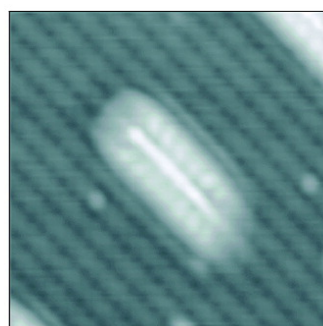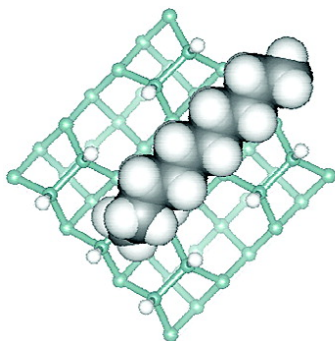Article

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Dispersion Interactions Enable the Self-Directed Growth of Linear Alkane Nanostructures Covalently Bound to Silicon

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Abstract: Current interest in methods for controllably adding organic molecules to silicon surfaces relates to proposed hybrid silicon-organic devices. It was recently shown that a "self-directed" growth process, requiring only limited scanned probe intervention, has the potential to permit rapid, parallel production of ordered molecular nanostructures on silicon with predefined absolute position, structure, composition, and extent of growth. The hybrid organic-silicon structures formed are bound by strong covalent interactions. In this work, we use scanning tunneling microscopy and density functional theory techniques to show that molecule-surface dispersion interactions enable the growth process and play a crucial role in the final configurations of the nanostructures.

Current interest in methods for controllably adding organic molecules to silicon surfaces relates to proposed hybrid silicon-organic devices.[1] It was recently shown that a "self-directed" growth process, requiring only limited scanned probe intervention, has the potential to permit rapid, parallel production of ordered molecular nanostructures on silicon with predefined absolute position, structure, composition, and extent of growth.[2] The hybrid organic-silicon structures formed are bound by strong covalent interactions. In this work, we show that molecule-surface dispersion interactions enable the growth process and play a crucial role in the final configurations of the nanostructures.

The self-directed growth process involves a radical addition reaction between an alkene molecule and a Si• on an otherwise hydrogen-terminated silicon surface. As a C−Si bond forms, the C−C π-bond breaks, creating a carbon-centered radical. For a chain reaction to ensue, the radical species must succeed in abstracting a hydrogen atom from an adjacent Si−H surface site, resulting in the formation of a stabilized chemisorbed molecule while creating a new silicon dangling bond and the opportunity for another molecule to react. This chain reaction was first proposed by Linford et al. in the wet-chemical formation of organic monolayers on silicon.[3] The process is shown schematically in Figure 1.

In the initial work, it was shown that styrene achieved chain reaction at low doses, typically 3 langmuir (L). Calculations
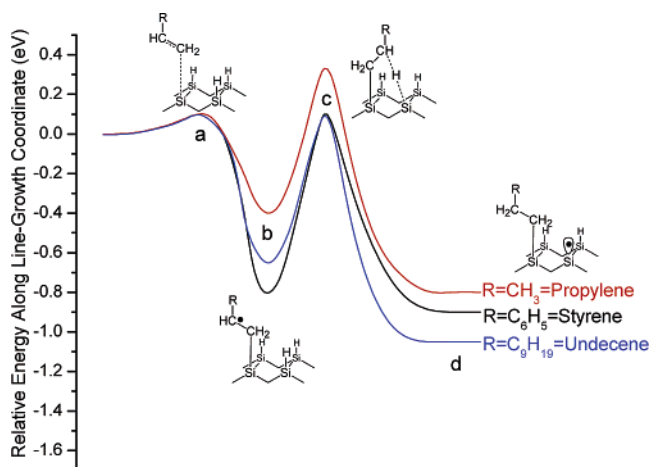

Figure 1. Schematic of energy changes and structures associated with the various steps associated with the chemisorption of a single molecule of styrene, propylene, and undecene on H−Si(100). (a) Radical addition transition state. (b) Addition product of alkene on silicon radical site. (c) Hydrogen-atom abstraction barrier. (d) Post-abstraction complex with radical site on neighboring silicon. Energies for the undecene reaction is the same as those of propylene but shifted to lower energies due to physisorption (vide infra).

indicate that styrene addition to a surface dangling bond is exothermic by ca. 0.8 eV. This radical intermediate is stabilized by delocalization of the unpaired electron into the benzene ring. The subsequent H-atom abstraction releases only ca. 0.1 eV. The energetics for propylene were found to be similar overall, but quite different in the partitioning of energy between the addition and H-abstraction steps. Calculations showed that the addition involving propylene results in an intermediate bound by ca. 0.4 eV and that the following abstraction reaction releases an additional 0.4 eV.[4] Experiments[2] revealed that, even at doses of 200 L, propylene does not undergo line growth. It is evident

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that the barrier to H-abstraction is substantially larger than the addition energy of propylene, and thus, for propylene, desorption occurs before H-abstraction can be achieved (see Figure 1). The key factor leading to styrene line growth is radical delocalization/stabilization of the intermediate species.[5]

In this work, we show that radical delocalization into a benzyl ring is not the only mechanism by which the addition intermediate can be stabilized. For sufficiently large molecules, weak, noncovalent interactions between molecule and substrate (physisorption) can stabilize the radical species sufficiently for H abstraction, and therefore line growth, to occur. As this new mechanism greatly reduces constraints on the structure of molecules used, a greater range of ordered, covalently anchored molecular nanostructures can now be automatically assembled than was originally anticipated.

An exhaustive study of alkenes has not been performed, but the molecules studied thus far show a clear trend: alkenes smaller than 1-heptene do not grow lines, while larger alkenes (tested up to 14 C atoms long) do grow lines on H−Si(100). STM images obtained form our initial survey work with various molecules are provided as Supporting Information. Here, we report results for 1-undecene as that species has been studied in the most detail.

The H−Si(100) surface exhibits rows of silicon dimers that run from the upper left to the lower right, as seen in the constant current STM image shown in Figure 2. The self-directed line-growth process does not proceed on a hydrogen-free silicon surface. The surface is terminated with hydrogen in a vacuum, resulting in one H atom bonded to each surface silicon atom, leaving the Si−Si dimer bonds intact.

The starting surface, shown in Figure 2A, has coverage of approximately 5% randomly distributed single dangling bonds as a result of incomplete H-termination. Those sites served as convenient growth initiation points. The raised bars in Figure 2B (near white in appearance) are lines of undecene molecules that have grown via the self-directed growth process.[6] Comparison of the before and after images shows that line growth has occurred.

The observed linear structures are consistent with multi-molecular assemblies, anchored along a contiguous line of surface attachment points, and wherein each molecule extends along the surface in a direction perpendicular to the dimer rows.

Registering a lattice matched grid over the images in Figure 3 supports association of the minor ridge within each molecular assembly with points of molecule-surface attachment. It appears that the broader feature within each line is due to the collection of saturated hydrocarbon chains lying upon the surface. Indeed, the individual molecules can be seen, and these fan-out somewhat. The spreading of the molecules is expected since the imposed spacing due to the silicon lattice is less than the van der Waals molecular separation expected for undecane.[7]

A surface with pre-existing undecene lines was exposed to styrene. Before and after images allow styrene lines to be unambiguously distinguished. Identification is straightforward
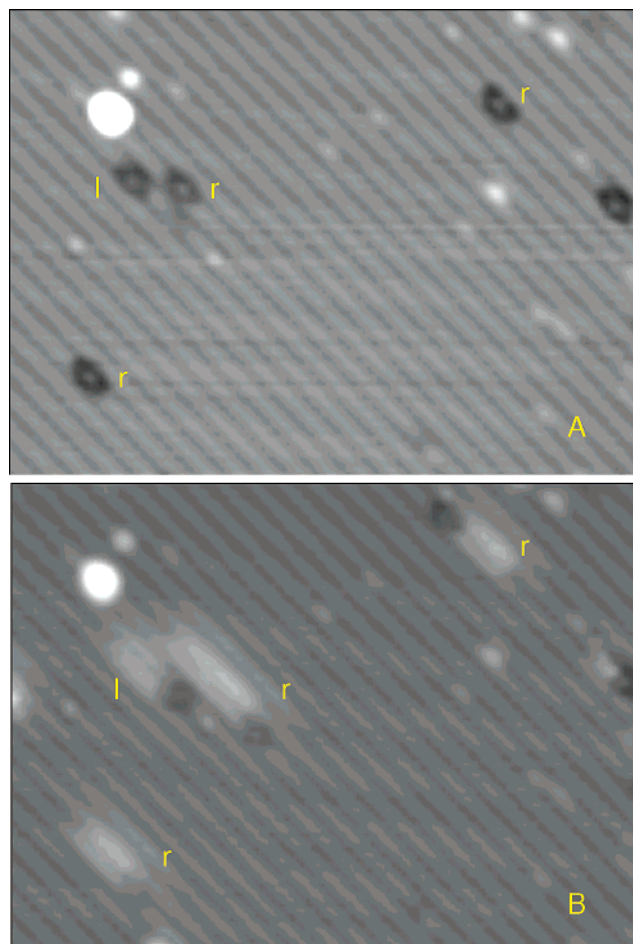

Figure 2. Constant current STM images on the H−Si(100) surface ($V_s = 2.0$ V, $I_s = 40$ pA) at $T = 298$ K. (A) Image of dangling bonds on the otherwise H-terminated surface. The dangling bonds lie on the left (l) or right (r) side of the dimer row. (B) After exposure of 10 L of 1-undecene. Grown lines extend out from the side of the dimer to which the molecule is anchored and lie flat on the surface. Image areas: 20×20 nm^2.

in any case as the styrene lines are narrower and approximately 1 Å higher in appearance, as seen in Figure 3.

Feature C in Figures 3 and 4 appears to have molecules fanning out from both sides of the points of attachment. Close examination reveals that the molecular sub-assemblies to both sides of the line of attachment have nominally single dimer spacing, just as in a normal single line. It is therefore not possible to reconcile this structure with molecules chemisorbed along one side of a dimer row and with the individual molecules lying on the surface in an alternating arrangement. Feature C is a double line, with individual molecules attached on both sides of a dimer row. This is a familiar observation in studies of styrene lines. Double lines result when a silicon dangling bond diffuses across a dimer, causing subsequent adsorption to be laterally displaced. With styrene, such a crossover abstraction most often leads to doubling back. With undecene, growth that jogs but is continuous in direction, as seen at D in Figures 3 and 4, more commonly occurs.

We began this discussion by stating that styrene and propylene add exothermically to silicon dangling bonds releasing approximately 0.8 and 0.4 eV, respectively. The greater stability of styrene addition is attributed to radical delocalization. Further calculation has shown that all 1-alkenes have the same addition energy, to within 0.1 eV. It must therefore be concluded that

(4) A recent DFT study of styrene and propylene line growth reported similar energetics. See: Kang, J. K.; Musgrave, C. B. *J. Chem. Phys.* **2002**, *116*, 9907−9913.
(5) We have exploited this type of radical stabilization to grow lines of vinyl ferrocene on H−Si(100). See: Kruse, P.; Johnson, E. R.; DiLabio, G. A.; Wolkow, R. A. *Nano Lett.* **2002**, *2*, 807−810.
(6) Dosing conditions are described in the Figure 2 caption.
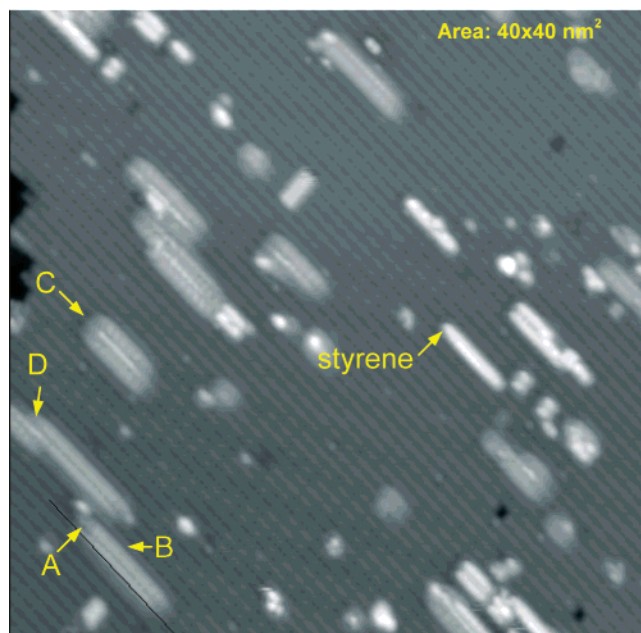(7) Ullman, A. *Chem. Rev.* **1996**, *96*, 1533−1554.

Figure 3. Constant current STM image of undecene (20 L) and styrene (10 L) on the H−Si(100) surface (V_s = 2.8 V, I_s = 40 pA) at T = 298 K. Surface height is denoted by a gray scale, ranging from 0 (black) to 0.59 nm (white). The minor bar at "A" denotes the location where undecenes are bonded to the surface. The bar feature at "B" results from the undecene chain lying down on the surface. Species at "C" indicates an undecene line that has "doubled-back", fanning the hydrocarbon chains on both sides of the central silicon dimer row. A styrene line is labeled for comparison. "D" indicates where a jog in the growing line has occurred.
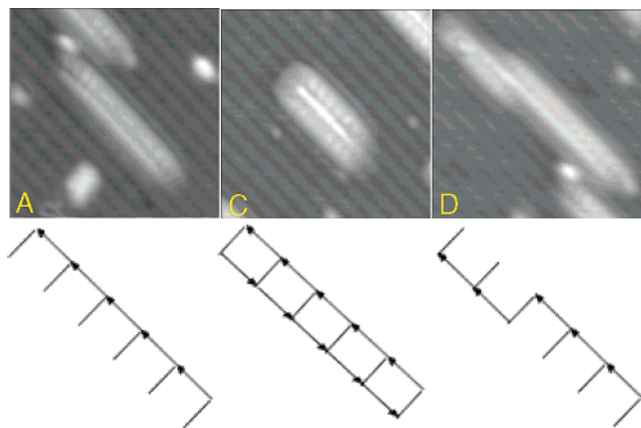

Figure 4. Enlargements of features indicated in Figure 3, with schematics indicating how growth proceeds (solid line = dimer row, arrow = incremental growth direction). STM image areas: 10 × 10 nm².

the longer alkene molecules gain extra stability as a result of more substantial dispersion interactions with the surface, as suggested in Figure 1. We assume that similar interactions play a role at all stages of line growth. That is, alkenes physisorb on the surface, retaining some freedom to diffuse laterally until a dangling bond is encountered. After adding to the dangling bond, a portion of the molecule remains physisorbed to the surface, including during H-atom abstraction.

With no experimental data with which to compare, we turned to theory to estimate the strength of the physisorption interaction. We calculated the interaction energy between a geometry optimized undecane molecule[8] and a rigid, hydrogen-terminated 108 silicon atom cluster using HCTH407[9]/6-31G(d).[10,12] These calculations yielded an estimate for the interaction energy of 0.25 eV, enough to make the H-atom abstraction reaction more competent than undecene desorption. The undecene line-growth energetics are now comparable to those of styrene (see Figure 1).[13] Our physisorption results are also in line with those reported in studies of the thermal desorption energetics of alkanes on different surfaces.[14] Additional physisorption interactions exist between individual undecane molecules in the ordered nano-structures that are formed.

We note that vinyl cyclohexane should display similar physical adsorption characteristics as styrene, and yet, no line was observed. In addition, it is notable that to grow lines with allyl benzene, which is larger than styrene and does not benefit from radical delocalization, requires doses ca. 10 times larger than those that result in styrene line growth. Taken together, these observations allow us to conclude that two stabilizing mechanisms are responsible for line growth on H−Si surfaces: Styrene line growth is facilitated largely by delocalization effects while alkene chains are stabilized almost exclusively by dispersion interactions with the surface. Thus, dispersion interactions are responsible for the formation of alkane nano-structures that are covalently bound to silicon surfaces. These findings indicate that a greater variety of organic molecules than originally expected can form self-assembled nanostructures on silicon surfaces.

Supporting Information Available: STM images of lines of 1-octene, 1-undecene, and 1-tetradecaene. This material is available free of charge via the Internet at http://pubs.acs.org.

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