Illuminating Silicon Surface Hydrosilylation: An Unexpected Plurality of Mechanisms

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ABSTRACT: Silicon is the cornerstone material of the semiconductor industry. As feature sizes on chips continue to decrease in size, the ratio of surface to bulk increases, and as a result, the role of surface defects, surface states and other subtle features play larger roles in the functioning of the device. Although silicon oxides have served the industry well as the passivation chemistry of choice, there is interest in expanding the repertoire of accessible and efficient chemical functional strategies available for use, and to fully understand the nature of these interfaces. For new applications such as molecular electronics on silicon and biochips, for example, there is a need to avoid the layer of intervening insulating oxide: A well-defined linkage of organic molecules through a silicon−carbon bond has great promise and appeal. Hydrosilylation, the insertion of an alkene or alkyne into a surface Si−H bond, is an ideal approach

to producing these covalent Si−C bonds, and can be carried out in a number of ways. Light-promoted hydrosilylation is promising because it is clean and direct and can be patterned via masking; it requires no additional reagents such as catalysts or input of thermal energy and thus may have reduced surface contamination and numbers of defects. In this perspective, we start by making connections between the molecular silane literature, and the first reports of UV-mediated hydrosilylation of an alkene on a silicon surface, a reaction that was assumed to operate via a radical mechanism. We then describe the unexpected development of four new mechanisms that have no obvious parallels with the molecular silane literature, and take place as a result of the solid state electronics of the underlying silicon itself. From exciton involvement, to the influence of plasmonics, to the role of photoemission, the area of silicon surface hydrosilylation has become incredibly rich, and undoubtedly still contains new reactivity to be discovered.

KEYWORDS: silicon, surface, mechanism, light, hydrosilylation, exciton, radical, porous silicon
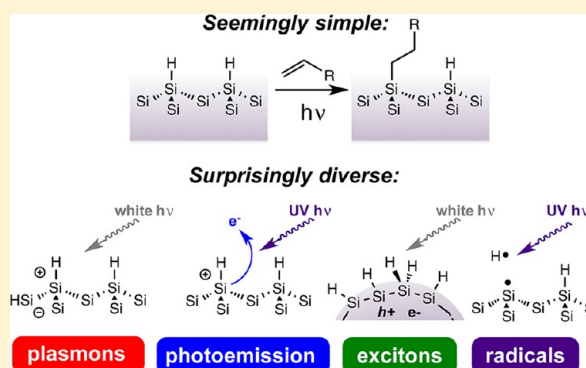
■ INTRODUCTION

Silicon is the single material on which the entire computer industry worldwide has grown; this ubiquitous element on the earth's crust, when in its crystalline, elementally pure form, has the ideal band gap, oxide surface chemistry, and etching properties to enable the manufacture of incredibly powerful integrated circuitry.[1] As feature sizes on silicon devices continue their seemingly relentless decrease, increasing scrutiny has been focused upon the surface of silicon, as its native oxide has proven problematic at shorter length scales.[2] New non-oxide-based chemical approaches toward the passivation of silicon surfaces may be required. A related and intriguing direction of research has been the integration of functional molecules, such as biomolecules, polymers, and molecules for molecular electronics applications, with silicon-based devices to enable new functionality from these organic-based materials, and from the silicon devices themselves.[3] The standard silicon oxide interface, rife with electrical defects and imprecise chemical composition, is typically too insulating to "communicate" electrically with individual molecules.[4] A more well-defined

interface is needed. In a landmark 1993 communication, Linford and Chidsey showed how hydrosilylation of alkenes on hydrogen-terminated surfaces could cleanly lead to direct silicon−carbon bond formation (Hydrosilylation outlined in Figure 1).[5] This general approach is ideal for interfacing molecules to silicon since it avoids the problem of a disordered surface oxide, and connects an organic molecule to the silicon through a stable covalent bond.[6]

The original chemistry proposed by Linford and Chidsey for surface hydrosilylation drew a direct connection with the molecular literature.[7] Under the conditions they employed, a peroxide initiator results in homolytic cleavage of the Si−H bond on the surface to produce a silicon dangling bond, a
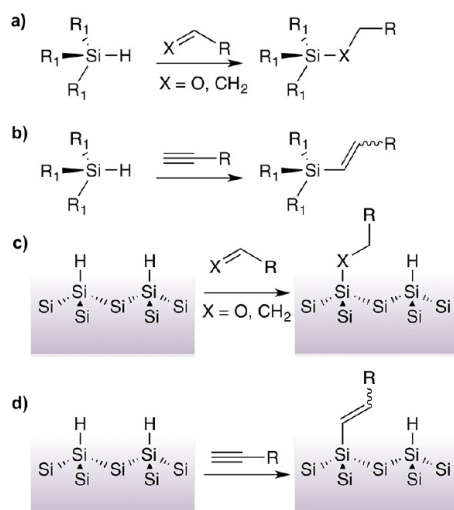
Figure 1. Examples of hydrosilylation of unsaturated molecules with molecular silanes and on a representative silicon surface, Si(111)-H. (a, b) Hydrosilylation of an aldehyde and an alkene, and an alkyne, with trisubstituted molecular silanes. (c, d) Hydrosilylation of an aldehyde, an alkene, and an alkyne, on Si(111)-H.

Figure 2. Representative examples of hydrogen-terminated silicon surfaces.

species akin to a silicon radical. Based upon the extensive work of Chatgilialoglu and co-workers,[8] it has been established that an alkene can add to a molecular silicon radical with little activation barrier to produce the a β-silyl radical with a covalent Si−C bond, which then abstracts a hydrogen from elsewhere to complete the reaction.[9] Thermal hydrosilylation most likely also proceeds via a similar mechanistic pathway, as is the case with silicon−based molecules.[2] This chemistry has been used to functionalize silicon with an incredible breadth of molecules, including simple aliphatics to complex conducting molecular wires, to DNA, and other biomolecules.[3]

Since 1993, other very interesting silicon−carbon bond-forming reactions on silicon surfaces began to appear that had no clear parallels with the chemistry of silane-based molecules. Electrochemical and photochemical reactions on hydrogen-terminated silicon surfaces used electrical potential or less energetic white light to drive reactions that appeared entirely unique and unprecedented.[2,3] By harnessing the properties of the underlying silicon-based material, this "old" material was discovered to have a previously unsuspected rich surface chemistry. In this perspective, we will focus on the role of illumination of silicon surfaces to yield radicals, excitons and other charge carriers in silicon that drive surface silicon−carbon bond-forming reactions. Although the product is a surface monolayer of organic molecules, the reactions proceed via mechanisms that take place as a result of the solid-state properties of the underlying crystalline silicon.

A very useful surface with which to start when functionalizing silicon via wet chemistry on both flat and nanostructured silicon is the metastable hydrogen-terminated interface (Figure 2).[6] From a chemist's perspective, the surface is chemically simple and clean as it appears as an array of Si−H$_x$ bonds, with no intervening oxide. Brief treatment of a flat, single-crystal sample of silicon with dilute HF (aq) yields the hydrogen termination in laboratory ambient, and the interface is sufficiently stable to withstand minutes in air before suboxidation commences. A high surface area variant of flat hydrogen-terminated silicon, called porous silicon, can be easily prepared via an electrochemical etch from standard silicon wafers in the presence of
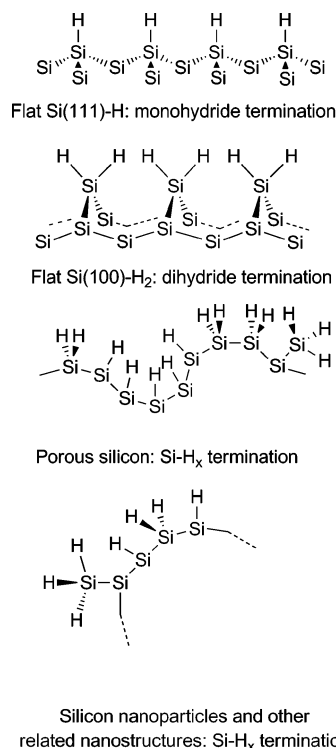
HF (aq); there are many reviews to lead the interested author to the appropriate synthetic approach.[10−12] Work over the past two decades has shown that the band gap of silicon is size-dependent, and so there has been an enormous effort to produce a range of morphologies of nanostructured silicon, starting with nanocrystalline porous silicon and then on to nanoparticles, nanowires, and nanorods.[13−15] Hydrogen termination of silicon nanoparticles and nanowires is performed in a similar manner, with HF (aq) exposure.[16]

Si−H bonds are well-known from the molecular silane literature to participate in hydrosilylation, a reaction that can be perceived as either an insertion reaction of an unsaturated bond into the Si−H bond, or cleavage of the Si−H bond across the unsaturated group, as shown in Figure 1.[17] The reaction is first shown for molecular silanes (Figures 1a and b), and silicon surfaces (Figure 1c, d). The mechanism can proceed via a variety of ways, including metal complex-based catalysis,[18] radicals (with or without an initiator),[8] or silylium-based cation chemistry.[19] Light-promoted hydrosilylation with molecular silanes has been enabled by ultraviolet wavelengths, and has been presumed to involve homolytic cleavage of the silicon−hydrogen bond to generate a silicon-based radical, as shown in Figure 3.[20] The light needs to be sufficiently energetic, on the order of ∼81 kcal/mol, which corresponds to a wavelength of approximately 354 nm.[21] The strength of this bond varies
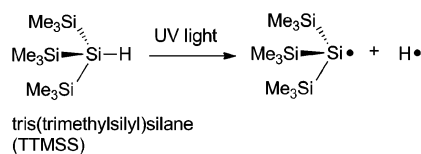

Figure 3. UV-induced dissociation of the Si−H bond in tris-(trimethylsilyl)silane, TTMSS, to produce a silicon-centered radical.

764

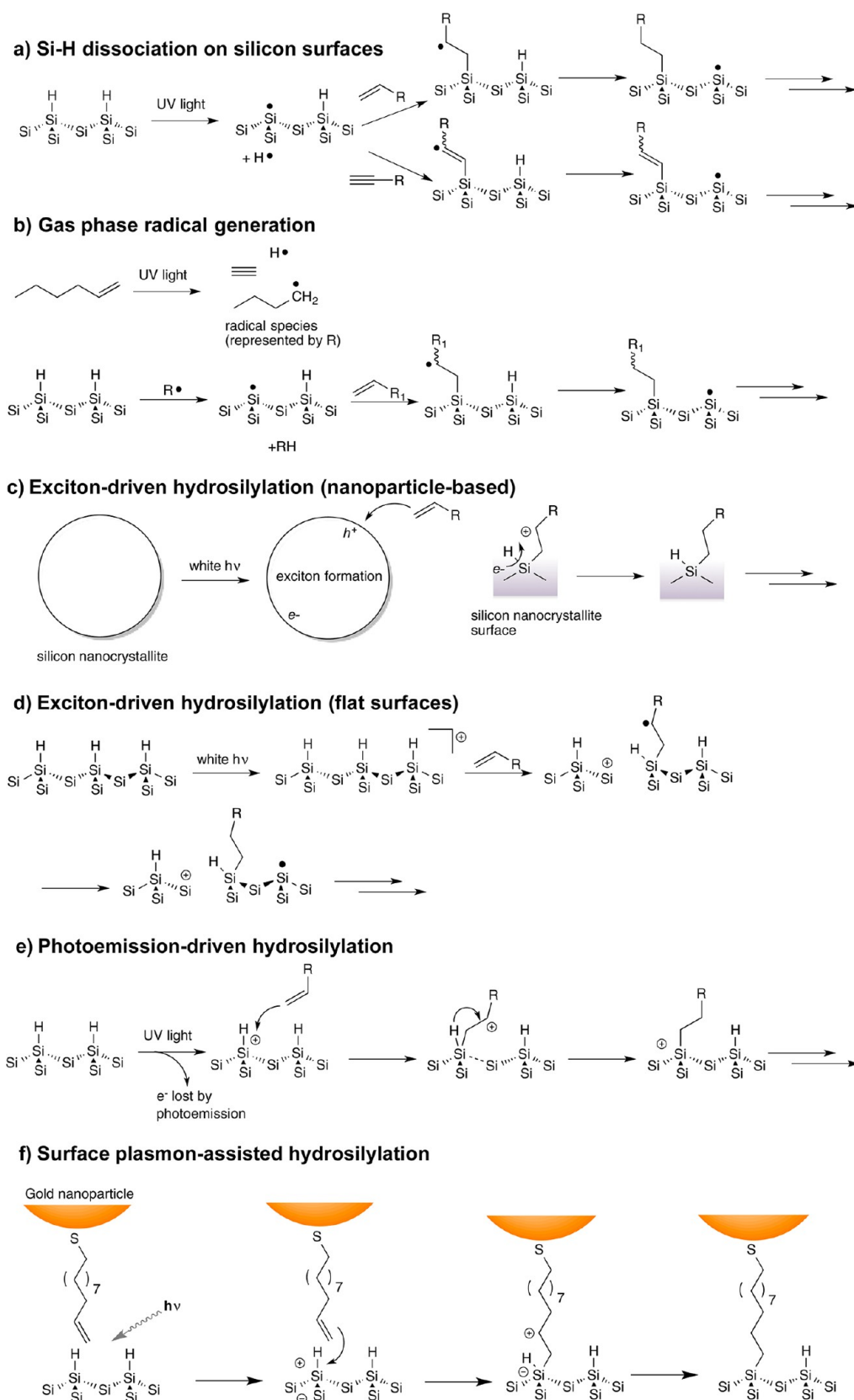dx.doi.org/10.1021/cm402120f | *Chem. Mater.* 2014, 26, 763−772

Figure 4. Proposed mechanisms for light-induced hydrosilylation on hydride-terminated silicon surfaces.

directly with the number of silicon substituents on the central Si−H group as they lower the energy required.[21b] For instance, The dissociation energy for tris(trimethylsilyl)silane, (Me$_3$Si)$_3$Si−H, is 11 kcal/mol lower than that of (alkyl)$_3$Si−

H.[21b] Because a silicon surface Si−H group is substituted by an infinite lattice of silicon atoms, the dissociation energy for this bond on a surface is also expected to be lower than that of a typical trialkylsilane.

The thoroughly investigated radical reactivity of $(Me_3Si)_3Si-H$ (and more recently, related polysilanes)[22] with unsaturated molecules served as the starting point for the understanding of the hydrosilylation on silicon surfaces; the initial assumptions were, with justification, that radical chemistry would be dominant. As will be described in this perspective, within the first few years following the first reports of hydrosilylation on hydrogen-terminated silicon surfaces, observations were presented that were not congruent with a straightforward radical mechanism. These questions grew more persistent with the discovery that less energetic white light could promote hydrosilylation under some circumstances, and that these reactions did not require activation of the surface of the silicon substrate. The "simple" radical mechanism had given way to several possible (and ostensibly simultaneously occurring) reaction pathways. Over the past 3 years, more than a decade since the first communication of light-promoted hydrosilylation on Si−Hₓ-terminated surfaces, yet another new and very intriguing mechanism has been proposed, and is currently being debated in the literature (vide infra). The current state of the art, and future directions related to the understanding of the mechanisms involved in light-driven silicon surface chemistry, will be the focus of this perspective. As summarized in Figure 4, the mechanistic overview will begin with light-promoted radical chemistry that has solid foundations in the molecular silane literature, but will then move into mechanisms that involve excitons, photoemission pathways, and plasmonic enhancement of excitonic hydrosilylation.

■ LIGHT-PROMOTED HYDROSILYLATION ON SILICON SURFACES

Si−H Dissociation on Silicon Surfaces (Figure 4a). The first report of light promoted hydrosilylation of 1-pentene on silicon surfaces appeared in 1997 by Chidsey and co-workers, who examined the resulting pentyl surfaces on Si(111)-H following irradiation with a mercury arc lamp (185 and 254 nm lines) for 2 h.[23] This work and follow-up papers proved the viability of a simple light-promoted approach and clearly demonstrated Si−C bond formation,[24] but provided no indication as to the mechanism in operation. Shortly afterward, UV-mediated hydrosilylation of two liquid unsaturated molecules, an aldehyde and an alkene, 1-octadecanal and 1-octadecene, on Si(111)-H was examined in detail.[25] The highest coverage of both the aldehyde and the alkene, as determined by FTIR spectroscopy, was noted to take place at a wavelength of 385 nm at slightly elevated temperatures (60 °C). The results were somewhat surprising since shorter wavelengths inexplicably led to lower coverage. The authors proposed a radical mechanism in which the Si−H bond dissociates upon irradiation to react with the alkene or aldehyde, based upon the known reactivity of silanes (Figure 4a).[25] These early results were promising for soft lithographic applications and surface patterning using light,[26] but more interestingly, hinted at the fact that the underlying mechanism, or mechanisms, may not exactly mirror those observed in molecular silanes.

A random walk based upon silicon radicals was proposed by Chidsey and co-workers that is based upon a UV-promoted Si−H cleavage initiation, as shown in Figure 5.[27] Dissociation of a Si−H bond with sufficiently energetic UV light leads to a silicon dangling bond (radical equivalent), which then reacts with the α-carbon of a primary alkene; molecular silane investigations using the tris(trimethylsilyl)silane radical has
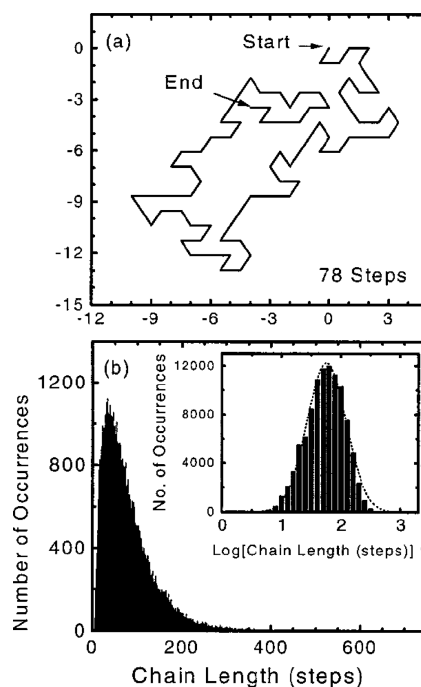

Figure 5. (a) Self-avoiding random walk for a dissociative (homolytic Si−H cleavage) reaction on a triangular lattice that is geometrically related to the Si(111)-H surface. b) Monte Carlo simulation (1×10^5 cycles) of the random walk process. Inset to (b) shows the number of occurrences of a walk versus the log of the number of steps. Figure reproduced with permission from ref 27. Copyright 2000 American Chemical Society.

shown that the reaction of this silicon radical and 1-pentene has essentially no activation barrier and is rapid (1×10^6 M^{-1} s^{-1}),[8] and leads to a β-silyl-substituted carbon radical that can may be quenched by either by plucking H• from a neighboring Si−H group, or from another alkene molecule. According to the Monte Carlo simulation in Figure 5, the number of steps taken is most likely less than 100 before the walk "traps" itself and thus ends. The random walk mechanism was substantiated by ultrahigh vacuum (UHV) experiments on Si(111)-H, in which a scanning tunneling microscope (STM) tip selectively removed very small number patches of surface hydrides to produce islands of silicon dangling bonds.[28] Upon exposure to gaseous styrene, much larger islands of an organic monolayer, presumably phenethyl groups, formed around the dangling bonds because of random walk growth via hydrosilylation.

Looking at another morphology of silicon, solubilized hydrogen-terminated silicon nanoparticles were subjected to UV light (254 nm irradiation) in the presence of a variety of primary alkenes, and thus the assumption for the reaction pathway was Si−H dissociation followed by the radical pathway (Figure 4a).[29] Hydrosilylation was observed as expected, but because of the nanoparticle platform, the silicon−hydrogen interfacial chemistry has the advantage that it can be monitored by ^{1}H NMR in deuterated chloroform. The proton NMR spectra of the silicon nanoparticles hydrosilylated in the presence of 1-dodecene suggest that both Markovnikov and anti-Markovnikov additions take place; typically, it had been assumed that the addition gives mainly the linear ≡Si(CH₂)₁₁CH₃. These results are intriguing, and point to an avenue of investigation that could be further developed to provide more insight into the underlying mechanism(s) in action.

Gas Phase Radical Generation (Figure 4b). Gas phase reaction experiments, in which the alkene is in a gaseous state over a hydrogen-terminated silicon wafer, seem to suggest that a different radical-based reaction pathway is in operation under these conditions.[30] If two Si(111)-H wafers are placed back-to-back in casual (nonelectrical) contact in a UHV chamber, and only one of the two wafers is irradiated with a UV pen lamp, hydrosilylation takes place on both wafers. This result points to gas phase migration of radical initiators from the irradiated area to the nonirradiated area. The authors propose photolytic breakdown of the alkene or aldehyde to generate R• that can then pull H• from the surface in a homolytic fashion, to generate silicon-based dangling bonds. These silicon-based dangling bonds then undergo the chain reaction hydrosilylation proposed in Figure 4a. Gas phase radicals may have sufficiently long lifetimes due to a lack of self-quenching reactions (i.e., R• + R• → R-R) to enable this mechanism to operate under these conditions; the corollary is that the solution phase may be detrimental to radical migration because of rapid quenching, although this hypothesis remains undetermined.

Exciton-Driven Hydrosilylation (Figure 4c, d). In 1998, white light was shown to be sufficiently energetic to promote hydrosilylation of alkenes and alkynes on photoluminescent porous silicon at room temperature to yield alkyl and alkenyl functionalized surfaces in minutes.[31] Photoluminescent porous silicon is an ensemble or matrix of isolated silicon nanocrystallites, and so has substantially different electronic properties than those of bulk single crystalline silicon. Upon absorption of a photon of sufficient energy by a nanocrystallite of silicon within the porous silicon matrix, an electron/hole pair, termed an exciton, is formed.[32] The exciton in porous silicon and other quantum confined silicon nanomaterials is relatively long-lived (microseconds), and upon recombination, can emit light via photoluminescence. Because white light is not expected to be sufficiently energetic to cleave Si−H bonds (vide supra), the attack of photogenerated holes on the surface in a nucleophilic fashion by primary aliphatic alkenes or alkynes was proposed as a possible mechanistic route to Si−C bond formation, as shown in Figure 4c. The holes would be derived from the electron−hole pair of an exciton. Localization of a positive charge on the surface of a hydride-terminated silicon nanoparticle could produce an intermediate that is akin to a silylium cation, a molecular intermediate shown to be involved in a class of hydrosilylation reactions.[19] The interaction of the alkene with the surface is followed by the formation of a silicon−carbon bond and a β-silyl-substituted carbocation that can then be neutralized with a neighboring H and the electron derived from the original exciton (to formally generate a hydride equivalent). Further evidence for an exciton-based mechanism was provided through the addition of low concentrations of energy- or charge-quenching agents that would rapidly annihilate the exciton before it could become involved in hydrosilylation.[33] The excitonic mechanism has no obvious molecular relative; for instance, tris(trimethylsilyl)-silane and 1-pentyne do not react even upon extended irradiation with white light.[33] The white-light promoted excitonic mechanism also proceeds cleanly on hydride-terminated silicon nanocrystals.[34]

If the formed exciton is indeed driving the hydrosilylation chemistry of porous silicon, one should be able to probe the energetics using electron acceptors to extract the electron from the electron/hole pair.[35] As described schematically in Figure 6a, porous silicon was irradiated with white light in the
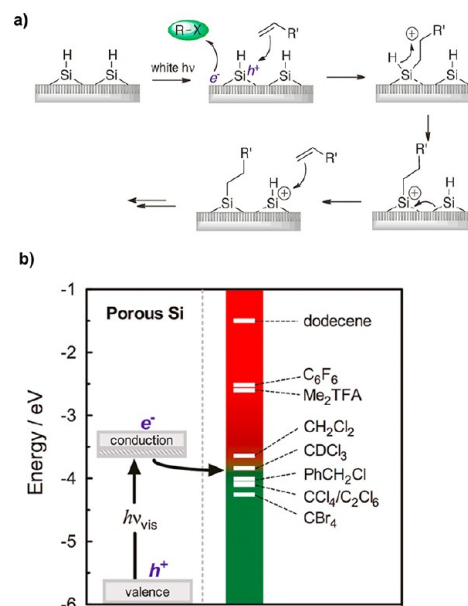

Figure 6. (a) Proposed mechanism for an enhanced hydrosilylation rate for the excition-mediated mechanism; electron abstraction by RX from the photogenerated exciton in porous silicon the hole, h+, in the silicon nanocrystal that is then attacked by the alkene. (b) Energy level diagram showing the approximate positions of the conduction and valence bands in a silicon nanocrystallite, and LUMOs of select oxidizing agents. Figures reproduced with permission from ref 35. Copyright 2011 American Chemical Society.

presence of 1-dodecene to carry out surface hydrosilylation. A number of different additives were added to the 1-dodecene solution, whose electron acceptor (LUMO) energy levels span a range, from below the conduction band of a silicon nanocrystallite, to far above (i.e., 1-dodecene), as shown in Figure 6b. Those oxidants whose LUMO levels were below that of the conduction band by ∼0.2 eV brought about strong increases in both the rate of the hydrosilylation reaction, and the final yield (coverage). For instance, C_2Cl_6 as an oxidant resulted in a doubling of the observed rate, and 5-fold increase in the yield (observed coverage) of the reaction, as followed by FTIR kinetics experiments. An example of the effects of two oxidants on the rate of 1-dodecene hydrosilylation on porous silicon is shown in Figure 7. Those oxidants whose LUMOs were higher than the conduction band of a silicon nano-crystallite showed no effects on either the rate or the yield of the reaction. Presumably, only those additives that are sufficiently oxidizing and fall below the conduction band energy are able to accept electrons. Radical involvement was not likely due to the lack of effect shown by butylated hydroxytoluene (BHT), a radical inhibitor, and by the lack of oxidation that would be expected if Si-X (X = Br, Cl) formation and hydrolysis (in laboratory ambient) took place. In addition, low concentrations of ferrocene (E_{ox} = +0.66 V vs SHE) are known to quench excitons in silicon via electron donation; when 14 mM ferrocene was added to 0.5 M C_2Cl_6-promoted reactions of 1-dodecene, the yield of hydrosilylation decreases several fold. In Figure 6, the color gradient of the center column changes from green to red, with green meaning that there was an observed increase in rate, and red meaning no change.

Monitoring the regioselectivity of the reaction is challenging by FTIR, but some details can be gleaned thanks in part to the
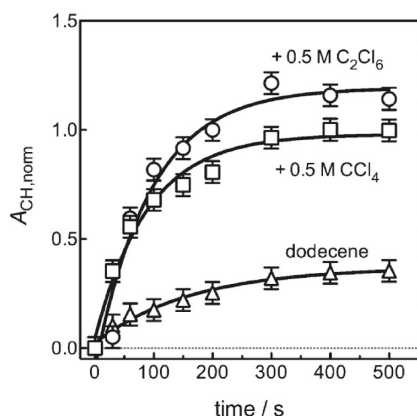
Figure 7. Example of the rate enhancement upon addition of an electron acceptor (0.5 M C_2Cl_6 and 0.5 M CCl_4) to a 1-dodecene solution. The y-axis is based upon the absorbance of the C—H stretching region in the FTIR spectra of the posthydrosilylated samples. Figure reproduced with permission from ref 35. Copyright 2011 American Chemical Society.

high surface area of the porous silicon that allows for a very high signal-to-noise ratio. When aliphatic 1-alkynes are hydrosilylated, they appear to produce predominately anti-Markovnikov *trans*-silicon-substituted alkenes on the surface, of the form ≡Si—CH=CH—R, as determined by the observation of a trans olefinic out-of-plane deformation γ(=CH) at ~980 cm^{-1}.[33,36] The lack of an obvious marker for silicon surface-substituted *cis*-alkenes, however, makes concrete quantification impossible. Use of a perfluorinated R group on the alkene RCH=CH$_2$ dramatically simplifies analysis of the resulting hydrosilylated product due to the reduced number of obscuring —CH$_2$ and —CH$_3$ groups, and the observation of a weak mode corresponding to a terminal methyl group could suggest Markovnikov addition to produce the branched product ≡Si—CH(CH$_3$)(CF$_2$)$_n$CF$_3$, although it could also be due to adventitious contamination by hydrocarbons on the hydrophobic surfaces.[33] As was stated earlier in the section on Si—H dissociation-based mechanisms, a detailed investigation of the resulting products could lead to new insights.

White-light promoted hydrosilylation of alkenes on flat silicon surfaces, including Si(100)-H$_x$ and Si(111)-H was shown to also be successful, but with greatly extended irradiation times (>10 h).[37] The authors proposed a related mechanism to that suggested for nanocrystalline porous silicon, in which a surface-localized positive charge is attacked by an alkene, resulting in a silicon—carbon bond (Figure 4c). The mechanism was further refined to incorporate elements of both the radical- and hole (h+)-based mechanisms, as shown in Figure 4d.[38,39] The authors propose that the hole weakens a surface Si—Si bond, which is then attacked by the alkene to produce the Si—C bond. Instead of generation of the positive charge on the β-C of the alkyl group, the authors suggest that this carbon has more radical character, and that the positive charge remains in the silicon. The persistence of the positive charge in this mechanism following completion of the

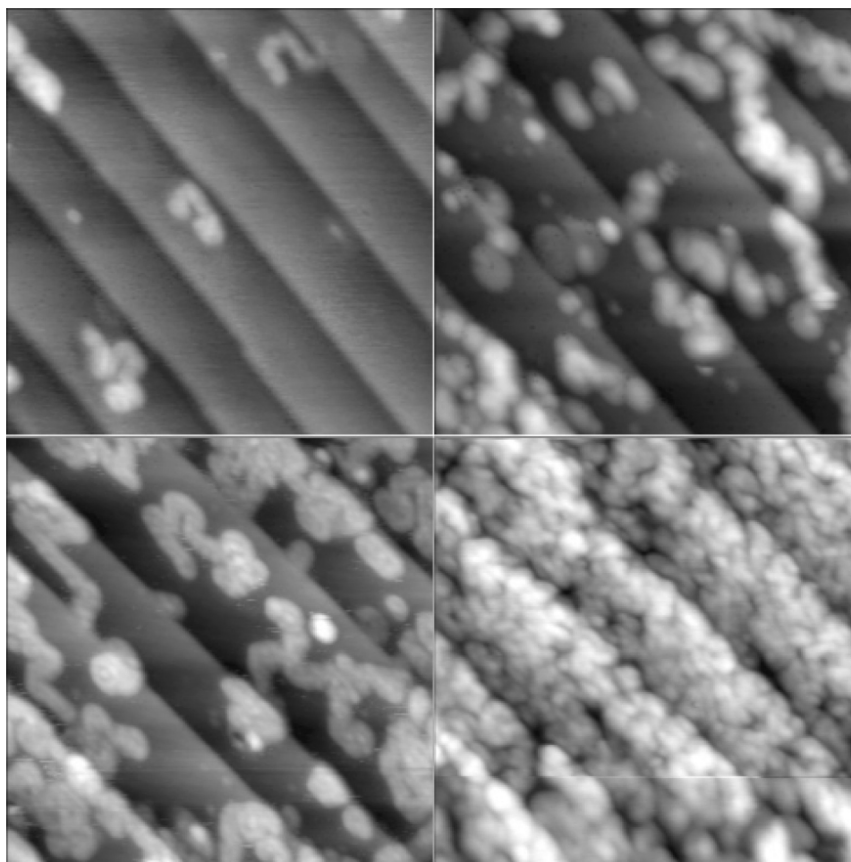**Figure 8.** Scanning tunneling microscopy (STM) images (200 × 400 Å^2) of Si(111)-H surfaces following white light (447 nm) promoted hydrosilylation with 1-decene over increasing lengths of time: top left = 3 min, top right = 15 min, bottom left = 30 min, bottom right = 120 min. Figure reproduced with permission from ref 40. Copyright 2004 American Chemical Society.

hydrosilylation event, needs to be determined. STM images of samples on Si(111)-H following irradiation with 447 nm light in 1-decene clearly show the growth of monolayer (1-decyl) islands on the Si(111) terraces (images reproduced in Figure 8).[40] The islands are suggestive of a meandering random walk that is self-limiting, similar to that observed with the STM tip-initiated hydrosilylation experiments (vide supra).

A very interesting mechanistic study to elucidate the role of excitons (or related light-promoted surface charges) on flat silicon was carried out by Chabal and co-workers.[41] Two surfaces were prepared in which both contain Si—H$_x$ groups. The first was a typical Si(111)-H surface, and the other was Si(100)/SiO$_2$/H that was prepared from the reaction of triethoxysilane on an oxidized Si(111) wafer. If the radical-based Si—H dissociation mechanism (Figure 4a) is in operation, then both surfaces should react in a similar manner with UV irradiation. When irradiated for the same length of time, the Si(100)/SiO$_2$/H surface did not undergo a hydrosilylation reaction with indene, whereas Si(111)-H did. In the case of Si(100)/SiO$_2$/H, any formed electron/hole pairs could not traverse the silica dielectric, thus preventing an exciton-based mechanism from proceeding. This creative set of experiments provides strong proof for the involvement of a mechanism that is based on charge generation at the silicon surface.

The mechanism of white-light-promoted hydrosilylation on flat silicon surfaces is more challenging to understand than that of porous silicon or nanoparticles because the photogenerated charges are not confined within a nanocrystal, as they are in porous silicon or an isolated nanoparticle. In addition, the much lower surface area of flat silicon compared with porous silicon renders analysis by FTIR more challenging, in addition to possible competition with dilute contaminants such as dissolved trace oxygen. Zuilhof and co-workers have gone to great lengths to overcome these challenges, and raised a number of very interesting questions about the white light promoted mechanism.[22,42] For instance, they have observed that over extended periods of time (24 h), hydrosilylation of alkynes is observed to proceed in the dark at room temperature, which they attribute to thermal excitation and generation of excitons in situ.[42] They also note that 1-alkynes are more reactive than 1-alkenes on flat surfaces due to "higher intrinsic reactivity, better stabilized intermediates, and an overall more exothermic reaction".[42] Similar trends have not been observed with porous silicon or nanoparticles, and so these results do point to yet another subtle mechanistic difference between excitonic-driven reactions on flat surfaces, and nanostructured silicon.

Computational studies appear to support the exciton-driven hydrosilylation reaction on silicon nanocrystallites, and other silicon surfaces.[43−45] The Galli group found that the activation barrier for hydrosilylation in a nanocrystallite is dramatically lowered upon absorption of a photon.[43] Interestingly, the authors suggested applying size-selective reactivity that uses the concept of an increasing band gap as quantum-confined silicon becomes smaller in size; for carefully chosen monochromatic light, the silicon nanoparticles that have too large a band gap (i.e., small diameter particles) will not react, whereas those with smaller band gaps that can absorb the photon and undergo surface hydrosilylation. This concept was experimentally demonstrated by Veinot and co-workers for hydrogen-terminated silicon nanocrystals.[46] Other computational work has also looked closely at the very fine details of Si—C bond

formation on silicon, including understanding which surface-bound H atoms might be extracted in a sequence of hydrosilylation events in a chain reaction.[47]

Photoemission-Driven Hydrosilylation (Figure 4e). In 2010, Hamers and co-workers proposed an alternative mechanism to Si—H dissociation for UV light promoted hydrosilylation, a mechanism driven by photoemission.[48] As shown in Figure 4e, UV light is sufficiently energetic to knock an electron directly from the conduction band, where it is captured by the acceptor levels of a molecule in the solution phase. Ejection of the electron leaves the silicon surface with a net positive charge that is then attacked by the alkene, leading to formation of the silicon—carbon bond, as has been suggested in several earlier mechanisms. The acceptor molecule in this study was the alkene itself, an α,ω-alkene that contains both a trifluoroacetamide group and a primary alkene (trifluoroaceta-mide-10-aminodec-1-ene, TFAAD). TFAAD has lower acceptor energy levels than 1-dodecene, and so coverage by the products of hydrosilylation on Si(111)-H surfaces were twice as high with this molecule than with the aliphatic alkene as determined by XPS. It was later shown that the trifluoroacetamide molecule (Me$_2$TFA), which does not have an attached alkene group, can also induce increases in surface coverage when added to a solution of 1-dodecene.[35] The small band gap of silicon (1.12 eV) may enable the reaction to proceed with high efficiency under these conditions, and thus may be generalizable to other low band gap semiconductors.[48] Longer wavelengths that do not have the energy to initiate photoejection of the electron would most likely proceed via the exciton mechanism.

The alkene with the electron accepting moiety used by Hamers et al., TFAAD, has a relatively high LUMO level, and thus a molecule with a lower empty orbital to accept the photoejected electron should better promote the hydrosilylation reaction on flat surfaces because of an increase in the reaction cross-section for generation of a surface-bound positive charge.[49] As shown schematically in Figure 9 and Table 1, the rate constants for 1-hexadecene on Si(111)-H increase by 2 orders of magnitude in the presence of phenylchloride and paradichlorobenzene (p-DCB). The k_{obs} in Table 1 vary from 1.1×10^{-3} s^{-1} with no additives, to $260 \pm 30 \times 10^{-3}$ s^{-1} with p-DCB. These results strongly support the photoemission mechanism since the better electron acceptors are the most
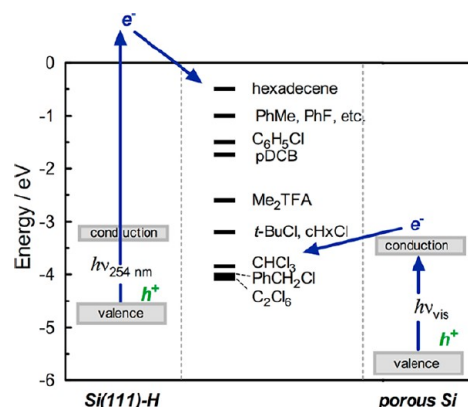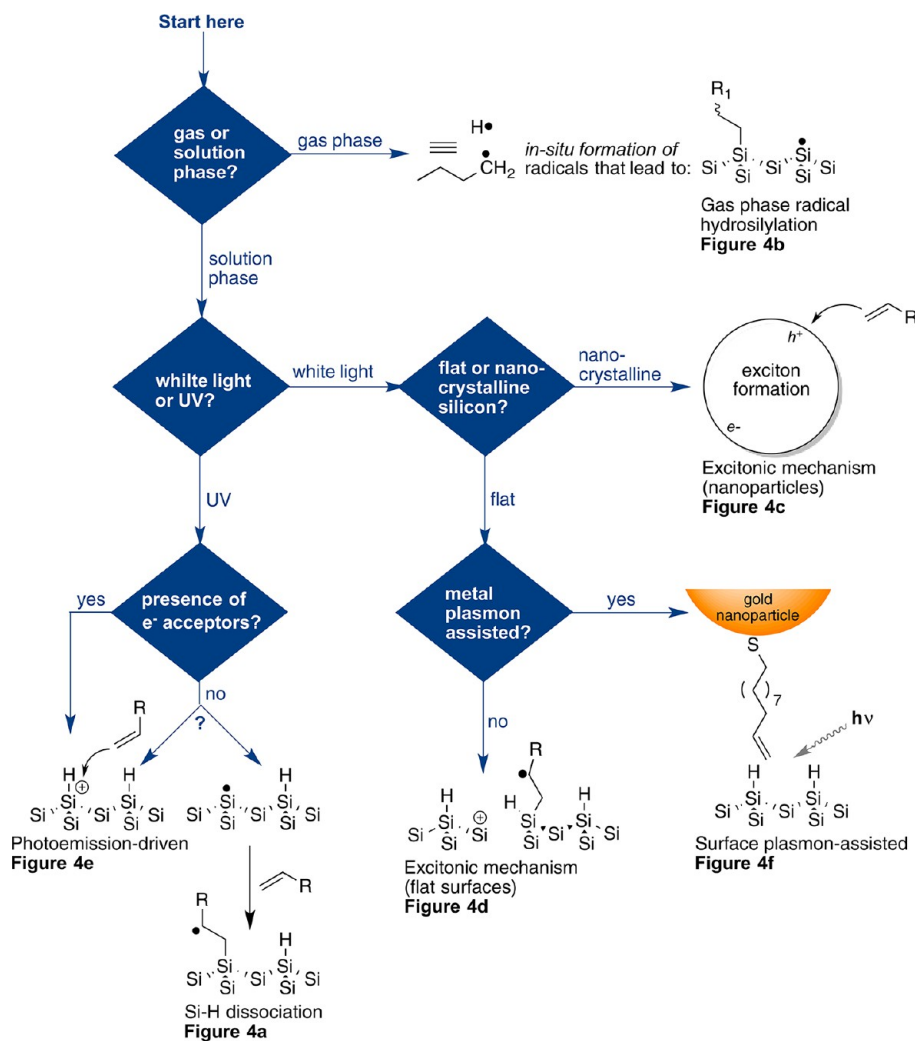

Figure 9. Energy level diagram for both porous silicon and Si(111)-H, showing the valence and conduction bands, and the LUMO energies of various additives. Figure reproduced with permission from ref 49. Copyright 2012 American Chemical Society.

Table 1. Rate Coefficients (k_{obs}) for UV-Initiated Hydrosilylation with 1-Hexadecene as the Alkene, and 0.25 M Additive[a]

additive	k_{obs} ($\times 10^{-3}$ s^{-1})	E_{red} (V)	$k_{(\bullet SiEt_3)}$[g] ($\times 10^6$ M^{-1} s^{-1})
none	1.1 ± 0.4	< -3.5	4.8
THN	6 ± 2	< -3	
PhOCH$_3$	12 ± 2	< -3	
PhF	18 ± 5	< -3	
PhCH$_3$	43 ± 3	< -3	1.2
PhCl	205 ± 20	-2.2	0.7
p-DCB	260 ± 30	-2.0	
BzCl	$[220 \pm 20]$	-0.5	20

[a]Reduction potentials of the additives are vs SHE in CH$_3$CN, and are accompanied by the rate constants for their reaction with the triethylsilyl radical for comparison.[54] Table reproduced with permission from ref 35. Copyright 2011 American Chemical Society.

effective at bringing about a dramatically increased rate. Interestingly, however, the screening of various oxidants also turned up evidence to support Si–H dissociation and surface-bound silicon dangling bonds or radicals. A series of results suggest that direct homolysis of Si–H bonds could be taking place simultaneously, and the very fast reaction between C–Cl group and Si• radicals occurs when the concentration of the C–Cl-containing additive is high. These results suggest that subtle changes in reaction conditions could allow for different mechanisms to manifest themselves; the extension of this thinking is that several mechanistic pathways could be operating simultaneously under a given set of parameters.

Surface Plasmon-Assisted Hydrosilylation (Figure 4f). In a very interesting new twist on silicon surface hydrosilylation, the Sugimura Group demonstrated that gold nanoparticles can have a significant influence on coverage on Si(111)-H.[50] As outlined in Figure 4f, a 20 nm gold nanoparticle is functionalized with an α,ω-alkene-terminated thiol; these gold nanoparticles have an absorption maximum in their UV−visible spectrum at 550 nm due to surface plasmons. When irradiated with visible light, the nanoparticles adhere to the Si(111)-H surface due to hydrosilylation between terminal alkenes and the silicon surface. Wavelength-dependent experiments showed that the highest coverage of gold nanoparticles on the Si(111)-H is obtained when the light has its maximum intensity closest to 550 nm, the plasmon absorbance of the gold. According to the authors, the gold nanoparticles are operating as "photon collectors", transferring the energy to the

Figure 10. Algorithm that maps out, to a first approximation, the light-induced hydrosilylation mechanism that may be predominant under a given set of conditions. The algorithm assumes the alkene or alkyne undergoing hydrosilylation is a simple aliphatic hydrocarbon.

silicon surface to enhance the hydrosilylation chemistry. Another explanation could be related to the enhanced electric fields nearby that assist in exciton dissociation, as has been proposed in bulk heterojunctions in organic photovoltaics.[51]

MECHANISTIC ELUCIDATION

Arriving at a conclusion as to which mechanism(s) is (are) in operation is certainly tricky, because of the fact that the final hydrosilylation products of the reaction appear identical. Figure 10 attempts to provide, to a first approximation, a simple algorithm to help delineate which mechanism may predominate under a given set of conditions. The algorithm starts with the phase of the reactants, gaseous or liquid, because there seems to be a subtle but distinct difference in the stability of the resulting alkene/alkyne-based radicals that form under UV irradiation: Low radical concentrations in the gas phase minimize recombination, and hence the persistence and diffusion of these radicals lead to reactivity in nonirradiated areas (Figure 4b). The second branch point distinguishes between UV- and white-light irradiation, as white light is too weak to break the surface Si−H bonds in a homolytic fashion or induce photoemission. The white-light-based mechanisms are then separated based upon the morphology of the silicon substrate, either flat or nanocrystalline (Figures 4c, d). Another branch point separates plasmon-mediated assistance of white-light induced hydrosilylation (Figure 4f). On the UV-induced hydrosilylation side of the algorithm, the next split differentiates based upon the presence of electron acceptors; it appears that the presence of appropriate electron acceptors strongly favors the photoemission mechanism (Figure 4e).[52] In the absence of obvious electron acceptors, aliphatic alkenes may still function as weak electron acceptors, but the radical-based Si−H dissociation-based mechanism may also operate (Figure 4a). Further research is needed to elucidate the role of both these mechanisms (photoemission versus Si−H dissociation) upon UV-irradiation, as suggested by the question mark ("?") at the branch point in Figure 10, as it remains unknown as to what proportion of each may be in operation. It must be emphasized that this algorithm is simply a starting point. For instance, if light of 350 nm were to be used, it is questionable as to whether a UV- or white-light-induced mechanism would predominate because the energy of this wavelength is close to the minimum required for Si−H bond cleavage.[21] It is hoped that Figure 10 will serve to promote more interest in mechanistic elucidation of hydrosilylation mechanisms on silicon surfaces, in general.

CONCLUSIONS AND FUTURE DIRECTIONS

An apparently simple reaction, $\equiv$Si−H + $h\nu$ → $\equiv$Si• + H• on a silicon surface, has turned out to be far richer than could have been imagined 15 years ago. The underlying silicon surface plays an important role, and thus the reactions on silicon cannot be considered as exclusively molecular in any sense — they fall into the category of true materials chemistry, as is befitting for the 25th anniversary of *Chemistry of Materials*. Many persistent questions remain, including a better understanding of the effect of the reaction conditions or environment on the reaction mechanism. What conditions would favor exclusivity of one over the other, or allow all three to proceed simultaneously? Second, what is the role of the large excess of alkenes, alkynes, and aromatics on a surface reaction? Computational studies of unsaturated molecules interacting with silicon point to a significant physorption on hydride-

terminated silicon surfaces.[53] The field (this paper included) continually sketches 'naked' Si−H surfaces in such reactions when in fact the interface may be responding to subtle electrochemical cues due to the close proximity of these molecules. Such an influence could favor, for instance, a mechanism that involves charge separation if the solvent environment generated a partial surface charge. Lastly, the role of plasmonics on excitonic mechanisms is growing rapidly in many areas, particularly organic photovoltaics and other systems requiring light management. This area of research could also be the source of many new directions for silicon surface chemistry, and surface science as a whole.

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REFERENCES

(1) (a) Keyes, R. W. *Rep. Prog. Phys.* **2005**, *68*, 2701. (b) Ieong, M.; Doris, B.; Kedzierski, J.; Rim, K.; Yang, M. *Science* **2004**, *306*, 2057.
(2) Thissen, P.; Seitz, O.; Chabal, Y. J. *Prog. Surf. Sci.* **2012**, *87*, 272.
(3) (a) Yu, H.-Z.; Li, Y.; Ou, L. M.-L. *Acc. Chem. Res.* **2013**, *46*, 258. (b) Ciampi, S.; Harper, J. B.; Gooding, J. J. *Chem. Soc. Rev.* **2010**, *39*, 2158. (c) Liu, Y.; Jhe, C.; Teplyakov, A. V. *Langmuir* **2012**, *28*, 15521.
(4) (a) Puniredd, S. R.; Jayaraman, S.; Yeong, S. H.; Troadec, C.; Srinivasan, M. P. *J. Phys. Chem. Lett.* **2013**, *4*, 1397. (b) Harada, Y.; Koitaya, T.; Mukai, K.; Yoshimoto, S.; Yoshinobu, J. *J. Phys. Chem. C* **2013**, *117*, 7497.
(5) Linford, M. R.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1993**, *115*, 12631.
(6) (a) Buriak, J. M. *Chem. Rev.* **2002**, *102*, 1271. (b) Li, Y.; Calder, S.; Cahen, D.; Haick, H.; Kronik, L.; Zuilhof, H. *Langmuir* **2012**, *28*, 9920. (c)
(7) Linford, M. R.; Fenter, P.; Eisenberger, P. M.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1995**, *117*, 3145.

(8) Chatgilialoglu, C. *Chem. Rev.* **1995**, *95*, 1229.

(9) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 3292.

(10) Huang, Z.; Geyer, N.; Werner, P.; de Boor, J.; Gösele, U. *Adv. Mater.* **2011**, *23*, 285.

(11) Tsang, C. K.; Kelly, T. L.; Sailor, M. J.; Li, Y. Y. *ACS Nano* **2012**, *6*, 10546.

(12) Thompson, C. M.; Nieuwoudt, M.; Ruminski, A. M.; Sailor, M. J.; Miskelly, G. M. *Langmuir* **2010**, *26*, 7598.

(13) Collins, G.; Holmes, J. D. *J. Mater. Chem.* **2011**, *21*, 11052.

(14) Bashouti, M. Y.; Sardashti, K.; Schmitt, S. W.; Pietsch, M.; Ristein, J.; Haick, H.; Christiansen, S. H. *Prog. Surf. Sci.* **2013**, *88*, 39.

(15) Zang, Z. Y.; Dobbie, A. R.; Cui, K.; Veinot, J. G. C. *J. Am. Chem. Soc.* **2012**, *34*, 13958.

(16) Lu, X.; Hessel, C. M.; Yu, Y.; Bogart, T. D.; Korgel, B. A. *Nano Lett.* **2013**, ASAP.

(17) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley & Sons: New York, 2000.

(18) Marciniec, B. *Coord. Chem. Rev.* **2005**, *249*, 2374.

(19) (a) Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677. (b) Lambert, J. B.; Zhao, Y.; Wu, H. *J. Org. Chem.* **1999**, *64*, 2729.

(20) Chatgilialoglu, C.; Lalevée, J. *Molecules* **2012**, *17*, 527.

(21) (a) Kopping, B.; Chatgilialoglu, C.; Zehnder, M.; Giese, B. *J. Org. Chem.* **1992**, *57*, 3994. (b) Wu, Y.-D; Wong, C.-L *J. Org. Chem.* **1995**, *60*, 821.

(22) Rijksen, B.; van Lagen, B.; Zuilhof, H. *J. Am. Chem. Soc.* **2011**, *133*, 4998.

(23) Terry, J.; Linford, M. R.; Wigren, C.; Cao, R.; Pianetta, P.; Chidsey, C. E. D. *Appl. Phys. Lett.* **1997**, *71*, 1056.

(24) Terry, J.; Linford, M. R.; Wigren, C.; Cao, R.; Pianetta, P.; Chidsey, C. E. D. *J. Appl. Phys.* **1999**, *85*, 213.

(25) Effenberger, F.; Gotz, G.; Bidlingmaier, B.; Wezstein, M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2462.

(26) Xia, Y.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 550.

(27) Cicero, R. L.; Linford, M. R.; Chidsey, C. E. D. *Langmuir* **2000**, *16*, 5688.

(28) Cicero, R. L.; Chidsey, C. E. D.; Lopinski, G. P.; Wayner, D. D. M.; Wolkow, R. A. *Langmuir* **2002**, *18*, 305.

(29) Hua, F.; Swihart, M. T.; Ruckenstein, E. *Langmuir* **2005**, *21*, 6054.

(30) Eves, B. J.; Lopinski, G. P. *Langmuir* **2006**, *22*, 3180.

(31) Stewart, M. P.; Buriak, J. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 3257.

(32) (a) Canham, L. T. *Appl. Phys. Lett.* **1990**, *57*, 1046. (b) Buda, F.; Kohanoff, J.; Parrinello, M. *Phys. Rev. Lett.* **1992**, *69*, 1272. (c) Canham, L. T. Applied Sciences−Optical Properties of Low Dimensional Silicon Structures. In *NATO Advanced Study Institute Series E244*; Bensahel, D. C., Canham, L. T., Ossicini, S., Eds.; Kluwer:Dordrecht, The Netherlands, 1993; p 81. (d) Fisher, D. L.; Gamboa, A.; Harper, J.; Lauerhaas, J. M.; Sailor, M. J. *Mater. Res. Soc. Symp. Proc.* **1995**, *358*, 507. (e) Coffer, J. L. *J. Lumin.* **1996**, *70*, 343. (f) Rehm, J. M.; McLendon, G. L.; Fauchet, P. M. *J. Am. Chem. Soc.* **1996**, *118*, 4490. (g) Baierle, R. J.; Caldas, M. J.; Molinari, E.; Ossicini, S. *Solid State Commun.* **1997**, *102*, 545. (h) Cullis, A. G.; Canham, L. T.; Calcott, P. D. J. *J. Appl. Phys.* **1997**, *82*, 909.

(33) Stewart, M. P.; Buriak, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 7821.

(34) Kelly, J. A.; Veinot, J. G. C. *ACS Nano* **2010**, *4*, 4645.

(35) Huck, L. A.; Buriak, J. M. *J. Am. Chem. Soc.* **2011**, *134*, 489.

(36) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Chapman and Hall: London, 1975; pp 50−61.

(37) Sun, Q.-Y.; de Smet, L. C. P. M.; van Lagen, B.; Wright, A.; Zuilhof, H.; Sudhölter, E. J. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 1352.

(38) Sun, Q.-Y.; de Smet, L. C. P. M.; van Lagen, B.; Giesbers, M.; Thüne, P. C.; van Engelenburg, J.; de Wolf, F. A.; Zuilhof, H.; Sudhölter, E. J. R. . *J. Am. Chem. Soc.* **2005**, *127*, 2514.

(39) Rijksen, B.; Pujari, S. P.; Scheres, L.; van Rijn, C. J. M.; Baio, J. E.; Weidner, T.; Zuilhof, H. *Langmuir* **2012**, *28*, 6577.

(40) Eves, B. J.; Sun, Q.-Y.; Lopinski, G. P.; Zuilhof, H. *J. Am. Chem. Soc.* **2004**, *126*, 14318.

(41) Langner, A.; Panarello, A.; Rivillon, S.; Vassylyev, O.; Khinast, J. G.; Chabal, Y. J. *J. Am. Chem. Soc.* **2005**, *127*, 12798.

(42) Scheres, L.; Giesbers, M.; Zuilhof, H. *Langmuir* **2010**, *26*, 10924.

(43) Reboredo, F. A.; Schwegler, E.; Galli, G. *J. Am. Chem. Soc.* **2003**, *125*, 15243.

(44) Cossi, M.; Boccia, A.; Marrani, A. G.; Zanoni, R. *J. Phys. Chem. C* **2011**, *115*, 19210.

(45) Wang, R.; Pi, X.; Yang, D. *J. Phys. Chem. C* **2012**, *116*, 19434.

(46) Kelly, J. A.; Shukaliak, A. M.; Fleischauer, M. D.; Veinot, J. G. C. *J. Am. Chem. Soc.* **2011**, *133*, 9564.

(47) Kanai, Y.; Selloni, A. *J. Am. Chem. Soc.* **2006**, *128*, 3892.

(48) Wang, X.; Ruther, R. E.; Streifer, J. A.; Hamers, R. J. *J. Am. Chem. Soc.* **2010**, *132*, 4048.

(49) Huck, L. A.; Buriak, J. M. *Langmuir* **2012**, *28*, 16285.

(50) Sugimura, H.; Mo, S.; Yamashiro, K.; Ichii, T.; Murase, K. *J. Phys. Chem. C* **2012**, *117*, 2480.

(51) Wu, J. L.; Chen, F. C.; Hsiao, Y. S.; Chien, F. C.; Chen, P.; Kuo, C. H.; Huang, M. H.; Hsu, C. S. *ACS Nano* **2011**, *5*, 959.

(52) Kolaskinski, K. W. *J. Am. Chem. Soc.* **2013**, *135*, 11408.

(53) Johnson, E. R.; DiLabio, G. A. *J. Phys. Chem. C* **2009**, *113*, 5681.

(54) (a) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5123. (b) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 3292.