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## Evidence for Initiation of Thermal Reactions of Alkenes with Hydrogen-Terminated Silicon by Surface-Catalyzed Thermal Decomposition of the Reactant

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New insights into the mechanism of thermal reactions of alkenes with hydrogen terminated silicon are presented. Scanning tunneling microscopy (STM) imaging at the early stages of the reaction of 1-decene with H/Si(111) at 150 °C confirm this reaction occurs via a propagating radical chain mechanism. In addition, evidence is presented for an initiation mechanism involving degradation of hydrocarbon molecules catalyzed by the silanol surface of Schlenk tubes commonly used in carrying out these reactions. Hydrogen-terminated silicon surfaces are found to be unstable in the "inert" solvent dodecane when heated at 150 °C in a Pyrex Schlenk tube. By contrast, the surfaces were significantly more stable at the same temperature when reactions were carried out in Teflon (polytetrafluoroethylene or PTFE). The thermal reaction of decene with H/Si(111) was found to proceed more rapidly in Pyrex than in PTFE, consistent with an impurity-based initiation mechanism.

#### Introduction

Interest in the molecular functionalization of hydrogenterminated silicon (Si–H) surfaces has grown rapidly since first reported by Linford and Chidsey,<sup>1</sup> largely due to envisaged applications in molecular electronics<sup>2–8</sup> as well as chemical and biological sensing.<sup>9–11</sup> Despite the considerable number of publications concerned with organic functionalization of Si–H in the 15 years since the initial report, questions surrounding the mechanism(s) responsible for monolayer formation remain unresolved. While scanning tunneling microscopy (STM) studies have confirmed that photochemical reaction,<sup>12</sup> as first proposed by Chidsey and co-workers,<sup>13</sup> the mechanism by which this reaction is initiated is a matter of ongoing debate. In the original report of monolayer

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formation, the reaction was initiated by the thermal decomposition of peroxy compounds. Subsequent reports revealed that alkenes would react in the absence of intentionally introduced initiator under both thermal<sup>13–15</sup> and photochemical initiation.<sup>16–18</sup>

While initially it was suggested that the thermal and photochemical processes led directly to Si–H bond breaking, this is inconsistent with existing data on the thermal and photochemical stability of the Si–H bond. The observation that visible light<sup>19–21</sup> could be used to initiate the reaction further ruled out direct photocleavage of the Si–H as the sole operable mechanism, as in this case the photons lack sufficient energy to break the Si–H bond. Studies of gas-phase photochemical reaction<sup>22</sup> of alkenes with Si–H have implicated alkyl radicals produced via photolysis of the alkenes as the initiating species, although this requires photons of wavelengths less than 200 nm. In the case of thermal reactions, trace oxygen is a possible initiator, as the abstraction of hydrogen by molecular oxygen to create a silyl radical has been observed in the molecule tris(trimethylsilyl)silane.<sup>23</sup> However, the

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activation energy for this process on the H–Si(111) surface has been calculated to be ~130 kJ/mol,<sup>24</sup> implying that this pathway can only account for reactions at temperatures exceeding 100 °C. Additional mechanisms are required to account for recent reports of spontaneous reactions (at room temperature, in the dark) of alkynes with the H-terminated surface.<sup>25,26</sup>

In this paper we present new insights into the mechanism for the thermal reaction of alkenes with H/Si(111). STM imaging of surfaces at the early stage of reaction clearly confirm that the thermal reactions at 150 °C do indeed proceed via the radical chain mechanism as for the photochemical reactions. Furthermore, the nature of the reaction vessel used to carry out the surface modification is found to play an important role in influencing the rate of reaction and the monolayer quality. Even supposedly unreactive alkanes are shown to react with the Si-H surface under thermal (150 °C) conditions in a Pyrex Schlenk tube. By contrast, when the thermal reaction is carried out in a Teflon (polytetrafluoroethylene or PTFE) vial, the reactivity is significantly reduced. The type of reaction vessel is also found to influence the reaction of alkenes with Si-H. Although the reaction proceeds more rapidly in Pyrex, the resultant monolayer quality was higher when the reaction was carried out in PTFE. These results provide evidence for an additional initiation mechanism involving catalytic decomposition of the hydrocarbons on the surface of the glass Schlenk tube, resulting in the formation of reactive intermediates that in turn produce the silicon dangling bonds necessary to initiate the radical chain reaction.

#### **Experimental Details**

**Materials.** ATR silicon crystals  $(25 \times 4.5 \times 1 \text{ mm}^3)$  were purchased from Harrick, and the silicon wafers were obtained from Virginia Semiconductor. Cleaning and etching solutions were clean-room grade. Sulfuric acid, 96% (H<sub>2</sub>SO<sub>4</sub>), and ammonium fluoride, 40% (NH<sub>4</sub>F), were purchased from J. T. Baker; hydrochloric acid, 30% (HCl), and ammonium hydroxide, 30% (NH<sub>4</sub>OH), were from Olin Microelectronic Materials; hydrogen peroxide, 30% (H<sub>2</sub>O<sub>2</sub>), was from Anachemica; and hydrofluoric acid, 48% (HF), was from Arch. Milli-Q water (18 M $\Omega$ ) was used for all experiments. 1-Decene (94%) and dodecane (99%) purchased from Aldrich were purified by filtration through a pad of Florisil (100-200 mesh from Aldrich) and then vacuum distilled at 5-10 mmHg (1-decene at 38-40 °C, dodecane at 80 °C). Silicon shards and attenuated total reflectance (ATR) elements were cleaned after reactions in a Soxhlet Extractor under argon with continuously refluxing 1,1,1-trichloroethane (TCE) purchased from Aldrich.

Surface Characterization. Scanning Tunneling Microscopy. STM images were obtained in constant current mode using an Omicron STM1 system operating in an ultrahigh vacuum system (base pressure  $< 1 \times 10^{-10}$  torr). The system is also equipped with a high-resolution electron energy loss spectrometer (HREELS), enabling characterization of the chemical state of the sample. Samples prepared in solution were transferred to the vacuum system via a load-lock. Once in vacuum, the samples were heated to 200 °C to remove physisorbed contaminants and facilitate stable imaging.

Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR). ATR-FTIR spectra were recorded using a Nicolet 6700 FTIR spectrometer at  $4 \text{ cm}^{-1}$  resolution. The ATR crystals were mounted in a purged sample chamber with the light focused normal to one of the 45 ° bevels. Background spectra were obtained using an oxidized surface.

Surface Wettability Measurements. Surface wetting properties were measured with a contact angle goniometer (model: Cam-Micro, Tantec, Inc.) under ambient conditions (18-22 °C, 50-60% relative humidity) using a collimated horizontal light beam to illuminate the liquid droplet.

Thickness Measurements. The thickness of organic monolayers were estimated using a Gaertner model L116S singlewavelength (633 nm) ellipsometer at an angle of incidence of 70°. The thickness was obtained using a two-layer model with n = 1.46 as the refractive index of the monolayer and the silicon substrate described by n = 3.85 and k = 0.02.

Surface Photovoltage (SPV) Measurements. A scanning Kelvin probe (KP Technology Ltd., Wick, Scotland) was used to measure the SPV, which provides a direct measure of bandbending (the difference in surface potential in the dark and under illumination). A white light fiber optic source was used to illuminate the surface; the light was determined to be of sufficient intensity to saturate the photovoltage. A motorized stage was used to scan the sample, allowing measurement of the SPV at 16 spatially distinct points to be collected per sample.

**Surface Preparation.** Cleaning and Hydrogen Termination. Single-sided silicon crystals were used once and discarded. ATR elements were cleaned and reused. All crystals were cleaned with piranha solution (3:1 H<sub>2</sub>SO<sub>4</sub>, 96%: H<sub>2</sub>O<sub>2</sub>, 30%) at 120 °C for 30 min, then rinsed with Milli-Q water. (Warning: Piranha solutions should be handled with care and kept isolated from organic materials.) ATR elements were then cleaned with 4:1:1 Milli-Q water/30% NH<sub>4</sub>OH/30% H<sub>2</sub>O<sub>2</sub> at 80 °C for 15 min, rinsed with Milli-Q water, and heated in 4:1:1 Milli-Q water/30% HCl/30% H<sub>2</sub>O<sub>2</sub> at 80 °C for 15 min then rinsed with Milli-Q water. Samples were hydrogen terminated by etching in degassed ammonium fluoride for 15 min followed by a brief rinse in deaerated Milli-Q water.

*Monolayer Formation.* Samples were cleaned and etched then dried using a stream of nitrogen and immersed in a deoxygenated solution of either 1-decene or dodecane in a Pyrex Schlenk tube or PTFE screw cap vial (equipped with PTFE inlet and outlet tubing through the cap) under continuously bubbling argon. The Schlenk tube and PTFE vials had 2 cm outer diameters and contained 4 mL of liquid; after bubbling at room temperature for 10 min, the reaction vessels were place in an aluminum heating block at 150 °C for the desired time. The vials were cooled to room temperature, and the samples were removed from the reaction vessel, washed with TCE in a Soxhlet for 20 min, and dried under a stream of nitrogen.

#### **Results and Discussion**

Figure 1 shows STM images taken at the early stages of the thermal reaction of decene with H-terminated Si(111). Clearly visible in Figure 1a are several monatomic height steps, separated by atomically flat terraces. On these flat terraces, several irregularly shaped islands with nominal heights of 4-5 Å are observed. HREEL spectra on this sample (not shown) confirm the presence of a submonolayer coverage of alkyl chains on the H–Si(111) surface, allowing the islands to be attributed to assemblies of decyl chains. Figure 1b shows a smaller area scan of a different region on the same sample showing a close up view of one of these island structures. The observation of the growth of irregularly shaped islands is consistent with the reaction proceeding via a propagating radical chain mechanism, as seen previously for

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**Figure 1.** UHV STM images of partially reacted (5 min. at 150 °C) H-terminated Si(111) surfaces: (A) 26 nm<sup>2</sup> image obtained at 43 pA with a sample bias of -2.6 V; (B) 12 nm<sup>2</sup>, 43 pA, -3.2 V.

photochemical reactions under solution or gas phase conditions.<sup>27,28</sup> In this mechanism, an alkene molecule reacts at an initiation site (Si dangling bond) via formation of a covalent silicon carbon bond, resulting in the formation of a radical on the  $\beta$ -carbon, which can abstract a hydrogen from an adjacent Si–H bond, creating a new dangling bond that reacts with an alkene, thus propagating a chain reaction.<sup>13</sup> On the H–Si (111) surface, this propagating chain reaction proceeds via a pseudo random walk process.<sup>17,28</sup>

Although the STM images confirm that the reaction proceeds via the radical chain mechanism, the question remains as to how the reaction is initiated (i.e., the origin of the initial dangling bond that starts the chain process). Although initially it was suggested that this could occur by thermally induced Si-H bond cleavage,<sup>13,29</sup> this scenario is unlikely in view of existing data on the thermal stability of this bond. Heating a H-terminated silicon surface in the absence of impurities will result in desorption of molecular hydrogen (generating pairs of dangling bonds). On the basis of the measured activation energy for this process ( $\sim 2.6 \text{ eV}$ ),<sup>30,31</sup> we can estimate that generation of dangling bonds at 150 °C is negligible. Therefore, it is highly likely that other mechanisms for silicon radical generation are responsible for initiating the reaction. As discussed in the introduction, molecular oxygen has been suggested as a possible initiator.<sup>24,32</sup>

We recently reported on the reaction of oxidized silicon surfaces with alkenes, observing signals in the X-ray photoemission spectrum corresponding to oxidized hydrocarbon.<sup>27</sup> In this study the thermal reaction of 1-decene with oxidized silicon surfaces was found to be consistent with Markovnikoff addition of the alkene to the silanol at lower temperature (80 °C and ~35 °C in the Rayonet photoreactor) and anti-Markovnikoff at higher temperature (150 °C). The X-ray photoemission spectrum of the high-temperature reaction showed evidence for the presence of carboxylic acid groups, indicating that the organic material had been oxidized. Hydroxylated surfaces (typically silica–alumina, which are more acidic) are well-known catalysts for cracking hydrocarbons, producing highly reactive intermediates.<sup>33</sup> To investigate the feasibility of an oxide-induced degradation of alkyl chains, the

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**Figure 2.** ATR-IR spectra of (A) a freshly etched Si-H surface, and (B) a Si-H surface after 1 h immersion in dodecane at 150 °C in a Pyrex vial and (C) after 1 min in 2% HF.

stability of H-terminated Si(111) in the "inert" solvent dodecane was investigated. The surface is expected to be unreactive in this solvent in the absence of a dedgradation pathway.

Figure 2 shows the ATR-FTIR spectrum of the H-terminated surface upon exposure to deaerated dodecane in a Pyrex Schlenk tube at 150 °C. The freshly etched sample (Figure 2a) shows a sharp peak at 2083 cm<sup>-1</sup> corresponding to the terrace Si-H monohydride stretch, along with a small amount of hydrocarbon contamination indicated by the C-H stretches observed in the 2800-3000 cm<sup>-1</sup> range. However, after reaction with dodecane for 1 h at 150 °C (Figure 2b), the Si-H peak is completely eliminated, and the growth of significant peaks in the C-H stretch region is observed. The spectra clearly indicate the alkylation of the surface under these conditions, presumably from the dodecane solvent. In contrast to the alkyl monolayers formed from the reaction of alkenes with H/Si(111), the alkylated surface from the dodecane reaction is unstable to etching in HF. After 1 min in 2% HF (Figure 1c), the hydrocarbon signal is significantly reduced, and Si-H modes are once again observed in the region from 2080 to 2150  $\text{cm}^{-1}$ . The removal of the hydrocarbon in HF is consistent with the alkyl chains being attached to the surface via an Si–O–C link, while the presence of multiple modes in the Si-H region (indicative of the formation of dihydride species) indicates that the initial reaction had also led to a significant amount of oxygen insertion into Si-Si backbonds. For the alkane to react with the Si-H surface, the organic must have been degraded elsewhere in the reaction vessel and then subsequently reacted with the surface. Given the propensity for hydroxyl groups to crack hydrocarbons noted above, the surface of the Pyrex Schlenk tube was implicated as the likely source of the dodecane degradation. Gas chromatography (GC) analysis of the solvent following the reaction did not show any changes in chemical composition. However, it should be noted that the exceedingly small concentrations of reactive intermediates are sufficient to degrade pristine Si-H surfaces.

To test the idea that it was the Pyrex surface that was responsible for the reaction on the silicon surface, the dodecane experiment was repeated in a Teflon (PTFE) vial. Figure 3 shows representative ATR-FTIR spectra for the reaction of a Si–H surface in dodecane using a PTFE vial. While the starting freshly etched Si–H surface exhibits the same characteristic 2083 cm<sup>-1</sup> peak, the spectrum after

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**Figure 3.** ATR-IR spectra of (A) a freshly etched Si-H surface and (B) a Si-H surface after 1 h immersion in dodecane at 150 °C in PTFE vial.

reaction is substantially different. Even after heating for 1 h in dodecane, the peak remains at approximately 70% the intensity of a freshly etched sample, and only minimal accumulation of hydrocarbon is apparent. Since no attempts were made to rigorously exclude oxygen (e.g., freeze-pump-thaw, or conduct reaction in a glovebox), the observed hydrocarbon accumulation could be due to trace oxygen or impurities. This provides evidence that silanol groups on the surface of Pyrex introduce additional degradation pathways for the hydrocarbon, which in turn can initiate a surface reaction.

Given these unexpected results, it was important to investigate the impact of reaction vessel on the reaction of alkenes with the Si-H surface. The properties of monolayers formed via thermal reaction of 1-decene for 1 h at 150 °C in both Pyrex and PTFE were compared. As for the dodecane reactions, 1-decene was filtered through Florisil then distilled under vacuum, and the purified reactant was then separated into two portions with one going into a Pyrex Schlenk tube and the other into a PTFE vial. The data in Table 1 represents the average of three separate experiments. On the basis of the integrated IR absorption intensity over the entire C-H stretching region, it is evident that the reaction in Pyrex led to an increased amount of hydrocarbons grafted to the surface. The film thicknesses determined by ellipsometry were also consistent with this trend, although the observed differences were within the experimental error. While the thermal reaction in Pyrex was essentially complete after 1 h, the IR integrated intensity and contact angle in PTFE continued to increase for longer reaction times. After 2 h reaction in PTFE, the contact angle was  $112 \pm 1^{\circ}$ . The observation that thermal reactions proceed more rapidly in Pyrex is consistent with the reaction being initiated by reactive intermediates generated by the thermally induced degradation of reactants/solvent on the surface of the reaction vessel. It is perhaps interesting to note that, although the reaction in Pyrex appears to increase the rate of monolayer formation, the contact angle for these samples was slightly lower, indicative of a poorer quality monolayer.

The impact of the reaction vessel on the electrical properties of the silicon was investigated by measuring the SPV by a Kelvin probe. Briefly, the surface potential is first measured in the dark and then under illumination and with the difference representing the degree of band-bending associated with charge trapped in electrically active defects at the organic/silicon interface.<sup>34,35</sup> Ideally, alkylation is expected to retain the extremely low density of electrically active defects and minimal band bending observed on H-terminated silicon surfaces. In fact, a small SPV (<100mV) is typically observed on alkylated surfaces, and can be attributed to the small degree of oxidation (oxygen insertion into silicon backbonds) that invariably occurs during monolayer formation. For the silicon doping densities used here, the observed SPV of ~70 mV corresponds to an interfacial charge density of <4 × 10<sup>10</sup> cm<sup>-2</sup>. Although the sample reacted in PTFE exhibited a slightly lower SPV than that in Pyrex, the observed difference is within the error bars.

A recent trend in organic functionalization reactions of hydrogen-terminated silicon surfaces, expressed in several publications, has been a push to "milder" reaction conditions. For photoinitiated reactions, this has involved the use of visible rather than UV light, whereas, in the case of thermal reactions, it has meant investigation of lower temperatures to initiate the reaction. For example, de Smet et al.<sup>32</sup> reported the thermal reaction of H-terminated porous silicon with 1undecene at 90-110 °C, considerably lower than the temperatures of >150 °C that are typically employed. When efforts were made to exclude oxygen and peroxides from the system minimal reaction was observed. This is consistent with our finding that, at 80 °C in an oxygen free environment, the Si-H peak is stable for extended periods of time in dodecane or toluene, and the reaction of 1-decene was inhibited (data not shown). These observations provide evidence for trace oxygen as a source of silyl radicals. Abstraction of hydrogen by molecular oxygen has been observed in the molecule tris (trimethylsilyl)silane,<sup>23</sup> a molecular analog of the H/Si(111) surface. However, the activation energy for this process was estimated to be  $\sim 130 \text{ kJ/mol}$ ,<sup>24</sup> implying that this pathway can only account for reactions at temperatures above ~100 °C. Recently this trend to mild reaction conditions has been extended further with two reports describing room-temperature reactions of alkynes with H-terminated silicon.<sup>25,26</sup> Although these reactions have been attributed to the molecular oxygen initiation mechanism discussed above, this is difficult to rationalize in view of the activation energy required for this process unless the chain length of the ensuing reaction is exceedingly long with the more reactive alkynes.

In summary, we have shown that thermal reactions of alkenes with H-terminated silicon proceed via the radical chain mechanism established for photochemically initiated reactions. Furthermore, we have provided evidence that these reactions can be initiated by the degradation of hydrocarbons catalyzed by the silanol groups on the surface of glass vessels typically used for these reactions. Even the "inert" solvent dodecane was observed to react with the Si-H surface at 150 °C when the reaction was carried out in a Pyrex Schlenk tube. This reaction was significantly inhibited in Teflon (PTFE) vials. The reaction of decene with H/Si(111) proceeded considerably more slowly in Teflon vessels (relative to Pyrex), although the resulting monolayers were of higher quality. These observations illustrate the impact of what is typically considered to be an inert reaction vessel on reactions of H-terminated silicon. The results also indicate the importance

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Table 1. Properties of Monolayers Formed by Reaction of 1-Decene in Either a Pyrex Schlenk Tube or a PTFE Vial with the Si-H Surface at 150
°C for 1 h

reactor	thickness (Å)	contact angle (°)	SPV (mV)	IR C–H peak area (AU)
Pyrex Schlenk PTFE vial	$13.6 \pm 1.3$ $12.2 \pm 1.0$	$107.6 \pm 1.0$ $109.1 \pm 0.8$	$-79 \pm 15 \\ -67 \pm 19$	$\begin{array}{c} 0.61 \pm 0.02 \\ 0.46 \pm 0.01 \end{array}$

of minor degradation pathways and traces of impurities in the initiation of surface reactions of H-terminated silicon, providing alternative (more plausible) mechanisms for the initiation of these reactions. In addition to molecular oxygen, impurities and reactive intermediates generated during the thermal reaction (and by implication the photochemical reactions) are a source of initiators of the solution-phase reaction of alkenes with Si-H surfaces.