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Photochemical Attachment of Organic Monolayers onto H-Terminated Si(111): Radical Chain Propagation Observed via STM Studies

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The formation of covalently attached monolayers on hydrogen-terminated silicon (H-Si) surfaces has been a topic of increasing interest over the past decade.¹ One of the major reasons for this is the possibility to functionalize the surface in a tailor-made fashion using the toolbox of synthetic organic chemistry.² This allows, for example, the attachment of bioactive moieties, such as DNA fragments,³ at a distance of less than 2 nm from bulk or porous Si, which opens up various possibilities for sensing and other optoelectronic applications.⁴ Recently, a mild method compatible with the fragility of biomolecules and which relies on the general procedure depicted in Figure 1 was reported by two of us.⁵ In this scheme a simple fluoride-induced etching step is followed by irradiation of a mesitylene solution of a ω -functionalized 1-alkene or 1-alkyne with visible light (e.g., 447 nm). By using this procedure it has, for example, been possible to attach labile sialic acid derivatives onto H-Si(100).⁶

For this reaction an exciton-based mechanism was proposed,⁵ similar to that advanced for the visible-light attachment of 1-alkenes onto porous silicon.⁷ This hypothesis was made on the basis of the observation that organic monolayers were formed more easily on n-type Si than on p-type Si, in analogy to observations made for attachment onto partially iodinated H-Si.⁸ However, apart from these observations little other mechanistic information is available. A significant open question is whether the attachment proceeds via a propagating radical chain reaction. Such a radical chain mechanism was shown to be operative for the reaction of styrene onto H-Si(111) and H-Si(100) under ultrahigh vacuum (UHV) conditions.^{9,10} It was shown that isolated dangling bonds (created by incomplete hydrogenation or by the STM tip) could react with styrene molecules in the gas phase (at pressures in the range 10^{-6} – 10^{-9} Torr) to create nanostructures of ~ 20 – 80 molecules per initial reactive site. As the growth process is controlled by the geometry of the surface, these chain reactions lead to the growth of straight lines on Si(100)⁹ and irregularly shaped islands on Si(111).¹⁰ However, it is not clear, a priori, that the mechanism operative in UHV is relevant for the wet chemical photochemical attachment reactions. Here we present STM and HREELS data on partially reacted H-Si(111) surfaces, providing further insight into the mechanism of these reactions.

Samples with a partial monolayer were obtained by irradiation (447 nm; Jelight pen lamp; 3 mW/cm² at 0.5 cm from the substrate; Ar atmosphere) of H-Si(111) samples immersed in a solution of 1-decene (doubly distilled, 0.2 M) in mesitylene for times insufficient to obtain complete coverage (<10 h), followed by extensive rinsing with 1,1,1-trichloroethane. The progress of the reaction was followed by inserting these samples into a UHV system equipped with STM (Omicron STM1) and HREELS (LK3000). Once in

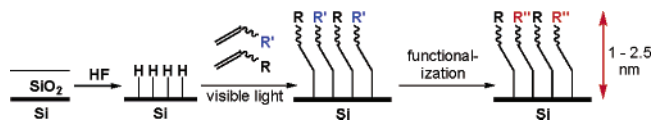


Figure 1. Visible-light attachment of functionalized monolayers onto silicon surfaces.

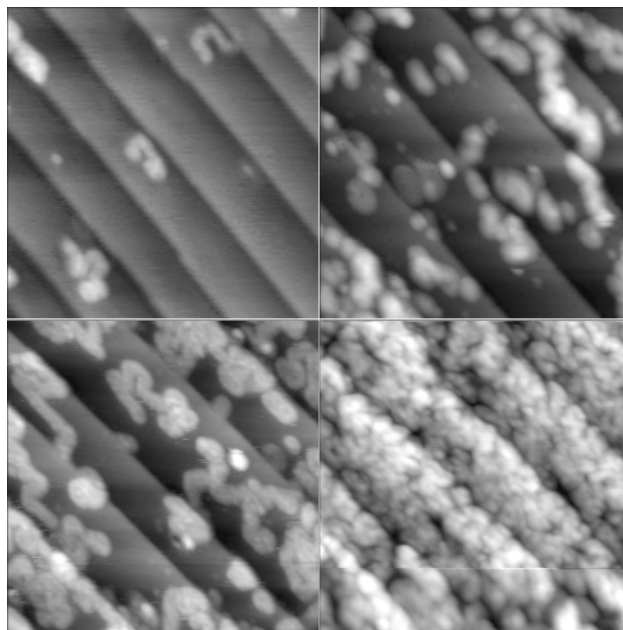


Figure 2. STM images ($400 \times 400 \text{ \AA}^2$) of incompletely covered H-Si(111) surfaces upon irradiation (447 nm) of a Si wafer in a 1-decene solution for 3 (top left), 15 (top right), 30 (bottom left), and 120 (bottom right) min. Images were acquired at 20 pA and sample biases of -2.7 to -3.8 V.

UHV, the samples were gently heated to ~ 100 – 200 °C to remove any residual physisorbed contaminants from the surface. Resulting STM images are presented in Figure 2.

As is obvious from the images in Figure 2, monolayer attachment of 1-decene proceeds via the formation of islands. Furthermore, the irregular, meandering shape of the islands suggest that these structures were formed by a process analogous to the self-avoiding, near-random walk radical chain mechanism proposed for UV-light-induced monolayer attachment.¹¹ Similar images were also obtained for photochemical reactions using styrene, although the islands in this case appear to be less extended. It is also clear from the images that longer irradiation times lead primarily to the nucleation of more islands rather than growth of larger islands. This is in agreement with island nucleation being the rate-limiting step along with the self-limiting nature of the subsequent chain reaction.^{10,11}

The progress of the attachment reaction has also been monitored with high-resolution electron energy loss spectroscopy (HREELS).

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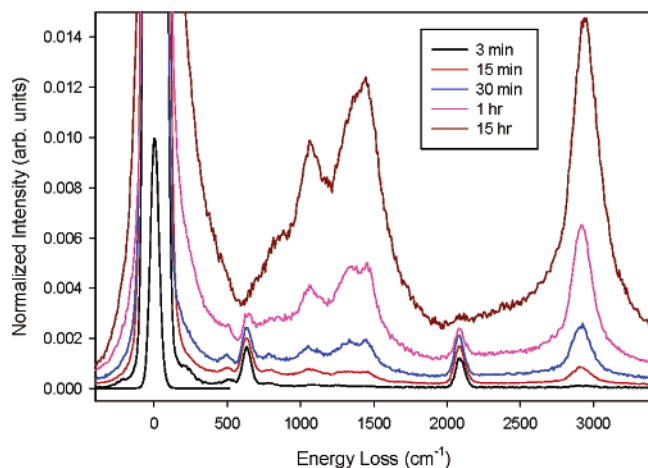


Figure 3. HREEL spectra (normalized to the elastic peak intensity) of visible-light (447 nm)-induced attachment of 1-decene on H-Si(111) after various irradiation times. The incident electron energy was 6 eV, and the elastic peak intensities were in the range of 10^4 – 10^5 cps.

HREEL spectra taken of partially 1-decene covered H-Si(111) samples are presented in Figure 3. At the start of the reaction strong peaks at 626 and 2085 cm^{-1} are visible, due to Si-H bending and stretching vibrations, respectively. These peaks decrease with increasing irradiation times.¹² At the same time the strong peaks growing in at 1060, 1360, 1440, and 2920 cm^{-1} can all be attributed to various modes associated with alkyl chains.¹³ In combination this set of data clearly confirms the gradual growth of the organic monolayer. Interestingly, the elastic peak intensity is found to be a measure of the atomic scale “roughness” of the surface. This intensity decreases by more than an order of magnitude as the monolayer grows in, reflecting increased nonspecular scattering from the partial monolayers. After reaching a minimum for irradiation times of ~ 1 h the elastic peak intensity begins to increase again as the monolayer is completed.

STM measurements at the earliest stage of the reaction facilitate the determination of the efficiency of the photochemical initiation. With a 3 mW cm^{-2} light flux at 447 nm, the photon flux adsorbed by the sample is $\sim 5 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$. Since ~ 10 islands are observed in a $500 \times 500 \text{ \AA}^2$ area after 3 min, the island nucleation rate is $\sim 2 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$. This implies each photon has $\sim 4 \times 10^{-7}$ probability of nucleating an island. Therefore, the initiation of the attachment reaction is a rather low-efficiency process.

While the data presented here confirm that monolayer growth occurs through a radical chain mechanism, it is not clear how the reaction is initiated. The UV-light-induced reaction has been proposed to start with the light-induced homolytic bond cleavage of Si, for which an energy of >3.4 eV (i.e. light of < 365 nm) is required.^{11,14} Since the visible-light-induced attachment employed here is initiated with photons of significantly less energy, homolytic bond cleavage can be excluded as the starting point for the reaction. Additionally, the 1-decene does not absorb any 447 nm light. Given the range of wavelengths (up to at least 700 nm)¹⁵ observed to initiate this reaction, it is therefore likely that photoexcitation of the Si wafer itself leads to reactive sites.

Plausible initiation mechanisms that can account for the available experimental data include exciton-based schemes involving surface-

localized holes which facilitate attack of the alkene nucleophile, resulting in the formation of Si-C bonds.^{5,7,8} However, given the low efficiency of the initiation process it is difficult to completely rule out the role of light-induced generation of radical species from impurities in solution (even given the highly pure reactants used here). Whatever the initiation event, it must involve the eventual formation of a carbon-centered radical on the attached alkene. This radical can then abstract a hydrogen atom from a nearby Si-H site, yielding a silicon radical which becomes a new reactive site for alkene attachment, leading to the chain reaction.

In summary, the mild photochemical attachment of organic monolayers onto H-Si proceeds via a gradual formation of monolayer islands. This is in agreement with a rate-determining initiation step (possibly involving the formation of surface-localized holes) yielding a propagating radical chain reaction and resulting in the growth of irregularly shaped islands. Interestingly, this means that this surface reaction proceeds similarly under both well-controlled UHV conditions and intrinsically much less controllable solution-phase conditions. Future work, involving exploration of how the initiation rate depends on wavelength as well as on the substrate doping type and density, is expected to shed further light on the nature of the initiation mechanism.

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