

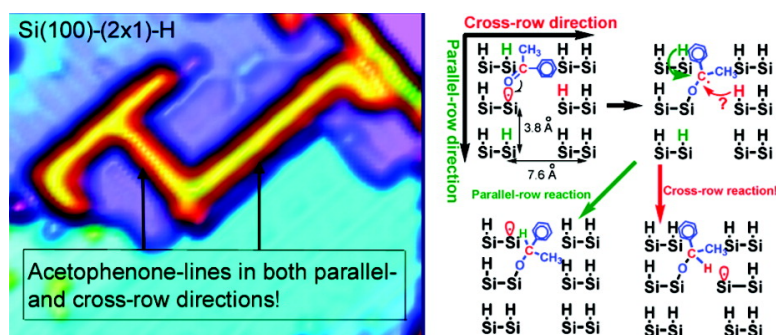
Article

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Self-Directed Chain Reaction by Small Ketones with the Dangling Bond Site on the Si(100)-(2 × 1)-H Surface: Acetophenone, A Unique Example

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Abstract: Using scanning tunneling microscope (STM) at 300 K, we studied the growth of one-dimensional molecular assemblies (molecular lines) on the Si(100)-(2 × 1)-H surface through the chain reaction of small ketone (CH₃COCH₃, PhCOPh, and PhCOCH₃) molecules with dangling bond (DB) sites of the substrate. Acetone and benzophenone show the growth of molecular lines exclusively parallel to the dimer row direction. In contrast, acetophenone molecules show some molecular lines perpendicular, in addition to parallel, to the dimer row direction. Most of the molecular lines perpendicular to the dimer row direction were grown by self-turning the propagation direction of a chain reaction from parallel to perpendicular directions relative to the dimer row. A chiral center created upon adsorption of an acetophenone molecule allows the adsorbed molecules to align with identical as well as alternate enantiomeric forms along the dimer row direction, whereas such variations in molecular arrangement are not observed in the case of acetone and benzophenone molecules. The observed molecular lines growth both parallel and perpendicular to dimer row directions appears to be unique to acetophenone among all the molecules studied to date. Hence, the present study opens new possibility for fabricating one-dimensional molecular assemblies of various compositions in both high-symmetry directions on the Si(100)-(2 × 1)-H surface.

Introduction

The π -conjugated organic molecules assembled in low dimension are promising as materials for future nano scale semiconductor devices.^{1–4} Among the various emerging techniques for fabricating such low dimensional system on surface, the use of dangling bond (DB) initiated radical chain reaction on the H-terminated Si (100) surface stands out because the position, length, and composition of the desired assembly can be precisely controlled.⁵ The H-terminated Si(100)-(2 × 1) surface consists of parallel rows of monohydride silicon dimers (H–Si–Si–H), where the interdimer distances along and across the dimer rows are 3.8 and 7.6 Å, respectively. The dimer spacing along the row (3.8 Å) makes the Si(100)-(2 × 1)-H surface an ideal template for fabricating one-dimensional (1-D) π -stacking system, where a significant π – π interaction exist among the aligned molecules.^{2,4} To date, only one type of ordered π -stacking system, where phenyl rings of adsorbed molecules aligned parallel to each other, has been fabricated along

one of the two high-symmetry directions on the Si(100)-(2 × 1)-H surface.^{5–7} However, ordered arrangements of π -conjugated systems in both high symmetric directions as well as variation in the π – π alignments are highly desirable from a practical point of view.

Varieties of molecules, as listed in the Table 1, were studied for fabricating 1-D molecular line on the Si(100)-(2 × 1)-H surface through chain reaction mechanism.^{5–16} It was observed that some molecules formed 1-D lines while others did not, although every molecule contains the main reactive functional group >C=C< or >C=O. The initial reaction occurs between the >C=C< or >C=O group and the DB site of the substrate, resulting into a carbon-centered (C-centered) intermediate radical of the adsorbed mole-

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Table 1. List of Various Molecules That Are Studied on the H-Terminated Si(100)-(2 × 1) Surface at 300 K for Growing One-Dimensional Molecular Line through the Chain Reaction Mechanism^a

name of molecule	chemical formulas	observation of molecular line on the surface	direction of growth
styrene ⁵	C ₆ H ₅ -CH=CH ₂	YES/NO	direction of growth
allylbenzene ⁸	C ₆ H ₅ -CH ₂ -CH=CH ₂	YES	along the dimer-row
vinylcyclohexane ⁸	C ₆ H ₁₁ -CH=CH ₂	NO	
4-vinylpyridene ⁹	C ₅ H ₄ N-CH=CH ₂	NO	
2,4-dimethylstyrene ⁹	(CH ₃) ₂ C ₆ H ₃ -CH=CH ₂	YES	along the dimer-row
4-methylstyrene ¹⁰	(CH ₃)C ₆ H ₄ -CH=CH ₂	YES	along the dimer-row
vinylferrocene ¹¹	(C ₅ H ₅)Fe(C ₅ H ₄)-CH=CH ₂	YES	along the dimer-row
long chain alkene ⁸	CH ₂ =CH-(CH ₂) _n CH ₃ (n ≥ 5)	YES	along the dimer-row
1-hexene and 1-heptene ¹³	CH ₂ =CH-(CH ₂) _n CH ₃ (n = 3,4)	YES at 180 K	along the dimer-row
allylmercaptan ^{9,14}	CH ₂ =CH-CH ₂ -SH	YES	across the dimer-rows
allylmethylsulfide ¹⁴	CH ₂ =CH-CH ₂ -S-CH ₃	NO	
trimethylenesulfide ¹⁵	(CH ₂) ₃ S	YES	along the dimer-row
benzaldehyde ⁷	C ₆ H ₅ -CH=O	YES	along the dimer-row
acetaldehyde ⁷	CH ₃ -CH=O	YES	along the dimer-row
cyclopropylmethyl ketone ¹⁶	(CH ₂) ₂ CHCOCH ₃	YES	random, no ordered line
acetone, ^{12, this work}	(CH ₃) ₂ C=O	YES	along the dimer-row
benzophenone ^{this work}	PhCOPh	YES	along the dimer-row
acetophenone ^{this work}	PhCOCH ₃	YES	along and across the dimer-row

^a 1-Hexene and 1-Heptene molecules were studied at both 300 and 180 K.

cule.^{5,7,14,17} This C-centered intermediate radical abstracts a H from the neighboring dimer site of the substrate, thereby creating a new DB site propagate the chain reaction (reaction scheme shown later). The stability of the C-centered intermediate radical is believed to be the key factor for growing a molecular line successfully.^{8,18,19} If the intermediate radical is stable enough to abstract a H from the substrate at certain temperature, then the reaction continues in a forward direction to form a molecular line. Otherwise, the intermediate radical might desorb before the H-abstraction event occur. Moreover, a molecular line already formed on the surface normally possesses a DB at the end, which may trigger a chain reaction in the reverse direction to erase the molecular line completely.^{8,13} Hence, the observation of a molecular line by an experimental means depends on the rate of reversed-chain reaction at the substrate temperature and the inactivation of the end DB.¹³

In the cases of successfully grown molecular lines, all molecules except allylmercaptan were observed to form molecular lines parallel to the dimer row (hereafter “parallel”) direction on the Si(100)-(2 × 1)-H surface. Allylmercaptan molecules form molecular line perpendicular to the dimer row (hereafter “perpendicular”) direction.¹⁴ Cyclopropylmethyl ketone undergoes chain reactions with poor directional selectivity, leading to random structures of the adsorbed molecules on the surface.¹⁶ On the relatively less stable H-terminated (3 × 1) surface, styrene molecules form molecular lines in “perpendicular” direction.^{20,21} Utilizing the directional selectivity of two different molecules, the successive growth of molecular lines in “perpendicular” and then in “parallel” direction on both (2 × 1) and (3 × 1) reconstructed Si(100)-H surfaces was achieved simply by changing gas molecule which was fed into the reaction chamber.^{12,21} Since allylmercaptan is the only molecule so far known that form well defined molecular lines in “perpendicular”, rather than “parallel”, direction on the Si(100)-(2 × 1)-H surface, the possibilities for forming molecular lines with varying compositions across the dimer row was limited.

In this study, we explored the chain reactions of acetone (CH₃COCH₃), benzophenone (PhCOPh), and acetophenone (PhCOCH₃) molecules with DB sites on the Si(100)-(2 × 1)-H surface using a scanning tunneling microscope (STM) at 300 K. As expected, molecular lines of acetone and benzophenone molecules grow through a chain reaction in “parallel” direction, and the adsorbed states of all molecules in a line are identical. In contrast, molecular lines of acetophenone molecules grow in both “parallel” and “perpendicular” directions. Depending on the spatial arrangement of methyl and phenyl groups, two different types of stacking sequences of adsorbed molecules in the acetophenone lines in “parallel” direction can result, according to our observations. The maximum that we observed the molecular lines grown in “perpendicular” direction on a freshly prepared H-terminated Si(100)-(2 × 1) surface is about 30%. These observations make the acetophenone molecule unique among the molecules studied to date. The growth of molecular lines of acetophenone molecules in ‘perpendicular’ direction opens new opportunity for fabricating nanoscale molecular circuit on the Si(100)-(2 × 1)-H surface.

Experimental Section

The experiments were performed in an ultrahigh vacuum (UHV) chamber with base pressure better than 5 × 10⁻¹¹ mbar. A variable temperature scanning tunneling microscope (Omicron VT-STM) was used. The Boron-doped silicon sample (0.01 Ωcm) was cleaned by prolonged annealing at ~850 K (~8 h) followed by repeated flashing up to 1400 K. The H-terminated surface was prepared by exposure to atomic H, generated by a hot W-filament (~2100 K), at the surface temperature of ~625 K. The freshly prepared H-terminated surface normally contains a dilute concentration of unpaired DB sites resulting from the incomplete H-termination,²² otherwise, the DB at a predefined position is generated using STM tip.²³ Benzophenone (solid), acetophenone (colorless liquid) and acetone (colorless liquid) purchased from Tokyo Chemicals Industries Co., Ltd. (TCI) were purified by pumping out the vapor above the liquid or solid phases. The molecules were dosed onto the silicon surface through electronically controlled pulse-valve doser. For high exposure, the benzophenone molecules were also dosed by opening a gate valve between the benzophenone ampule and the silicon sample. In the case of benzophenone, the ampule was slightly heated during exposure. The amounts of molecule dosed are expressed in

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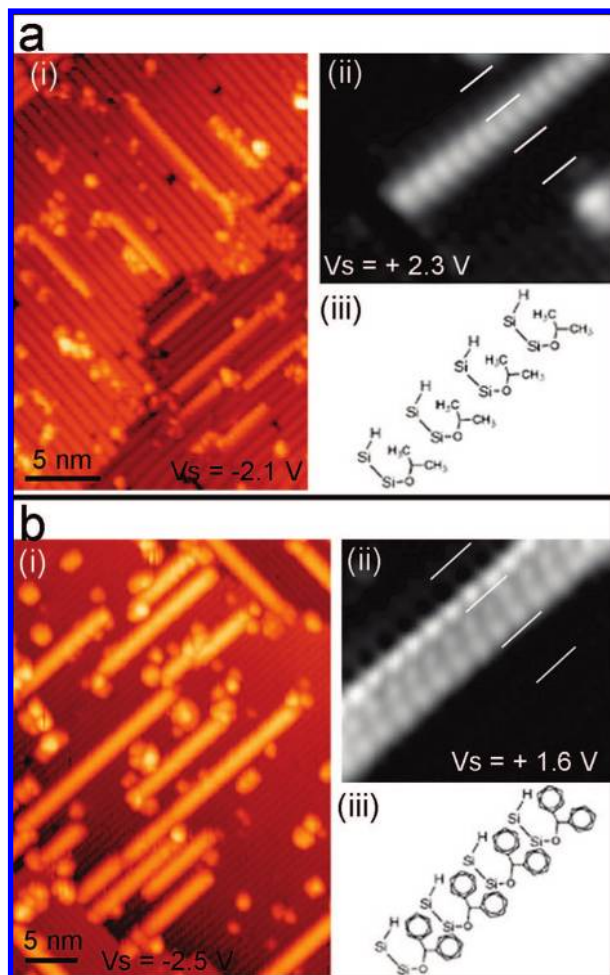


Figure 1. STM images of the Si(100)-(2 × 1)-H surface exposed to a(i) ~0.02 L of acetone (CH₃COCH₃) and b(i) ~50 L of benzophenone (PhCOPh) molecules at 300 K. The zoomed STM images and schematic model of molecular lines formed by acetone and benzophenone molecules are shown in the right panel of (a) and (b), respectively. Parallel white lines are drawn through middle of the underlying dimer-row. All images were acquired at the sample bias indicated with $I_{\text{tunnel}} = 0.2$ nA.

Langmuir ($1 L = 1 \times 10^{-6}$ Torr·s), which is estimated from the background pressure reading by BA (Bayard-Alpert) gauge during the exposure.

Results

Acetone and Benzophenone. Figure 1, parts a(i) and b(i), shows the STM images of the Si(100)-(2 × 1)-H surface exposed to ~0.02 L of acetone and ~50 L of benzophenone molecules at 300 K, respectively. Many bar-like structures, whose contrast is brighter than that of underlying dimer rows in STM image, are observed on each terrace of the Si(100)-(2 × 1)-H surface. In addition to those bar-like structures, some bright protrusions of adsorbed molecules and/or defect sites can also be seen [Figure 1, parts a(i) and b(i)]. Those bar-like structures are ascribed to the molecular line formed through the chain reaction of the respective molecules with the DB sites of the substrate.^{5,12} It is clear from Figure 1, parts a(i) and b(i), that the growth of the molecular lines by both acetone and benzophenone molecules are unidirectional on the Si(100)-(2 × 1)-H surface, i.e., the molecular lines lie only in “parallel” direction (parallel-row molecular line). In addition, no double lines where both of the silicon dimer atoms are occupied by the adsorbed molecules are observed. Note that the formation

of a double lines, which limits the length of molecular line on the surface, is common for other molecules, such as benzaldehyde, acetaldehyde, and styrene due to the higher stability of the double line compared to single line.^{5,7,19b} The simple comparison of aldehyde and ketone suggests that the additional methyl or phenyl group causes the strong steric hindrance between two molecules adsorbed on the same Si—Si dimer, which prohibits the formation of double lines in the present cases.

The spatial arrangement of methyl/phenyl groups in adsorbed acetone/benzophenone molecules within a molecular line can be seen in high-resolution images of the unoccupied states, as shown in Figure 1a(ii)/1b(ii). The molecular line formed by acetone molecules was resolved into many small protrusions aligned in “parallel” direction. Each oval-shaped protrusion is ascribed to the individual adsorbed acetone molecule. The registration of these small protrusions with respect to the underlying dimer row suggests that all of the adsorbed molecules are bonded to the silicon atoms lying on the same side of the dimer row, as shown schematically in Figure 1a(iii). In the case of benzophenone, pairs of small protrusions located on one side of the underlying dimer row [indicated by white lines in Figure 1b(ii)] are ascribed to the adsorbed molecules. Note that the other half of the reacting dimer row appears brighter than the normal H-terminated dimer row, which may result from overlapping the contrast of the silicon dimer with that of adsorbed molecules or the buckling of the reacting dimer. The uniform appearance of the small protrusions and their alignment with respect to the underlying dimer row indicates that the adsorbed states of all molecules in the line are identical in both cases, i.e., the spatial arrangements of methyl and phenyl groups in the adsorbed molecule are identical in every molecule in the line, as shown schematically in Figure 1, parts a(iii) and b(iii).

Acetophenone. Figure 2a shows an STM image of the Si(100)-(2 × 1)-H surface exposed to ~10 L of acetophenone molecules at 300 K. As observed for acetone and benzophenone molecules (figure 1), many molecular lines were formed on the Si(100)-(2 × 1)-H surface by exposure to acetophenone as seen in Figure 2a. It is remarkable that the molecular lines formed by acetophenone lie both in “parallel” and “perpendicular” directions on a given terrace. The molecular lines lying in “perpendicular” direction (cross-row molecular lines) are indicated by black arrow. The contrast of molecular lines in “parallel” and “perpendicular” directions are similar in the STM image; this establishes that both cross-row and parallel-row molecular lines were formed by same chemical species. The cross-row molecular lines of adsorbed acetophenone molecules are clearly distinguishable from those of allylmercaptan molecules; a cross-row molecular line formed by pre-exposure to a small amount (~0.02 L) of allylmercaptan molecules is indicated by the blue arrow.¹⁴ We estimate that almost 30% of the molecular lines formed by acetophenone molecules in Figure 2a lie in “perpendicular” direction. However, STM observations on several freshly prepared H-terminated surfaces after exposure to acetophenone suggest that this percentage of cross-row molecular lines varies depending on the surfaces, for reasons that remain unclear. Apparently, the higher concentration of dark defect sites (missing dimer and/or dihydride) on the surface favors the higher number of cross-row molecular lines.

Figure 2b shows a high-resolution STM image of the Si(100)-(2 × 1)-H surface containing a few molecular lines formed by acetophenone molecules. One can easily recognize that two different types of molecular arrangements exist in parallel-row

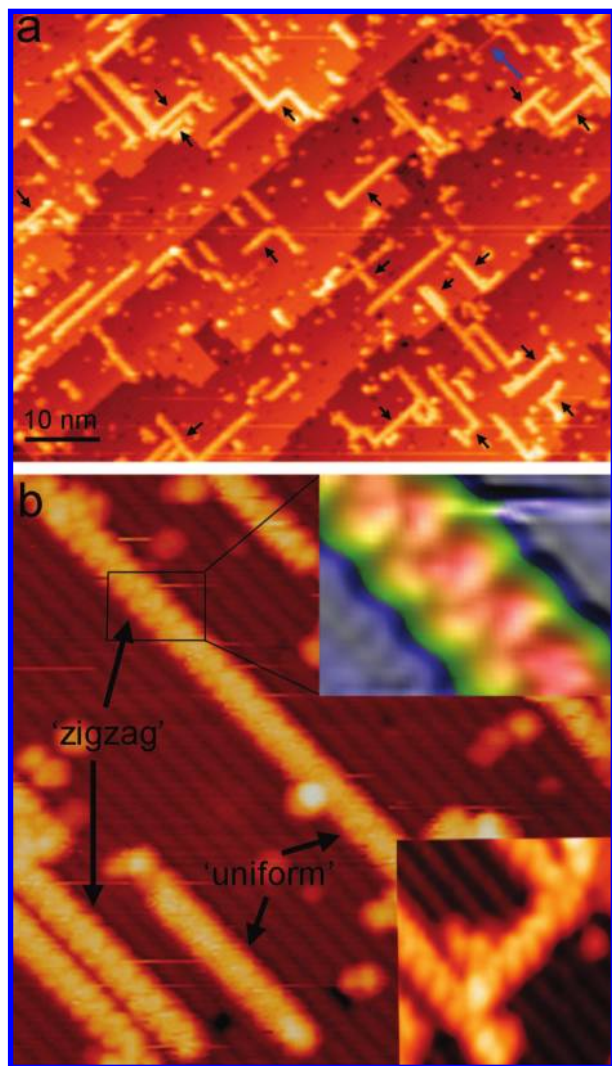


Figure 2. (a) STM images of the Si(100)-(2 × 1)-H surface exposed to ~10 L of acetophenone (PhCOCH₃) molecules at 300 K. Before acetophenone exposure, the surface was pre-exposed to a small amount (~0.02 L) of allylmercaptan molecules. The black arrows indicate molecular line grown perpendicular to the dimer-row direction. The blue arrow indicates a cross-row molecular line formed by allylmercaptan molecules. (b) A high-resolution STM image of a few molecular lines of adsorbed acetophenone (PhCOCH₃). Two different appearances of the molecular lines are indicated as “zigzag” and “uniform”. Upper right inset: zoomed-in 3D view of a “zigzag” line. Lower right inset: high-resolution image of a cross-row molecular line. Parallel-row molecular lines are also seen. $V_{\text{sample}} = -2.1$ V; $I = 0.2$ nA.

molecular lines. Some of the molecular lines resolved into many small protrusions, which are arranged in zigzag pattern in “parallel” direction (indicated as “zigzag”), while others appear as uniform bar-like structure (indicated as ‘uniform’). These two different types of molecular arrangements can be seen together even in the same molecular lines, however, the boundary between the two arrangements cannot be clearly determined. By looking into hundreds of such highly resolved molecular lines in STM images, we found that almost 70% of the molecular lines consist of zigzag arrangement of the small protrusions. In the case of cross-rows molecular lines, only the zigzag arrangements of small protrusions are observed, as shown in the lower right inset of figure 2b. We never observe the interconversion of those two different molecular arrangements during scanning at typical sample biases (~2.5 V).

One can observe that some of the cross-rows molecular lines in Figure 2a are connected with parallel-row molecular lines, while others are isolated. These interconnected molecular lines might have formed either by a self-turning chain reaction, initiated at a particular DB site, from one high symmetry direction to another, or by meeting of two independent molecular lines originating at two different DB sites. To monitor the growth of such interconnected molecular lines, we performed a controlled experiment. Figure 3 shows a series of selected area STM images of the freshly prepared Si(100)-(2 × 1)-H surface exposed to increasing amount of acetophenone molecules at 300 K. These images (Figure 3, parts a–d) clearly show the stepwise growth of several molecular lines of acetophenone molecules. Careful inspection of the images shown in Figure 3 reveals that some of the molecular lines initially grown in “parallel” direction at lower exposures have ultimately grown in “perpendicular” direction from a certain point at higher exposure; the initial growth direction of those selected molecular lines and their turning points are indicated by blue and black arrows, respectively. As Figure 3 shows, the turning point indicated by black arrows is located within the clean area (defect free region) of the H-terminated surface. The present series of the STM images indicate that the most of the cross-row acetophenone lines were grown following the growth of the respective parallel-row molecular line. However, a few independently grown cross-row molecular lines were also observed. In rare cases, the continuous growth of a parallel-row molecular line from the cross-row molecular line can be seen. Note that the uniformity of a freshly grown molecular line can be destroyed by the prolonged scanning at the same area or scanning at higher sample bias (>3.0 V), as seen in some of the molecular lines in Figure 3, parts c–d.

Discussion

Uniqueness of Acetophenone. The molecules (CH₃COCH₃, PhCOPh, PhCOCH₃) examined in the present study contain only the >C=O reactive group. Hence, the molecular lines observed in Figures 1–3 were formed through a common chain reaction mechanism involving >C=O group and DB site of the substrate, as shown in Figure 4.^{7,12} Although the reactions leading to the formation of molecular lines by these molecules are basically similar, the directional selectivity of acetophenone molecules (PhCOCH₃) is different from that of acetone (CH₃COCH₃) and benzophenone (PhCOPh). Mediated by the substrate, the radical chain reaction of acetophenone molecules can proceed in both “parallel” and “perpendicular” directions, whereas the acetone and benzophenone molecules undergo chain reaction only in “parallel” direction. Indeed, all of the molecules that form well-defined molecular lines undergo chain reactions in either “parallel” or “perpendicular” direction, as listed in Table 1.^{5–15} Thus, the present study clearly demonstrates that acetophenone is a unique example of an organic molecule that can lead a DB initiated chain reaction to propagate in “perpendicular”, in addition to “parallel”, directions either independently or continuously from “parallel” direction on the Si(100)-(2 × 1)-H surface.

The high-resolution STM image of the molecular line formed by acetophenone (Figure 2b) indicates that adsorbed molecules may attain two different types of molecular arrangements along the dimer row direction. In the “uniform” line, the geometric configuration of all molecules seems identical, as observed in the case of acetone and benzophenone. In contrast, the more commonly observed “zigzag” line consists of two different geometric orientations of the adsorbed molecules that can be

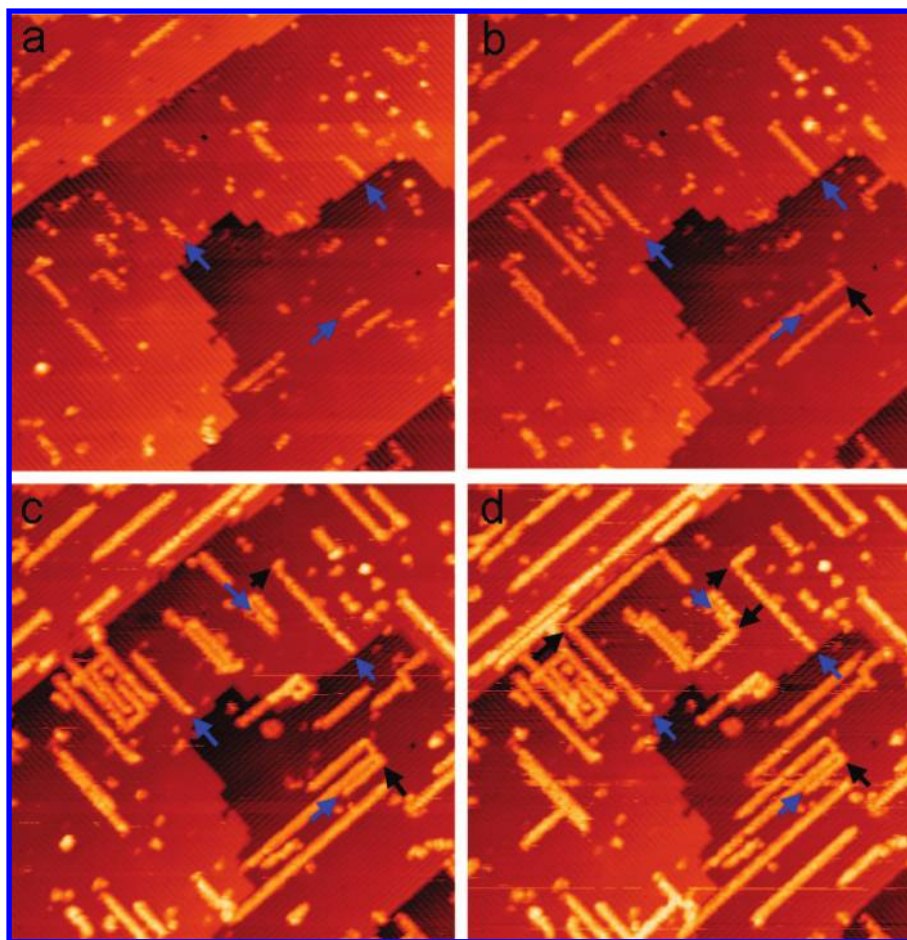


Figure 3. A series of STM images measured at the same area of a Si(100)-(2 × 1)-H surface after exposure to increasing amount of acetophenone (PhCOCH₃). The exposure for (a), (b), (c), and (d) were ~0.5 L, ~1 L, ~3 L, and ~8 L, respectively. Blue arrows indicate the initial growth of some selective molecular lines along the dimer row direction that ultimately turned to the cross-row direction. The point of self-turning from a parallel-row to a cross-row direction is indicated by black arrows. Scan area = 62 × 62 nm². $V_{\text{sample}} = -2.2$ V; $I = 0.2$ nA.

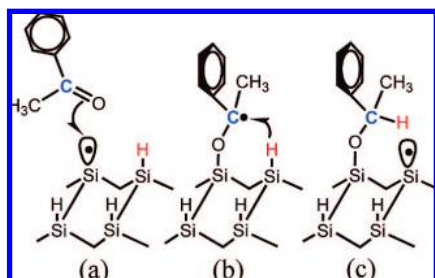


Figure 4. Schematic of the chain reaction mechanism of acetophenone (PhCOCH₃) and a DB site of the Si(100)-(2 × 1)-H surface along the dimer row direction.

described in terms of their absolute configurations. One can see in Figure 4c that a chiral carbon atom was created after the adsorption of acetophenone, which did not happen for benzophenone and acetone molecules. Since the H atom bonded to the chiral carbon atom comes from the substrate, it is likely that this H atom is always oriented toward the propagation direction of the chain reaction because of the rotational constraint on the adjacent adsorbed molecule. Hence, depending on the spatial orientation of the CH₃ and Ph groups, the chiral carbon atoms may attain the absolute configuration of R or S. Thus, the creation of a chiral center allows the acetophenone molecules to attain one of two possible stacking sequences (RSRS and RRR or SSS) along the growth direction. The

observed “zigzag” pattern of small protrusions of adsorbed acetophenone molecules (Figure 2b) is attributable to the alternate configurations (RSRS–) of the chiral carbons along the direction of the chain reaction, as shown schematically in Figure 5 (first row). Molecular arrangements in the “uniform” and cross-row line are also shown in Figure 5. It seems that the adsorbed acetophenone usually attains the alternate configuration to minimize the steric hindrance between methyl groups. Note that methyl groups lying on the same side of the dimer row experience a significant steric hindrance, which was indicated by the occasional reversed chain reaction in acetone line even at room temperature.¹²

Directional Selectivity of Chain Reaction. The directional selectivity of a chain reaction on the Si(100)-(2 × 1)-H surface is determined by the selective abstraction of the H atom from the substrate by the intermediate radical of adsorbed molecule.^{8,9,14,15,19b} When the intermediate radical abstracts the H from the adjacent dimer in the same row, as shown in Figure 4b, the reaction proceeds in “parallel” direction. Alternatively, if the intermediate radical can abstract the H from the nearest dimer of the next row, then the reaction might proceed in “perpendicular” direction, as observed earlier in the case of allylmercaptan.¹⁴ Note that in the case of allylmercaptan, a S-centered intermediate thiyl radical is believed to form transiently at the end group of the anchored molecules, which can easily reach to the next dimer row to abstract the H.¹⁴

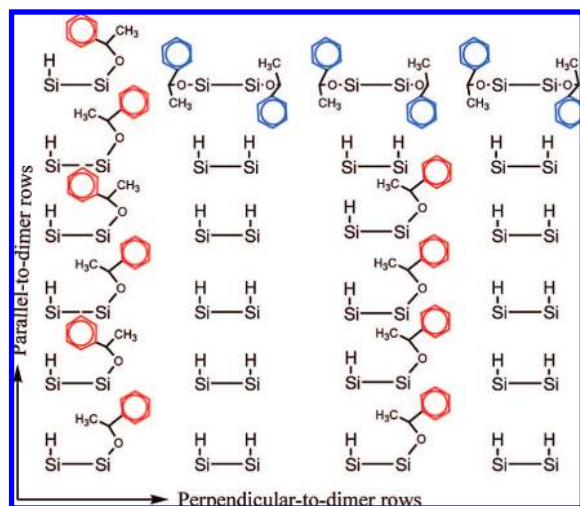


Figure 5. Schematic of the different types of molecular stacking of adsorbed acetophenone (PhCOCH_3) molecules along and across the dimer-row direction on the $\text{Si}(100)-(2 \times 1)\text{-H}$ surface.

However, the distance of C-centered intermediate radical of adsorbed acetophenone from the anchored Si atom is comparable to that of styrene. A theoretical calculation of the radical chain reaction of styrene molecules on $\text{Si}(100)-(2 \times 1)\text{-H}$ suggests that H abstractions in “parallel” and “perpendicular” directions have the energy barrier of ~ 21 and ~ 29 kcal/mol, respectively.^{19b} The higher energy barrier (~ 29 kcal/mol) in the “perpendicular” direction is related to the larger distances from the C-centered radical to the nearest H of the next dimer row, and that causes all of the molecules except acetophenone to follow the reaction path exclusively in “parallel” direction. Thus, the formation of some cross-row molecular lines by acetophenone molecules (Figures 2a and 3) cannot be explained by considering the normal interdimer distances (7.6 \AA) in “perpendicular” direction.

It can be predicted from the previous calculation that a small displacement ($\sim 0.2 \text{ \AA}$) of the silicon atom (bonded to the radical intermediate) toward the next row can bring the C-centered radical close enough to abstract the H in the “perpendicular” direction.^{19b} There are two possible ways that the silicon atom bonded to the C-radical can get closer to the next row. One is the buckled structure of the silicon dimer at which the C-radical is anchored, and another is a complex reaction involving the breaking of silicon dimer through the insertion of O. Since the contrast of parallel-row and cross-row molecular lines in the STM images are similar, the possibility of molecular decomposition leading to O insertion can be completely ruled out. However, the buckled silicon dimers are common on the bare $\text{Si}(100)$ surface. Because of the higher electronegativity of an O atom compared to a Si atom, the silicon dimer bonded to O in an adsorbed molecule may attain a buckled structure. However, the buckled structure of a silicon dimer linked to the C-centered radical cannot alone account for the different growth modes of acetophenone compared to benzophenone and acetone. We argue that, in conjunction with the buckled dimer, the strong tendency of acetophenone molecule to attain alternate configurations plays an important role in propagating some chain reactions in “perpendicular” direction. One of the two configurations (R or S) of the adsorbed molecules perhaps induces the

adjacent C-radical to be directed toward the nearest H of the next dimer row. Once the growth direction is switched to the “perpendicular” direction, the sterically controlled alternate geometry of the adjacent molecules may help to maintain the growth direction. However, an elaborate computational calculation is needed to explore the details of the cross-row chain reaction by acetophenone on the $\text{Si}(100)-(2 \times 1)\text{-H}$ surface.

New Possibilities in Molecular Lines. The cross-row molecular lines formed by acetophenone and allylmercaptan¹⁴ on the $\text{Si}(100)-(2 \times 1)\text{-H}$ surface differ by their relative intermolecular distances within the molecular line. In the case of allylmercaptan molecules, the adsorbed molecules were separated by the same distance as that between rows, (7.6 \AA) i.e., a molecular line consists of one molecule per dimer across the rows.¹⁴ In the case of a cross-row acetophenone line, both of the silicon dimer atoms are bonded to adsorbed molecules, as shown in Figure 5. Hence, the molecules were densely packed in “perpendicular” direction and thus appeared similar to the molecules aligned in the “parallel” direction in the STM images (Figures 2 and 3). The discovery of the cross-row chain reaction by acetophenone molecules and the sterically controlled molecular arrangements along the growth orientation open new possibilities for fabricating tunable one-dimensional assemblies in both high-symmetry directions on the $\text{Si}(100)-(2 \times 1)\text{-H}$ surface. We expect that the present study will promote further experiments with various molecules to design molecular architecture using the H-terminated $\text{Si}(100)$ surface as a template.

Conclusions

The interactions of acetone (CH_3COCH_3), benzophenone (PhCOPh), and acetophenone (PhCOCH_3) molecules with the DB sites on the $\text{Si}(100)-(2 \times 1)\text{-H}$ surface were studied using scanning tunneling microscope (STM) at 300 K. All of these molecules undergo a chain reaction with a dangling bond (DB) site of the substrate and form well defined molecular lines on the surface. Benzophenone and acetone grow molecular lines exclusively in “parallel” direction. In contrast, acetophenone molecules show the molecular lines in both “parallel” and “perpendicular” directions. Reflecting the chiral configuration of the adsorbed acetophenone molecule, two different types of molecular stacking sequences were observed in “parallel” direction. In addition to some isolated cross-row lines, the interconnected junctions of cross-row and parallel-row molecular lines of adsorbed acetophenone are frequently observed. The controlled experiments reveal that most of the cross-row molecular lines in the junctions grew by self-turning the growth direction of the respective parallel-row line. These growth modes and the sterically controlled arrangement of adsorbed acetophenone molecules are unique among all the molecules studied to date. The growth of molecular lines in both “parallel” and “perpendicular” directions by acetophenone molecules open new possibilities for fabricating tunable one-dimensional molecular assemblies in both high-symmetry directions on the $\text{Si}(100)-(2 \times 1)\text{-H}$ surface.

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