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# Topographic and spectroscopic analysis of ethylene adsorption on Si(111)7×7 by STM and STS

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A study of the adsorption of ethylene $C_2H_4$ on Si(111)7×7 at room temperature by scanning tunneling microscopy and scanning tunneling spectroscopy is reported. No significant change in the surface reconstruction is observed. The spatial distribution of the surface reaction has been analyzed on an atom-by-atom basis. Reacted and unreacted sites have been selectively imaged. A higher reactivity of the adatoms in the faulted subunits with respect to those in the unfaulted subunits is reported. Furthermore, the center adatoms are more reactive than the corner adatoms. On the basis of this distribution of reacted atoms, the adsorption site is assigned. The proposed bond model implies that an ethylene molecule is bonded to a pair of adjacent Si adatom–rest atom. It is also shown that the adsorption process affects not only the surface atoms directly involved in the chemical bond with the ethylene molecules, but also some of the neighboring adatoms.

## I. INTRODUCTION

The surface chemistry of unsaturated hydrocarbons on silicon single crystals has been the object of several studies performed by our group and other groups with synchrotron radiation photoemission and HREELS (high-resolution electron-energy-loss spectroscopy).$^{1-4}$ While the electronic states and the nature of the chemical bond between adsorbed molecules and surface atoms have been probed with the above-mentioned spectroscopies, the structural information obtained was only indirect and averaged over a relatively large surface area. To obtain direct and local information such as the reacted site(s), the spatial distribution of the surface reaction, the possible local change in surface reconstruction, and the change in the local density of states (LDOS) of the surface atoms involved in the interaction with the adsorbed molecules, scanning tunneling microscopy and spectroscopy (STM and STS) have been used to provide information on an atomic scale from both geometric and electronic points of view.$^{5-7}$

Ethylene, $C_2H_4$, is known to adsorb on Si(111)2×1 in a molecular form (without decomposition). From photoemission data, a close correspondence is found between the relative ordering and energy position of spectral features of the free molecule and the molecule adsorbed on Si, indicating that the C-C $\pi$ bond is not broken.[2] However, the C-C bond length for the adsorbed molecule derived from HREELS measurements is intermediate between double and single bonds, with a partial rehybridization of the molecular orbitals in the adsorption process.[1] Therefore the proposed bond model implies the interaction of an intact molecule with two Si surface atoms. For ethylene on Si(111)7×7, similar conclusions have been drawn from HREELS (Ref. 3) and photoemission data.[4] Here we report on an investigation by STM and STS of the adsorption of ethylene on Si(111)7×7, at room temperature and as a function of coverage.

The Si(111)7×7 surface has been studied extensively with a variety of spectroscopic techniques, and in recent years has been the object of many STM investigations.[8] The most accepted model to date (the dimer-adatom-stacking fault, or DAS model) implies several different types of potentially reactive surface sites. In the unit cell these sites are 12 adatoms, six rest atoms, nine dimers, and one corner hole. The adatoms are included in two triangular subunits slightly different because of a surface stacking fault, therefore called faulted ($F$) and unfaulted ($U$). The rest atoms are triply coordinated Si atoms on the surface. The dimers are on the side of the triangular subunits.[9] One of the goals of the present experiment is therefore to single out the specific reactive sites where the interaction between ethylene and the surface takes place.

The first experimental result is the identification of the Si atoms which interact with adsorbed molecules. We observe that the saturation coverage is much less than one monolayer, and it is $\approx 0.2$ monolayers. No significant changes are observed in the surface reconstruction due to the adsorption process. We conclude that the reaction involves some of the adatoms, and those in the $F$ subunits are more reactive than those in the $U$ subunits. Among the adatoms we can separate center and corner adatoms, and center adatoms are more reactive than corner adatoms. We also observe that the spatial distribution of the reacted sites changes as a function of exposure and time, which hints at a mobile precursor state. These sites are identified as the pairs of adjacent Si adatom–rest atom in the unit cell. Furthermore, there is

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a strong change in the LDOS for the atoms which react directly with the ethylene molecules, but the adsorption process also affects atoms which are not directly involved in the chemical bond with adsorbed molecules.

## II. EXPERIMENTAL

The Si substrate consisted of *n*-type Si(111) wafers ($0.6\times1$ cm) of resistivity $\rho\approx1-10$ $\Omega$ cm. A reconstructed Si $7\times7$ surface was obtained by repeatedly flashing the sample at 1150 °C by joule heating with a current of $\approx9$ A. The base pressure of the UHV chamber was $<3\times10^{-10}$ Torr. The temperature of the sample surface was checked by an optical pirometer. Surface reconstruction and cleanliness were monitored by reflection high-energy electron diffraction (RHEED).

The scanning tunneling microscopy (WA Technology) consists of a UHV attachment with an antivibration stacking of stainless-steel plates and viton balls. The lateral resolution of the microscope is estimated from measurements done in air on cleaved surfaces of graphite, and it is of the order of 1–2 Å, while the accuracy in the lateral displacement is ±0.05 Å. STM images were acquired at 300 K and a constant tunneling current of $\approx1$ nA. Tungsten tips were prepared by chemical etching. Further experimental details are reported elsewhere.[10]

Ethylene was a research-grade product (Union Carbide, purity 99.98%). The gas was let inside the vacuum chamber through a leak valve. During the exposures the pressure was kept at $10^{-6}$ Torr (uncorrected gauge reading). We exposed the reconstructed Si surface to ethylene while obtaining STM images, and we also recorded STM topographs after the gas flow was stopped. Typical total exposures were 2700 L (1 L$=10^{-6}$ Torr s).

## III. RESULTS AND DISCUSSION

### A. Topographic results

In Fig. 1 we report a topograph of the clean Si(111)$7\times7$ surface, obtained by several annealings at $\approx1150$ °C and checked by RHEED. In both the images related to the empty states [Fig. 1(a)] and to the filled states [Fig. 1(b)] the 12 adatoms of the unit cell are clearly visible. The slight difference in brightness for the *F* and *U* subunits in negatively biased topographs reported in the literature[8] is evident in Fig. 1(b). The percentage of defects is rather small, less than 2%.

To monitor the effects of the interaction between ethylene and the surface, we obtained STM topographic images in the dynamical regime, i.e., during the surface exposure to the $C_2H_4$ flow. In Fig. 2 we report a series of images taken on the same surface area and with the same bias (+1.5 V) as a function of exposure. We notice that the surface reconstruction does not show significant changes due to the interaction between the molecules and the surface, since the $7\times7$ superstructure is largely preserved. The main experimental evidence is the apparent formation of holes whose number increases as a function of the exposure. The relative number of reacted versus unreacted atoms indicates that the ethylene does not form a monolayer on the Si surface, but the saturation coverage is $\approx0.2$ monolayers. This is analogous to data obtained by independent measurements [x-ray photoemission spectroscopy (XPS)] for acetylene on Si, where the adsorption process is similar to the present case.[2,11]

The same apparent hole formation was reported for adsorption of other small molecules on Si(111)$7\times7$, such as

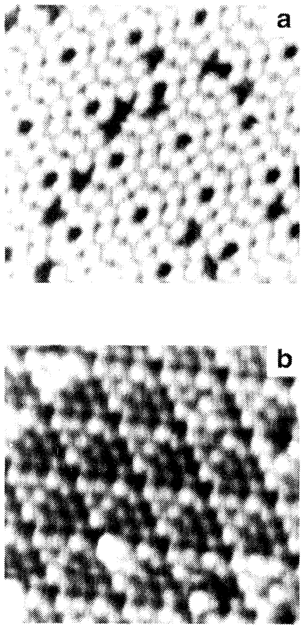

FIG. 1. Constant-current ($I_t=1.0$ nA) topographs of the clean Si(111)$7\times7$ surface. The surface area ($115\times115$ Å$^2$) is imaged with (a) positive bias ($V_b=+1.5$ V); and (b) negative bias ($V_b=-1.5$ V).

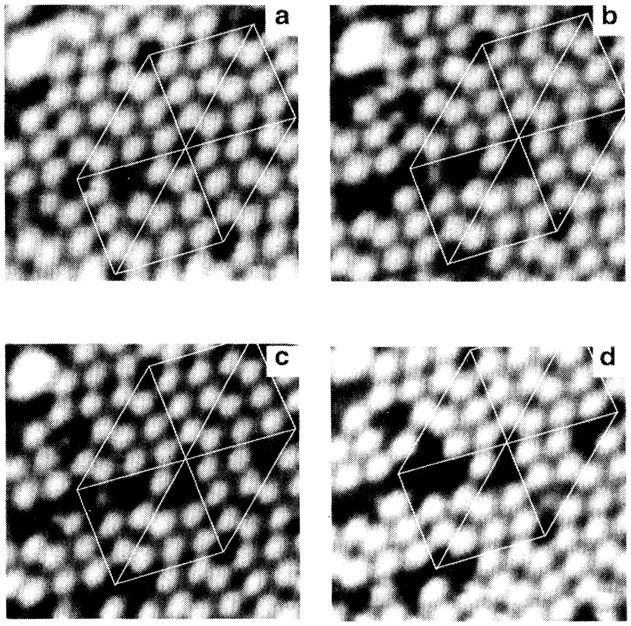

FIG. 2. $70\times70$-Å$^2$ topographs of a given Si(111)$7\times7$ surface area exposed to ethylene as a function of exposure: (a) 300, (b) 400, (c) 500, and (d) 600 L. The bias is $V_b=+1.5$ V.

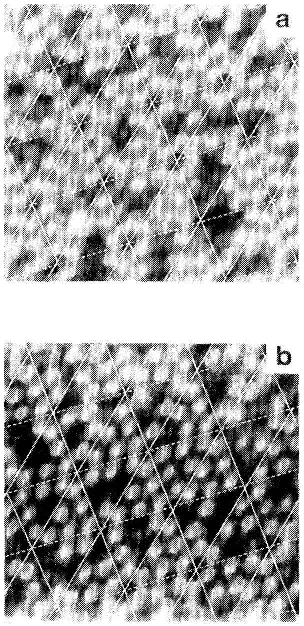

FIG. 3. 110×110-Å$^2$ images of a given Si(111)7×7 surface area as a function of bias: (a) $V_b = +1.5$ V; and (b) $V_b = +2.0$ V. The overall unit-cell pattern is marked.

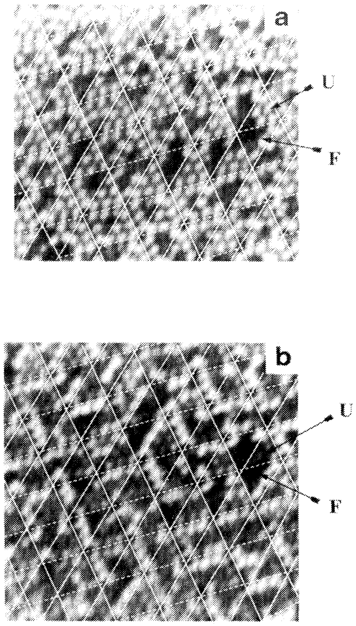

FIG. 4. 180×180-Å$^2$ topographs of a given Si(111)7×7 surface area after exposure to ethylene for opposite bias voltages: (a) $V_b = +1.5$ V; and (b) $V_b = -1.5$ V. The overall unit-cell pattern is marked and the faulted (*F*) and unfaulted (*U*) subunits are identified.

$H_2O$,[5] $NH_3$,[6] and $C_2H_2$.[7] However, brightness changes do not correspond to real vacancies induced by the chemisorption process, but they are rather related to a change in the LDOS for the reacted adatoms. In fact these adatoms become visible again when the bias is changed, while the real defects look dark, also as a function of bias. In Fig. 3 we report a series of images taken on the same surface area as a function of bias. Some adatoms appear as dark holes at +1.5 V sample bias, and become brighter when the bias is increased up to +2.0 V, since higher-lying unoccupied states are imaged. For the adsorption of water on Si(111)7×7, the darkness of the reacted atoms was also attributed to a change in the LDOS. When the species which form a chemisorption bond with the Si surface atoms do not have low binding-energy states, there is a net reduction in LDOS due to the adsorption process, and therefore the reacted sites appear as holes.[5] The same argument can be invoked in our case, and it is also consistent with the fact that we are not able to directly observe the $C_2H_4$ molecules, because both the filled and empty energy levels of the adsorbate are too far from the Fermi level ($E_F$). In fact, from the photoemission valence spectra we observe that the first localized molecular orbital of ethylene is at ≈7 eV below $E_F$. In other cases reported in the literature, molecules with extended electron delocalization were clearly imaged on a Si surface, at variance with the present data set.[12] We also notice that the intensity for some of the adatoms shows the opposite behavior, i.e., adatoms which are bright at a bias of +1.5 V darken at +2.0 V. This behavior has been reported also for $NH_3$ on Si(111)7×7, and attributed to chemical inhomogeneity of the tip at high bias voltages: tip atoms with different tunneling probabilities can affect not only the image resolution, but also the relative intensity.[6] Another element to take into account is the fact that at high bias voltages desorption phenomena can be induced, as noted for $H_2O$ on Si(111)7×7.[5]

Another interesting experimental finding is shown in Fig. 4, where a given surface area biased at positive or negative bias is compared. The reacted adatoms appear as holes at both positive and negative biases, but for negative bias there is an additional effect: some of the adatoms which are visible appear brighter than others. Therefore it seems that the adsorption affects the adatoms in two different ways. Since the adatoms belong to *F* and *U* subunits, it is interesting to compare the relative reactivity of the two triangles. Our experimental evidence is that the *F* adatoms react more than the *U* adatoms. The ratio between reacted *F* and *U* adatoms is not constant, but it increases in the range 1.2–4 during the exposure to ethylene, and decreases to 2.5–3.0 after the gas flow is stopped. One possible explanation comes from the fact that there is a remarkable asymmetry between the local density of dangling-bond states close to $E_F$ in the *F* and *U* subunits of the unit cell.[13] This difference in LDOS can have the consequence of preferential molecular adsorption on *F* subunits if the precursor state for the adsorption is mobile. This hypothesis is supported by the fact that the spatial distribution of the reacted sites changes as a function of exposure and time. The higher reactivity of the *F* adatoms observed by STM is also reported in the literature for acetylene on Si.[7]

We can also notice that in the negatively biased topographs (Fig. 4) the adatoms which look brighter are mostly located in the *F* subunits. A similar experimental finding is reported for $O_2$ on Si(111)7×7,[5] and explained by the presence of two different adsorption sites for O atoms. In our case, since the adsorption of ethylene is nondissociative, there is only one type of chemisorption bond, and the existence of more than one adsorption site is unlikely. The brightness of some of the *F* adatoms can therefore be justified in terms of a change in the LDOS due to nearby reacted adatoms (the dark sites in Fig. 4) (see the discussion in Sec. III B). Inside the same subunit we can also distinguish between the corner and center adatoms. We observe that the reactivity of the corner and center adatoms is different, and the average ratio is precisely 2:1 between reacted center and corner adatoms. A similar experimental finding for acetylene on Si was explained on the grounds of surface topography,[7] and a similar explanation can be invoked in our case. Namely, photoemission and HREELS data show that the adsorption of $C_2H_4$ on Si is nondissociative, and the proposed bond model implies an interaction of the molecule with two Si surface atoms.[3,4] Therefore, we should single out two Si atoms of the unit cell whose bond distance is compatible with the molecular one. Since the C-C bond distance is $\approx 1.4$ Å, and typical Si-C bond lengths are in the range 1.9–2.1 Å,[14] the only possibility for the $C_2H_4$ molecule to bond to two Si surface atoms is between an adatom and a rest atom (the corresponding relaxed bond distances are 4.48 Å for a corner/center adatom and a rest atom), since the bond distance between all the other possible pairs is much too long.[15] Therefore the ethylene molecular axis should be tilted by $\approx 13°$ with respect to the surface plane. A schematic drawing of the proposed adsorption site is shown in Fig. 5. This model also explains the higher reactivity of the center adatoms with respect to the corner adatoms: from the DAS model it is known that corner adatoms have one neighboring rest atom, while center adatoms have two. Therefore in our case the probability of a center adatom reacting is twice as much as that for a corner adatom.

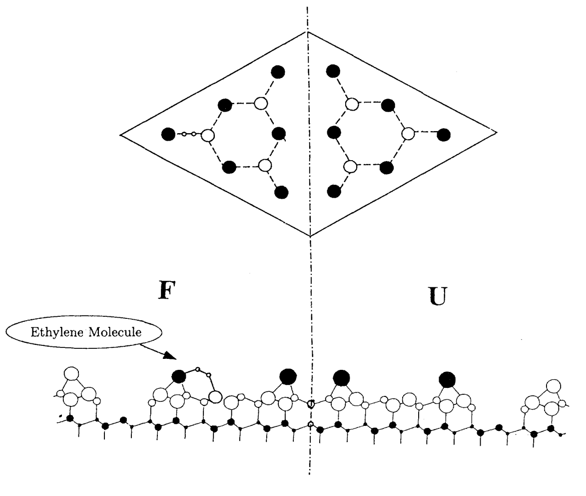

FIG. 5. Schematic drawing of the proposed adsorption site. Top: top view of the surface reconstruction; bottom: side view. In the top part only Si adatoms and rest atoms are shown. Faulted and unfaulted subunits are marked with *F* and *U* capital letters, respectively. The possible adsorption sites are all the silicon adatom (filled dots) and rest atom (open dots) pairs. For the sake of clarity, only the carbon atoms of one ethylene molecule (smallest open dots) are drawn.

### B. Spectroscopic results

In Fig. 6 we report a series of normalized conductance curves taken on a clean Si surface, and on a Si surface exposed to $C_2H_4$ in two different areas: namely, a reacted and an unreacted subunit. Literature data for a Si clean surface are reported for comparison.[6] For the clean surface, we averaged our data over several scans and also averaged the literature data over atom-resolved spectra taken at different atomic sites (a rest atom, a corner adatom, and a center adatom). The agreement between the two spectra for the clean surface in Fig. 6(a) is quite good. The characteristic peak at $-0.8$ V is due to resonant dangling-bond states centered on the rest atoms, while the shoulder closer to $E_F$ (within $\pm 0.5$ V) is related to adatom dangling-bonds states.[6,8,13] If we compare our STS data for clean and adsorbate-covered Si surfaces, we can draw some interesting conclusions. If we examine the curve for the unreacted subunit, we can see that the main difference with respect to the clean surface is a slight change in the relative intensity of the spectral structures. The difference is much more significant if we

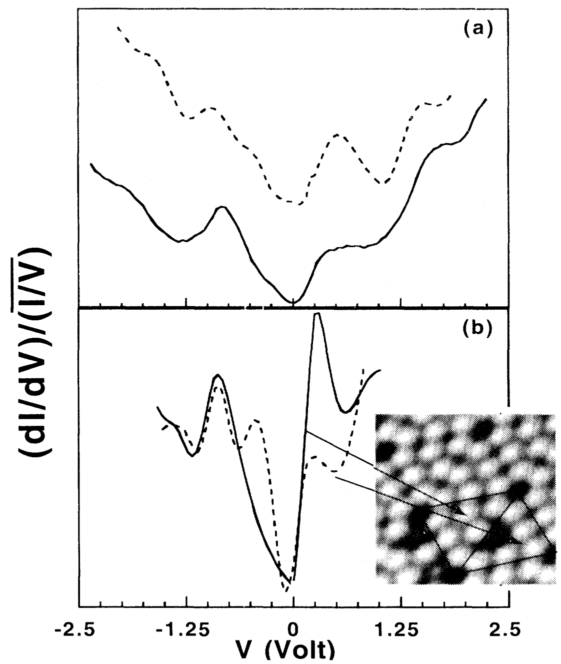

FIG. 6. (a) Normalized conductance curves $(dI/dV)\overline{(I/V)}$ of the Si(111)7×7 clean surface. Dotted curve: our data; solid curve: site-averaged conductance curve from Ref. 6. (b) Normalized conductance curves of the Si surface exposed to $C_2H_4$ for reacted (dotted line) and unreacted (solid line) subunits. The two spectra are scaled at $-0.8$ V. In panel (a) the spectra are shifted vertically for the sake of clarity.

compare the data for the reacted subunit with the curve for the clean surface. The shoulder at $-0.5$ V in the clean-surface spectrum turns to a peak in the reacted-surface spectrum. This peak can be related to the brighter adatoms which are visible in topographs taken with negative bias [see Fig. 4(b)]. We can explain its increase in relative intensity as being due to dangling-bond states localized on some of the adatoms which do not bond to the adsorbed molecules, but which are nevertheless affected by the adsorption process. In fact, the LDOS for atoms which are directly involved in the bond should change in the opposite direction (moving away from $E_F$). Since, according to the proposed bond model, each reacted site involves a pair of adjacent Si rest atom–adatom, the relative weight of dangling-bond states localized on unreacted adatoms should increase with respect to the clean surface, which explains the change of relative intensity of the $-0.8$- and $-0.5$-V spectral components, and the brightness change of some of the unreacted adatoms in the topographs.

## IV. CONCLUSION

The interaction between ethylene and the Si(111)7×7 surface has been investigated by STM and STS. We conclude that the surface reconstruction does not show a significant change due to the adsorption process. The spatial distribution of the reacted Si atoms has been obtained, and the adsorption site has been assigned on the basis of the map of reacted atoms and bond lengths of the various possible Si atom pairs of the 7×7 reconstruction. The adsorption process causes a change in the LDOS, not only for the surface atoms directly involved in the adsorbate-substrate bond, but also in some of the neighboring atoms. The adatoms in the faulted subunits are more reacted than those in the unfaulted subunits. The ratio between reacted atoms in the faulted and unfaulted subunits is $>1$, but it is not constant as a function of time, therefore hinting at a mobile precursor state. The most likely bond model implies the $C_2H_4$ molecule bonded to a pair of adjacent Si adatom–rest atom.

## ACKNOWLEDGMENTS

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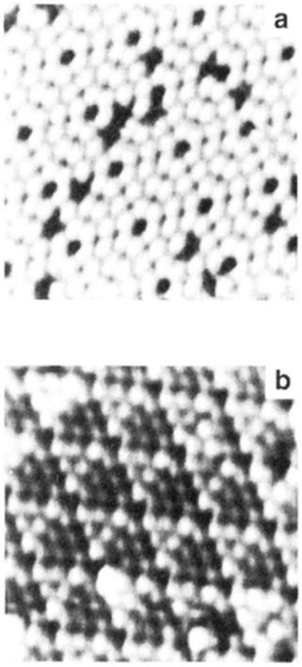
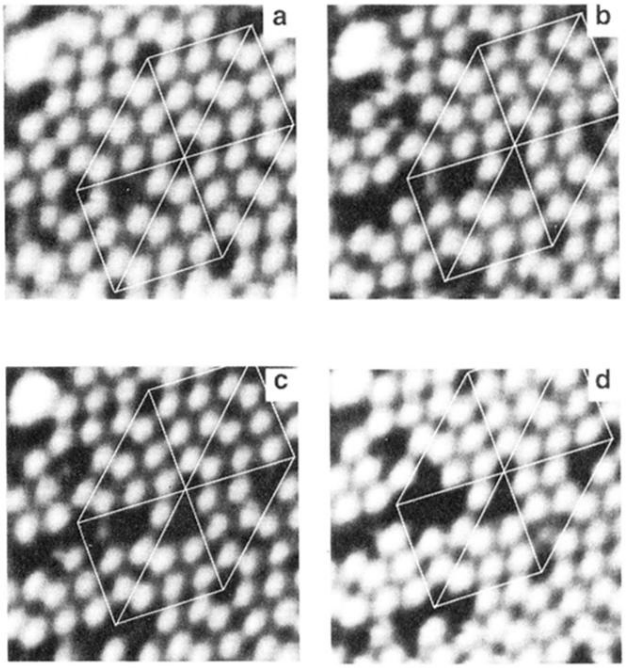


FIG. 1. Constant-current ($I_t = 1.0$ nA) topographs of the clean Si(111)7×7 surface. The surface area ($115 \times 115$ Å$^2$) is imaged with (a) positive bias ($V_b = +1.5$ V); and (b) negative bias ($V_b = -1.5$ V).



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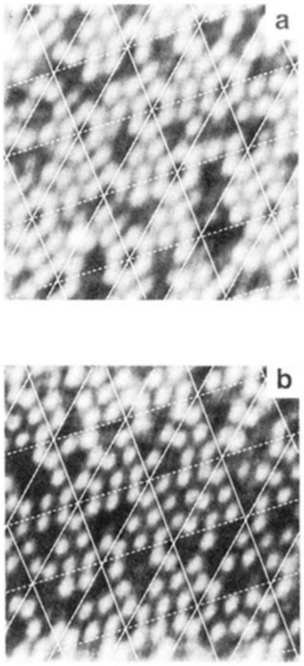


FIG. 3. 110×110-$\mathring{A}^2$ images of a given Si(111)7×7 surface area as a function of bias: (a) $V_b = +1.5$ V; and (b) $V_b = +2.0$ V. The overall unit-cell pattern is marked.

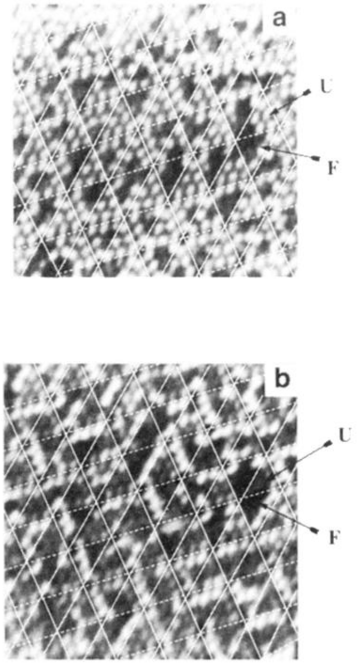
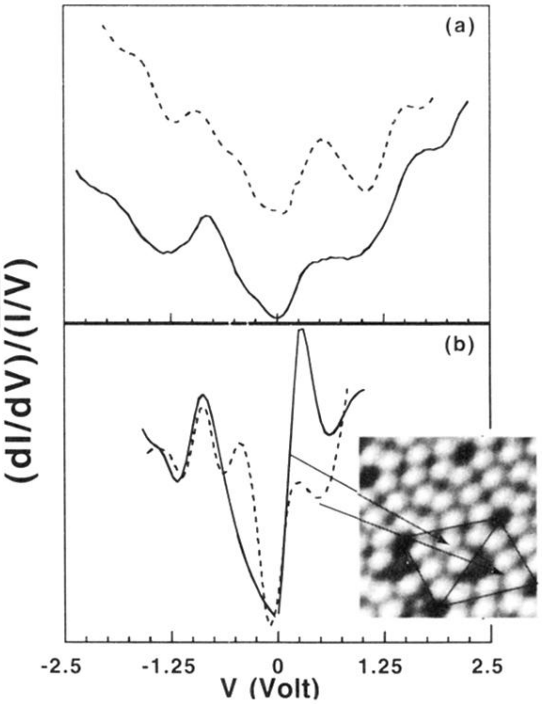


FIG. 4. $180 \times 180$-$\mathring{A}^2$ topographs of a given Si(111)$7 \times 7$ surface area after exposure to ethylene for opposite bias voltages: (a) $V_b = +1.5$ V; and (b) $V_b = -1.5$ V. The overall unit-cell pattern is marked and the faulted ($F$) and unfaulted ($U$) subunits are identified.



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