

Initial adsorption configurations of acetylene molecules on the Si(001) surface

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Initial adsorption configurations of acetylene molecules on the Si(001) surface are investigated by scanning tunneling microscopy (STM) and *ab initio* pseudopotential calculations. Three distinctive features are observed in the STM images at low coverage. The comparison of the atomic resolution STM images with the simulation reveals that there are basically *two* kinds of di- σ bonding configurations: (i) on-top over a single dimer and (ii) end-bridge between two successive dimers in the same dimer row. The third feature is identified to be a pair of end-bridge di- σ configurations occupying the same two dimers. The tetra- σ bonding configurations are not found. The existence of the two kinds of di- σ bonding configurations can resolve the apparently conflicting results of the existing studies.

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The hydrocarbon molecules on the Si(001) surface attract increasing attention to grow carbon related materials like SiC (Ref. 1) and to fabricate strain-controlled nanostructures.² They are also important to understand the interface structure between organic and inorganic materials for the future molecular electronic devices.³ Among various hydrocarbons, acetylene is a prototype to achieve these purposes. It is the simplest molecule which can be effectively dissociated on the surface by heating.

For the last decade the adsorption of acetylene molecules on the Si(001) surface has been studied intensively by many experimental techniques and theoretical calculations.^{4–17} The early studies on this system focused on the issue of whether the Si dimer which is bonded with a molecule is retained or cleaved. A general consensus has been reached, that is, the reacted Si dimers are intact.^{4–6} A far more important issue, which is under heavy debate, is the adsorption geometry and the consequent carbon orbital configurations. Two local adsorption geometries of an acetylene molecule on the Si(001) surface are competing: di- σ versus tetra- σ configurations (see Fig. 1). They differ in the number of substrate Si atoms with which an acetylene molecule makes bonds: two in di- σ and four in tetra- σ configurations. Their intramolecular configurations thus contrast, possessing a double bond (C=C) with sp^2 and a single bond (C—C) with sp^3 rehybridized orbitals, respectively.

The di- σ adsorption configuration has been proposed in early experimental and theoretical studies^{4,5,7} and reaffirmed by a recent scanning tunneling microscopy (STM) study.⁸ The feature in the STM images was interpreted as acetylene molecules sitting parallel on top of the Si dimers (on-top di- σ). It has been further supported by several experimental studies using high-resolution electron-energy-loss spectroscopy (HREELS),⁹ photoelectron diffraction,¹⁰ near-edge X-ray absorption fine structure (NEXAFS), and valence-band photoemission spectroscopy.¹¹ On the other hand, Wolkow has raised the possibility of the tetra- σ adsorption.¹² Subsequently, the existence of the tetra- σ adsorption was claimed in recent photoelectron diffraction imaging¹³ and core-level photoemission¹⁴ experiments.

Theoretical calculations have provided interesting perspectives.^{15–17} While the most stable of the considered configurations was on-top di- σ , a different adsorption configuration—the so-called end-bridge configuration—was shown to be comparably stable. In this configuration, an acetylene molecule bridges two adjacent dimers in the same dimer row by attaching to one atom of each dimer, and forms another type of di- σ configuration. The tetra- σ geometries with the C-C axis of the acetylene molecule being parallel (*p*-bridge) or at right angle (*r* bridge) with respect to the dimer direction, was shown to have much smaller adsorption energies. In one of the studies, the most energetically unlikely *p*-bridge tetra- σ geometry has been suggested to exist at room temperature by the kinetic effect and energy barrier.¹⁶

In this paper, we report a combined study of atomic resolution STM experiment and *ab initio* calculation on the initial adsorption configurations of acetylene molecules on Si(001) surface at room temperature. We made an experimental STM observation of C₂H₂ molecules in the theoretically proposed end-bridge di- σ geometry which exist as *single* and *paired* configurations, in addition to the previously reported on-top di- σ configuration. We have not observed any feature which can be related to the tetra- σ configurations. This leads us to conclude that a *single* acetylene molecule is adsorbed on the Si(001) surface by forming two σ bonds with either one or two Si dimers.

Experiments were performed using a homemade STM in an ultrahigh vacuum chamber with a base pressure below 2×10^{-10} Torr. The Si(001) surface was cleaned by repeated

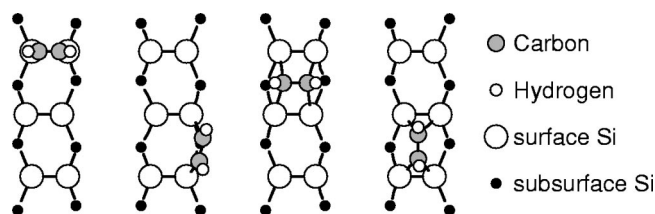


FIG. 1. Schematic view of proposed adsorption geometries: di- σ (on-top and end-bridge) and tetra- σ (*p*-bridge and *r*-bridge) configurations from left to right.

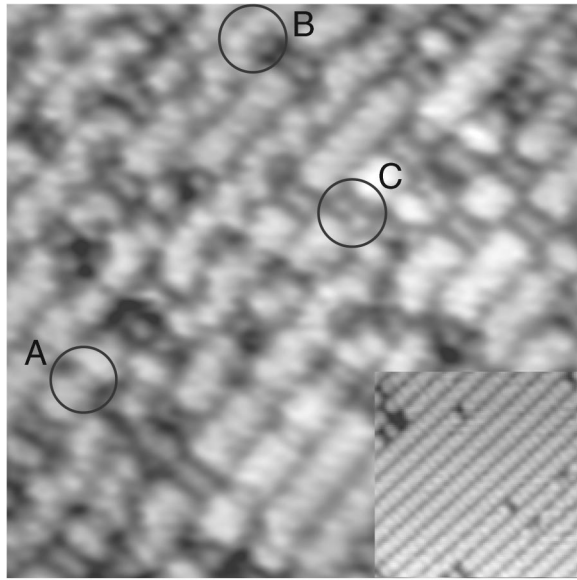


FIG. 2. A filled state STM image of $\text{C}_2\text{H}_2/\text{Si}(001)$ with three dominant features labeled A, B, and C. The sample bias voltage is -2.5 V and the tunneling current is 0.3 nA. The inset shows the typical clean $\text{Si}(001)-2\times 1$ surface with defect density of 4%.

flashes up to 1450 K,¹⁸ and confirmed by STM. Acetylene gas was dosed onto the sample at room temperature by back-filling the chamber. The structure of the $\text{C}_2\text{H}_2/\text{Si}(001)$ was investigated by STM at room temperature.

Figure 2 shows a typical STM image of $\text{C}_2\text{H}_2/\text{Si}(001)$ at low coverage. In the image, there are three dominant features labeled A, B, and C. (The numbers of A, B, and C in the image are 19, 22, and 20, respectively.) Type A occupies a single dimer site, and appears slightly depressed compared with the clean Si dimers. Type B spans two dimers in a dimer row and makes an asymmetric appearance. Type C also occupies two dimer sites along the dimer row but with a symmetric appearance. Some (about 17) features which cannot be identified as either of those three features are also observed in the image. They are of diverse characters and difficult to categorize into another type of adsorption configuration. We consider that they are related to the defects which appear with a similar density on the $\text{Si}(001)$ surface.

The enlarged images and the height profiles of the three features are shown in Fig. 3 to provide detailed information of atomic structure.

Type A [Fig. 3(a)]. It appears narrower in the dimer direction. Its height profile contains only a single maximum in both directions along and across the dimer row. We interpret this as the on-top di- σ configuration. It appears similar to the STM image of an ethylene molecule adsorbed on the $\text{Si}(001)$ surface.¹²

Type B [Fig. 3(b)]. Two bright spots are located at one side and a single weak protrusion at the other side of the dimer row. In addition, the Si dimer buckling appears to be pinned in the neighborhood of this feature. The height profiles crossing the weak protrusion show that a local maximum is located midway between two dimers along the dimer row but displaced towards one edge of the dimer row. We note that this feature is distinct from the so-called C-defect,

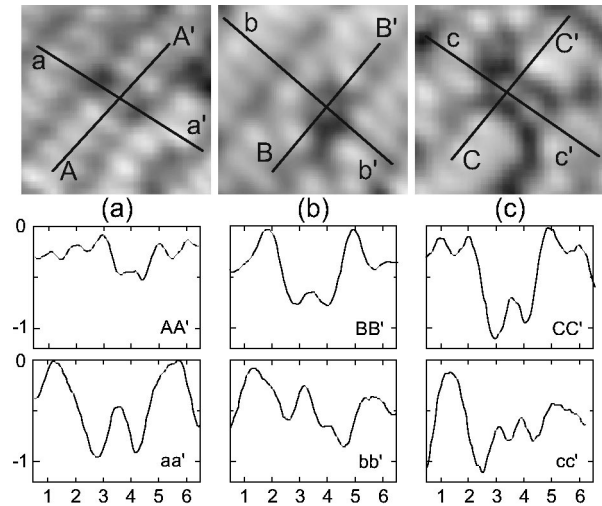


FIG. 3. The magnified image of each feature found in Fig. 2 and the height profiles along two orthogonal paths passing through the local maximum. (a) Type A, (b) type B, and (c) type C features. The vertical and horizontal axes are in the unit of \AA and the surface lattice constant 3.84 \AA , respectively.

which does not have such a local maximum, on the clean $\text{Si}(001)$ surface.¹⁹ We interpret the weak protrusion as an acetylene molecule adsorbed in the end-bridge di- σ configuration and the two bright spots as the Si dangling bonds. This feature was missing in the previously published STM images but the existence of the end-bridge configuration has been theoretically predicted based on its considerably large adsorption energy.^{15–17}

Type C [Fig. 3(c)]. Like the on-top di- σ , it appears symmetric in both dimer and dimer row directions. The main difference from the on-top di- σ feature is that the height profile in the dimer direction (cc') consists of two local maxima, which are aligned with the node between two dimers of the neighboring dimer row. We interpret this feature as a pair of acetylene molecules adsorbed on both edges of the two successive dimers in the same dimer row—a paired end-bridge. The double maxima of this feature can be reasonably reproduced by simple superposition of two end-bridge di- σ configurations. In some of these features, the two local maxima are less distinct. This is supposed to be related with slightly different local environment around each feature such as the geometry of underlying Si dimers. As a matter of fact, this feature was observed and assigned to the on-top di- σ configuration in a previous STM study,⁸ but reinterpreted later as the tetra- σ configuration by Wolkow.¹² A similar interpretation was also made in a recent STM work.²⁰

To test our assignment of the features observed in the STM image, we have performed the *ab initio* pseudopotential calculations within the local-density approximation (LDA),²¹ using the Vienna *Ab initio* Simulation Package.²² We used a plane-wave cutoff of 300 eV, the theoretical lattice constant of 5.39 \AA , Γ -point sampling for Brillouin-zone integration, and ultra soft pseudopotentials.²³ The $\text{Si}(001)$ surface was modeled by a six layer slab separated by 19 \AA vacuum with (4×6) surface supercell. Acetylene molecules were adsorbed on $c(4\times 2)$ reconstructed surface and the op-

TABLE I. Adsorption energies (E_{ads}) of single and double molecular adsorption configurations.

Number of C_2H_2	Configuration	E_{ads} (eV/ C_2H_2)
Single	on-top di- σ	3.20
	end-bridge di- σ	3.00
	r -bridge tetra- σ	2.55
	p -bridge tetra- σ	1.80
Double	double on-top di- σ	3.19
	paired end-bridge di- σ	3.35

posing surface was passivated by hydrogens. All adsorbate atoms and the top four Si layers were allowed to relax until their rms forces were smaller than 0.01 eV/Å. The constant-current STM images were simulated within Tersoff-Hamann approximation²⁴ under the applied external electric field²⁵ of -0.4 V/Å. In order to simulate the symmetric dimer in the experimental STM image at room temperature, the LDA images from the oppositely buckled dimers were averaged.

Educated from the experimental observations and the available theoretical results, we have calculated the *ab initio* total energies for (i) four single molecular adsorption configurations (on-top di- σ , end-bridge di- σ , p -bridge tetra- σ , and r -bridge tetra- σ) and (ii) two paired molecular adsorption geometries (paired end-bridge and double on-top di- σ configurations). The calculated adsorption energies are shown in Table I. Among four single molecular adsorption geometries, the on-top di- σ configuration has the largest adsorption energy, 3.20 eV. While the tetra- σ configurations have significantly smaller adsorption energies compared to the on-top configuration (1.80 for p -bridge and 2.55 eV for r -bridge), the end-bridge di- σ configuration has comparably large adsorption energy of 3.00 eV. Adsorbing C_2H_2 at one end of the two Si dimers involved in the end-bridge configuration, two dangling bonds are created at the opposite end. This accounts for the adsorption energy reduction of the end-bridge configuration compared to the on-top configuration despite the similar di- σ nature of the Si-C bonds. Our results on a single molecular adsorption are in agreement with the previous calculations.^{16,17}

With the significantly smaller adsorption energies of the two tetra- σ geometries, it is natural to expect that the acetylene molecules would not be adsorbed in these configurations. This implies that the acetylene adsorption will proceed

either by single molecular adsorption in two kinds of di- σ configurations or by forming their complexes if the single molecular adsorbates interact attractively. The last two rows in Table I shows the adsorption energies of the di-molecular complexes. Two acetylene molecules adsorbed in two adjacent on-top di- σ sites have almost the same adsorption energy per molecule compared with the single molecular adsorption. This implies that acetylenes adsorbed in on-top di- σ configuration hardly interact with each other. On the other hand, when adsorbed in end-bridge configuration, two adsorbates turn out to interact strongly attractively. The interaction energy, the energy gain by forming the paired end-bridge configuration, is around 0.7 eV. The attractive interaction is originated from the full compensation of the dangling bonds in the single end-bridge configuration by the additionally adsorbed C_2H_2 .²⁶ As a result, the paired end-bridge configuration has larger adsorption energy per molecule than the single molecular on-top di- σ configuration (3.35 versus 3.20 eV/ C_2H_2).

The STM images were simulated using the fully relaxed geometries with the applied bias voltage of -0.75 V. Five of them are illustrated in Fig. 4. The simulated STM images for the on-top di- σ [Fig. 4(a)] and the end-bridge di- σ [Fig. 4(b)] are in good accordance with the experimental data in Figs. 3(a) and (b). The simulated image for the paired end-bridge di- σ configuration in Fig. 4(c) matches well with the experimental image of the type C in Fig. 3(c). In contrast, the simulated images of the p -bridge and r -bridge tetra- σ configurations [Figs. 4(d) and (e)] show quite different characteristics from the experimental features in Fig. 3. From both the energetics and the simulated STM images, it is evident that the three features observed in the experiment are (i) on-top, (ii) end-bridge, and (iii) paired end-bridge di- σ configurations and the tetra- σ configurations are not observed at all.

Based on our findings, we propose a scenario on the acetylene adsorption on Si(001) extendable to high coverage. Acetylene molecules are adsorbed in *only* two kinds of di- σ configurations: on-top and end-bridge. The larger population of the end-bridge di- σ over the on-top di- σ configuration at low coverage, despite its smaller adsorption energy at low coverage, comes from the larger number of the available adsorption site by a factor of 2. When the coverage increases the acetylene molecules would have more chances to meet other molecules and form more stable complex such as the paired end-bridge di- σ configuration which has the lowest

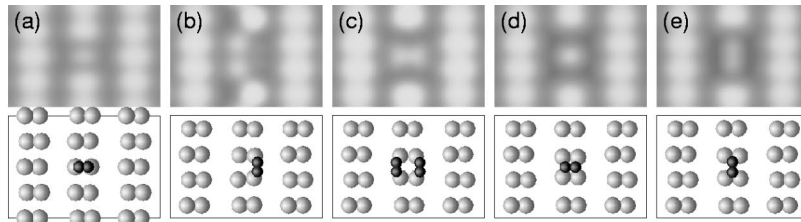


FIG. 4. The simulated STM images of different $\text{C}_2\text{H}_2/\text{Si}(001)$ configurations. (a) On-top di- σ , (b) end-bridge di- σ , (c) paired end-bridge di- σ , (d) p -bridge tetra- σ , and (e) r -bridge tetra- σ configurations. The gray and the black balls are the dimerized Si atoms and the C atoms of the acetylene molecule, respectively. The hydrogen atoms are not represented.

energy. Thus the population of the paired end-bridge (type C in Fig. 2) is expected to increase rapidly at higher coverages.²⁰

The above picture for the acetylene adsorption on Si(001) can account for most of the existing experimental results in a consistent way. The complete removal of the Si dangling bonds at saturation in photoemission study¹⁴ is accountable with paired end-bridge di- σ (or mixture of on-top and paired end-bridge di- σ) without having to assume tetra- σ configurations. The saturation coverage can be as large as 1.0 monolayer (ML) in accordance with the conclusion from the thermal desorption experiment.²⁷ It should be noted that the 0.5-ML saturation coverage was drawn from the $p(2 \times 2)$ arrangement with the mis-assigned on-top di- σ configuration at saturation in the previous STM study.⁸ The decrease but retainment of the $\pi_{C-C,\parallel}^*$ resonance peak of the adsorbed C_2H_2 molecule in the NEXAFS is compatible with di- σ configurations with sp^2 rehybridized orbitals, either the on-top or the end-bridge.¹¹ The symmetry reduction in the adsorption geometry from C_{2v} symmetry concluded from the HREELS results⁹ is exclusively reconcilable by the existence of the low-symmetry end-bridge di- σ configuration.^{17,28} The

only exception which cannot be accommodated within this picture is the photoelectron diffraction holography data by Xu *et al.*,¹³ claiming the tetra- σ configuration.

In conclusion, we have found that there exist only two different di- σ configurations at low coverage and room temperature: on-top and end-bridge. The acetylene molecules in the end-bridge configuration interact attractively and easily form the paired end-bridge, which is another feature observed in our STM image. The tetra- σ configuration is not observed and found to be unlikely from theoretical calculations. These results comply well with most of existing experimental and theoretical studies.

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²⁸The symmetry can be reduced in another way by distorting the adsorption geometry of either on-top di- σ or tetra- σ configurations. However, it was not found in the full coverage calculation with $p(2 \times 2)$ periodicity.