Sulfur-induced $c(4\times4)$ reconstruction of the Si(001) surface studied by scanning tunneling microscopy

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Scanning tunneling microscopy and low-energy electron diffraction have been used to study the adsorption and subsequent thermal desorption of molecular sulfur from the Si(001) surface. Room-temperature adsorption of sulfur resulted in the formation of an overlayer, displaying a high density of vacancies or defects, with the underlying Si(001) surface retaining the (2×1) reconstruction. Annealing this surface to 325 °C leads to the desorption of the sulfur overlayer and the appearance of coexisting $c(4\times4)$ and (2×1) surface reconstructions. Our data suggest that the $c(4\times4)$ reconstruction is an adsorbate-induced structure in which the sulfur creates defects during the desorption process. High-resolution filled- and empty-state images of the $c(4\times4)$ surface lead us to propose a missing-dimer defect model for this reconstruction.

There have been a number of scanning tunneling microscopy (STM) studies of the clean Si(001) surface which have revealed that the surface consists of parallel dimer row (2×1) reconstructions with both buckled and nonbuckled dimers.[1,2] A $c(4\times4)$ reconstruction of the Si(001) surface has been reported by a number of authors from both low-energy electron diffraction (LEED) and recently published STM studies. Wang, Lin, and Wang[3] induced the $c(4\times4)$ reconstruction by thermally annealing the Si(001)-(2×1) surface for several minutes at 580–630 °C in an ultrahigh vacuum (UHV), while Kato et al.[4] and Ide and Mizutani[5] both reported that the $c(4\times4)$ reconstruction formed following exposure of the Si(001) surface to hydrogen and annealing at 570–690 °C. While the precise details of the structural models proposed by these authors for the $c(4\times4)$ surface reconstruction differ, they all propose variations of missing-dimer defect structures. Zhao, Jia, and Yang[6] have reported the observation of a Si(001)-$c(4\times4)$ reconstruction following a surface preparation procedure involving the deposition of lead, annealing to 300 °C, and the subsequent deposition of additional lead. More recently, Uhrberg and co-workers[7] have used STM to investigate the atomic structure of this metastable $c(4\times4)$ phase, created through hydrogen exposure and subsequent annealing in the 600–700 °C range. First-principles total-energy calculations, in conjuction with filled and empty STM images, led them to propose a "mixed ad-dimer" model consisting of both buckled dimers oriented parallel to the original dimer rows and symmetric dimers along the original (2×1) dimer rows. In this paper we report the appearance of a $c(4\times4)$ reconstruction on the Si(001)-(2×1) surface following thermal desorption of an adsorbed sulfur layer deposited *in situ*. Filled- and empty-state STM images of the $c(4\times4)$ surface are con-

sistent with a missing-dimer defect model.

A theoretical study of the structural and electronic properties of a group-VI element (sulfur or selenium) terminating the Si(100) surface has been performed by Kaxiras.[8] He investigated the possibility of terminating the ideal Si(1×1) bulk configuration with a group-VI adsorbed monolayer saturating the surface dangling bonds, as has been observed for the sulfur-terminated Ge(100) surface by Weser et al.[9] By considering both the chemical reactivity and induced stress inherent in the formation of such a terminated Si(100) surface, he concluded that such a termination was energetically unfavorable for sulfur. A photoemission core-level study of the adsorption of molecular sulfur on the Si(100) surface was carried out by Weser et al.[10] They reported that for room-temperature adsorption, the sulfur bonded to the surface atoms and the surface retained the (2×1) reconstruction with no evidence of additional spots related to an ordered overlayer. When the adsorption process was studied at 200 °C they found evidence from the presence of higher oxidation states of silicon that sulfur was penetrating into the bulk.

The UHV tunneling microscope used in this work was from Omicron Vakuumphysik GmBH (base pressure 6×10^{-9} Pa) and the vacuum vessel also contained a four-grid LEED/AES (Auger electron spectroscopy) system. The Si(001) samples were cut from commerically available wafers (Wacker). After rinsing in acetone and ethanol, the samples were clamped into a tantalum holder and inserted into the prebaked UHV chamber and repeatedly annealed to 900 °C by an electron-beam heater and cooled slowly. Sample temperature was monitored by a thermocouple mounted on the sample holder. The resulting surface produced a sharp (2×1) LEED pattern, which when imagined by STM revealed the two domain

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(2×1) dimer row reconstruction on terraces tens of nanometers wide, separated by monatomic steps. The clean Si(001) surface was then exposed to a beam of molecular sulfur in a connecting chamber with a base pressure of 2×10^{-8} Pa. The home built electrochemical cell, as described by Heegemann et al.,[11] was operated under the conditions required to produce a beam of almost exclusively S_2 molecules. The sulfur-covered surface was subsequently annealed to 325 °C over a 15-min period with an equivalent time for cooling which helped to minimize thermal drift of the piezoelectric elements of the STM. A range of bias voltages from -2 to $+2$ V and tunneling currents between 0.2 and 0.5 nA were used in the STM imaging.
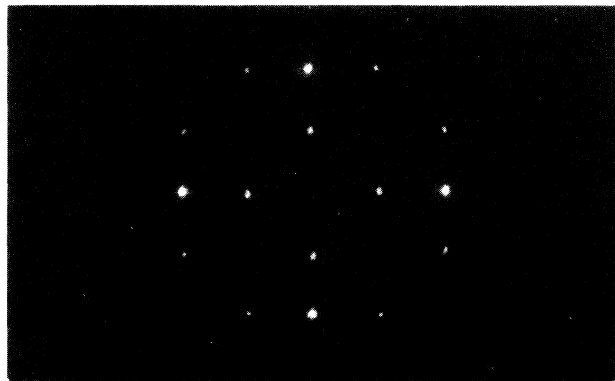
The LEED pattern for the sulfur-covered Si(001) surface is shown in Fig. 1(a). The (2×1) reconstruction spots are clearly visible, the only difference noted from the clean surface pattern is an increase in background intensity. This behavior was also observed by Weser et al.[10] in their study of room-temperature adsorption of sulfur. An estimate of the sulfur coverage from the attenuation of the Si (90-eV) Auger line, with respect to the signal for the clean surface, would indicate an approximate thickness of 1–2 monolayers. The fact that there appears to be no structural rearrangement following sulfur adsorption suggests that interaction between the sulfur and the silicon surface at room temperature is weak. The STM image of the sulfur-covered surface illustrated in Fig. 1(b) reveals the presence of an overlayer with a high density of vacancies. The distance between adjacent maxima in tunneling image is dependent on the direction of measurement. This distance, when measured along the direction of the underlying silicon dimer rows, indicates a separation of 4–5 Å while the distance perpendicular to this amounts to 7–8 Å. From this we deduce that sulfur adsorbs preferentially along dimer rows. From these results it is evident that, for room-temperature adsorption, there is no ideal (1×1) sulfur-terminated reconstruction. By investigating the variations in the intensity of the sulfur (152-eV) Auger line across the surface, it was established that the sulfur coverage was homogeneous, again in good agreement with the observation of Weser et al.[10]

The sulfur-covered surface was then heated to 325 °C over a 15-min period, annealed at this temperature for 5 min, and cooled over a 15-min period. Auger spectra taken at different positions of the surface revealed either no sulfur signal or a very small signal just above the detection limit of the system used (approximately 0.1 monolayer coverage). This suggests that most of the sulfur was desorbed during the annealing cycle with a small amount either remaining on the surface or diffusing into the crystal as was reported by Weser et al.[10] for adsorption at 200 °C. Similar observations have been made for the thermal desorption of sulfur from the Si(111)-7×7 surface.[12] Figure 2 illustrates the sharp c(4×4) LEED pattern observed for the annealed surface. There were no changes in this pattern across the whole surface; therefore, we do not believe that sulfur directly contributes to the c(4×4) reconstruction, but rather that it is an adsorbate-induced structure involving only silicon atoms. However, as noted by Wang, Lin, and Wang,[3] all the (2×1) LEED spots coincide with the integral and half-order spots of the c(4×4) reconstruction; therefore the c(4×4) can coexist as domains on the (2×1) structure.

The filled- and empty-state STM images of the surface illustrated in Figs. 3(a) and 3(b), respectively, clearly show an ordering of features along the original (2×1) dimer row direction. As in the images presented by Uhrberg et al.,[7] the brightest features in Fig. 3(a) outline the c(4×4) periodicity; however, the presence of these
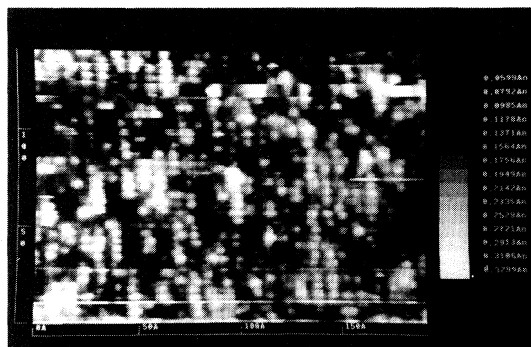
(a)

(b)

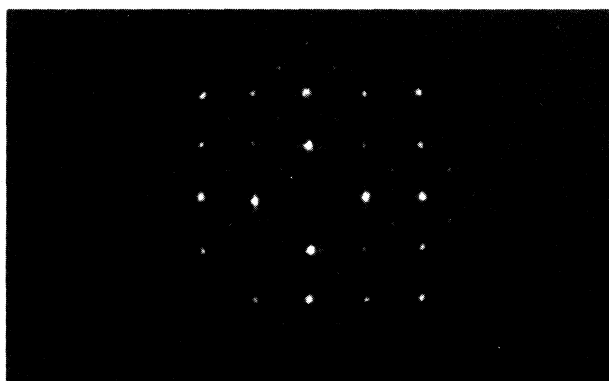FIG. 1. (a) The (2×1) LEED pattern (E_p =41 eV) and (b) the STM image observed for the sulfur-covered surface.

FIG. 2. The c(4×4) LEED pattern (E_p =66 eV) observed for the annealed silicon surface.

features is not necessary for the surface to exhibit this symmetry. From a comparison of the filled- and empty-state images of these features in Figs. 3(a) and 3(b) we attribute them to symmetric dimers along the original (2×1) dimer rows, in agreement with the proposal of Uhrberg et al.[7] On the right-hand side of Fig. 3(a), (2×1) dimer rows can be observed (indicated by the A arrow) which are seen to split in the empty-state image in Fig. 3(b). This splitting along the (2×1) dimer rows is identical to the splitting of the brightest feature observed in the $c(4 \times 4)$ region of the surface, confirming that this is indeed a symmetric dimer. A comparison between the
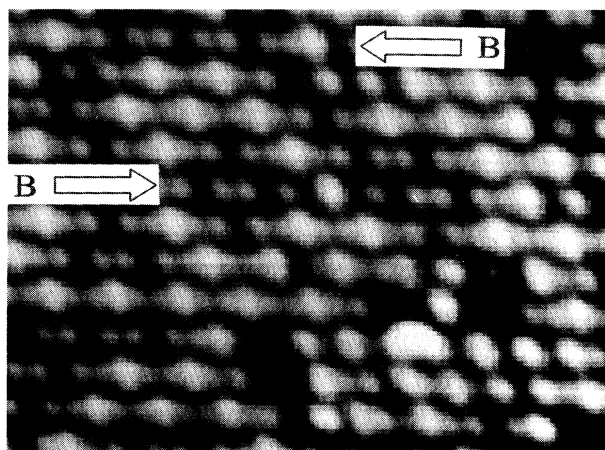
FIG. 4. A high-resolution picture of the filled-state image in an area 130×100 Å. The B arrows indicate dimer row without "high dimers" present.

height of these dimers in the $c(4 \times 4)$ pattern with the dimers along the (2×1) dimer rows indicates that they are at the same height. We believe that these "high dimers" in the $c(4 \times 4)$ pattern are the same as the feature resolved by Ide and Mizutani.[5] Areas of the surface in Fig. 3(b) are visible (indicated by the B arrows) where this "high dimer" is absent and there is an underlying pattern consisting of protrusions alternatively spaced by approximately 10 and 6 Å along the rows. This can be more clearly seen for the filled-state image in Fig. 4 which allows the detailed structure of these underlying features to be more clearly resolved. It is also apparent that the "high dimer" is only ever observed in the 10-Å spacing along the original dimer rows. Again, Uhrberg et al.[7] have similarly observed this variation in spacing between such neighboring features which creates the $c(4 \times 4)$ symmetry. They attribute these protrusions to buckled, parallel ad-dimers in their "mixed ad-dimer" model. For silicon dimers, such buckling has been shown to give rise to charge transfer from the "down" to "up" atom resulting in the filled-state image corresponding to predominant tunneling from the "up" atom.[13] Conversely, the empty-state image should be dominated by tunneling to the "down" atom. However, a detailed comparison between the empty-state images in Fig. 3(b) and the filled-state image in Fig. 4 reveals a direct registry between the periodicity of these underlying features in both images. Unfortunately, due to degraded resolution in the filled-state image in Fig. 3(a), it was not possible to observe the detail of the underlying structure for a direct comparison with Fig. 3(b). Nevertheless, since we can use the position of the symmetric "high dimer" as a reference point in both filled- and empty-state images, it is possible to confirm that there is no shift in registry between the positions of the underlying features, within experimental error. This is inconsistent with these features originating from buckled dimers since there should be a shift in registry between the filled- and empty-state images resulting in an inversion in the positions of the alternative "long-short" spacings along the dimer rows. We therefore propose that these protrusions consist of dimers which have
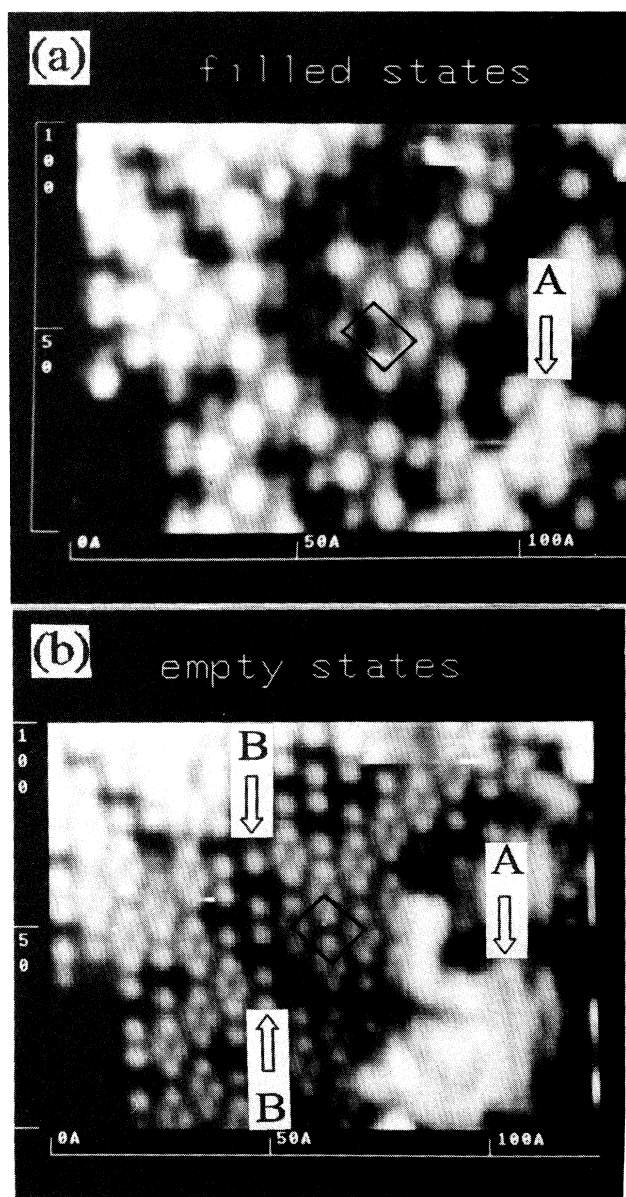

FIG. 3. The filled- (a) and empty- (b) state STM image of the same surface acquired simultaneously, showing the $c(4 \times 4)$ structure coexisting with (2×1) dimer rows on the right indicated by the A arrows. The B arrows indicate a region of the surface with no "high dimers" present.

an increase in the degree of π bonding between the dangling-bond states resulting from an increased degree of planarity of the $c\,(4\times4)$ structure. This would explain the narrowing in the width of the underlying dimer feature with respect to the high dimer in the filled-state image and the inability to resolve the splitting in the empty-state image of these underlying features. The increase in planarity of the $c\,(4\times4)$ surface reconstruction, as first outlined by Pandey,[14] is due to the presence of a high number (between 25% and 50%) of missing-dimer defects. The differences in our interpretation of the STM images from that of Uhrberg et al.[7] can be attributed to our ability to individually resolve protrusions in both filled- and empty-state images which are in direct registry. A schematic model of the $c\,(4\times4)$ reconstruction consistent with the experimental observations is presented in Fig. 5(a) with the unit cell outlined. However, a model which satisfactorily accounts for the above experimental observations must be able to explain the identical alternating periodicity observed in both the filled- and empty-state images. A possible surface reconstruction consistent with this experimental observation would consist of alternate missing dimers and interstitial dimers resulting in a nonuniform spacing of the remaining surface dimers as schematically illustrated in Fig. 5(b). This structure would be a composite of missing-dimer defects as proposed by Pandey[14] alternating with interstitial dimers as proposed by Ihara et al.[15] along the original dimer rows and would not require the presence of the "high dimer" in order to reproduce the $c\,(4\times4)$ surface reconstruction observed.

Unlike previous studies,[3-5,7] the appearance of the $c\,(4\times4)$ phase occurred at a desorption temperature of 325 °C, much lower than the 600–700 °C anneal needed to create this reconstruction after hydrogen exposure. Furthermore, our observation that above a temperature of 700 °C the $c\,(4\times4)$ surface transformed irreversibly to the (2×1) reconstruction is close to the 730 °C temperature determined by Uhrberg et al.[7] for this transition. Again, from a comparison with previous studies, we propose that the surface reconstruction as described in this paper occurs as a result of defects created in the silicon surface region during the desorption of sulfur. Kaxiras[8] suggested that since the S-Si bond energy is larger than the Si-Si bond energy, this could result in the formation of volatile Si_nS_m molecules rather than a stable S:Si(100)
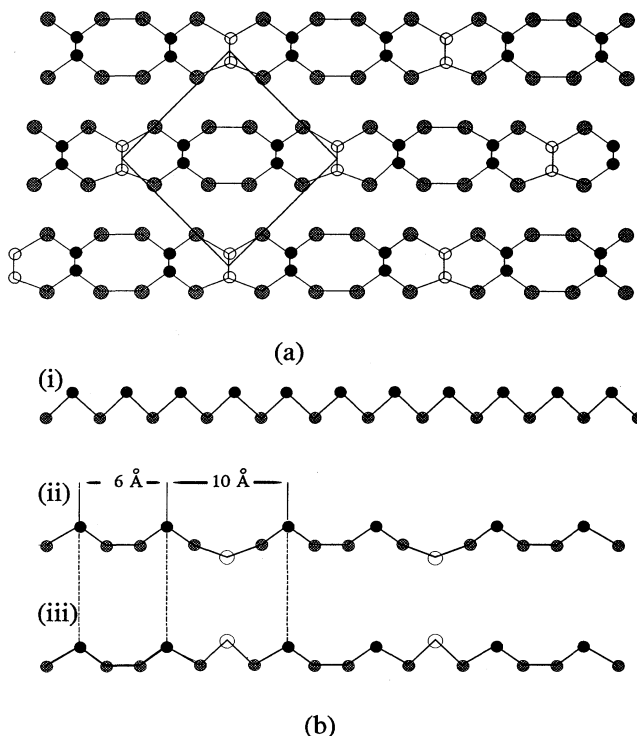

(a)

(b)

FIG. 5. (a) Proposed structural model of the $c\,(4\times4)$ surface, with open circles representing the possible sites of "high dimers," solid circles representing the dimers along the original (2×1) dimer rows, and shaded circles representing the second-layer atoms. (b) Section (i) original dimer rows; section (ii) missing dimers interspaced with interstitial dimers; and section (iii) missing dimers interspaced by "high dimers."

configuration. This could well be a possible source of surface defects as indeed would be the penetration of sulfur atoms in to silicon at elevated temperatures as reported by Weser et al.[10]

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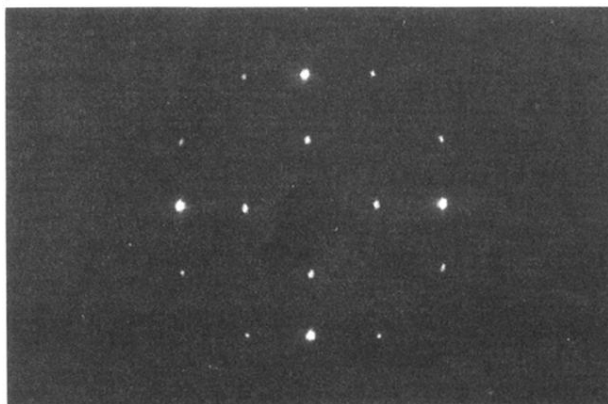[12]L. Koenders, P. Moriarty, and G. Hughes (unpublished).

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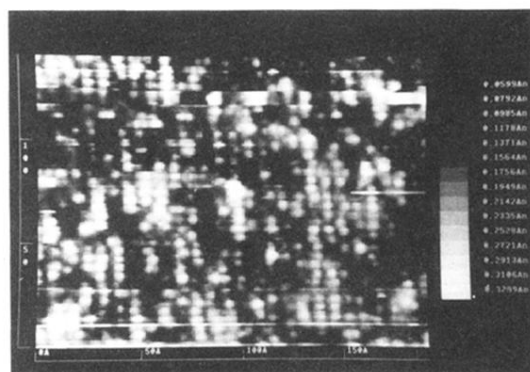[15]S. Ihara, S. L. Ho, T. Uda, and M. Hirao, Phys. Rev. Lett. 65, 1909 (1990).

(a)

(b)

FIG. 1. (a) The (2×1) LEED pattern $(E_p = 41 \text{ eV})$ and (b) the STM image observed for the sulfur-covered surface.
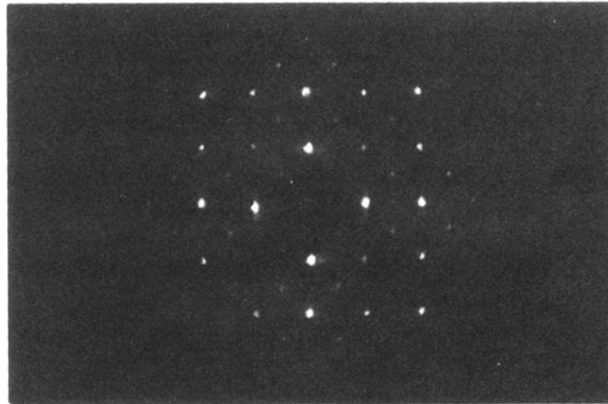
FIG. 2. The $c(4 \times 4)$ LEED pattern ($E_p = 66$ eV) observed for the annealed silicon surface.
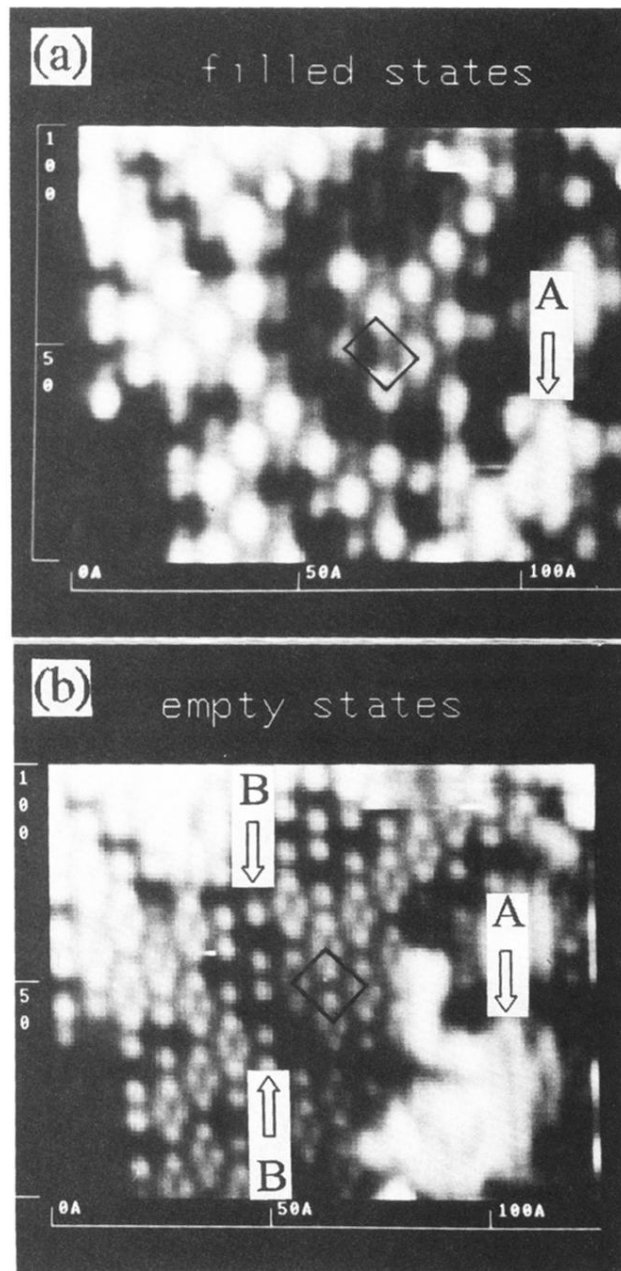
FIG. 3. The filled- (a) and empty- (b) state STM image of the same surface acquired simultaneously, showing the $c(4\times4)$ structure coexisting with (2×1) dimer rows on the right indicated by the A arrows. The B arrows indicate a region of the surface with no "high dimers" present.
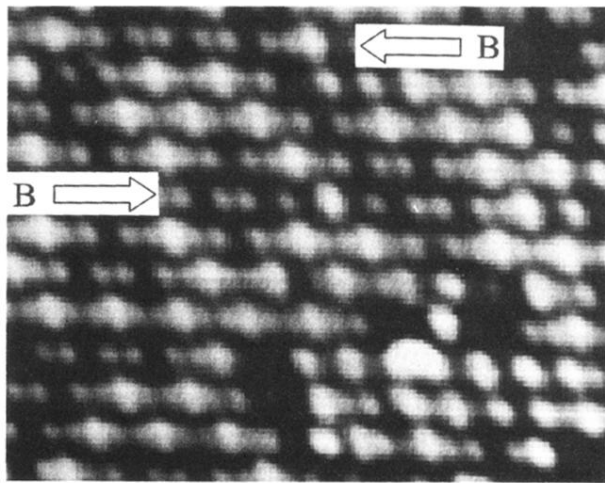
FIG. 4. A high-resolution picture of the filled-state image in an area 130×100 Å. The B arrows indicate dimer row without "high dimers" present.