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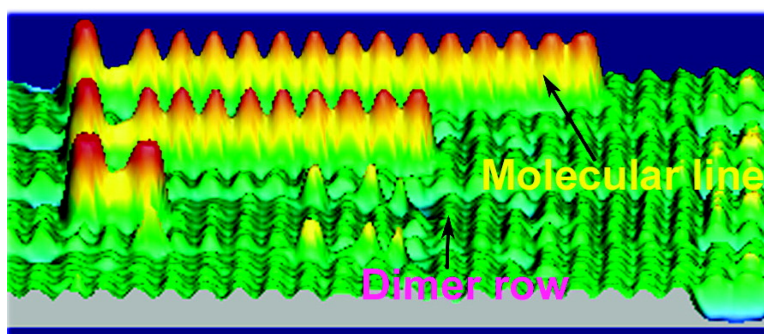

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Controlled Fabrication of 1D Molecular Lines Across the Dimer Rows on the Si(100)−(2 × 1)−H Surface through the Radical Chain Reaction

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The fabrication of organic nanostructures on silicon surface has received much attention for its potential application as a basic electronic component as well as the connecting wire in a variety of molecular scale devices.[1] The particular interest is focused on the self-directed growth of covalently bonded 1D molecular lines on the H-terminated Si(100)−(2 × 1) surface through radical chain reactions initiated at an unpaired dangling bond (DB) site.[2−7] In all of the previous studies with various molecules,[2−4,6] molecular line growth has succeeded only along the dimer rows on Si(100)−(2 × 1)−H. From the technological points of view, designing a molecular system that undergoes chain reaction across the dimer rows is highly desirable, which ultimately leads to the steering of growth direction on a 2D surface. In this communication, we report the rapid fabrication of covalently bonded 1D functional molecular lines across the dimer rows on the Si(100)−(2 × 1)−H surface at room temperature. Unlike self-assembly of 1D metal ad-dimer lines across the Si dimer rows on bare Si(100) surfaces,[8] location, length, and direction of the molecular line in the present study are precisely controllable.

To date, styrene,[2,3,7] vinyl ferrocene,[4] and long-chain alkenes ($C_8 \sim C_{14}$) result in molecular lines along the dimer rows on the Si(100)−(2 × 1)−H surface; however, several other alkenes do not.[6] For example, alkenes smaller than 1-heptene, vinyl cyclohexane, 4-vinyl pyridine, etc. do not show any line growth even after large exposure on the Si(100)−(2 × 1)−H surface containing a dilute concentration of DB resulting from the incomplete H-termination.[6] Despite those reports,[6] the chemistry of the thiyl radical suggests that a thiol-ene system, such as allyl mercaptan (ALM), $CH_2{=}CH{-}CH_2{-}SH$, is a good candidate for growing molecular lines across the dimer rows on the Si(100)−(2 × 1)−H surface. The experimental procedures, including sample preparation and hydrogen termination processes in the present study, are similar to those reported elsewhere.[3]

Figure 1a shows the scanning tunneling microscopy (STM) image of the Si(100)−(2 × 1)−H surface, which contains a dilute concentration of DB, exposed to ~3 L (1 L = 1 × 10^{-6} Torr•s) of ALM molecules at 300 K. The parallel lines observed in all the scanning regions are the H-terminated silicon dimer rows. The random isolated bright protrusions and dark depressions are the defects, such as bare dimers, missing dimers, etc. on the surface.[9] Additionally, four lines of small protrusions running across the dimer rows, as indicated by "molecular lines" in Figure 1a, are also observed. These lines are randomly distributed all over the surface, which suggest that the STM tip has no role in the growth of these lines; 100% of the observed lines lie across the dimer rows. The high-resolution zoomed-in STM image (Figure 1b) reveals that each protrusion in the lines has two parts, the "head" and "tail", as indicated in Figure 1b. The head of a protrusion is located on the edge of a dimer row, and its tail is on the preceding row (discussed later). The observed lines are stable even at 650 K (Figure 1c) and for at least 10 days in vacuum at 300 K, which ensures that the molecules in the lines are chemically bonded to the silicon substrate.

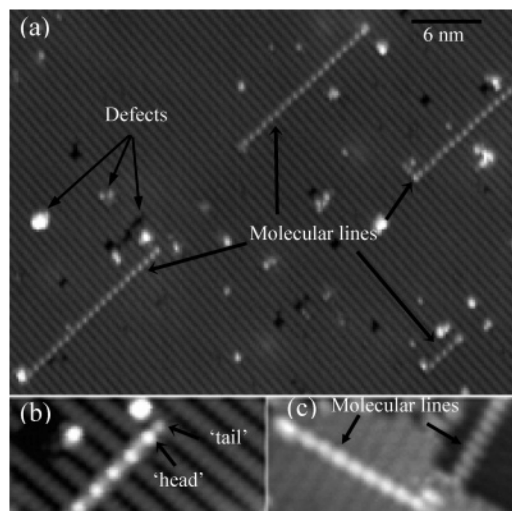

Figure 1. (a) STM image of the Si(100)−(2 × 1)−H surface containing a dilute concentration of dangling bonds exposed to ~3 L (Langmuir) of allyl mercaptan ($CH_2{=}CH{-}CH_2{-}SH$) molecules at 300 K. V_{sample} = −2.5 V; I = 0.2 nA. (b) High-resolution zoomed-in image of the molecular line at 300 K. V_{sample} = −1.2 V; I = 0.2 nA. (c) STM image at 650 K. V_{sample} = −3.0 V; I = 0.2 nA.

To see if the growth of the line is due to the chain reaction of ALM molecules with the DB on the surface, we also have performed controlled experiments as shown in Figure 2. Figure 2a shows a series of selected area STM images of (a1) the H-terminated Si(100)−(2 × 1) surface and (a2−a5) the surface exposed to an increasing amount of ALM molecules after creating an unpaired DB using the STM tip at the position shown in Figure 2a1.[10] Unfortunately, a nearby bigger protrusions, indicated by white arrow (Figure 2a2), also appeared, which might be a defect resulting from the tip-induced multiple H-desorption.[10] Figure 2b1 shows a DB site at the left side of a surface dimer, which is exposed to ALM molecules (Figure 2b2−b3). The gradual growth of molecular lines, initiated at a DB site, with increasing ALM exposure clearly suggests that molecular lines (Figures 1 and 2) are formed through a chain reaction mechanism. By monitoring the growth of a number of lines, we confirmed that the single DB initiates the growth of the line; hence, the defect (as in Figure 2a2) has no role in the line growth, and the tail of a protrusion was resolved only at the starting molecule of the line. In molecules other than the starting one, the tail is overlapped with the head part, that is, the molecules in line are tilted and arranged in cascade fashion. The growth direction from the initiation point depends on the location of the DB on a

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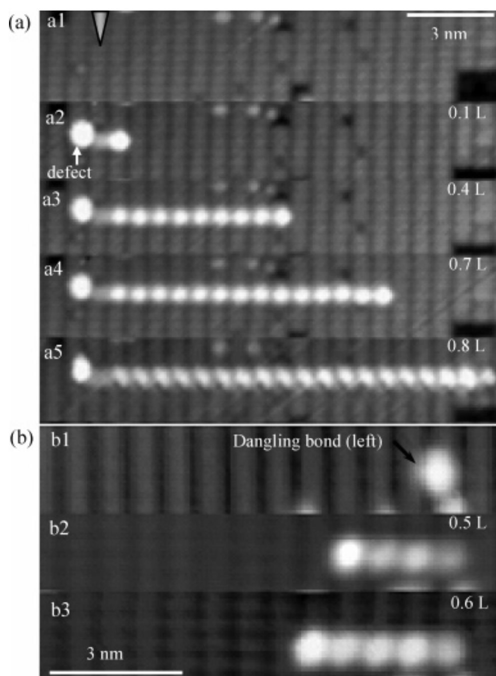

Figure 2. (a) Series of STM images showing stepwise growth of the molecular line of adsorbed allyl mercaptan (a2−a5), initiated at a dangling bond created in (a1), across the dimer rows on the Si(100)−(2 × 1)−H surface. (b) Direction of the line growth with respect to the location of DB on a dimer. The total exposures are indicated in L (Langmuir). V_{sample} = −2.5 V; I = 0.2 nA.

dimer; that is, the line proceeds to the left (as in Figure 2b) or right (as in Figure 2a) side of the dimer row if the DB is located at the left (Figure 2b1) or right side on a dimer, respectively. We observed that, once the growth of the line starts, it continues to grow with increasing exposure of ALM molecules until the growing line encounters pre-existing defects, such as a missing dimer, DB, or other kinds of defects.

Similar to the case of styrene,[3] some lines grow much faster than others, and some DB exhibit no line growth. In addition to the proposed autocatalytic effect,[3] some other factors, such as reverse reaction, barrier to DB diffusion, substitution reaction of the −SH group with the DB, and lack of the molecule reaching the DB site, may also contribute to the observed phenomena.

In accordance with the reported mechanism for the chain reaction of alkene molecules triggered at the DB site,[3,11] the possible reaction mechanism for the formation of an ALM line on the Si(100)−(2 × 1)−H surface is schematically shown in Figure 3. While propylene ($CH_2{=}CH{-}CH_3$) and allyl methyl sulfide ($CH_2{=}CH{-}CH_2{-}S{-}CH_3$) do not show any line growth, the −SH group in ALM seems to play an important role in the stabilization of the intermediate radical in Figure 3b, which has been reported to be the key for the successful growth of the molecular line.[3,6] The chemistry of the C (carbon)-centered radical in the thiol molecule suggests that the radical centered at C can be transferred on S (sulfur) through tautomerism and results in a thiyl radical (Figure 3c), which is expected to be stable enough to abstract a H from the substrate.[12]

We think the distance between the stable intermediate radical and the anchoring site of the molecule is one of the factors that determines the selectivity in the direction (across or along the dimer rows) of line growth. It is evident that the length of the ALM molecule makes it possible that a radical on the S atom (Figure 3c) reaches the nearest H on the next dimer rows and abstracts it. However, it is not known at this stage whether the structure of

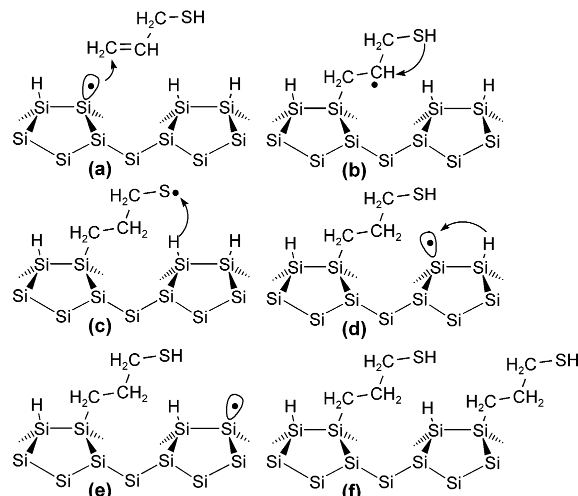

Figure 3. Proposed reaction mechanism of allyl mercaptan molecule with an unpaired dangling bond on the H-terminated Si(100)−(2 × 1) surface.

Figure 3e is achieved through the abstraction event (Figure 3c) followed by hopping of DB (Figure 3d) or directly through abstraction of the second H on the dimer. An elaborate computational simulation is needed to explore the energetics of the reaction steps and adsorbed states of the ALM on the surface. Consistent with the high-resolution STM image of the ALM line, the adsorbed ALM is schematically shown by Figure 3f. The head and tail indicated in the inset of Figure 1b may correspond to the SH and hydrocarbon part of the adsorbed molecules, respectively.

In conclusion, we succeeded in the rapid fabrication of covalently bonded 1D functional molecular lines with predefined location, direction, and length across the dimer rows on the Si(100)−(2 × 1)−H surface. The present observation provides a means to make a predesigned interconnection of molecular lines running along and across the dimer rows.

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