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The Mechanism of Photohydrosilylation on Silicon and Porous Silicon Surfaces

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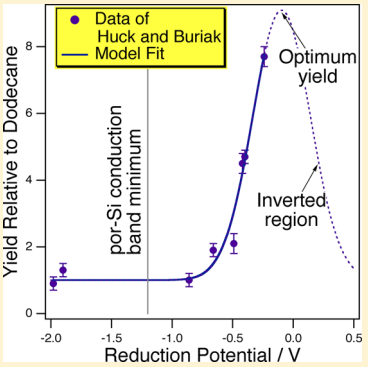
ABSTRACT: Visible or UV light activates H-terminated Si surfaces because of the presence of a photogenerated hole in a Si−Si back-bond. Enhancing the lifetime of this hole at the surface increases reactivity. On the basis of photodynamics and electron transfer theory, the prevalence of two mechanisms of photoactivation (internal photoemission versus interband photoexcitation followed by electron transfer) are explored. To act as an effective trap, an acceptor state for the excited electron must either be populated directly by photoexcitation or the state must lie in a band gap (or both). It is predicted that oxidants with a properly positioned acceptor level will enhance the reactivity of porous silicon or silicon nanocrystals in a size selective manner.



INTRODUCTION

The ability to tune the solubility, wettability, and dissolution behavior of nanocrystalline silicon (nc-Si) by variations in surface termination makes porous silicon (por-Si) an ideal vehicle for drug delivery.[1−3] Silicon nanoparticles exhibit improved solubility in polar solvents when longer alkyl chains are attached to them.[4] Carboxylic acid-terminated Si nanoparticles do not exhibit cytotoxicity, whereas amine-terminated Si nanoparticles do.[5] H-terminated surface are easily resorbed,[6,7] whereas derivatization can inhibit the corrosion of por-Si surfaces.[8] Decelerated dissolution can slow the release of a steroid that has been loaded into the pores.[9]

Sailor and co-workers followed up the first thermal modifications of Si surfaces with work on the photoreactivity of por-Si surfaces.[10−12] Direct patterning of crystalline Si (c-Si) surfaces with adsorbed alkoxide layers by photoactivation soon followed.[13,14] Chidsey[15−17] and Buriak[14,18−20] extensively studied the photo-initiated hydrosilylation of Si and por-Si surfaces.

Stewart and Buriak implicated excitons in the reaction mechanism.[18] Sun et al.[21] extended this mechanism by invoking a surface localized valence band hole coupled to radical formation and propagation. Reaction proceeds by nucleophilic attack of the Si surface at the site excited by the presence of the hole. In a chain reaction, this is followed by H abstraction from a neighboring site that allows for radical propagation.

Experiments consistent with the involvement of photogenerated holes to enhance reactivity of Si−H bonds on both extended surfaces and nanoparticles have been performed by a number of groups.[22−25] However, controversy still exists regarding the details of the mechanism and how the reactivity of the holes can be enhanced. Huck and Buriak[20] have found that for white light illumination the addition of oxidants possessing an acceptor level can enhance photoreactivity if the level resides below the conduction band minimum. They ascribe this to the oxidant's ability to overcome the exciton binding energy.

Hamers and co-workers have shown that UV excitation can be quite effective at grafting of terminal alkenes not only to Si,[26,27] but also to diamond and other carbon surfaces.[28] They illuminated Ar-sparged neat alkenes in contact with a surface with 254 nm light at ∼10 mW cm^{-2}. They suggested[26] that internal photoemission is important during the grafting. Internal photoemission is electron transfer from the solid substrate to an acceptor species in solution by direct photoexcitation. They demonstrated that this mechanism works particularly well with diamond surfaces and molecules that possess an acceptor level that resides below the vacuum level of the solid. Huck and Buriak[29] found that aromatic groups are particularly effective at enhancing reactivity with H-terminated Si surface under 254 nm irradiation.

In this report, I discuss the photodynamics responsible for photochemistry at Si surfacesand then develop a quantitative model to fit the data of Huck and Buriak, which takes into consideration both internal photoemission and electron transfer in enhancing the rate of reaction. This work puts a firm theoretical foundation under the suggestion in ref 26 that the rate of reaction is enhanced because removal of the electron from the substrate increases the lifetime of the hole that initiates reactivity.

RESULTS AND DISCUSSION

The initiator of UV- and visible-irradiation-induced photochemistry by nucleophilic attack at H/Si surfaces is a thermalized hole at the top of the valence band not Si−H

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bond cleavage. By conservation of energy, the Si−H bond could in principle be photodissociated with a photon of wavelength $\lambda \leq 410$ nm. There are, however, no electronic transitions at this wavelength. In fact, direct photodissociation of the Si−H bond only begins to occur with a measurable probability at a wavelength around 157 nm.[30,31] Thermalized holes are involved in the mechanism of photoinitiated etching of Si in HF.[32−34] On the basis of electronic state energetics, Kolasinski has unambiguously determined[34] that the hole resides in a Si−Si backbond bulk state localized near the surface. The hole is not located in the Si−H bond, nor is it capable of dissociating the Si−H bond. This state is the active state in the exciton model of Stewart and Buriak.[18]

We need to consider what can influence and even enhance the reactivity of the valence band hole. Foremost, the hole must not recombine effectively with a conduction band electron. Band bending can lead to separation of these carriers, especially when only a fraction of the surface is illuminated.[33,35] When the nucleophile is strong, such as F^-, this promotes significant reactivity. Hence, localized but not full surface laser excitation with above band gap radiation of Si in HF(aq) leads to formation of por-Si in the area that contains the holes: the irradiated area of n-type Si[36] or the unirradiated portion of p-type Si.[33] Faster and more reliable reactivity on both n- and p-type wafers is induced if the hole and electron are not only separated, but if the electron is completely removed from the Si substrate all together. This is accomplished in stain etching in which an oxidant in solution removes an electron and injects a hole into the valence band.[37−39]

The solid state electronic energy ε in electronvolts in which the vacuum level is used as the energetic origin $\varepsilon_{vac} = 0$ is related to the electrochemical reduction potential E in volts by[40]

$$\varepsilon = -4.43 \text{ eV} - eE \quad (1)$$

The energetic origin of the electrochemical energy scale is the standard hydrogen electrode (SHE) at 0 V, which has a work function of 4.43 eV, and e is the elementary charge on the electron. The band structure of por-Si depends on the nanocrystallite size distribution because of quantum confinement.[41] For example, $E_C = -0.22$ V versus SHE and $\varepsilon_{gap} = 1.12$ eV for 1 Ω cm p-type Si(100) in 2 M HF.[42] However, for a particular preparation of por-Si, Rehm et al.[43] found $E_C = -1.20$ V and a band gap of $\varepsilon_{gap} = 2.6$ eV.

Excitation of electron hole pairs requiring above band gap radiation requires significantly bluer photons on por-Si ($\lambda_{gap} \leq$ 480 nm, for the visibly photoluminescent sample of Rehm et al.) or sufficiently small nanocrystals of Si as compared to c-Si ($\lambda_{gap} \leq 1110$ nm) because of band gap widening. Photoemission is possible once the photon energy exceeds the work function. However, since Si is a semiconductor, the density of states is necessarily low at the Fermi energy ε_F and is only the result of defect states. Unless these defects are close to the surface, it is unlikely that photoelectrons released from them can actually leave the sample before collisional relaxation. Photoelectron production occurs to a substantial extent only when photons can promote electrons from the energy of the valence band maximum ε_V. This requires ultraviolet light of $\lambda_{VB} \leq 240$ nm on c-Si or $\lambda_{VB} \leq 210$ nm on por-Si.

Internal photoemission removes the excited electron from the Si and thereby lowers the recombination rate with the valence band hole. The hole has a longer lifetime than if the electron were excited to the conduction band. This intrinsically increases the effective reactivity of the hole toward nucleophilic attack by a solution phase species such as terminal alkenes. Hamers and co-workers achieved a high probability for internal photoemission by choosing molecules with an acceptor level under the Si vacuum level and by using 254 nm light. It should be noted that while charge transfer is generally most rapid to the lowest energy acceptor state, internal photoemission is possible not just to the lowest available state (the acceptor level corresponding to the reduction potential) but to any energetically accessible acceptor level.

To increase the hole lifetime, the excited electron must be transferred to a trap state. An excited state such as $|S3\rangle$ in Figure 1 is unstable and relaxes with a lifetime on the order of a f1

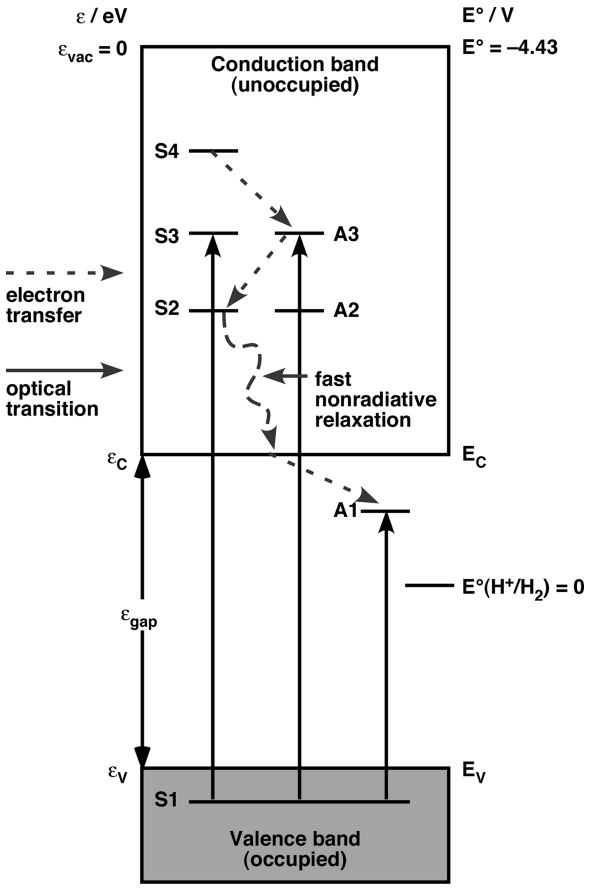

Figure 1. S1, S2, S3 and S4 represent substrate electronic states within the valence or conduction bands. A1, A2 and A3 represent molecular acceptor states in solution phase or adsorbed species.

few femtoseconds, rapidly relaxing to the conduction band minimum. This is very short compared to the radiative recombination time that determines the lifetime of electrons at the conduction band minimum in well-passivated Si, which has a lifetime on the order of a few nanoseconds to tens of microseconds, depending on temperature, surface termination, and nanocrystallite size.[44,45]

To significantly increase the hole lifetime, the electron must be transferred to a long-lived adsorbate state. Candidate states $|A1\rangle$ and $|A3\rangle$ are shown in Figure 1. As mentioned above, population of these states can be accomplished by internal photoemission. The rate of radiative excitation W_{fi} from initial state $|i\rangle$ to final state $|f\rangle$ is given by the Fermi golden rule expression

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$$W_{fi} = \frac{2\pi}{\hbar} |V_{fi}|^2 \rho(\varepsilon_{fi}) \quad (2)$$

where the transition dipole matrix element is $V_{fi} = \langle f|\vec{\mu}|i\rangle$ and $\rho(\varepsilon_{fi})$ is the power density at the resonance energy ε_{fi}. The transition dipole matrix element depends on the orbital nature of the initial bulk state and the final acceptor state. Therefore, there is no reason for the internal photoemission probability to depend in a direct way on the reduction potential.

Consider two degenerate levels, one in the conduction band $|S3\rangle$ and one localized on a molecular acceptor $|A3\rangle$. There are two ways to populate the state $|A3\rangle$. The first is direct photoexcitation from a valence band state $|S1\rangle$. Whether the probability of an optical transition is greater for $|S1\rangle \rightarrow |S3\rangle$ or $|S1\rangle \rightarrow |A3\rangle$ depends on the relative magnitude of the transition dipole matrix elements $|S3\rangle|\vec{\mu}|S1\rangle$ compared to $|A3\rangle|\vec{\mu}|S1\rangle$.

The second way to transfer the electron into $|A3\rangle$ is optical excitation to $|S3\rangle$ followed by an electron transfer event $|S3\rangle \rightarrow |A3\rangle$. Here we assume that the molecules are weakly coupled (physisorbed or nonspecifically adsorbed) to the Si surface such that Marcus theory can be used to calculate the rate of electron transfer.[46]

The rate of electron transfer from the conduction band can be written

$$R_{inj} = c_{ox} N_C k_{max} W(E) \quad (3)$$

where N_C is the density of states in the conduction band, k_{max} is the optimal rate constant, and $W(E)$ is the Marcus hop probability factor that depends on the relative position of the acceptor level compared to the energy of the valence band edge E_C. For an oxidant with Nernst potential E_{ox}

$$W(E) = \exp[-((E_C - E_{ox} + \lambda_e)^2/4\lambda_e k_B T)] \quad (4)$$

λ_e is the solvent reorganization energy (about 0.5−1.5 eV for organic species at a semiconducting electrode), and k_B is the Boltzmann constant. k_{max} occurs when the activation Gibbs energy $\Delta G^{\ddagger}$ vanishes as defined by

$$\Delta G^{\ddagger} = (E_C - E_{OX} + \lambda_e)/4\lambda_e = 0 \quad (5)$$

This condition defines the onset of the inverted region for electron transfer. Lewis and co-workers,[47−51] have measured a value of $k_{max} \approx 10^{-25}$ to 10^{-24} m^4 s^{-1} with Si, ZnO, InP, and GaAs electrodes. They have shown that this value is consistent with the maximum magnitude of k_{max} calculated quantum mechanically from

$$k_{max} = \frac{2\pi}{\hbar} |H_{DA}|^2 \beta^{-1} (4\pi\lambda_e k_B T)^{1/2} \frac{l_{Si}}{\rho_A^{2/3} (6/\pi)^{1/3}} \quad (6)$$

where l_{Si} is the effective coupling length in the semiconductor, $\beta \approx 1$ Å is the tunneling range parameter, and H_{DA} is the coupling matrix element for the electron transfer Hamiltonian H_{et} between the donor and acceptor levels $|D\rangle$ and $|A\rangle$. The coupling matrix element H_{DA} depends on orbital overlap and symmetry. Thus, it varies exponentially with distance r from the distance of closest approach r_m according to

$$|H_{DA}|^2 = |\langle D|H_{et}|A\rangle|^2 = V_0 \exp[\beta(r - r_m)/2] \quad (7)$$

What should be apparent from Figure 1 and eqs 3−7 is that as long as $|A3\rangle$ lies above E_C, there always exists a state $|S2\rangle$ that lies at lower energy than $|S3\rangle$. Therefore, the activation Gibbs energy for electron transfer $|A3\rangle \rightarrow |S2\rangle$ must be less than for $|S3\rangle \rightarrow |A3\rangle$, and the rate of electron transfer out of $|A3\rangle$ must be greater than rate of electron transfer into $|A3\rangle$. In other words, $|A3\rangle$ can never act as an electron trap state in the two-step mechanism as long as it resides above the conduction band minimum. A higher energy state such as $|S4\rangle$ could only efficiently transfer electrons to $|A3\rangle$ if the electron transfer rate were competitive with nonradiative relaxation in the conduction band, which is unlikely. $|A3\rangle$ can only act as a trap state if electron transfer to the conduction band is slow compared to the direct optical excitation rate and the rate of diffusion of the molecule away from the surface.

On the other hand, a state such as $|A1\rangle$, which resides in the band gap, can act as an effective trap state. Electron transfer from $|A1\rangle$ into the conduction band is slow because of the need for thermal activation to go back up to the conduction band at higher energy. The rate of electron transfer to the valence band is low because of the low density of empty states in the valence band.

On the basis of these considerations, I constructed a model based on photochemistry induced by two competing processes: (1) direct photoexcitation by internal photoemission and (2) charge transfer via the conduction band by electrons that have relaxed to the conduction band minimum. The rate of photochemistry is determined by the concentration of holes at the surface. Holes are produced by photoexcitation and lost by recombination. Assuming that the only holes to react are those that are made free of recombination by removal of the excited electron by direct internal photoemission or charge transfer, the yield is represented by the sum of these two contributions

$$Y(\lambda_{ex}, E_{red}, \lambda_e, E_C) = R_{direct,ox}(\lambda_{ex}) + R_{inj}(E_{red}, \lambda_e, E_C) \quad (8)$$

The rate of direct excitation of the particular oxidant ox depends on the excitation wavelength λ_{ex}. To minimize the number of parameters in the model, this rate is taken to be a constant R_{direct}. Although this may seem a severe approximation, note that a sufficiently small λ_{ex} will always be able to make a resonant transition from an appropriate initial state in the valence band and that Huck and Buriak utilized a white light source for irradiation. Monochromatic irradiation of the surface would be more likely to produce values of R_{direct} that vary from one species to the next as expected according to the resonance and density of states dependences in eq 2. Because the lifetime of electrons excited high in the conduction band is so short, $R_{inj} = 0$ for any state above the conduction band minimum ($E_{red} < E_c$). Therefore, the yield of species i relative to dodecene is

$$Y_{rel} = \frac{Y_i}{Y_d} = \frac{R_{direct} + R_{inj,i}}{R_{direct}} = 1 + R_{inj,i}/R_{direct} \quad (9)$$

Substituting from eq 6 and further limiting the number of parameters by assuming $k_{max} = 5 \times 10^{-25}$ m^4 s^{-1} and λ_e is the same for the solvated oxidants, a two-parameter model is obtained to fit the relative yield data of Huck and Buriak (Figure 2).[20] The result is an excellent fit with $R_{direct} = (5.2 \pm 1.2) \times 10^{26}$ m^{-2} s^{-1} and $\lambda_e = 1.1 \pm 0.06$ eV. The fit was weighted by the reported experimental uncertainty and uncertainties of fit parameters are reported at 95% confidence limits.

Recall that the band gap and E_C depend on the nanocrystallite size. This engenders the self-limiting nature of Si etching in acidic fluoride solutions that leads to nanostructure

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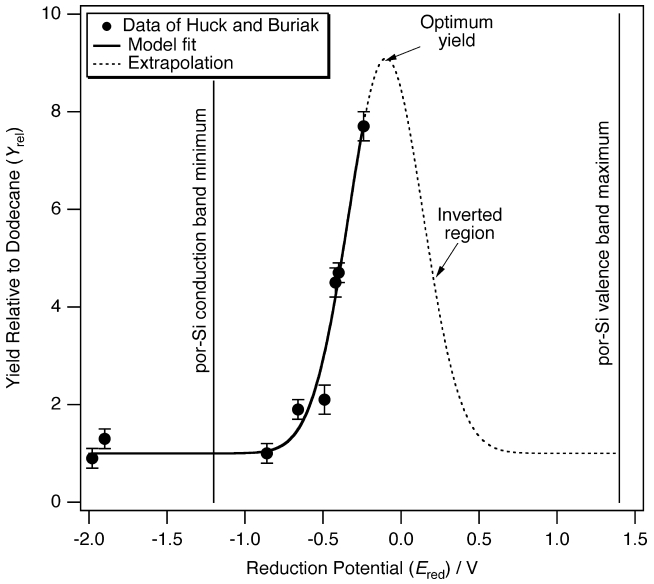

Figure 2. The result of a weighted fit of eq 9 to the data of Huck and Buriak.[20] The conduction band minimum and valence band maximum positions indicated are for the case of por-Si referenced in the text. After attaining the optimal rate constant, the yield is predicted to plunge in the inverted region.

formation.[41] Therefore, it is possible not only to tune the rate of photoinduced electron transfer from the conduction band to $|A1\rangle$, but also to tune this according to the size of the nanocrystalline Si object (pore wall or nanocrystal) that is in contact with the molecular acceptor level. The rate of electron transfer is tuned by choosing E_{ox} and λ_e appropriately because the optimal electron transfer rate occurs at

$$E_C - E_{ox} + \lambda_e = 0 \quad (10)$$

As noted above, the band gap of c-Si corresponds to the energy of a photon with wavelength λ_{gap} = 1110 nm, but for por-Si, λ_{gap} = 480 nm. Therefore, by choosing blue or UV light, we can excite electrons across the band gap of all nanocrystallites in a sample. Alternatively, by choosing a redder wavelength, we can preferentially excite only the larger nanocrystals.

A molecule with E_{ox} = −0.2 V and λ_e = 1.0 eV would accept electrons from the por-Si at the optimal rate. However, since it is resonant with the conduction band, it would be a poor trap state for c-Si. This molecule would very effectively enhance the photo reactivity of small nanocrystals but do much less to enhance the reactivity of large crystallites and flat Si surfaces.

A molecule with E_{ox} = +0.78 V and λ_e = 1.0 eV would accept electrons from the c-Si at the optimal rate but would lie in the inverted region for por-Si, thus acceping electrons at a much lower rate. Consequently, we can bias reactivity toward flat surfaces or larger crystallites or to smaller crystallites by choice of excitation wavelength and by choice of the acceptor molecule.

CONCLUSIONS

Internal photoemission can be quite effective at promoting photoreactivity, especially not only when the acceptor level resides in a band gap, but also when the level is strongly optically coupled to the valence band. Diamond is an exceptionally well-suited material because of its extremely wide band gap and a vacuum level positioned below the conduction band minimum. Indeed, Hamers and co-workers have exploited this for efficient covalent modification of diamond and other carbonaceous surfaces.[27,28] A two-step photoexcitation/charge transfer mechanism is most efficient when the acceptor level resides in a band gap, which quantitatively explains the results of Huck and Buriak.[20] Monochromatic excitation may lead to more complex behavior of the direct photoexcitation rate than implied in eq 9. Nonetheless, with judicious choice of the excitation wavelength, redox potential of the acceptor level and the reorganization energy of the acceptor molecule, it is possible to construct photochemical surface modification schemes that will size selectively react with nanocrystalline Si.

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Notes

The authors declare no competing financial interest.

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