# Extending Molecular Lines on the Si(100)-2 × 1 Surface: A Theoretical Study of the Effect of Allylic Mercaptan Adsorbates on Radical Chain Reactions

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ABSTRACT The reaction mechanism for the adsorption and growth of allylic mercaptan (ALM) at a defect site on the Si(100)-2 × 1 surface has recently been proposed. The adsorbate structure is believed to be a branched or linear ALM molecule forming a bridge across silicon dimer rows on the Si(100)-2 × 1 surface. Subsequent reactions at the radical site formed by an ALM adsorbate have not been studied previously. We have now calculated the reactivity of ALM, acetone, and styrene at radical sites formed by an ALM adsorbate. The reactivity of ALM and acetone is unaffected by adjacent ALM adsorbates. The same is true for styrene reacting adjacent to a linear ALM adsorbate. A branched adsorbate significantly destabilizes a styrene adsorbate, making styrene more likely to desorb than to react further. The origin of this destabilization is the partially broken silicon dimer bond. These results are consistent with available experimental observations and support the proposal of a branched ALM adsorbate bridging dimer rows.

SECTION Surfaces, Interfaces, Catalysis
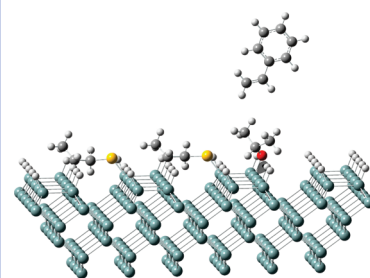
Silicon-based devices form the core of the modern microelectronics industry.[1] While the semiconductor industry's reliance on silicon may not continue indefinitely, the large infrastructure supporting silicon-based devices gives strong support to the idea that future devices will be built upon a silicon framework. The limits of the current technology will be reached around the year 2020 as device dimensions shrink to ever smaller sizes.[2-5] A promising research direction to circumvent this limitation is the direct functionalization of surfaces to create molecular-scale devices.[6-15] A small number of molecules (possibly a single molecule) could be used to form a nanoscale device. Some of the fundamental work geared toward this goal has been focused on the chemistry of organic molecules with silicon surfaces. While there is still much work to be done in this area, some initial progress has been achieved by exploiting the surface chemistry of organic molecules to form nanoscale patterns on the silicon surface.[16-45]

The nascent field of silicon surface nanopatterning has many unanswered questions. One of the most difficult questions is how to make complex patterns. Some of the techniques used to functionalize silicon have been the Grignard reaction,[12,46-48] reactions at defect sites,[16,17,21,22,24,25,30-32,35,39,42] and dehydrative cyclocondensation reactions.[49] Reactions at defect sites offer a powerful strategy for exploring the science of functionalization, particularly the reaction of olefins or carboxyl groups with surface dangling bonds. This technique was first discovered by Lopinski et al. for the reaction of styrene on Si(100) surfaces.[38] The dangling bonds may be the result of incomplete hydrogen passivation of the surface or may be created on the surface by a scanning tunneling microscope (STM) tip. The chemistry for this class of reactions follows a chain-reaction-type mechanism; a surface silicon radical reacts with a carbon−carbon or oxygen−carbon double bond to create a silicon−carbon[18,19,24,25,27,30,32,37,38] or a silicon−oxygen bond[26,28,29,31] between the molecule and the surface, and this shifts the radical site to the adsorbed molecule that then reacts with an adjacent surface silicon, shifting the radical back to the surface. This chemistry has been shown to occur with a number of molecules and has also demonstrated not to occur for other related molecules.

These molecular-scale lines are envisioned to act as interconnects for nanoscale devices. In some cases, for example, styrene, a line of adsorbed molecules acts as a wire, while in other cases, that is, long-chain alkanes, further modification would be required.[40] To make interconnects on a surface, predictable growth in at least two distinct directions is required. The directional anisotropy of the Si(100)-2 × 1 surface makes this possible.[17,22,39] Most molecules, for example, styrene and acetone, grow preferentially "along" dimer rows on the of the Si(100)-2 × 1 surface.[24,26−29,32,33,35,38] A few molecules are known to grow "across" dimer rows, including allylic mercaptan (ALM) and acetopheone;[17,22,24,28,29,39] of these, only ALM grows *exclusively* across dimer rows. The mechanism for growth of molecules along dimer rows has been well-established.[32] For across dimer growth, several

(a) Si(100)-2×1 Four Dimer Model with
Branched ALM Adsorbate

(b) Si(100)-2×1 Four Dimer Model with
Linear ALM Adsorbate

(c) Si(100)-2×1 Two Dimer Model with
Branched ALM Adsorbate

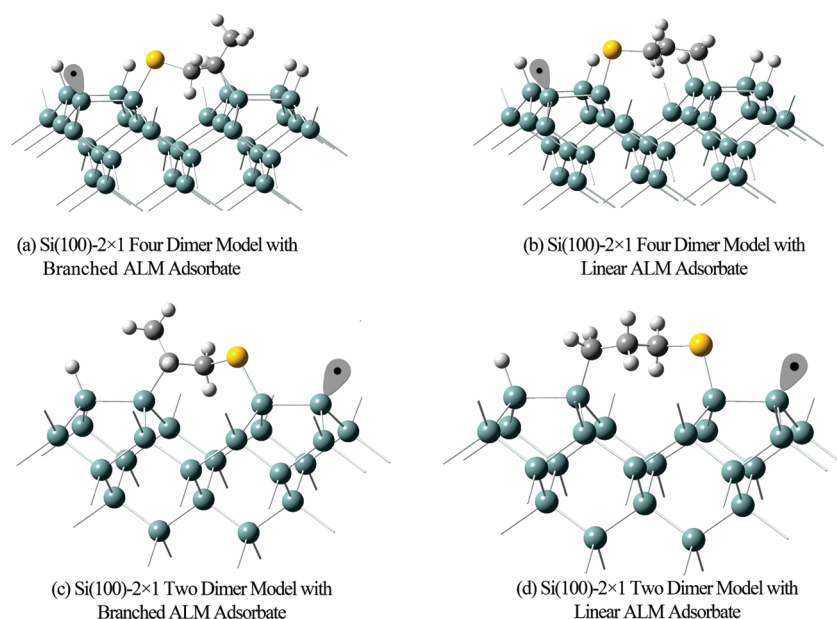(d) Si(100)-2×1 Two Dimer Model with
Linear ALM Adsorbate

Figure 1. The models used in this study containing four surface dimers (top) and two surface dimers (bottom). Branched ALM adsorbates (a) and (c) are shown on the left, and linear ALM adsorbates (b) and (d) are shown on the right. The light blue spheres represent silicon, the small white spheres represent hydrogen, the gray spheres represent carbon, and the yellow spheres represent sulfur. Radicals are shown with gray orbitals containing black dots.

initial mechanisms have been proposed, with our proposed mechanism explaining the key experimental observations.[17,22,39] This mechanism proposes that the initial reaction of ALM occurs to form a primary carbon radical[39] and results in a bridged structure across dimer rows linked by a silicon−sulfur bond, Figure 1a. Our proposed bridged product is similar to one suggested previously by Choi and Cho, though some of the details are different (branched in our model versus linear in their model).[17] One point which is not fully understood in our previous work is whether the branched ALM adsorbates would be too strained to form a line on the surface. An alternate possibility would be a line of branched ALMs interspersed with linear ALMs to relieve the strain. If this is the case, we would expect ALM lines composed of both branched and linear bridging ALM molecules. This consideration leaves open the possibility that the terminating ALM molecule could be either branched or linear.

From these observations, we would like to consider two important questions. Both concern the reactivity of the dangling bond at the terminal point of an ALM line on the Si(100)-2 × 1 surface. The first question that we address is how the initial reactivity of a second ALM molecule is affected by the presence of the first ALM on the surface. The second question that we consider is why it is possible to react with acetone but not styrene at the end of an ALM line. To answer these questions, we have examined the reactivity of ALM, acetone, and styrene at the terminal dangling bond site with an ALM adsorbate. The reaction mechanisms for the initial reaction of ALM on the Si(100)-2 × 1 surface have been proposed by several groups but not yet verified.[17,22,24,39] For reactions occurring at the terminal site of the ALM line, there are two possible starting points, the branched or the linear ALM adsorbate, Figure 1. Since the efficacy of the initial mechanism has not yet been determined and it is possible that linear ALMs may exist within a line of branched ALMs, we have examined the reactions for both branched and linear structures.

We first compare and contrast reactions of ALM at radical sites on the hydrogen-passivated surface to those on surfaces containing branched and linear ALM adsorbates. The reaction of the first ALM across the silicon dimer bond creates a bridge with a silicon−sulfur bond, Figure 1a and c. The largest change after forming the bridged structure involves the silicon dimer bond distance. The silicon dimer bond of the passivated surface is 2.47 Å, and the distance between dimers is 5.32 Å (surface containing a single radical). After the reaction of ALM forming a linear structure, the silicon dimer distance is increased slightly (at the dimer forming the silicon−carbon bond) to 2.48 Å, and the distance between dimers is reduced slightly by 0.01 Å. A branched ALM adsorbate yields a much larger perturbation to the bond distances, with a silicon dimer distance of 2.53 Å and an interdimer distance of 5.05 Å (difference of 0.27 Å from the reference). It is clear that part of the strain caused by the shorter branched structure merely extends the dimer bonds and would not be expected
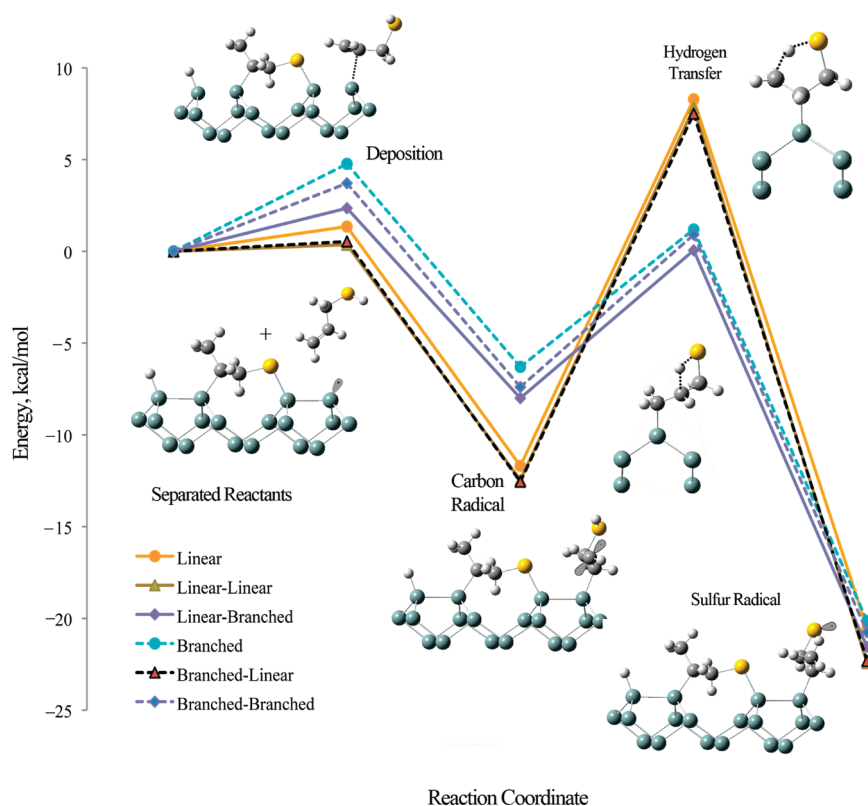
Figure 2. Reaction coordinate of a second ALM reacting on the Si(100)-2 × 1 surface. Only the reaction path of an ALM forming a branched adsorbate reacting next to a branched adsorbate is shown, with the exception of the hydrogen-transfer step that is shown for both branched and linear adsorbate reactions. Lower-layer hydrogen and silicon atoms are omitted for clarity. The light blue spheres represent silicon, the small white spheres represent hydrogen, the gray spheres represent carbon, and the yellow spheres represent sulfur. Radicals are shown with gray orbitals containing black dots, and black dotted lines are bonds breaking and forming during a reaction.

to cause significant buckling of the surface as previously thought.[22]

Several of the reaction paths for a second ALM molecule reacting on the Si(100)-2 × 1 surface starting from the surface with an adsorbed ALM are shown in Figure 2. There are four possible reaction pathways for the second ALM, reaction at a linear ALM adsorbate site to form either a branched or linear ALM adsorbate (linear−linear and linear−branched) or reaction at a branched ALM site to create either a linear or branched ALM adsorbate (branched−linear and branched−branched). The proposed reaction sequence closely follows the previously established mechanism.[32] We have calculated the initial reaction steps up to the formation of the sulfur radical. The reaction proceeds by the interaction of the olefin functional group with the surface radical to form a carbon radical on the ALM and a carbon−silicon bond. The carbon radical can then rearrange to form a sulfur radical, which subsequently reacts with the adjacent dimer. The reactions following the sulfur radical formation require much larger models that we plan to investigate in the future.

As can be seen from the reaction profiles in Figure 2, the radical formation at either the linear or branched adsorbate is little perturbed by the presence of the initial ALM molecule. The largest variance of the reactions between surfaces with adsorbates and those without is the initial deposition barrier. This could be expected since the largest perturbation to the

structure is to the length of the dimer bonds. The smallest differences in deposition energy are for the linear−linear and branched−linear reactions. These are within 1−2 kcal/mol of the deposition without an adsorbate. Since the bonds are very slightly perturbed for the linear adsorbate, we would not expect to see a significant difference. The reactions at branched sites have slightly more variance but are not significantly different from the reactions without ALM adsorbates. From these results, several inferences can be made. The adsorbed ALM does not significantly stabilize the adsorption of a second ALM. While it is possible that there may be an effect with longer lines, studies with larger models are needed to explore this. The strain induced by a branched adsorbate does not significantly destabilize the initial deposition of a second molecule.

The reactions of styrene and acetone with radical sites on the Si(100)-2 × 1 have been extensively studied.[24,27,32,33,38,43] These molecules are known to react at defect sites on the hydrogen-passivated Si(100)-2 × 1 surface, but only acetone reacts at the end of ALM lines on the Si(100)-2 × 1 surface. The reaction of styrene follows a pathway where the initial reaction is the loss of a double bond and formation of a silicon−carbon bond. The carbon radical then abstracts a hydrogen from a site along the dimer row to create a silicon surface radical. Acetone contains no olefin group; therefore, it reacts through the carbon−oxygen double bond to form a silicon−oxygen bond
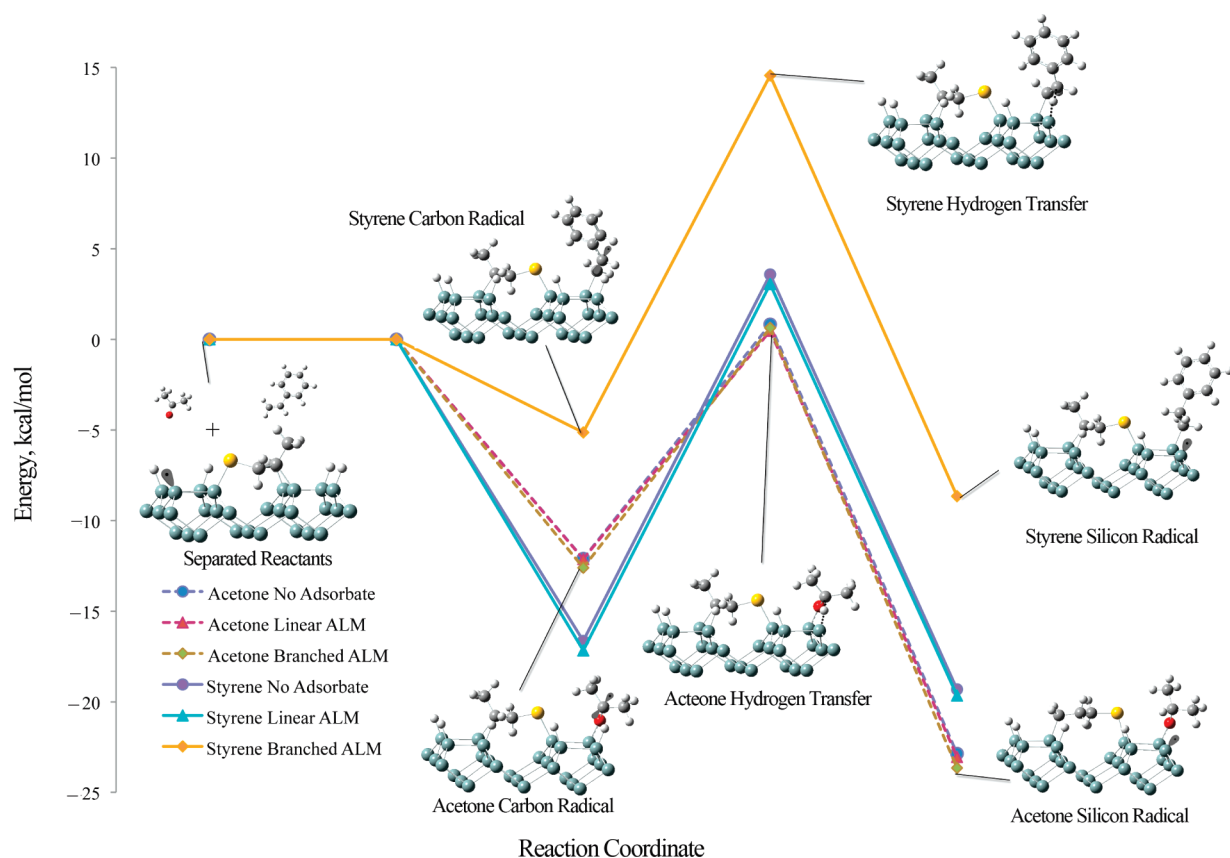
Figure 3. Reaction coordinate of styrene and acetone reacting on the Si(100)-2 × 1 surface at the end of an ALM line. Only some of the structures are shown, that is, the acetone and styrene products with the branched ALM adsorbate. Reactions and structures with linear ALM are analogous. Lower-layer hydrogen and silicon atoms are omitted for clarity. The light blue spheres represent silicon, the small white spheres represent hydrogen, the gray spheres represent carbon, and the yellow spheres represent sulfur. Radicals are shown with gray orbitals containing black dots, and black dotted lines are bonds breaking and forming during a reaction.

and a carbon radical. The radical can then abstract a hydrogen from a neighboring dimer; as is the case with styrene, only along dimer growth has been observed.[26,28,29]

As can be seen in Figure 3, the reaction of styrene is affected by the adjacent ALM molecule for branched ALM but not for linear ALM. Acetone is unaffected by adjacent adsorbates. This provides an interesting explanation for the experimental observations of styrene versus acetone growth at the end of ALM lines on the Si(100)-2 × 1 surface.[26] The growth of acetone lines is the same since the electronic and structural perturbation of the ALM does not affect the stability of subsequent abstraction. From these results, one would predict that styrene may adsorb to the surface but is much more likely to desorb rather than to undergo a hydrogen abstraction reaction if it is adjacent to a branched ALM. If the terminal ALM is linear, then styrene will react almost as if no ALM is present. STM observations show an interaction of styrene with the end of an ALM line (formation of an "S" feature) but no line growth.[26] These calculations along with the STM observation support our proposal of a branched bridging ALM adsorbate at the end of an ALM line. With these results, it is not possible to rule out interspersed linear bridging adsorbates. It can be concluded these would be as reactive as a silicon radical on the hydrogen-passivated surface with styrene.

It has been shown previously that the reactivity of styrene is controlled by the stability of the adsorbed molecule.[32] This conclusion is based on the low barrier to adsorption. In fact, the barrier for the reaction of the carbon−carbon and carbon−oxygen double bonds with the silicon radical is, in most instances, a few kcal/mol.[19,34] The relative energies of the forward and reverse reaction barriers is the most important factor in determining line growth on the Si(100)-2 × 1. The highest barrier for acetone and styrene is the hydrogen abstraction along the dimers rows. Acetone adsorbates with the silicon radical of the hydrogen-passivated surface are less stable than the corresponding styrene adsorbates by ∼4 kcal/mol but have a very low overall barrier to reaction, < 1 kcal/mol. A possible source of this reactivity is the weakly stabilizing effect of the electronegative oxygen next to the carbon radical. Moreover, the oxygen does not significantly destabilize the transition state for hydrogen abstraction. These factors are relatively unaffected by the partially broken silicon dimer bond on the branched ALM adsorbate. Styrene radicals, on the other hand, are stabilized on the surface by radical delocalization through the phenyl ring and through hyperconjugation of the radical with the surface silicon. This is unaffected by the linear ALM adsorbate, which changes the silicon dimer only slightly. However, the stability of the

adsorbed styrene is significantly affected by the adjacent branched ALM on the surface by ~10 kcal/mol. The source of the destabilization is the partially broken silicon dimer bond. A similar effect may be present for other carbon−carbon double bonds reacting at a radical site with the same chemistry, that is, carbon radical formation with immediate hydrogen abstraction. This is not the case for the reaction of a second ALM since it rearranges to form the sulfur radical before hydrogen abstraction.

We have calculated the reaction profiles (minima and transition states) for the reactions of ALM, styrene, and acetone at the radical site adjacent to a bridging ALM on the Si(100)-2 × 1 surface. Our results indicate that the reactivity of ALM and acetone are unchanged when reacting with a silicon radical adjacent to an ALM adsorbate. Styrene reactivity is affected only if the terminal ALM is a branched adsorbate. In this case, the styrene is destabilized by ~10 kcal/mol and is not expected to undergo further reaction. This final observation is in accordance with the experimental observation that styrene interacts with the radical at the end of an ALM line but does not form a molecule line. Acetone and ALM will react at the radical site at a rate similar to that observed without the ALM adsorbate.

COMPUTATIONAL DETAILS

The structure of the Si(100)-2 × 1 surface is well-known.[1] The 2 × 1 reconstruction gives a series of dimer rows separated by troughs, Figure 1. To model this surface, we have used several clusters. The critical points of the reaction pathway (true minima and transition states) of ALM with the Si(100)-2 × 1 surface require a $Si_{23}H_{27}$ cluster model containing two surface dimers, Figure 1. This smaller model is possible since the deposition and rearrangement reactions (vide infra) do not occur along the dimer rows. For the acetone and styrene reactions on the surface, we use the larger $Si_{35}H_{32}$ model, Figure 1. This model contains four dimers, which is large enough to model the hydrogen abstraction along dimer rows. Cluster models similar to these have been used in the past and were reliable for a variety of different chemistries.[50] When constructing cluster models, the truncated bonds are terminated with hydrogen. To mimic the extended surface and to avoid unphysical relaxation, hydrogen atoms below the second layer and silicons below the third layer are frozen in their ideal crystal positions during optimization, in accordance with the well-established procedure.[50] In order to reduce the forces from proximate hydrogens, a fifth layer of silicon was added to the two-dimer model. The fifth layer was not added to the four-dimer model too because the benefit of avoiding proximate hydrogens was outweighed by the increase in the computational cost of adding more heavy atoms to the cluster.

To maintain computational tractability with accuracy, we have used hybrid density functional theory with Becke's three-parameter exchange functional along with the Lee−Yang−Parr correlation functional (B3LYP).[51−53] While deficiencies have been noted with hydrogen abstractions, the performance for systems of this type (hydrogen abstraction via a carbon or oxygen radical) has been sufficient. The basis

set used in our model chemistry is the Pople-style double-ζ basis set with polarization functions on all of the hydrogen and heavy atoms.[54] This gives an overall model chemistry of B3LYP/6-31G(d,p). Transition states and minima were characterized using analytic second derivatives. Calculations were performed using the Gaussian suite of programs.[55]

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