

## Unique behavior of acetophenone molecules in growing one-dimensional molecular assemblies on the Si(100)–(2 × 1)–H surface

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**Introduction.** The  $\pi$ -conjugated organic molecules assembled in low dimension are promising as materials for future nano scale semiconductor devices.<sup>1,2</sup> 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.<sup>3</sup> To date, a variety of organic molecules have been studied on the Si(100)-(2 × 1)-H surface.<sup>3,4</sup> However, only one type of ordered  $\pi$ -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 surface. From the practical point of view, ordered arrangements of  $\pi$ -conjugated systems in both high symmetric directions as well as variation in the  $\pi$ - $\pi$  alignments are highly desirable. Here, we explore the interactions of acetone (CH<sub>3</sub>COCH<sub>3</sub>), benzophenone (PhCOPh) and acetophenone (PhCOCH<sub>3</sub>) molecules with the DB sites on the Si(100)-(2 × 1)-H surface using scanning tunneling microscope (STM) at 300 K.<sup>5</sup>

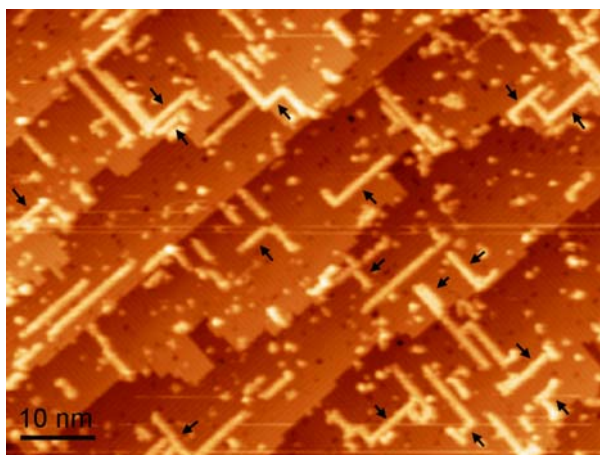
**Experimental.** The experiments were performed in an ultra-high vacuum (UHV) chamber with base pressure better than  $5 \times 10^{-11}$  mbar. The Boron-doped silicon sample (0.01  $\Omega$ cm) was cleaned by prolonged annealing at  $\sim 850$  K ( $\sim 8$  hours) followed by repeated flashing up to 1400 K. The H-terminated surface was prepared by exposure to atomic H, generated by a hot W-filament ( $\sim 2100$  K), at the surface temperature of  $\sim 625$  K. The H-terminated Si(100)-(2 × 1) surface consists of parallel rows of monohydride silicon dimers (H-Si-Si-H), where the inter-dimer distances along and across the dimer rows are 3.8 and 7.6 Å, respectively. The freshly prepared H-terminated surface normally contains a dilute concentration of unpaired DB sites resulting from the incomplete H-termination, otherwise, the DB at a predefined position is generated using STM tip. Benzophenone (solid), acetophenone (colorless liquid) and acetone (colorless liquid) molecules were dosed onto the silicon surface through electronically controlled pulse-valve or through a gate valve.

**Results and Discussions.** All the molecules, acetone (CH<sub>3</sub>COCH<sub>3</sub>), benzophenone (PhCOPh) and acetophenone (PhCOCH<sub>3</sub>), were observed to undergo a chain reaction with the dangling bond (DB) site of the substrate and form well defined molecular lines on the surface. The directional selectivity of acetone and benzophenone is similar to that of acetaldehyde or benzaldehyde molecules,<sup>6</sup> i.e., benzophenone and acetone form molecular lines exclusively parallel to the dimer row direction. In contrast to acetone and benzophenone, acetophenone molecules show the molecular lines both parallel and perpendicular to the dimer rows directions, as shown in figure 1. The molecular lines that lied perpendicular to the dimer row direction were estimated to be  $\sim 30\%$  of the total number of molecular lines on a typical surface. 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.

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, as revealed in high-resolution STM images (not shown). Such variations in molecular arrangement were not observed in the case of acetone and benzophenone molecules. About 70% of the molecular lines lying parallel to the dimer row directions consist of alternate enantiomeric forms of adsorbed molecules. The strong tendency of attaining the alternate geometries of adsorbed molecules in parallel to the dimer row direction seems to play the key role in propagating some chain reactions perpendicular to the dimer row direction by acetophenone molecules.

The growth of molecular lines in both high-symmetry directions and the sterically controlled arrangement of adsorbed acetophenone molecules are unique 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.



**Figure 1.** STM image of the Si(100)-(2 × 1)-H surface exposed to ~ 10 L of acetophenone (PhCOCH<sub>3</sub>) molecules at 300 K. The black arrows indicate molecular line grown perpendicular to the dimer-row direction.  $V_{\text{sample}} = -2.1 \text{ V}$ ;  $I = 0.2 \text{ nA}$ .

## References

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