Journal of the Korean Physical Society, Vol. 69, No. 1, July 2016, pp. 52∼55

Direct Visualization of a Cycloaddition Reaction on Frozen Asymmetric Si Dimers at Room Temperature

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(Received 12 May 2016)

We firstly report an experimental visualization of a cycloaddition reaction on RT frozen asymmetric Si dimers. The frozen Si dimers with a local c(4 × 2) order were prepared by pinning flip-flopping Si dimers by using molecules. This RT pristine c(4 × 2) structure was used to determine what Si atom of an asymmetric Si dimer bonds to a molecule at the initial stage of the RT cycloaddition reaction, which has been a long-standing puzzling issue. This made it possible to compare directly experimental cycloaddition reactions with theoretical ones. As a prototype for the experiment, a 1,3-butadiene molecule adsorbed between Si dimer rows was used. The 1,3-butadiene molecule was found to prefer a symmetric Si pair on the frozen Si dimers, *i.e.*, two electrophilic lower atoms of asymmetric Si dimers. This result is consistent with the theoretical prediction that a 1,3-diene molecule prefers a symmetric Si pair on the Si(001)c(4 × 2) surface. This experimental approach can also be applied to other studies for the adsorption of a molecule on a Si(001) surface at room temperature.

PACS numbers: 68.35.Ja, 68.35.Md
Keywords: Si(001), 1,3-butadiene, Cycloaddition, Symmetric and asymmetric dimers
DOI: 10.3938/jkps.69.52

I. INTRODUCTION

Chemical reactions of unsaturated hydrocarbon and heterocyclic aromatic molecules on Si surfaces have become a subject of intense attention because of potential applications such as molecular electronics [1–3]. Recent studies of the reactions have focused on cycloaddition reactions and their pathways on the Si(001)2 × 1 and Si(111)7 × 7 surfaces [4–10]. One of puzzling issues in the studies is that, for the cycloaddition reactions on the Si(001)2 × 1 surface, the frozen asymmetric Si dimers adopted in theoretical approaches have not been successfully realized in experiments [4–13].

The Si(001)2 × 1 surface consists of asymmetric Si dimers which flip-flop at room temperature (RT) and freeze at low temperature forming a c(4×2) or a p(2×1) phase [14,15]. Of note is that most experiments on cycloaddition reactions on the Si(001)2 × 1 surface were performed at RT. For example, a 1,3-diene molecule was found to form a [4 + 2]-like cycloaddition product after bonding with a flip-flopping Si pair at RT by using scanning tunneling microscopy (STM) [16–18]. In contrast, theoretical calculations have used frozen asymmetric Si dimers with a c(4 × 2) or a p(2 × 1) order [4, 12]. This suggests that a 1,3-diene molecule, located between Si dimer rows, prefers a symmetric Si pair on the Si(001)c(4 × 2) surface [6] and an asymmetric Si pair on the Si(001)p(2 × 1) surface [12]. Accordingly, the extremely-frequent flip-flop motion of Si dimers at RT has limited direct comparison of the theoretical results with the experimental data. If the gap between the the-

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oretical and the experimental results is to be closed, an experiment on a molecule adsorption on frozen asymmetric Si dimers is required.

In this paper, we first report an experimental visualization of a cycloaddition reaction on RT frozen asymmetric Si dimers. The frozen Si dimers with a local c(4 × 2) order were prepared by pinning flip-flopping Si dimers by using molecules. This made possible a direct comparison of experimental cycloaddition reactions with theoretical ones. As a prototype for the experiment, a 1,3-butadiene molecule adsorbed between Si dimer rows was used. The 1,3-butadiene molecule was found to prefer a symmetric Si pair on the frozen Si dimers, *i.e.*, the two lower atoms of asymmetric Si dimers. This result is consistent with a theoretical prediction that a 1,3-diene molecule prefers a symmetric Si pair on the Si(001)c(4 × 2) surface [4]. This experimental approach can also be applied to other studies on molecule adsorption on the RT Si(001) surface.

II. EXPERIMENTS

STM images were acquired using a commercial variable-temperature STM system(Omicron, Germany) with a base pressure below 1×10^{-10} Torr. All STM images shown here were measured in a constant current-mode, and the purity of 1,3-butadiene was checked by using a quadrupole mass analyzer (QMA). The base pressure of the vacuum system was lower than 1×10^{-10} Torr. A boron-doped Si(001) wafer (5 − 12 cm) was degassed at 800 °C for several hours and repeatedly annealed to 1250 °C by direct-current heating to obtain a clean 2 × 1 surface. The 1,3-butadiene from Sigma-Aldrich was purified by prolonged pumping before use on the clean Si(001)-2 × 1 surface. Dosing was performed from a backfilled gas line into the chamber. The exposure was recorded in langmuir (1 L = 10^{-6} Torr·s).

III. RESULTS AND DISCUSSION

STM images, shown in Figs. 1(a) and 1(b), were measured at RT with constant currents of −1.5 nA for the filled state and 1.0 nA for the empty state. Flip-flopping Si dimers were imaged as elliptical shapes in both the images, and five different adsorption sites of a 1,3-butadiene molecule and C-defect were found, as reported previously in the case of a 1,3-hexadiene molecule [16, 17]. Figs. 1(c) and 1(d) show a STM image and a schematic figure, respectively, of two representative adsorption sites of 1,3-butadiene molecules, indicated by B and C, on two different types of interdimer-bridge. We can also easily distinguish B from a C-defect by whether there is a bright protrusion in an intradimer site. The bright protrusion originates from highly occupied molecular orbital(HOMO) π-state of two left-carbon atoms after a

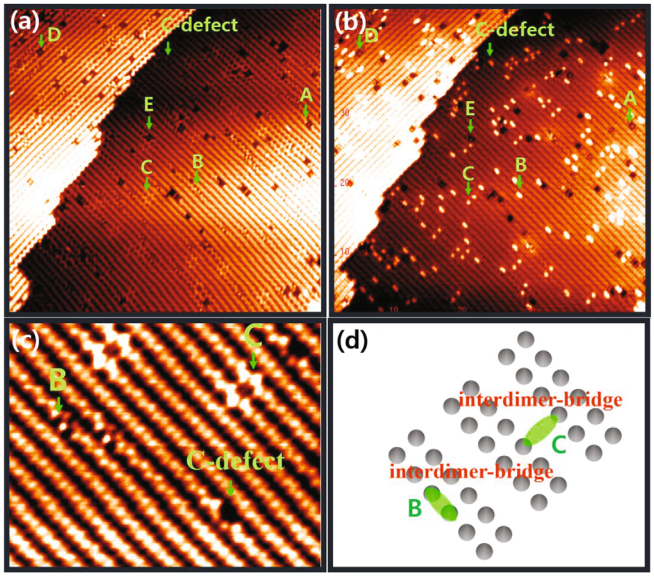

Fig. 1. (Color online) STM images of the Si(001)2 × 1 surface with V_s = (a) −1.5 V and (b) 1.0 V after adsorptions of 1,3-butadiene molecules. Five different adsorption sites (A, B, C, D, E) of a 1,3-butadiene molecule and a C-defect were found, as reported previously in the case of a 1,3-hexadiene molecule. Two typical types (B, C) of adsorption sites from the 1,3-butadiene molecule are shown in (c) and the atomic structure models are described in (d).

4 + 2 cycloaddition reaction with silicon atoms while the C-defect originates from H and OH adsorbed on two neighboring lower Si atoms, as reported previously [19–22]. Here, the C adsorption site must be examined intensively in order to focus on the adsorption pathway.

As shown in Fig. 2(a), the filled-state STM image shows a zigzag order of bright circles near the C site, where the bright circle originates mainly from the π state of the upper atom of an asymmetric Si dimer [16, 18]. This indicates that the 1,3-butadiene molecule at the C site induces a local c(4 × 2) order of an asymmetric Si dimer. In the empty-state STM image, two bright protrusions are observed. The protrusions can be assigned to unsaturated Si dangling bonds of the upper Si atom produced by the bond between the lower Si atom and a 1,3-butadiene molecule, as reported previously in the case of a 1,3-cyclohexadiene molecule [16,18].

Such a cycloaddition reaction of a 1,3-diene molecule with RT flip-flopping asymmetric Si dimers leaves an unresolved problem for the following reasons: The flip-flopping motion of the asymmetric Si dimer has a frequency of a few terahertz, and the reaction time of a cycloaddition reaction is shorter than a few picosecond [14, 15]. Thus, it is not obvious in a STM image what Si atom of the flip-flopping asymmetric Si dimer bonding with a 1,3-diene molecule at the initial stage of the reaction. In addition, a STM image shows only a final product. Therefore, the charge distribution of a Si pair bonding with a 1,3-diene molecule at the initial stage

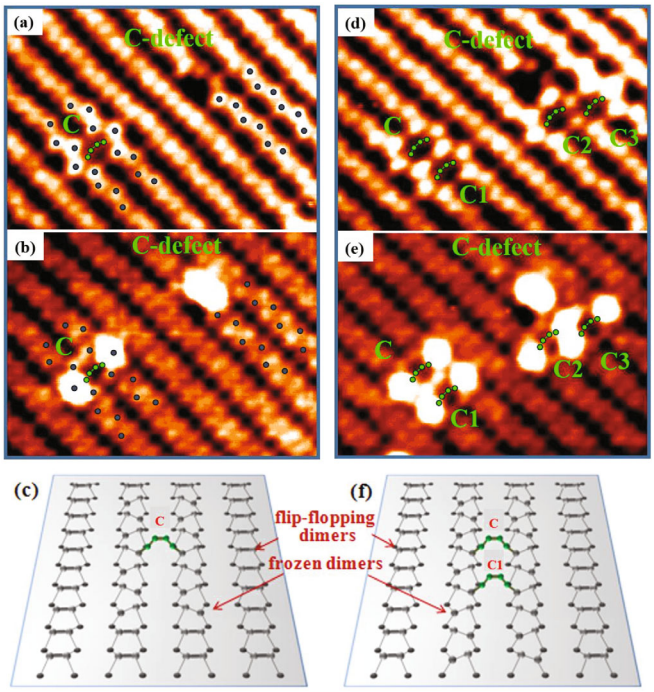

Fig. 2. (Color online) STM images of the Si(001)2 × 1 surface with (a)−(d) $V_s = -1.5$ and (b)−(e) $V_s = 1.0$ V (a)−(b) before and (d)−(e) after additional adsorptions of 1,3-butadiene molecules. The 1,3-butadiene and the water molecule, used to make a pristine local c(4 × 2) structure, are indicated by C and C-defect, respectively. The 1,3-butadiene molecules added to the pristine c(4 × 2) structure are indicated by C1, C2, and C3. (c) and (f) shows the atomic structure models of the C site before and after additional adsorptions of 1,3-butadiene molecules, respectively.

of the reaction, which plays a critical role in selecting its reaction pathway, cannot be determined experimentally. Accordingly, theoretical calculations for a [4 + 2]-like cycloaddition reaction of a 1,3-diene molecule have remained conflicting. A 1,3-diene molecule located between Si dimer rows was suggested to prefer a symmetric Si pair, *i.e.*, two lower Si atoms on the Si(001)c(4 × 2) surface, as shown in Fig. 3(a) [6]. On the Si(001)p(2 × 1) surface, a 1,3-diene molecule was suggested to bond with an asymmetric Si pair, *i.e.*, an upper and a lower Si atom, as shown in Fig. 3(b) [12].

To clarify the conflicting theoretical calculations and close the gap between theoretical and experimental results, we prepared a local c(4 × 2) structure of frozen asymmetric Si dimers at RT using 1,3-butadiene molecules. In this experiment, the 1,3-butadiene molecule at the C site, among the six different adsorption sites, was more efficient in producing the local c(4 × 2) structure. The c(4 × 2) structure was also produced by a dissociated product of a water molecule called a C-defect, which is indicated in Fig. 1(a) [20–22]. Here, the bright ellipse in the empty-state STM image is produced by unsaturated dangling bonds of the upper atoms of

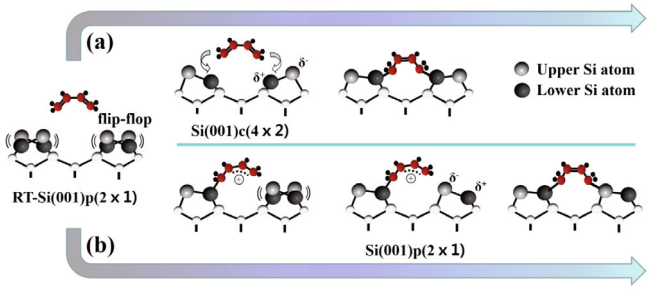

Fig. 3. (Color online) [4 + 2]-like cycloaddition reactions of a 1,3-butadiene molecule with asymmetric Si dimers on the Si(001) surface: (a) a concerted pathway in the case of the Si(001)c(4 × 2) surface and (b) a stepwise pathway in the case of the Si(001)p(2 × 1) surface.

asymmetric Si dimers bonding with H and OH.

The RT Si(001) surface with the local c(4 × 2) order of frozen asymmetric Si dimers was exposed to 1,3-butadiene molecules. Figs. 2(d) and 2(e) show filled- and empty-state STM images after additional adsorptions of 1,3-butadiene molecules. We emphasize that the region in Figs. 2(d) and 2(e) are the same as those in Figs. 2(a) and 2(d). To image the same region, we used the following procedure: Before the additional adsorptions of 1,3-butadiene molecules, the STM tip was moved away from the imaged region by 800 nm. After the adsorptions, we moved the STM tip back to the imaged region and finally confirmed whether the region was the same as the region imaged using a large defect or a step edge structure. The empty-state STM image in Fig. 2(e) shows that three 1,3-butadiene molecules, indicated by C1, C2 and C3, were adsorbed additionally on the surface. Among the three sites, the C1 and C3 sites show clearly where the added molecules were adsorbed on the RT pristine local c(4 × 2) surface. The empty-state images of the C1 and the C3 sites are identical to that of the C site. This indicates that the added 1,3-butadiene molecules make the same final product with the C site. In other words, the added 1,3-butadiene molecules were adsorbed between Si dimer rows and bonded with the two lower atoms of the frozen asymmetric Si dimers, where the atomic structure of the C1 site is drawn in Fig. 2(f). This leads to a conclusion that a 1,3-butadiene molecule adsorbed between Si dimer rows prefers a symmetric Si pair, *i.e.*, two electrophilic lower Si atoms, on the c(4 × 2) structure. The RT frozen asymmetric dimer, thus, elucidates obviously which Si atom of an asymmetric Si dimer bonds with a molecule in a cycloaddition reaction.

Such a cycloaddition reaction of a 1,3-diene molecule with a symmetric pair on a semiconductor surface was also reported for the C(001) and the Si(111) surfaces [9, 23, 24]. To bond with a symmetric pair through a cycloaddition reaction, the reaction should follow a concerted reaction pathway without an intermediate state, as shown in Fig. 3(a). On the other hand, when bonding with an asymmetric pair, a stepwise reaction is preferred,

as shown in Fig. 3(b). Thus, the 1,3-butadiene molecule adsorbed between Si dimer rows obviously bonds with a symmetric pair on the RT Si(001) surface and forms a [4 + 2]-like cycloaddition product through a concerted pathway. A possibility still exists that a stepwise pathway is chosen on the symmetric pair. If sublayers of a Si structure are distorted by a molecule's adsorption, consequently resulting in asymmetric pair, the existence of a molecule-induced asymmetric pair would make a stepwise pathway possible, as suggested theoretically [6].

IV. CONCLUSION

A local c(4 × 2) structure of frozen asymmetric Si dimers was successfully prepared on Si(001) surface at room temperature by using adsorptions of 1,3-butadiene and water molecules. The RT pristine c(4 × 2) structure was used to determine what Si atom of an asymmetric Si dimer bonds with a molecule at the initial stage of the RT cycloaddition reaction, which has been a long-standing puzzling issue. The 1,3-butadiene molecules added to the pristine c(4 × 2) structure revealed that a 1,3-butadiene molecule adsorbed between Si dimer rows preferred to bond with two electrophilic lower atoms of asymmetric Si dimers on the Si(001)c(4 × 2) surface, which is consistent with a theoretical prediction and the concerted reaction mechanism should not be ruled out.

ACKNOWLEDGMENTS

This work was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) (Grant Nos. NRF-2009-0073117 and NRF-2015M2A2A6A01045343) and by the Converging Research Center Program (2013K000306) funded by the Ministry of Science, ICT and Future Planning (MSIP).

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