Si(100)-$c(4\times4)$ metastable surface observed by scanning tunneling microscopy

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The atomic arrangement of a Si(100)-$c(4\times4)$ metastable surface is investigated using scanning tunneling microscopy (STM). The structure is formed on a Si(100) surface by exposing to hydrogen with a pressure of 2×10^{-5} Torr at 700 °C over 30 min. A comparison of filled- and empty-state STM images indicates the existence of a single dimer on the top layer in the $c(4\times4)$ unit cell. This result contradicts all previously proposed structural models, which have a missing dimer in the unit cell. The structure revealed by the present study is in reasonable agreement with the characteristic low-energy-electron-diffraction pattern previously reported.

Many reconstructions can be formed on a Si(100) surface. (2×1), $c(4\times2)$, and $p(2\times2)$ structures were observed by scanning tunneling microscopy (STM) (Ref. 1) and were confirmed to be dimer reconstructed structures. Small Ni impurity induces $(2\times n)$ $(6<n<10)$ structures, which were revealed by STM to have a complex missing dimer structure.[2] A $c(4\times4)$ structure on a Si(100) surface has been predicted by Pandey[3] based on a total-energy calculation. He proposed a π-bonded defect model. The existence of the $c(4\times4)$ periodic surface was found on Si(100) in experiments by Wang, Lin, and Wang[4] and Kato *et al.*[5] using low-energy electron diffraction (LEED). Wang, Lin, and Wang reported that $c(4\times4)$ reconstruction appeared on Si(100) surfaces through suitable thermal annealing, and that the transition between $c(4\times4)$ and (2×1) is reversible. On the other hand, Kato *et al.* reported that $c(4\times4)$ formed on a surface prepared by hydrogen exposure and subsequent annealing. They regarded the $c(4\times4)$ as a metastable structure on Si(100). Kato *et al.*[5] proposed a missing dimer model from the LEED pattern analysis of missing spots on a $c(4\times4)$-H surface based on structure factor calculation. However, the proposed model is merely one of the several possible structures obtained from the diffraction analysis.

STM has the potential to probe surfaces in real space and at atomic resolutions. In this study, the surface structure of Si(100)-$c(4\times4)$ is examined using STM. By comparing the filled- and empty-state STM images with those of (2×1), we are able to discuss the dimer arrangement on the $c(4\times4)$ surface.

This study used a STM equipped with a field-ion-microscope (FIM) device. This device is capable of monitoring the tip structure and removing oxidation layers from the tip surface by field evaporation *in situ*. The design of our STM unit was similar to that developed by Demuth *et al.*[6] The configuration of the combined STM and FIM apparatuses was similar to the "FI-STM" apparatus developed by Sakurai *et al.*[7] The ultrahigh-vacuum (UHV) chamber for STM experiments was also equipped with LEED optics and a cylindrical mirror analyzer (CMA) for Auger electron spectroscopy (AES). Base pressure of the UHV chamber was in the 10^{-11}-Torr region. The sample was transferred from the STM stage to the surface analysis stage in the UHV chamber to obtain surface characteristics by LEED or AES. The samples were mirror polished p-type Si(100) wafers cut into 5×12 mm^2 dimensions. The resistivity of the sample was 0.01–0.02 Ω cm. The samples were cleaned in the same manner as that reported by Swartzentruber *et al.*[8] The temperature of the sample was measured by optical pyrometer. After cleaning the sample, the surface was checked by LEED and AES together with the STM observation of the (2×1) surface structure. The tips were made of a tungsten wire, electrochemically etched. At the STM stage, the tips were cleaned by the field evaporation technique and checked by observing the crystal FIM image of the tungsten. Normally, in our series of experiments, the FIM images appeared after several kilovolts had been applied to the tip.

A $c(4\times4)$ structure was prepared with a method similar to that reported by Kato *et al.*[5] Keeping the clean (2×1) sample at 700 °C by resistivity heating, we exposed it to a 2×10^{-5}-Torr H_2 atmosphere. During the exposure, H_2 molecules were partly dissociated by the ion gauge filament that was used to monitor vacuum pressure. After exposure for 30 min (corresponding to 36 000

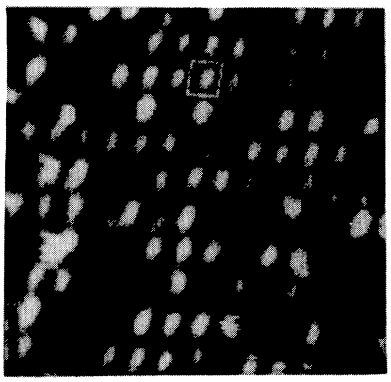
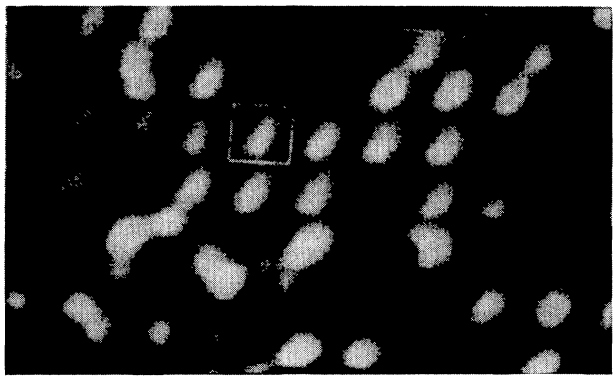


FIG. 1. STM image of the Si(100)-$c(4\times4)$ surface with sample at -1.5 V. Image is displayed as a gray scale, where the white and black correspond to high and low, respectively. The $c(4\times4)$ unit cell is indicated by a square.

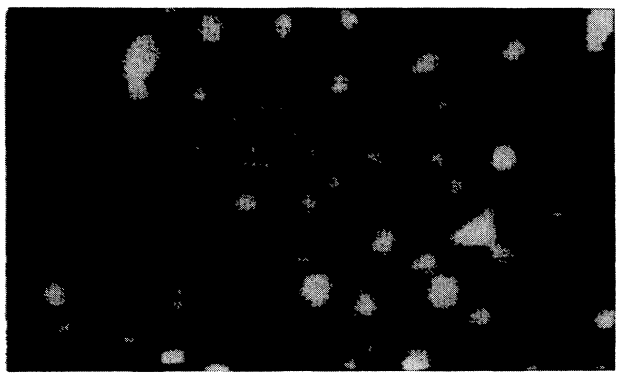
L), H_2 gas was pumped out and the sample was cooled down to room temperature. The samples prepared in this way were also checked by observing their $c(4\times4)$ LEED patterns. We also tried to prepare the $c(4\times4)$ surface using the method reported by Wang, Lin, and Wang.[4] However, we were unsuccessful in obtaining a $c(4\times4)$ surface through this method.

All STM images were obtained using a constant current mode by maintaining the tunneling current at 2.0 nA. The filled- and empty-state images were acquired simultaneously at the same position on the surface by changing the sample bias voltage in alternate line scans. This acquisition presented two different bias images of the same area with an identical tip. The locational differences between the two simultaneously acquired images were negligible. This was confirmed by applying the same voltage to both sample biases. The X and Y piezoelectric devices were calibrated from the image of Si(100)-(2×1), as the distances are well known.

Figure 1 shows a STM image (-1.5-V sample bias) of the sample showing a $c(4\times4)$ LEED pattern. In this image protrusions are arranged in a period of $c(4\times4)$. Figures 2(a) and 2(b) show the filled- and empty-state STM images, respectively. The filled-state image was taken at a -1.5-V sample bias and the empty-state image at a $+1.5$-V sample bias. In the empty-state image [Fig. 2(a)],



(a)



(b)

FIG. 2. (a) Filled- and (b) empty-state STM images of $c(4\times4)$ simultaneously acquired on the same area. Sample bias voltages are -1.5 and $+1.5$ V, respectively.

two protrusions are visible in the $c(4\times4)$ unit cell. A comparison of the filled- and empty-state images indicates that the two protrusions on the empty-state image in the $c(4\times4)$ unit cell are located at both ends of the beanlike protrusion of the filled-state image.

In our study, the $c(4\times4)$ surface was prepared by hydrogen exposure. As the samples were heated at 700 °C throughout the exposure, all hydrogen atoms were completely desorbed.[5,9] Therefore, the $c(4\times4)$ structure observed in this study is a structure formed solely by silicon atoms without hydrogen. As the (2×1), $c(4\times2)$, and $p(2\times2)$ structures of Si(100) are all accepted as reconstructions produced by the dimerization of silicon atoms, we believe that the silicon atoms on the $c(4\times4)$ structure also dimerized. In the STM image, each dimer on the (2×1) surface is observed as a single beanlike protrusion in the filled-state image and as dual split protrusions in the empty-state image.[10] The features of both have also been confirmed through our STM. In $c(4\times4)$ STM images displayed in Figs. 2(a) and 2(b), a similar feature is seen in each unit cell. This indicates that a single dimer exists in the uppermost layer in a $c(4\times4)$ unit cell. The second-layer atoms that are invisible to our STM should dimerize to reduce the number of dangling bonds.

Two structural models [Figs. 3(a) and 3(b)] have been proposed as the $c(4\times4)$ structure which assumes the presence of one missing dimer in a unit cell. In our $c(4\times4)$ STM images, dimers are represented as being somewhat large. One might interpret these protrusions as three dimers which undergo electrical structure changes due to the missing dimer. However, missing dimers observed in the $(2\times n)$ surface[2] do not have such change in electrical structure as we observed in both bias images. We believe that this large protrusion is due to the absence of neighboring dimers which cause lateral spread of wave functions at a far distance from the surface and prevent the observation of second-layer atoms.

Kato *et al.*[5] reported LEED patterns after dissociated hydrogen was adsorbed on the $c(4\times4)$ surface. In their patterns all $(\frac{1}{2}+n,\frac{1}{2}+m)$ LEED spots (n and m are integers) disappeared at any incident electron energy, retaining $c(4\times4)$ symmetry. Applying the structural analysis method proposed by Yang and Jona,[11] we will obtain only three possible structures for the $c(4\times4)$-H (Fig. 4) which satisfy the missing spot conditions. Atom-

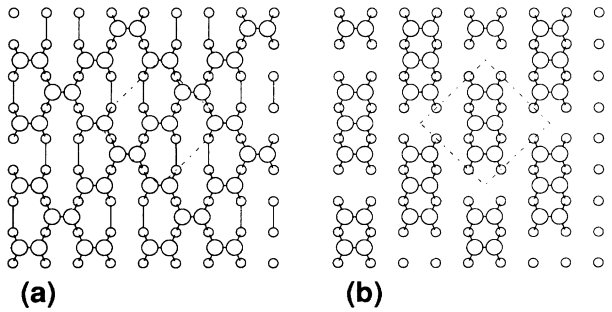


FIG. 3. Schematic illustrations of previously proposed $c(4\times4)$ structural models. (a) π-bonded defect model by Pandey (Ref. 3) and (b) missing dimer model by Wang, Lin, and Wang (Ref. 4) and Kato *et al.* (Ref. 5).

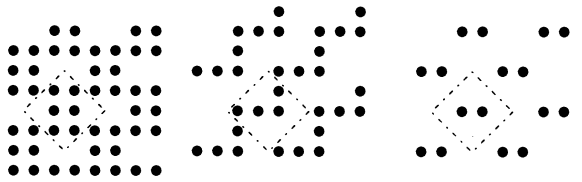


FIG. 4. All possible structural models for $c(4\times4)$-H satisfying missing spot conditions in LEED patterns. In each figure, circles indicate identical atoms or groups of atoms.

ic hydrogen breaks dimer bonds on Si(100) forming dihydride. So the $c(4\times4)$ structure must be one of either of the dimerized models of Fig. 4. From these considerations the only possible structural model that satisfies both missing LEED pattern of $c(4\times4)$-H and filled- and empty-state images of our STM observation is the single dimer model proposed above.

Many theoretical studies have been carried out on the Si(100) surface. Most of these studies are restricted to the small unit cell, so that the stability of $c(4\times4)$ reconstruction was unable to be adequately discussed. The missing dimer defect structures have been discussed by Pandey,[3] whereas the silicon ad-dimer structure has not been investigated theoretically as far as we know. In the case of Al, Ga, or In, ad-dimer structures on Si(100) have been reported[12–14] and theoretically investigated,[15] in which ad-dimers of Al, Ga, or In arrange in a (2×2) or a (2×3) periodicity. In the future, it would be interesting to theoretically study the stability of silicon ad-dimer structures.

In summary, we have proposed a metastable $c(4\times4)$ structure formed on a Si(100) surface by hydrogen exposure and heat treatment. The filled- and empty-state STM images taken of the same area revealed the existence of a single dimer on the top layer in the $c(4\times4)$ unit cell. This result rules out all previously proposed structural models, but is consistent with the characteristic LEED pattern reported by Kato *et al.*[5]

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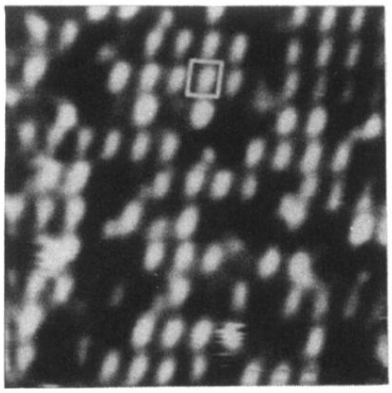
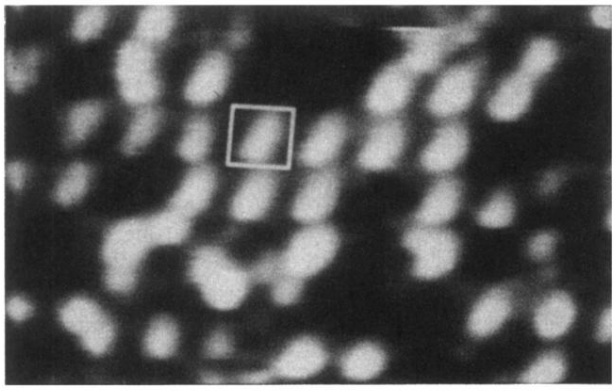
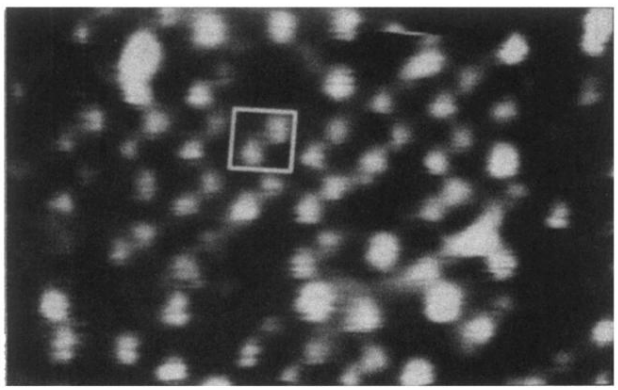


FIG. 1. STM image of the Si(100)-$c(4\times4)$ surface with sample at -1.5 V. Image is displayed as a gray scale, where the white and black correspond to high and low, respectively. The $c(4\times4)$ unit cell is indicated by a square.



(a)



(b)

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