system where a fully acetylenylated Si(111) surface ($\text{Si}-\text{C}\equiv\text{CH}$) was coupled, albeit in *ca.* 7% yield, to a solution coumarin azide derivative. The observed poor outcome of the 'click' step was reasoned to be a direct consequence of the significant steric hindrance introduced upon conversion of densely packed surface alkynes to the corresponding immobilized triazole species. However, the study of Heath and co-workers was motivated towards a full surface passivation, with every surface silicon atom site grafted to an sp-hybridized carbon atom,^{102,124} as distinct from an average of every second silicon surface atom as achieved on a Si(111) surface using hydrosilylation (see Section 2.2.2).^{31,111} Hence no attempt was made to achieve better surface coverage in the 'click' step.

Gooding and co-workers have recently reported the use of an α,ω -diacetylene molecule to passivate the Si(100)-H surface forming an acetylene-decorated interface that allows for the immobilization of solution phase azides in satisfactory yields (>40%).¹²⁸ The surface modification approach investigated is outlined in Fig. 19 and benefits from the use of an highly selective and efficient conjugation method, *i.e.* CuAAC reactions. 1,8-Nonadiyne **a** was chosen as a convenient candidate for the evaluation of the outcome of this synthetic strategy because it exhibits a number of key properties. Being commercially available, no synthetic effort was required. Further, its symmetrical nature allowed the intended alkyne-terminated monolayer to be prepared in a single-step hydrosilylation procedure (as opposed to two step halogenation/alkylation routes). Further derivatization of this organic structure using CuAAC reactions proceeded to afford hydrolytically resistant 1,4-disubstituted surface triazole species through a coupling

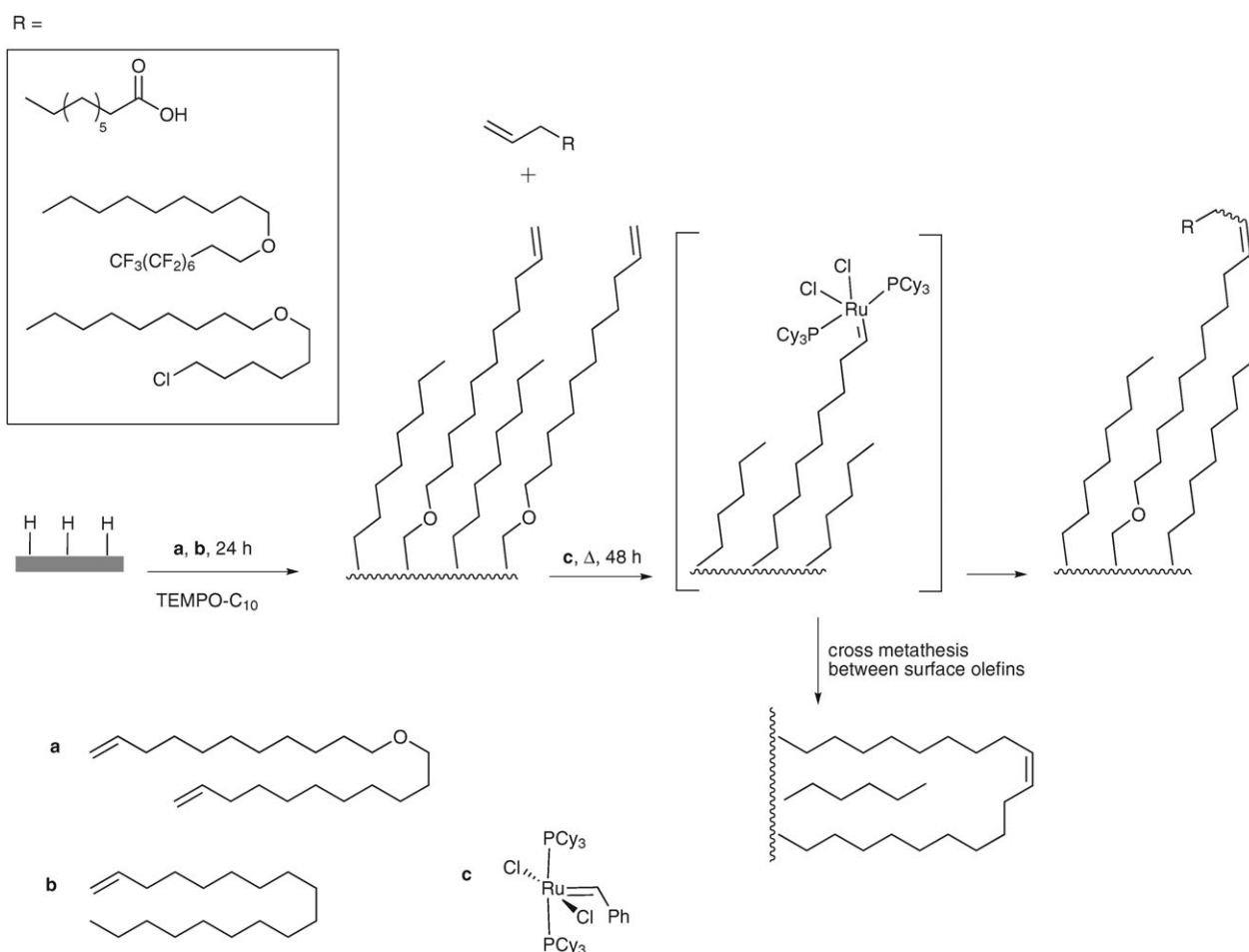


Fig. 18 Cross-metathesis reactions between an alkene-terminated Si(111) layer and 1-alkenes. Mixed layers were prepared from a (α,ω -diene) and b (1-alkene) in the presence of traces of TEMPO-C₁₀. In the presence of first generation Grubbs' catalyst (c), the diene at the distal end was further reacted with ω -functionalized 1-alkenes to yield carboxylic acid-, fluoride- and chloride-terminated layers (ref. 236).

procedure that did not require protection/activation steps and was generally insensitive to steric factors. A range of alkyl and aryl azides, with different chemical functionalities, were used in this process without the need to vary the reaction conditions and without any apparent disruption of the base monolayer. Furthermore, improved 'click' coupling efficiencies were achieved for SAMs composed of a mixture of 1,8-nonadiyne **a**/1-heptyne (**a** mole fraction, χ_{sln} , in the hydrosilylation mixture ranging from 1.0 to 0.05). With progressive dilutions of the diyne a species, close to quantitative 'click' yields were approximated by electrochemical methods for a χ_{sln} value of 0.05.¹⁵²

Modified Si(100) surfaces produced using this procedure have found applications in the preparation of redox assemblies for aqueous environments,^{152,248,249} antifouling surfaces,^{128,250} and have allowed for the first example of covalently immobilized porphyrins (Ni(II) β -azido-*meso*-tetraphenylporphyrin **h**, Fig. 19) attached to the substrate *via* the β -pyrrolic position.²⁵¹ In particular, the 'click' immobilization of azidomethylferrocene (**i** in Fig. 19) has been proved by Gooding and co-workers as viable and efficient method toward ferrocenyl-modified Si(100) electrodes that showed no evidence of silicon oxide species even after prolonged cycling between -100 and 800 mV in

aqueous electrolytes.¹⁵² The authors proposed that π - π interactions between alkyne moieties at the distal end provide a surface that is resistant to silicon oxidation. Evidence for this conclusion comes from a deviation from ideality of the surface electrochemistry as the dialkyne is diluted with 1-heptyne such that the distal alkynes are diluted. This approach opens the door to the application of modified silicon electrodes in the field of bioelectronics, and 'clicked' Si(100) electrodes presenting isonicotinic acid derivatives have been reported for the direct electrochemistry of cytochrome *c*.²⁵²

3.5 Reactions of halo-alkyl monolayers

As detailed in Section 3.2.1, alternative grafting routes appear to be operating during the hydrosilylation of ω -bromo-1-alkenes.¹³⁶ The presence of alternative binding modes, as well as the direct abstraction of bromine atoms by surface silyl radicals, has not hampered the preparation of well-behaved Si(100) electrodes and Si-molecular monolayer junctions.^{137,253} Nucleophilic halide/azide exchange is a well established synthetic protocol in solid-state systems,^{254–257} and Prato and co-workers have recently demonstrated its applicability for the modification of non-oxidized silicon surfaces.²⁵³ A three-step procedure, consisting

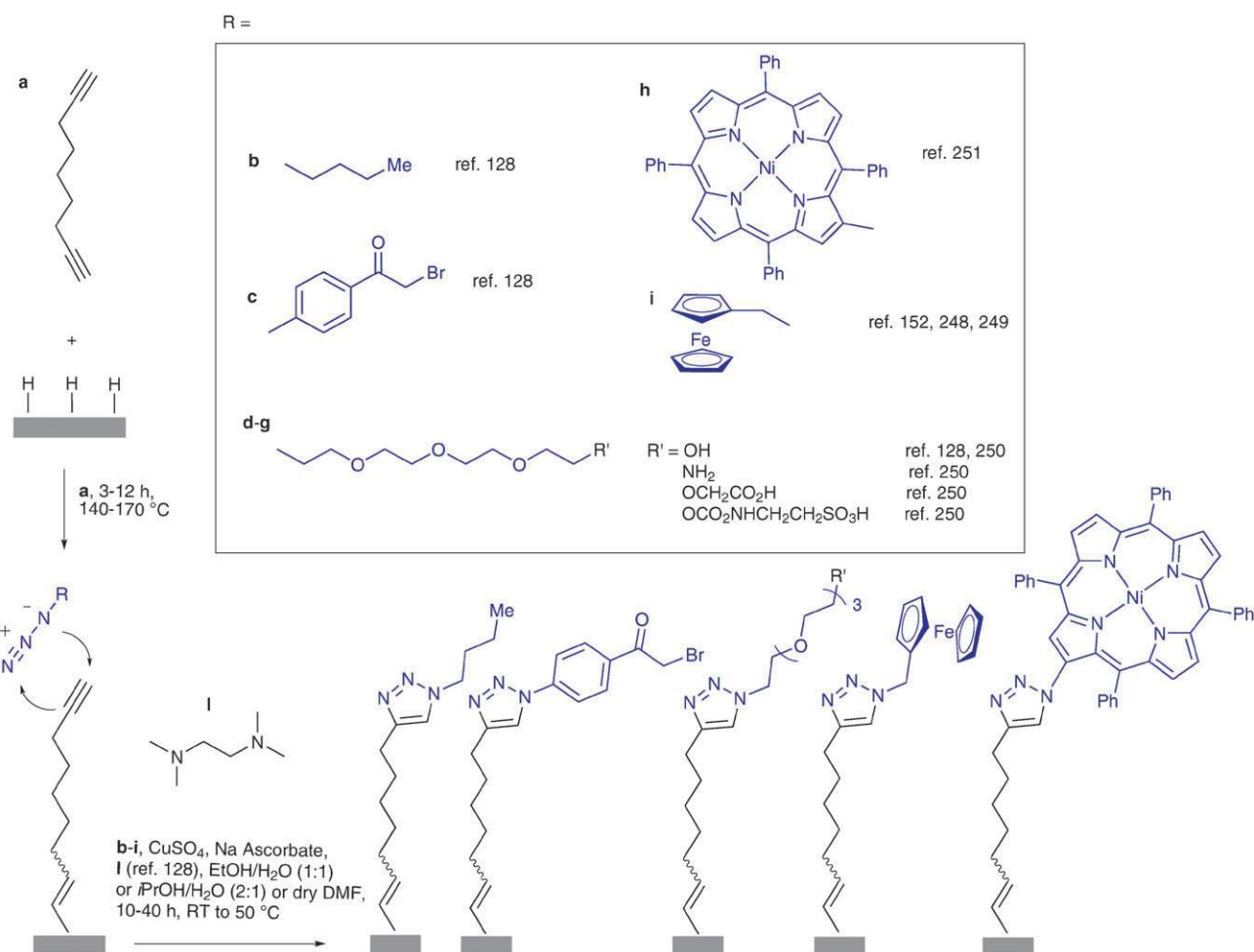


Fig. 19 Huisgen-type 'click' cycloaddition reactions on acetylene-terminated silicon (100) surfaces.

of the photochemical anchoring of 11-bromo-1-undecene onto Si(100)-H, followed by treatment with sodium azide and reaction of the azide-decorated surface with ethynylferrocene *via* 'click' chemistry, was used to prepare ferrocenyl electrodes. Despite this preparative protocol requiring the use of anhydrous solvents for each step, the ferrocene-bearing Si(100) electrodes, as prepared, showed significant levels of SiO_x species. Nevertheless, cyclic voltammetry in dry acetonitrile showed only a modest 30% decrease in the peak current intensity after *ca.* 1000 Fe^{II}/Fe^{III} oxidation/reduction cycles. More recently Cahen and co-workers have used the chemical manipulation of terminal bromine groups (-Br) in 1-bromo-1-undecene Si(111) SAMs to correlate chemical changes with electrical changes in MIS junctions.¹³⁷ The authors have shown how an improved packing density, resulting from the hydrolysis of -Br terminal groups to hydroxyl functionalities (-OH),²⁵⁸ was accompanied by an increased effective Schottky barrier height and a decreased junction ideality factor.¹³⁷

4. Chemical and biochemical sensing: selected examples

Biosensors research is a rapidly expanding field, with a broad spectrum of applications and transduction schemes

available. For example, optical, morphological and electrochemical properties of porous silicon have been exploited to prepare a range of platforms for chemical or biological molecule sensing.^{55,259-261} More often, (bio)chemical silicon-based sensors have used MIS structures (metal-insulator-semiconductor) and the ability of biomolecular binding events to modulate the conductance near the surface of a semiconductor.^{262,263} A general problem with standard (*i.e.* oxidized) silicon-based chemical sensors is low selectivity to different analytes of many oxidic transducer layers.²⁶⁴ However, this problem can be overcome by controlling the surface chemistry of the putative sensing interface through one of the wet-chemical methods described in the previous sections of this review. Numerous examples have appeared in the literature,^{53,59,62,207,209,259,265} and diverse transduction schemes are available. These schemes range from monitoring chromate ions concentrations by deflection of quaternary ammonium salt-terminated silicon AFM cantilevers²⁶⁶ to electrochemical impedance spectroscopy measurements of DNA- and antigen-modified Si(111) electrodes toward a label-free sensor for detecting interactions with complementary DNA oligonucleotides,⁵³ and antibodies.²⁰⁷ The following are therefore only selected examples from an expanding field.

4.1 Molecular oxygen detection

Charge trapping at *tert*-butylhydrazine amide-modified undecylenic acid Si(111) layers ($-\text{CO}-\text{NH}-\text{NH}-\text{C}(\text{CH}_3)_3$) has been demonstrated by Lopinski and co-workers for the detection of molecular oxygen.²²¹ The occurrence of electric field-induced second harmonic generation (EFISH), a technique largely used to study charge trapping at oxidized silicon surfaces,²⁶⁷ was used to monitor the charging of the hydrazide monolayers, and did not require electrical contacts with the sensor (*i.e.* the modified silicon sample) to be made.

Molecular oxygen adsorbed onto the SAM can act as an electron acceptor, with charged O^{2-} species being able to induce appreciable band bending in the underlying semiconductor. Enhancement of EFISH upon exposure of the hydrazide SAM to air was attributed to this electron trapping event. However, the interpretation of the experimental EFISH data was complicated by (i) plausible sample perturbation by photogenerated charge carriers (*i.e.* a laser light is needed to for optical second harmonic generation), (ii) 'ageing' in air of the modified silicon samples (IR spectral data), (iii) ionized hydrazide species actively acting as trap for holes, and (iv) charge trapping being influenced by moisture, even in the absence of oxygen.

4.2 Biomolecules detection

'Gating' effects at modified semiconductor surfaces open vast possibilities for attractive electrochemical transduction schemes of molecular events occurring at chemically modified semiconductor surfaces.²⁶⁸ As discussed extensively elsewhere,^{262,269} opposite to the situation in metals, electric fields can penetrate a large distance into a semiconductor and consequently shift energy levels near the surface region (*i.e.* band bending in the space charge layer, SCL).⁹⁵ The binding of charged or polar species, as well as the presence of surface states (*i.e.* available energy levels in the band gap eventually occupied by electrons escaping the silicon lattice), can thus lead to changes in band bending and alter conductivity near the semiconductor surface (Fig. 20). Alternating-current (AC) electrochemical impedance spectroscopy (EIS) can be used to probe this field-effect by monitoring conductivity changes in the semiconductor space charge region. Both frequency- and potential-dependent EIS measurements have been used to demonstrate the direct (*i.e.* label-free) binding of DNA and antibodies at monolayer-modified Si(111) surfaces.^{53,207} The method does not require the use of either auxiliary redox agents (*e.g.* ferricyanide/ferrocyanide,^{270,271} 2-anthraquinone-monosulfonic acid^{19,272,273}) or large bias voltages. For example, by selecting an appropriate AC frequency (*ca.* 10^4 – 10^6 Hz), and biasing the electrode into depletion, it is possible to enhance sensitivity toward field-effects induced in the semiconductor by the binding of charged species. Hamers and co-workers have demonstrated that stable, reproducible and distinct (*i.e.* well outside any statistical fluctuation) changes in the impedance response can be measured when either p- or n-type DNA-modified substrates are exposed to solutions containing complementary DNA strands.⁵³ On the other hand, the electrochemical response to non-complementary DNA strands (four-base mismatch) was indistinguishable

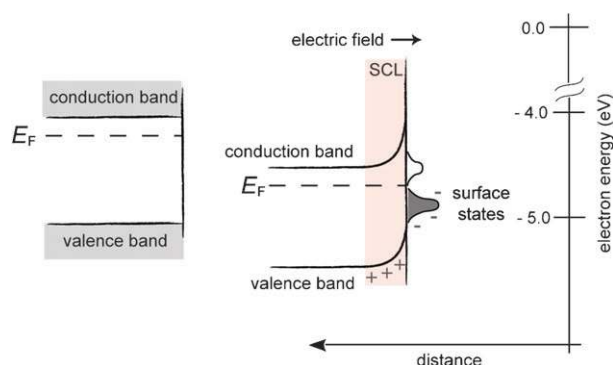


Fig. 20 Energy level diagram for n-type semiconductors. Electrons escape the semiconductor lattice until near-surface (*i.e.* SCL) electric fields oppose to a further electrons migration toward the surface. An electric field pointing toward the semiconductor surface is schematically depicted as an upward band-bending.

from that elicited by denaturation of the hybridized device. Interpretation of the experimental data, to fully understand the physical basis of the EIS response, requires refinement of the electrical equivalent circuit models depicted in Fig. 21. The overall impedance is largely controlled by the properties of the space charge region (R_{scl} and C_{scl}) and by the molecular layer resistance (R_{org}). In brief, regardless of the doping level (from 0.005 to 10 Ω cm) similar trends were found within the same doping type group, with upward band-bending observed upon hybridization. In the case of p-type substrates this field-effect resulted in a decreased resistance of the SCL (R_{scl}) upon DNA binding, as expected for a decrease in the depleted region due to the electric field arising from negative charges of the DNA phosphate back-bone (Fig. 22a). Conversely, in n-type electrodes the binding of a complementary strand gave a depletion region of increased resistance and decreased capacitance, and was thus consistent with an increased band-bending (Fig. 22b). It is worth mentioning that hybridization also resulted in changes of the molecular layer conductivity (R_{org}), with opposite trends observed in p- and n-type substrates. These changes are believed to be dictated by the nature of the electrolyte/SCL field interactions, but at present a conclusive explanation is still lacking and will be needed to fully elucidate the signal transduction process of similar biosensing EIS devices.

A significant implementation of this field-induced effect approach to the sensing of biomolecules was recently reported by the same group for the direct and label-free detection of antigen–antibody interactions.²⁰⁷ Hamers and co-workers demonstrated that EIS measurements at a single AC frequency can afford information on the binding of a specific antibody to its surface-confined antigen (Fig. 13). This last report represents a significant technological advance since, as stressed by Abbott,²⁷⁴ the fabrication of protein biochips appears to face more serious challenges than for the corresponding DNA systems.²⁷⁵ We also note that major advantages of this label-free field-effect approach include (i) the lack of interference with the protein's activity and/or with its structure, as on the other hand is expected if dyes are used to tag the analyte in conventional fluorescence-based methods, and (ii) simplified protocols, with no need for post-incubation rinsing

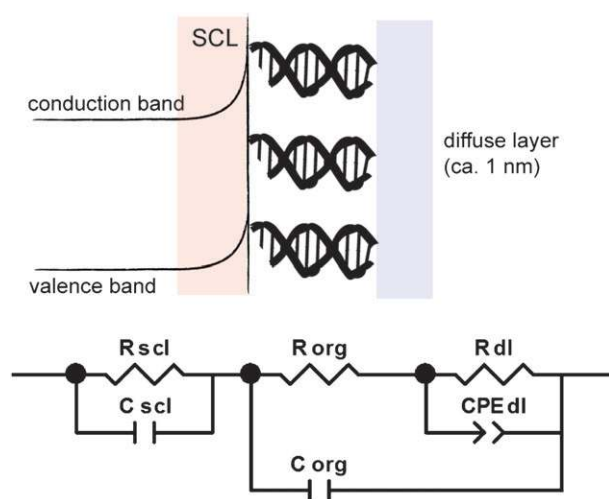


Fig. 21 Schematic representation of DNA-modified Si(111) surfaces and electrical equivalent circuit used to fit experimental EIS data and explain physical changes in the sensing device upon DNA hybridization (ref. 53).

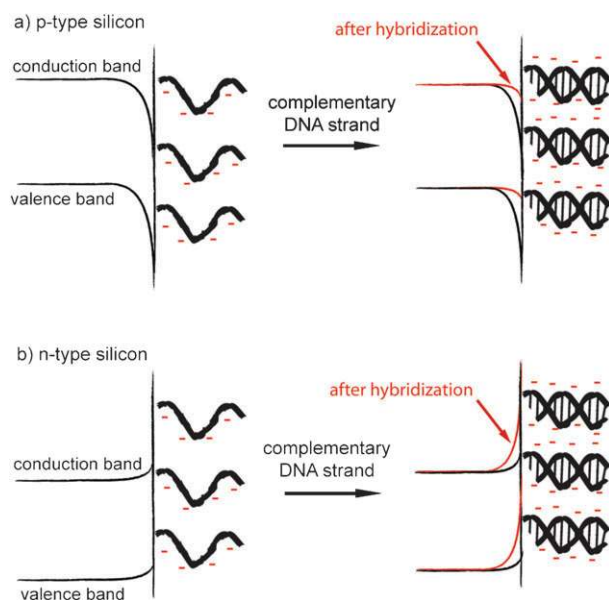


Fig. 22 Schematic depiction for the changes in the semiconductor near-surface fields upon DNA hybridization at (a) p- and (b) n-type silicon-based biosensors (ref. 53). Single-strand DNA sequences were immobilized according to the procedure of Strother *et al.* (ref. 49).

procedures of the sensing surface as required for fluorescence measurements.

It is very important to note that the electronic properties of such sensing surfaces will be very sensitive to defects in the device surface. Therefore only minor densities of electrically active traps, even below 10^{-5} monolayers equivalent, can lead to appreciable band-bending and have a detrimental effect on the sensing capabilities. The fabrication of robust monolayers resistant to aqueous environments will therefore be imperative to allow for further progress in the area of monolayer-modified field effect silicon sensing devices.

5. Summary and perspectives

Si(111) hydrogen-terminated silicon surfaces, as prepared through standard, widespread, chemical etching procedures are the prime example of *electrically* well-behaved semiconductor surfaces. If kept in fluoride-containing electrolytes, the silicon-hydride surfaces display minimal band bending and show the lowest to-date reported charge recombination velocities (*ca.* 0.25 cm s^{-1}).⁷² However, the Si-H surface is chemically unstable and prone to oxidation,⁷⁹ yielding a Si-SiO₂ interface²⁷⁶ which displays surface recombination velocities higher than 3 cm s^{-1} .²⁷⁷

As discussed in Section 3, provided that care is taken, silicon-carbon linked organic monolayers offer a convenient approach to chemically and electrically well-passivated silicon surfaces. The organic-semiconductor structure promises to expand the performances and applications of conventional semiconductor devices, with novel biosensing interfaces²⁵⁹ and high-density memory storage^{40,44,215} among the envisioned devices. For example, surface-bound molecules either charged or polarized can influence the energy levels near the surface (*i.e.* changes in the band-bending) and alter the conductivity of the substrate.^{53,207} This molecular gate¹²⁹ approach has stimulated vast research,^{43,63,64,129,278} but despite encouraging recent reports,²⁷⁹ at present the development of real-world molecular electronics, such as high density memories,^{40,41} remain a long-term target. Serious practical obstacles toward the fabrication of a real device still exist. These include complex wiring,⁴⁵ the required stability with regards to a large number of read-write cycles,²⁸⁰ and the requirement to minimize the damage to the organic layer after a solid contact is made.^{67,165,281}

While a practical molecular memory device would be required to withstand extreme operational conditions,²⁸⁰ on the contrary, real-world applications of modified silicon surfaces in the field of chemical²⁶⁶ and biological sensing appear to be less demanding.⁶⁰ The design of tailored interfaces benefits from numerous chemical strategies now available for the reaction of the Si-H surface with organic molecules. Nevertheless, a continuing challenge is in the development of robust chemistries to prevent side reactions, most notably oxidation, at the silicon surface. Although simple Si-C linked alkyl layers, with minimal traces of silicon oxides, are relatively simple to obtain, and particularly for the Si(111) surface, preparation of functional layers, as required in the design of complex, chemically well-defined sensing interfaces, is still a field rich in challenges and opportunities.

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