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# UV-Induced Grafting of Alkenes to Silicon Surfaces: Photoemission versus Excitons

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Molecular layers on silicon are of intense interest for their ability to control the chemical, physical, and electronic properties of surfaces.[1,2] One commonly used method for preparing such layers involves reacting a terminally unsaturated organic molecule with a Si surface that has been passivated with a layer of hydrogen. The subsequent reaction to graft the molecule to the surface is typically initiated by radical initiators, heat, or light.[3−12] The photochemical grafting of alkenes[7−12] is particularly attractive because the reaction produces densely packed, stable molecular films and provides a means for direct photopatterning of specific functional groups[8] that can be used to link biomolecules[13−15] and other more complex molecular structures to silicon surfaces.

Despite the many studies concerned with photochemical functionalization of Si−H, the mechanism(s) of monolayer formation have remained unclear. The mechanism is generally partitioned into an initiation step and subsequent propagation. Studies of the latter have suggested that radicals are likely involved.[16−20] However, the initiation step remains controversial. Studies of nanoporous silicon using visible light suggested an exciton mechanism in which light produces electron−hole pairs, with the holes inducing nucleophilic attack by the alkenes. (This mechanism is hereafter called the *exciton mechanism*). Other studies have suggested that UV excitation is able to cleave Si−H bonds to produce surface radicals.[9] However, studies using radical traps found no evidence for surface radicals but did find that grafting could also be initiated slowly using visible light.[11,12,19,21] Theoretical studies have suggested that localized electronic excitations play a role.[20]

*Here we show that the photografting efficiency on Si using UV light is independent of the photoexcited carrier lifetime, which cannot be explained by the exciton mechanism.* We further show that there are differences in reactivity among 1-alkenes having different functional groups at the distal end that cannot be explained by previous mechanisms but are consistent with a photoemission mechanism similar to that recently detected on diamond[22] using sub-bandgap illumination. *These studies present new mechanistic insights into the photochemical functionalization of Si surfaces and suggest that photoemission is a previously unrecognized mechanism for initiating grafting of alkenes to silicon using UV light.*

Float-zone (FZ)-purified Si(111) substrates were used in all of the experiments. We intentionally introduced Au as a dopant into some of the FZ samples to reduce the bulk carrier lifetime,[23−25] as described in the Supporting Information (SI). All of the samples were cleaned by exposure to ozone, then etched in 48% HF for 1 min followed by 40% $NH_4F$ for 15 min, and finally rinsed with deionized water. (**Caution!** *HF is highly dangerous and must be handled with extreme care.*) Liquid reagents were continually purged with Ar. This procedure yielded very flat H-terminated Si ("H−Si") surfaces, as verified by X-ray photoelectron spectroscopy (XPS). Atomic force microscopy images showed very flat surfaces with root-mean square roughnesses of 0.17 and 0.22 nm over 1 μm × 1 μm regions for the H−Si and gold-doped H−Si ("H−Si/Au") samples, respectively. To graft alkenes to the surfaces, the H−Si samples were covered with a layer of argon-purged reactant, covered with a fused silica window, and illuminated with UV light (254 nm, ~10 mW/cm$^2$) in a sealed cell under dry, oxygen-free conditions. Three alkenes were investigated (Figure 1): trifluoroacetic acid-protected 10-aminodec-1-ene (TFAAD, Almac Sciences), 10-*N*-Boc-aminodec-1-ene (tBoc, Astatech, Inc.), and 1-dodecene (Fluka, ≥99.8%). TFAAD and tBoc were purified by vacuum distillation. After reaction, the samples were sonicated in chloroform, ethanol, and methanol and then dried under $N_2$.

We measured the lifetimes of photoexcited carriers in H−Si and H−Si/Au samples using transient microwave reflectivity, as shown in the SI. These measurements yielded lifetimes of 25 μs for H−Si and 0.3 μs for H−Si/Au, confirming that Au doping reduces the lifetime of photoexcited carriers by a factor of ~100.

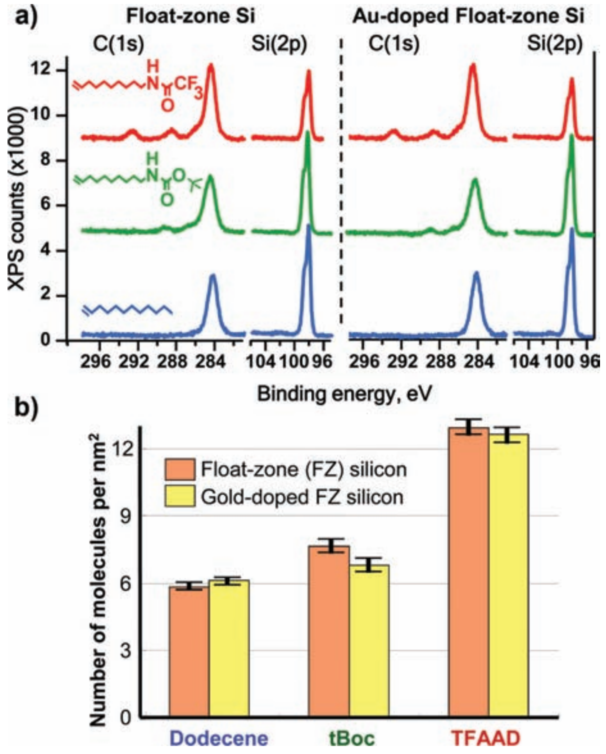

***Figure 1.*** (a) XPS spectra comparing grafting with three different molecules onto H-terminated samples of (left) FZ Si and (right) Au-doped FZ Si. (b) Resulting numbers of molecules per unit area.

Figure 1a shows C(1s) and Si(2p) XPS spectra comparing the grafting of these three molecules onto regular (H−Si) and gold-doped (H−Si/Au) Si samples after 15 min. The spectra confirmed successful grafting of all three molecules. No features were evident at 102−106 eV in the Si(2p) spectrum, demonstrating that surface

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oxidation was negligible. Control samples that were not illuminated (see the SI) showed no significant grafting. XPS peak areas were used to calculate the numbers of molecules per unit area, yielding the results in Figure 1b. Analysis procedures and inelastic scattering corrections are described in the SI.

Figure 1 demonstrates two important facts: First, for each molecule investigated, the absolute grafting efficiency on Au-doped Si is nearly identical to that on the pure FZ Si. Second, there are differences in reactivity between alkenes with different groups at the distal end. These molecule-dependent differences in reactivity were further verified using IR spectroscopy measurements, as shown in the SI.

The comparison of regular and Au-doped samples allowed us to immediately rule out the bulk exciton mechanism as the primary pathway. In an exciton mechanism, the steady-state concentration of photoexcited carriers scales inversely with the lifetime of those carriers. We measured a 100-fold difference in the lifetimes of the pure and Au-doped samples, implying that under illumination these samples should have a 100-fold difference in photoexcited carrier concentration. However, they showed nearly *identical* reactivity.

The differences in the reactivities of the three different molecules of similar size imply that the functional group at the distal end plays a role not explained by previous mechanisms. XPS and FTIR data show that both H−Si and H−Si/Au react most efficiently with TFAAD, followed by tBoc and 1-dodecene. Notably, this trend is identical to that observed on amorphous carbon and diamond surfaces and correlates with the electron affinity of the molecules predicted using density functional theory.[26] In contrast, the previously proposed exciton mechanism and Si−H homolytic cleavage mechanisms predict that all alkenes of similar size should react with the same efficiency.

We explain our results by noting recent studies showing that grafting of alkenes to diamond can be initiated by photoemission of electrons from the surface into electron-acceptor levels of the adjacent alkenes. In the case of diamond, the very large bandgap (5.5 eV) precludes creation of excitons, so even a relatively inefficient process such as photoemission can play a dominant role. *Our results here suggest that photoemission can also dominate as an initiation process with smaller-bandgap semiconductors, such as silicon, in which both exciton and photoemission pathways are possible.*

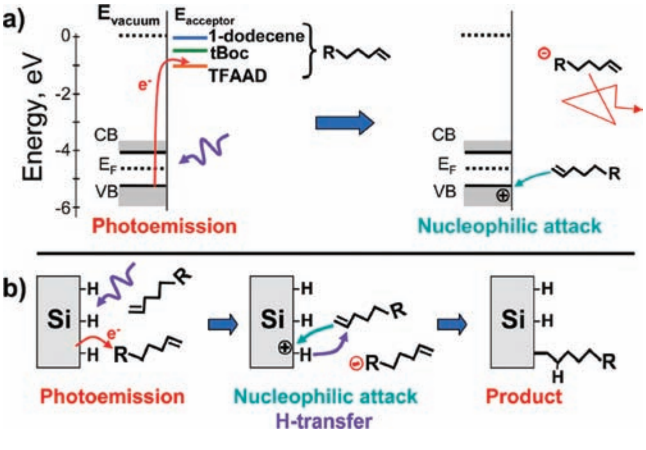

***Figure 2.*** Photoemission mechanism for UV-initiated grafting of alkenes to H-terminated Si surfaces: (a) photoemission to an acceptor level followed by nucleophilic attack by the C=C group of a second alkene; (b) overall result of the grafting reaction. Acceptor levels in (a) are from refs 26 and 22.

Figure 2 illustrates the likely reaction pathway. UV light initiates photoemission from Si into the acceptor groups of the reactant molecules or another electron acceptor. This leaves a valence-band hole that facilitates nucleophilic attack by the alkene group. While both the photoemission and exciton mechanisms involve creation of a valence-band hole, there are important distinctions that affect the efficiency of grafting. In the exciton mechanism, the concentration of holes at the surface is strongly reduced by bulk and surface recombination processes. In contrast, photoemission leaves the sample with a net positive charge from *persistent* holes that do not have corresponding conduction band electrons with which to recombine. Thus, the grafting efficiency is unaffected by recombination, and the sample can be restored to neutrality only by inducing an oxidation reaction at the surface.[22]

In the case of silicon, our results suggest that at short wavelengths, where photons can excite electrons to acceptor levels of the reactant molecules, photoemission is more efficient than the exciton mechanism, even though both are energetically possible. At longer wavelengths, it is likely that only the exciton mechanism can take place. Thus, the precise mechanism of grafting depends on the wavelength and electronic structure of the molecules. A key point is that because photoemission is essentially irreversible, it may be a very effective way of initiating surface grafting reactions on Si and other materials.

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**Supporting Information Available:** Procedures for Au doping of Si samples; microwave reflectivity measurements of carrier lifetimes; XPS data analysis procedures, including inelastic scattering corrections; dark control experiments; and IR measurements confirming molecule-dependent reactivity. This material is available free of charge via the Internet at http://pubs.acs.org.

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