

Acetylene adsorption on Si(111)(7×7): A scanning-tunneling-microscopy study

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The microscopic adsorption state of acetylene (C_2H_2) on Si(111)(7×7) at room temperature has been studied by using scanning tunneling microscopy. The center adatoms are more reacted than the corner adatoms in a ratio of about 2:1 upon the adsorption of acetylene. It is predominantly the adatoms in the faulted subunit that are reacted by acetylene, rather than those in the unfaulted subunit, indicating that acetylene is initially in a mobile precursor state. No significant restructuring of surface Si atoms is observed. It is proposed that acetylene is di- σ bonded to the pair of adjacent Si adatom and Si rest atom, saturating Si dangling bonds of the Si(111)(7×7) surface.

I. INTRODUCTION

The reaction of acetylene (C_2H_2) with Si surfaces has attracted great interest experimentally¹⁻⁵ and theoretically,^{6,7} as the prototype reaction of chemical vapor deposition⁸ and gas-source molecular-beam epitaxy⁹ of silicon carbide, as well as the low-pressure synthesis of diamond film from hydrocarbon.¹⁰

The adsorption of acetylene on Si(111)(7×7) is the first step of whole reactions towards carbide formation. A vibrational electron-energy-loss-spectroscopy (EELS) study² has shown that acetylene is molecularly adsorbed and the carbon-carbon triple bond of acetylene is rehybridized to a state between single and double bond on Si(111)(7×7) at 300 K. It is proposed that acetylene is di- σ bonded to two adjacent Si atoms saturating dangling bonds. A molecular orbital study⁶ has supported this model using an idealized-structure model for the Si(111) surface. A recent semiempirical quantum-chemical study using a 49-Si atom cluster⁷ has also supported the rehybridization of adsorbed acetylene, but they have predicted that a significant restructuring of the silicon surface atoms takes place by the adsorption of acetylene.

In this paper, we have studied the adsorption of acetylene on Si(111)(7×7) at 300 K using scanning tunneling microscopy (STM). STM provided the atomic-scale information in real space about silicon surface chemistry, for example, H,¹¹⁻¹⁴ O₂,¹⁵⁻¹⁷ H₂O,¹⁷ NH₃,¹⁸ etc. on Si(111)(7×7). The first objective of this study is to reveal

the selectivity of surface dangling bonds on Si(111)(7×7) for acetylene adsorption. The second objective is to elucidate whether or not a significant restructuring of the silicon surface atoms takes place upon acetylene adsorption.

II. EXPERIMENT

The experiments were carried out in an ultrahigh vacuum chamber containing an STM, a four-grid retarding field analyzer for low-energy electron diffraction and Auger electron spectroscopy, and a quadrupole mass spectrometer for gas analysis.¹⁹ The base pressure of the vacuum system was $< 1 \times 10^{-10}$ Torr.

Constant current topographs (CCT) were obtained as STM images. A typical tunneling current was 0.1 or 1.0 nA for a fixed sample bias between -3.0 and 3.0 V. STM tips were made by electrochemically etching tungsten wires (0.5-mm diameter). STM images shown here are not corrected for thermal drift.

The silicon samples were *n*-type (P-doped) (1-100 Ω cm) Si(111) wafers. The Si(111)(7×7) clean surface was prepared by heating the crystal up to $\sim 1250^\circ\text{C}$, and was cooled slowly. During this preparation, a background pressure was maintained below 1×10^{-9} Torr. Research-grade C_2H_2 (99.6 mol % purity) was used. The acetylene gas was introduced to the UHV chamber through a variable leak valve, and the pressure was monitored with a nude ion gauge.

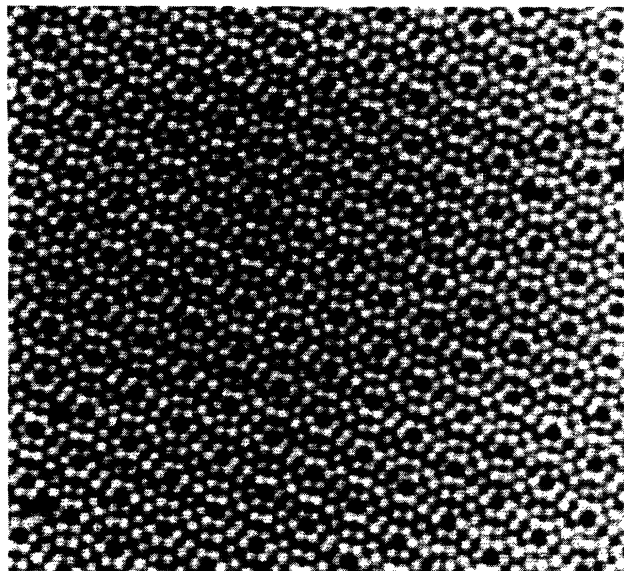


FIG. 1. A constant-current-topograph (CCT) image of clean Si(111)(7×7) at room temperature. Sample bias (E_S)=2.0 V. Tunneling current (I_t)=1.0 nA. Note that the amount of vacancies is very small: $\sim 300 \times 300 \text{ \AA}^2$.

III. RESULTS

After cleaning the Si sample by heating, we usually waited for a few hours to cool the sample down to room temperature, and the thermal drift was minimized. Figure 1 shows a typical STM topograph of the Si(111)(7×7) clean surface with a sample bias at 2.0 V. A CCT image of the positive sample bias corresponds to the unoccupied states of the Si(111)(7×7) surface, and the 12 adatoms are visible in the unit cell.²⁰ A few vacancies of adatoms are seen, but they are always less than 1% of total adatoms according to the inspection of many different areas. Mostly the vacancies are “center” adatoms rather than “corner” adatoms, which are adjacent to the corner hole in the dimer-adatom-stacking fault (DAS) structure of the Si(111)(7×7) surface.²¹ The nearly perfect Si(111)(7×7) surfaces like Fig. 1 were essential for our purposes.

Figures 2(a) and 2(b) show STM topographs of the Si(111)(7×7) surface exposed to 3500-L C_2H_2 [1 langmuir (L) = 10^{-6} Torr s] with the sample biases at 1.5 and 3.0 V, respectively. Upon the adsorption of acetylene, some adatoms become dark [Fig. 2(a)]. However, this is not due to the vacancies of Si adatoms, because these adatoms are visible for the sample bias at 3.0 V [Fig. 2(b)]. Therefore, the change of the brightness of adatoms is due to the change of electronic density of states by the acetylene adsorption. It is noted that real vacancies look dark even at the sample bias at 3.0 V.

In order to probe the reaction selectivity of different adatoms (corner and center adatoms) in the different triangular subunits that contain the stacking-faulted layer and the unfaulted layer, both negative and positive biases were applied to the sample. Figures 3(a) and 3(b) show STM topographs of the same Si(111)(7×7) surface ex-

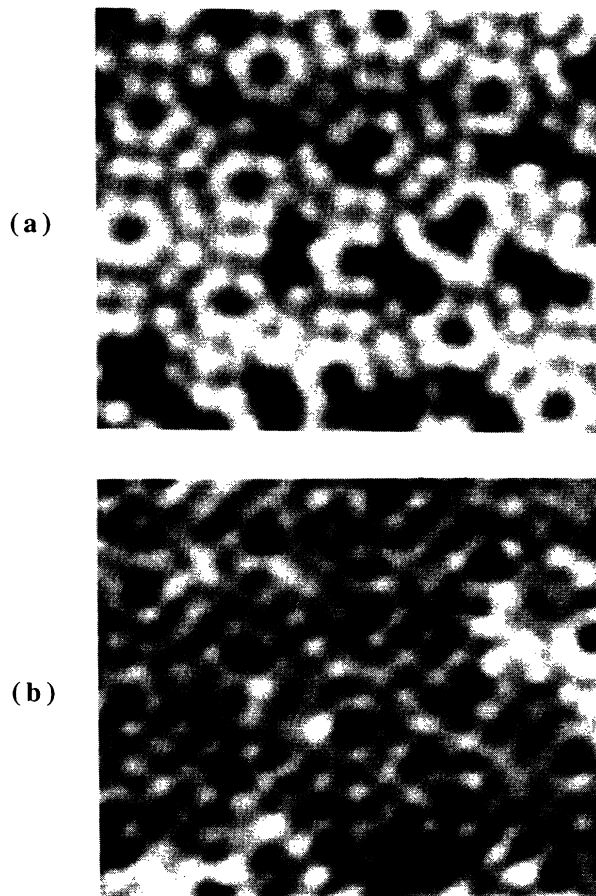


FIG. 2. CCT images of the Si(111)(7×7) surface exposed to 3500-L C_2H_2 at room temperature [(a) $E_S=1.5$ V, $I_t=0.1$ nA, (b) $E_S=3.0$ V, $I_t=0.1$ nA]. $\sim 105 \times 95 \text{ \AA}^2$.

posed to 3500-L C_2H_2 at the sample biases of +2.0 and -2.0 V, respectively. In the case of negative sample bias, the adatoms in the faulted subunit show brighter protrusions of adatoms than those in the unfaulted subunit.²⁰ Figure 3(c) is a schematic diagram showing the location of the reacted adatom sites in the same region [center adatoms (\circ); corner adatoms (Δ)]. The unfaulted subunits are shaded. In Fig. 3, 25 center adatoms and 14 corner adatoms are dark. Of the 39 dark adatoms, 31 are located in the faulted subunits and eight are in the unfaulted subunits. According to the inspection of several different regions on the same surface, the situations are quite similar: center adatoms preferentially reacted rather than corner adatoms in a $\sim 2:1$ ratio, and the adatoms in the faulted subunits reacted in more than a 3:1 ratio compared to those in the unfaulted subunits. It is noted that real vacancy defects may be included, but they should be within the experimental error because the amount of vacancies is less than 1% of all adatoms in the present experiments. In addition, it is interesting to note that more than three adatoms in a triangular subunit do not react in most cases.

Figure 4 shows a three-dimensional topograph of the Si(111)(7×7) surface exposed to 5000-L C_2H_2 at room

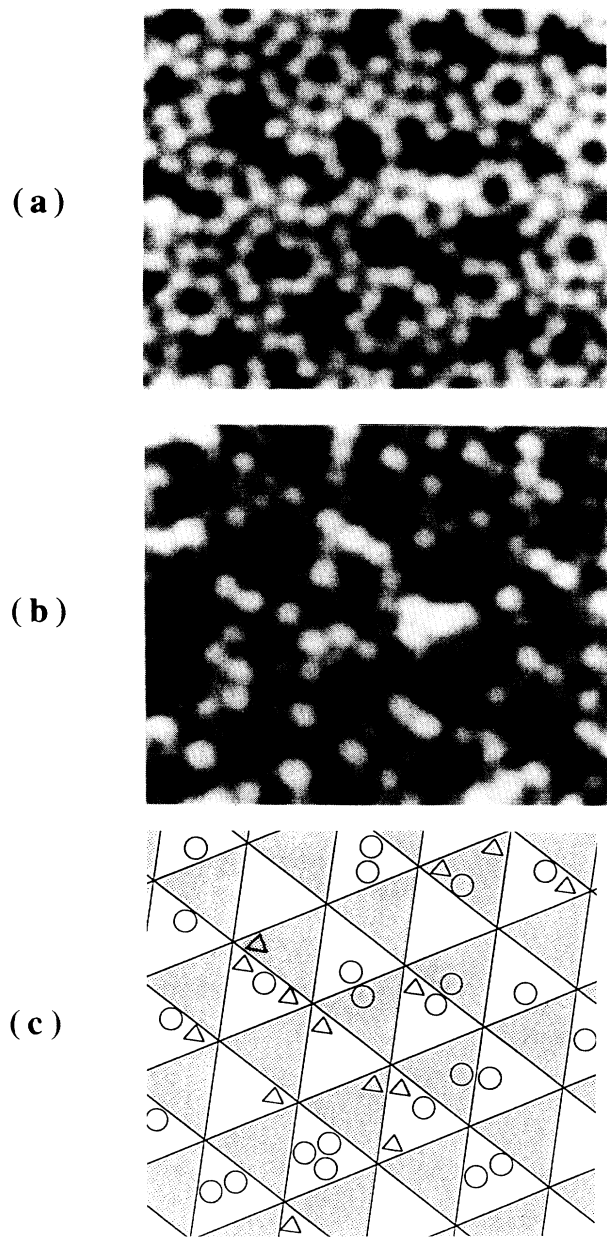


FIG. 3. CCT images of the Si(111)(7 \times 7) surface exposed to 3500-L C₂H₂ at room temperature [(a) $E_S=2.0$ V, $I_t=0.1$ nA, (b) $E_S=-2.0$ V, $I_t=0.1$ nA]. (c) A schematic diagram of the same region. \circ , reacted-center adatoms; \triangle , reacted-corner adatoms. The unfaulted subunits are shaded. $\sim 115 \times 105 \text{ \AA}^2$.

temperature. It is seen that more adatoms have become dark and the tendency of preferential occupation by center adatoms rather than corner adatoms is similar (*the ratio is still* $\sim 2:1$). However, the ratio of reacted adatoms in the faulted subunits to those in the unfaulted subunits becomes smaller ($\sim 2:1$). Thus, the adatoms in the unfaulted subunits have reacted with acetylene more slowly than those in the faulted subunits, and this preferential adsorption is kinetically controlled. Although a small distortion of adatoms around “dark” adatoms can be seen, no significant restructuring of Si adatoms is observed.

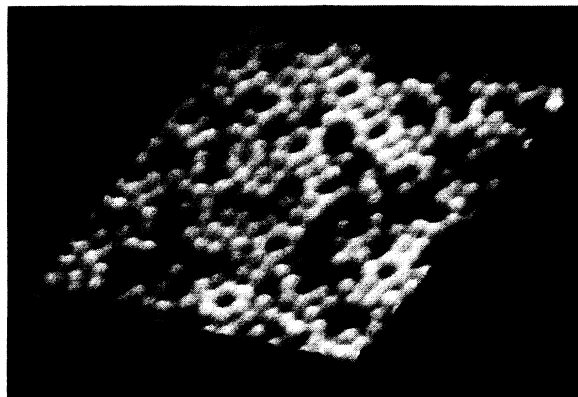


FIG. 4. A three-dimensional CCT image of the Si(111)(7 \times 7) surface exposed to 5000-L C₂H₂ at room temperature [$E_S=0.5$ V, $I_t=1$ nA]. $\sim 150 \times 150 \text{ \AA}^2$.

Within the present experimental conditions, we could not observe a direct image of acetylene, probably because the energy levels of adsorbed acetylene are away from the Fermi level (E_F).⁶

IV. DISCUSSION

In this section, we will inspect several models of adsorbed C₂H₂ on Si(111)(7 \times 7), and we will propose a possible structural model that agrees with the results of EELS (Ref. 2) and theoretical calculation,⁶ and can explain the present STM results.

On Si surfaces such as Si(111)(7 \times 7) and Si(100)(2 \times 1), acetylene molecules react with the dangling bonds of Si surface atoms, and the chemisorption bond formation between Si and C atoms occurs.^{1–5} Therefore, we focus here on the interaction between acetylene and the dangling bonds on Si(111)(7 \times 7).

First of all, a π -bond model, where acetylene is bonded to a single dangling bond (an “on-top” site), is excluded, judging from EELS (Ref. 2) and theoretical⁶ results. Thus, the adsorption to a single dangling bond of adatom, rest atom, or corner hole can be neglected.

Next, we will consider a di- σ bonded acetylene, which has been proposed by the EELS (Ref. 2) and theoretical⁶ studies. According to the DAS model of Si(111)(7 \times 7),²¹ there are seven different combinations of two neighboring Si atoms that have dangling bonds: (1) corner-adatom–corner-adatom, (2) corner-adatom–center-adatom, (3) center-adatom–center-adatom within a subunit, (4) center-adatom–center-adatom across a dimer row, (5) corner-adatom–corner-hole, (6) corner-adatom–rest-atom, and (7) center-adatom–rest-atom (Fig. 5). The direct distances between two Si atoms in the cases of (1)–(7) are 6.65, 7.68, 7.68, 6.65, 7.85, 4.57, and 4.56 \AA , respectively.²² On the other hand, the typical bond lengths of SiC and CC are 1.8–2.1 \AA (Refs. 6 and 23) and 1.2–1.5 \AA ,²³ respectively. Thus, in order to make the di- σ bond, the distance of two Si atoms must be less than 5.7 (equal to $2.1 \times 2 + 1.5$) \AA , provided that significant displacements of surface Si atoms do not occur. In fact, Fig. 2(b) shows no such displacements. Therefore, the cases of (1)–(5) can be excluded. In addi-

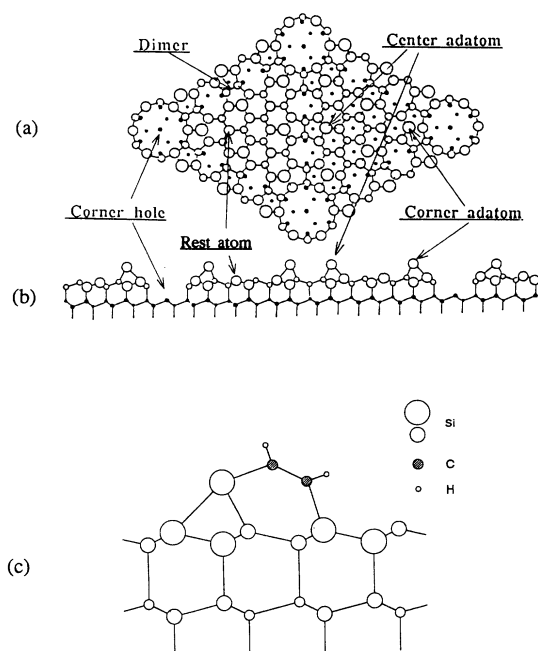


FIG. 5. The DAS model of the Si(111)(7×7) surface (Ref. 21): (a) a top view, and (b) a side view. (c) A proposed model of acetylene di- σ bonded to the pair of an adjacent Si adatom and a Si rest atom.

tion, if the case of (2) or (3) occurs predominantly, the number of dark adatoms in a subunit should be even. However, no such results are observed in the STM images (Figs. 2–5). In case (4), a pair of dark center adatoms across a dimer row should be observed, but there is no evidence for this. Moreover, in cases (1) and (5), predominantly the corner adatoms should be involved, but this contradicts the present results.

On the whole, it is most probable that acetylene is di- σ bonded to the pair of an adatom and a rest atom [cases (6) and (7)]. This model can also explain the preferential occupation by center adatoms rather than corner adatoms in a $\sim 2:1$ ratio. A center adatom has two neighboring rest atoms, but a corner adatom has only one. Thus, statistically, for the di- σ bond formation reaction, center adatoms can be involved with a rest atom two times faster than corner adatoms. In addition, within this model, more than three adatoms in a triangular subunit cannot be involved because the number of rest atoms with a dangling bond is three in the subunit. This also agrees with the present STM results.

It should be mentioned that rest atoms are not clearly seen in the CCT images in the present experimental conditions because adatoms are very predominant. Thus, strictly speaking, the reactivity of adatoms is directly observed in the present studies. However, the experimental results (STM and EELS) suggest the involvement of a rest atom for the di- σ -bonded acetylene (see the above discussion). Atom-resolved scanning tunneling spectroscopy will clarify this directly, as in the case of dissociative adsorption of NH_3 on Si(111)(7×7).¹⁸

A similar preferential reaction (center adatom:corner adatom = 2:1) is observed for the dissociative adsorption

of H_2O on Si(111)(7×7).¹⁷ Avouris and Lyo have postulated that only an adatom–rest atom pair can act in a concerted fashion for the chemisorption reaction of H_2O on Si(111)(7×7).

There is another site preference in the present system: the adatoms in the faulted subunits are more reacted than those in the unfaulted subunits. Two possible factors can be postulated. One may be the strain-energy difference of adsorbed structures, owing to the structural difference of subunits. Another factor may be the difference in electronic structure. A constant-current topograph with a negative sample bias clearly shows the difference of density of states (DOS) between the faulted and unfaulted subunits.^{18,20} Recent theoretical studies^{24,25} have also revealed the difference in DOS's between the faulted and unfaulted subunits: the DOS of adatoms in the faulted subunit is mainly distributed around E_F . The local DOS's could have an effect on a precursor state for chemisorption. The kinetically controlled preferential adsorption in the faulted subunits indicates that acetylene is initially in a mobile precursor state.⁵ Thus, the latter factor is plausible. However, further studies are needed to determine which factor plays an important role.

When the (7×7) surface is exposed to 5000-L acetylene, more adatoms are reacted, but still no rearrangement of Si atoms of the DAS structure is observed (Fig. 4). Around dark reacted adatoms, a small distortion of unreacted adatoms may be seen, although this may not be due to real distortion but due to the changes of electronic structure by acetylene adsorption.

A recent theoretical calculation using a fairly large Si cluster has predicted that significant restructuring of surface Si atoms is induced by acetylene chemisorption.⁷ However, the present STM results show no such restructuring. This may be ascribed to the fact that their model cluster is not large enough to describe a real surface, i.e., the Si(111)(7×7) surface.

Finally, we should note a low sticking probability ($< 10^{-4}$) of acetylene on Si(111)(7×7) at room temperature, as compared with the cases of dissociative adsorption of other molecules such as O_2 (Refs. 15–17 and 26) and NH_3 ,^{18,27} etc. This may be ascribed to the fact that acetylene is *molecularly* adsorbed on the specific sites [the adatom–rest-atom pairs: cases (6) and (7)] in a concerted fashion on Si(111)(7×7).

V. SUMMARY

Some of the important results and conclusions in this study are summarized as follows.

(1) No significant rearrangement of surface Si atoms on Si(111)(7×7) is observed upon acetylene adsorption.

(2) The center adatoms are more reacted than the corner adatoms by a ratio of $\sim 2:1$ upon the adsorption of acetylene on Si(111)(7×7).

(3) It is predominantly the adatoms in the faulted subunit that are reacted by acetylene rather than those in the unfaulted subunit, indicating that acetylene is initially in a mobile precursor state.

(4) It is proposed that acetylene is di- σ bonded to the pair of adjacent Si adatom and Si rest atom saturating dangling bonds on Si(111)(7×7).

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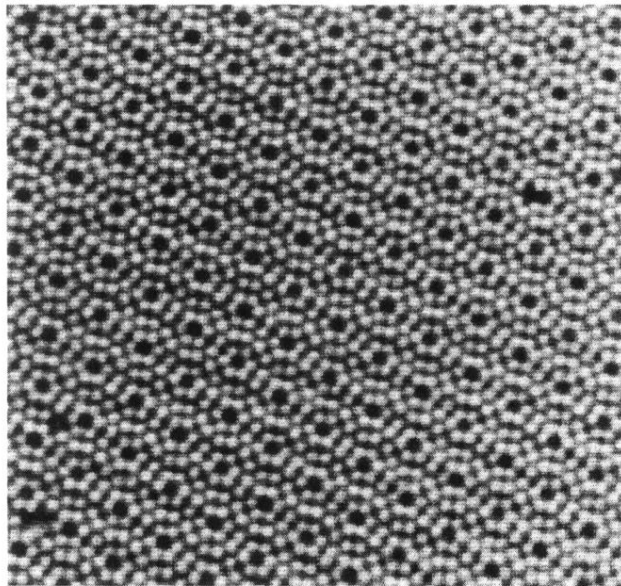


FIG. 1. A constant-current-topograph (CCT) image of clean Si(111)(7 \times 7) at room temperature. Sample bias (E_S)=2.0 V. Tunneling current (I_t)=1.0 nA. Note that the amount of vacancies is very small: $\sim 300 \times 300 \text{ \AA}^2$.

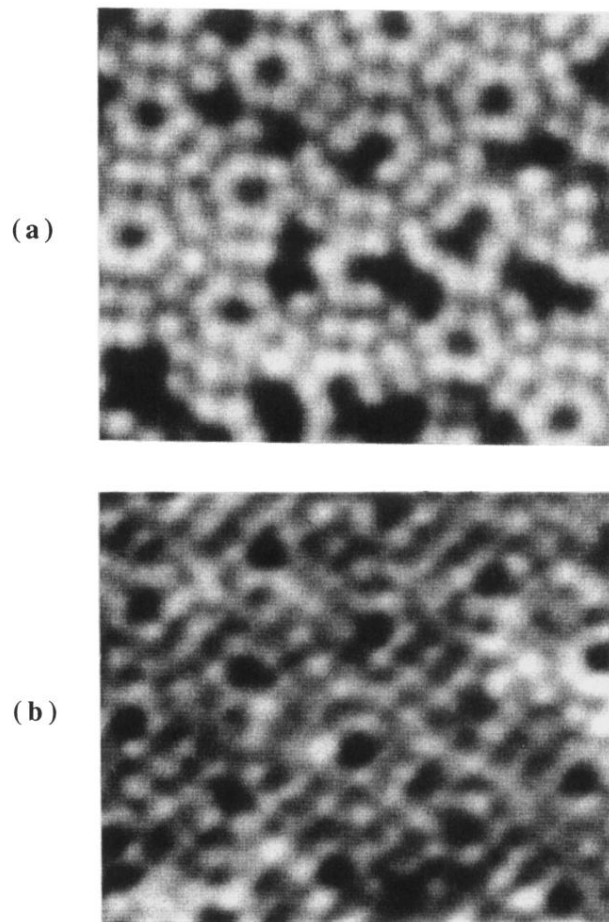


FIG. 2. CCT images of the Si(111)(7 \times 7) surface exposed to 3500-L C₂H₂ at room temperature [(a) $E_S=1.5$ V, $I_t=0.1$ nA, (b) $E_S=3.0$ V, $I_t=0.1$ nA]. $\sim 105 \times 95$ Å.

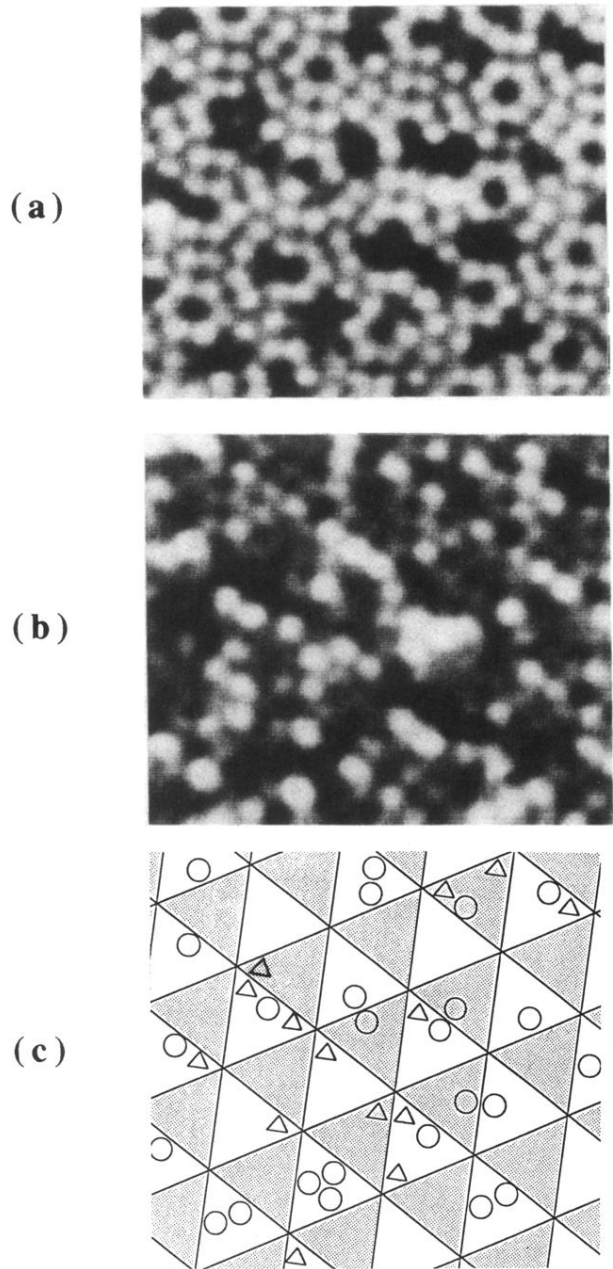


FIG. 3. CCT images of the Si(111)(7×7) surface exposed to 3500-L C₂H₂ at room temperature [(a) $E_S = 2.0$ V, $I_t = 0.1$ nA, (b) $E_S = -2.0$ V, $I_t = 0.1$ nA]. (c) A schematic diagram of the same region. ○, reacted-center adatoms; Δ, reacted-corner adatoms. The unfaulted subunits are shaded. $\sim 115 \times 105 \text{ \AA}^2$.

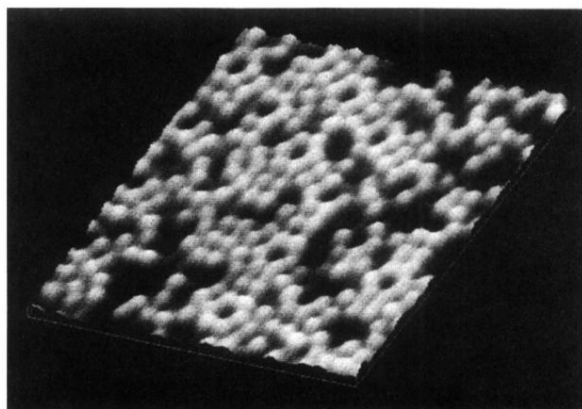


FIG. 4. A three-dimensional CCT image of the Si(111)(7×7) surface exposed to 5000-L C₂H₂ at room temperature [$E_S=0.5$ V, $I_t=1$ nA]. $\sim 150 \times 150 \text{ \AA}^2$.