Step structure of Si(110)-(16×2) and adsorption of H_2O

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The Si(110)-(16×2) surface has a complex reconstruction containing alternating up and down atomic steps with a periodicity of 5 nm. By studying the electronic states around the step edges with scanning tunnel microscope (STM), and by adsorption of water molecules, we are able to propose a model of the step structure. It requires the removal of seven atoms from the stepped (1×1) surface, and simulated STM images from density functional theory are in excellent agreement with experiment. We also found that water forms a perfectly ordered array on the upper terrace of the stepped reconstruction.

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I. INTRODUCTION

Understanding the atomic structure of complex semiconductor reconstructions is of enormous scientific and industrial importance. The most famous example, the Si(111)-(7×7) reconstruction, has become a universally recognized image and required many years of patient work; even the simpler Si(001) surface generated much controversy on the way to being solved. The Si(110) surface has a complex reconstruction known as (16×2), with 64 atoms in the surface unit cell; the surface is also chiral,[1] making it attractive for chemical experiments. This is in stark contrast to the III-V semiconductors which have a simple relaxation on this surface. As well as the inherent scientific interest in complex reconstructions, the Si(110) surface is becoming important in microelectronics;[2–4] it is therefore imperative to understand the (16×2) reconstruction. Lack of a reliable model is a crucial problem in further research on this surface.

There are two key features of the reconstruction: first, regular steps giving alternately raised and lowered terraces; and second, ringlike features on the terraces which exhibit four or five bright lobes in scanning tunnel microscope (STM) at different bias voltages. While there have been several suggestions for the structure of these ring structures,[5–8] none of them can explain all available experimental data; moreover, the only proposed step structure[5] does not match STM images for the steps, which are a key part of the reconstruction. The reconstruction indicates that significant mass transfer must occur during formation; recent modeling of diffusion barriers on the (1×1) surface[9] indicates that adatom diffusion will be fast at temperatures used for annealing.

The steps in the Si(110)-(16×2) reconstruction alternate between up and down and are in $[\bar{1}12]$ or $[1\bar{1}2]$ directions, forming upper and lower terraces which can be seen in Fig. 1; the ring structures on the upper and lower terraces are equivalent. Most previous studies focused on the terrace structure only while completely missing out the step structure. Yet the step edges have fundamental importance, especially for nucleation processes because steps often act as nucleation centers. An indication of the complexity of the step edges is found in recent experiments on Ge deposition on Si(110),[10] where up to 0.6 ML can be deposited without qualitative change to the STM appearance of the terraces (indicating step-edge adsorption).

We used variable bias STM and density-functional theory (DFT) calculations to propose a structural model of the step edge. We also explored the response of the surface to water molecules and found that water adsorbs preferentially on the step edges; this provides a tool to probe the surface states around steps which are difficult to reach by STM.

II. METHODS

Experiments were performed in a commercial UHV STM chamber JEOL JSTM-4500XT at base pressure less than 1×10^{-8} Pa. P-doped samples with resistivity 0.01–0.1 Ω cm were used. A single domain reconstruction was prepared by the flash-anneal procedure proposed in

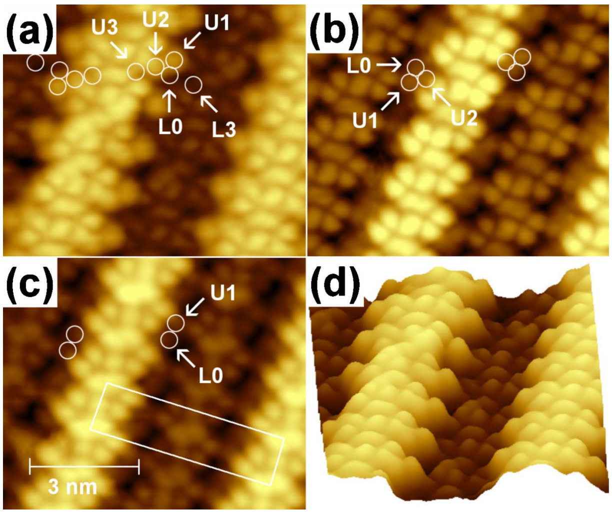

FIG. 1. (Color online) STM images of clean Si(110)-(16×2) surface at various sample bias. The locations of various electronic states around the step edges are marked (though not all are visible in these images). (a) V_S=−1.0 V, (b) −0.3 V, and (c) +0.8 V; all images are 8 nm×6.7 nm. (d) Three-dimensional rendering of (a). A scale bar and the fundamental (16×2) unit cell are marked in (c).

Ref. 11. H_2O molecules were obtained by thermal desorption from a molybdenum surface heated to 600 K. Pressure during H_2O exposure was 2×10^{-7} Pa and dosage was 97% clean.

DFT calculations were carried out with the gradient-corrected Perdew-Burke-Ernzenhof[12] generalized gradient approximation exchange-correlation functional and a plane-wave basis set, as implemented in the VASP code.[13,14] The computational cell contained 11 Si layers terminated with a H layer at the bottom. A plane-wave cutoff of 250 eV was used, which provided force and energy convergence. The Brillouin zone was sampled using a $(1\times4\times1)$ Monkhorst-Pack grid, which also converged forces and energies. STM images were simulated using the Tersoff-Hamann approach.

III. RESULTS

Figure 1 shows a set of STM images of a clean Si(110)-(16×2) surface taken at various biases. The images of rings in the middle of the terraces are well known.[8] However, we have observed several key electronic states associated with the steps which have not been described before. The positions of these newly observed electronic states are marked in Fig. 1(a), with states on the upper terrace marked U1, U2, and U3 and states on the lower terrace marked L0 and L3; however, not all of these states are clearly visible in this figure, as the bright pentagonal rings cause low contrast of the step-edge states in normal STM images; we focus on showing these states using other imaging techniques below. The two most distinct states are U1 and U2, which can be observed with the highest contrast at V_S about -1 V [Fig. 1(a)]. At low negative sample biases, we can also observe a state marked L0, which forms a characteristic triangle with U1 and U2 [Fig. 1(b)]. The L0 state is difficult to observe on a clean surface but it becomes more visible when the surface is exposed to water molecules, as will be described below. It is also possible to observe U1 and L0 in the empty states [Fig. 1(c)] but the contrast is very poor; therefore we will concentrate on filled state images. U1, U2, and L0 are the only surface states at the step edge which can be found in simple topographic images of a clean surface. The other states marked in Fig. 1(a), U3 and L3, appear as dark features between two neighboring rings and are important when considering water adsorption.

To further examine the properties of these step-edge states, we sought the most effective molecule to adsorb onto the surface, in effect to titrate away the step-edge states. We tested hydrogen but found that it was not specific to step edges; moreover, its low sticking coefficient, combined with the necessity of cracking made the experiment sensitive to contamination and therefore difficult to interpret. By contrast, water has a sticking coefficient close to 1, and it adsorbs preferentially on the step edges, which makes it a perfect tool for probing the observed electronic states.

The process of water adsorption on other Si planes—both high and low indices—has been studied before.[15–19] The major adsorption path at room temperature is dissociation into H+OH, with each of the groups bound to one Si atom; these Si atoms become dark in STM images.[20] Saturation of one Si dangling-bond state is often connected with charge transfer to a neighboring Si atom which becomes brighter in STM.[15,16,18] This effect is very strong when breaking a π bond.[21] The dissociative reaction pathway has a sticking coefficient close to 1, which is attributed to presence of π bonds on most Si surfaces.[17] The exception is Si(111)-(7×7) surface which contains only dangling bonds: the sticking coefficient is at least one order of magnitude lower and total decomposition to O+H+H with oxygen entering Si backbonds is observed as an alternative reaction pathway.[17]

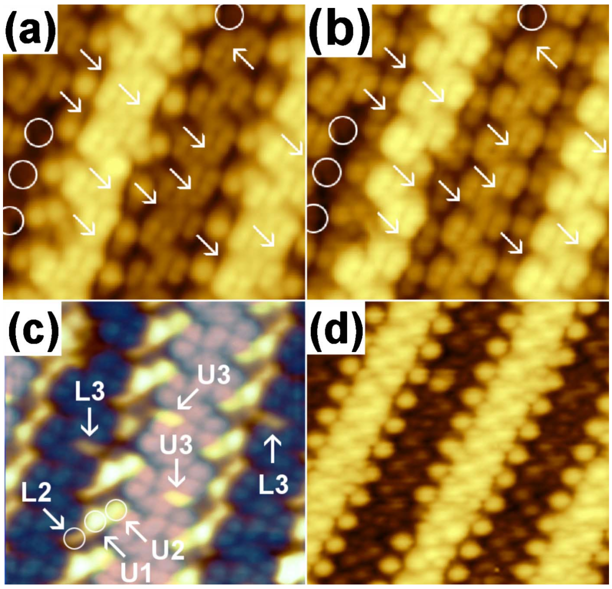

FIG. 2. (Color online) (a) and (b) show the same area of the surface following exposure to 0.06 L of H_2O, at bias voltages V_S $=-1.0$ and -0.5 V. The arrows indicate U3 and L3 positions brightened by adsorbed H_2O molecules. Circles show lower terrace pentagons missing due to adsorbed water. (c) A map of $(dI/dV)/(I/V)$ taken at -0.8 V (gold/light) overlaid by topography (blue/dark). The L2 states can be clearly observed, as indicated in the lower left. Arrows marked L3 and U3 point toward adsorbed H_2O. (d) A larger image of the surface following exposed to 0.7 L H_2O, $V_S=-1.4$ V. Water forms a perfectly ordered array on the upper terrace. Images (a)–(c) are 8 nm×8 nm while (d) is 12 nm×12 nm.

Figures 2(a) and 2(b) show the result of exposing the surface to 0.06 L of water ($1\ \text{L}=1.33\times10^{-4}$ Pa s). Arrows in Fig. 2(a) point toward U3 and L3 positions which become bright in comparison to the clear surface; we deduce that this is due to adsorbed H_2O fragments. The U2 state disappears next to each bright U3 state with perfect reproducibility. We conclude that both the darkening of U2 and brightening of U3 is caused by adsorption of fragments from a single H_2O molecule. The L3 sites, marked by arrows in Fig. 2, also became bright; since the upper and lower terraces appear completely symmetric, we must find an equivalent of the U2 state on the lower terrace. The L0 state would be a logical candidate but these remain bright after water adsorption [as can be seen by comparison of Figs. 1(b) and 2(b)]. While the necessary L2 state cannot be observed directly in topography images, it can be observed in a map of normalized conductance, $(dI/dV)/(I/V)$, taken at suitable sample bias. This is shown in Fig. 2(c) for $V_S=-0.8$ V. The map was measured

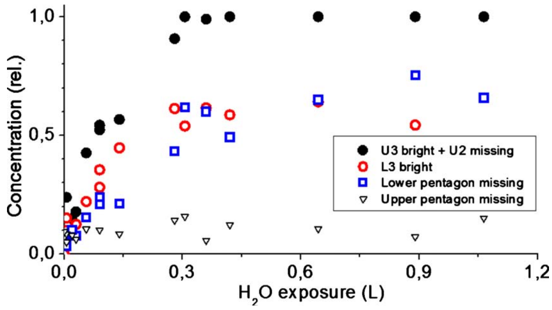

FIG. 3. (Color online) A plot showing percentage occurrence of different features related to water adsorption as a function of water exposure.

using a lock-in detector in the same way as in Ref. 7. The $(dI/dV)/(I/V)$ image (gold/light) contains only states at the step edge and is covered by topography (blue/dark) measured simultaneously. The L2 states may be now directly observed in a position which is perfectly symmetric to U2. The L3 and U3 states, which have been brightened by adsorption of water fragments, are marked by arrows in Fig. 2(c). In the context of the previous work on other surfaces, these results suggest that the U2/L2 states behave in a similar manner to dangling bonds and the U3/L3 states in a similar manner to π bonds on the Si(100)-(2×1) surface. We note that the presence of both dangling bonds and π bonds in the (16×2) reconstruction was predicted by hydrogen thermodesorption experiments.[22]

Increasing the dose of water leads to the formation of a new structure. Figure 2(d) shows a larger area of the surface, after exposure to 0.7 L H_2O. Water fragments have formed a perfectly ordered array on the upper terrace; on the lower terrace, some similar features are observed but without the perfect long-range order. The reason for this is that there are more types of adsorption sites on the lower terrace: Figs. 2(a) and 2(b) show that there are several pentagons missing on the lower terrace (marked by crosses) following low coverage water adsorption. The fraction of missing pentagons on the lower terrace increases with water exposure and saturates at value 0.65±0.10 (about 2/3). The fraction of bright L3 sites saturates at the same value. Figure 3 shows how the fraction of different sites changes with water exposure for the L3, the U2/U3 pair and the pentagons on upper and lower terraces. We see that the ordered array on the upper terrace is produced relatively early and is associated with the U2/U3 pair. The ordering does not occur on the lower terrace because of some link between the brightening of the L3 site and the disappearance of the lower pentagon. There is some kind of competition between these two reaction pathways, even though the features may appear next to each other; they are not mutually exclusive. We always find a few pentagons missing on the upper terrace as well but the ratio of 5–10 % is independent of water exposure which suggests that they do not react with water molecules.

We now turn to the task of constructing a model of the step edges. Figure 4(a) shows a schematic atomic model of an unreconstructed Si(110) surface with atomic steps. The model is overlaid on an STM image, which allows us to determine precisely the positions of the surface states on the surface. Of the four different ways to assign the lattice to the STM image, we follow the scheme proposed by An *et al.*;[8] their STM images of areas of disordered (16×2) reconstruction reveal zigzag rows of surface atoms which buckle [with one side going down and the other rising, exactly as happens on III-V (110) surfaces]. These images of buckled zigzag lines are in excellent agreement with structures we found using our DFT calculations [buckled lines can be seen in Figs. 4(c) and 4(d)]. We see from Fig. 4(b) that the U1, U2, L0, and L2 states may be well explained as dangling bonds of atoms marked by crosses. U3 and L3 are attributed to a Si-Si bond similar to π bonds on Si(100)-(2×1). There are also seven atoms in the unreconstructed surface (labeled by

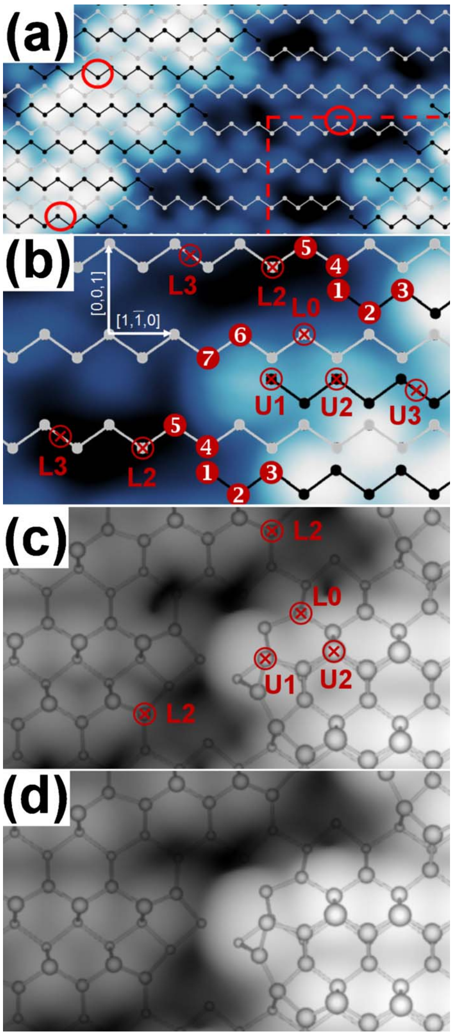

FIG. 4. (Color online) (a) STM image of 16×2 reconstruction at V_S=−1.0 V covered by atomic lattice of unreconstructed surface containing atomic steps. Circles mark U3/L3 states brightened by water adsorbed from the residual atmosphere in the STM chamber. The image is 7 nm×3.6 nm. (b) Detail from box marked in (a). Crosses mark atoms related to the dangling bonds of surface states U1, U2, L0, and L2. The U3 and L3 states may be explained as Si-Si bonds. The seven marked atoms must be removed. (c) and (d) show calculated STM images and structure of the step edge with the seven atoms removed as proposed in (b) and with buckling. V_S=−0.4 V and −1.0 V, respectively. Higher atoms are shown larger.

numbers 1–7 in the figure) not seen in STM images.

The positions of the step-edge states are in disagreement with the adatom-tetramer-interstitial (ATI) model.[5] This model posits a tetramer and two adatoms next to each step. The U1 and U2 states do not agree with the positions of these adatoms but rather correspond to substrate atoms in the zigzag rows. Adatoms always appear much brighter than zigzag rows in our DFT calculations, which suggests that the (16×2) reconstruction does not have those adatoms near the step edge.

We have built various models of the step edge and relaxed the resulting structures in DFT, and then generated STM images for various sample biases. However, we have not included the ring structures in these models, as the structure of these features has not been determined unambiguously; moreover, none of the previously proposed models can explain all available experimental data. Instead we left the terraces unreconstructed. Without the rings, we cannot search for the lowest surface energy between different structures but will instead use the similarity to STM images as the criterion for fitness for a particular model. We found two key features which are necessary for obtaining good agreement between the calculation and experiment: first, the buckling of the substrate zigzag rows is important and must take on a particular orientation; and second, the model as introduced in Fig. 4(a) contains many surface atoms which were not observed in the experiment (atoms labeled 1–7). For the model to match STM, the surface states from these excess atoms must be removed, either by removing the corresponding atoms or by finding a suitable reconstruction which converts the Si atom from three coordinated to four coordinated.

Recent calculations[23] show that defects in the unreconstructed Si(110) surface are energetically favorable compared to the clean surface [specifically, removing two neighboring atoms from a flat Si(110) surface removes two dangling bonds and gives an energy gain of 0.48 eV]. This suggests that the best way to reconcile the basic model in Fig. 4 and the STM images is simply to remove the excess atoms. Atoms 1 and 2 must be removed to keep general shape of the step. The removal of atom 1 changes atom L0 from four-coordinated to three-coordinated. Therefore with atom 1 present we would never see the L0 state in STM images. Removing the pairs $(4+5)$ and $(6+7)$ creates the stable defect found in our recent calculations; this is exactly what is required to match the STM images. The last excess atom (number 3) was removed both because its dangling bond is not observed in STM and to ensure symmetry between upper and lower terraces. Removing these seven atoms to create our model means that the upper and lower pentagons will both be bordered by a step with the same atomic structure.

The model which fits best the experimental data is shown in Figs. 4(c) and 4(d), with atomic models superimposed on simulated STM images. We found that the U1 atom must be buckled up, otherwise the U1 state becomes blurred in calculated STM images, especially at low sample bias. In experiment, a sharp, round shape of U1 is always observed. Consequently the states U1, U2, and L0 form a characteristic triangle at low negative sample bias and the L0 state disappears at higher sample bias as observed in experiment. The L2 state is not directly visible in the calculated STM images, which is in agreement with our experiment. However, the corresponding atom is present in the structure. Our calculations do not show any signs of the formation of π-like bonds at positions L3 and U3; instead, a simple buckling typical for the unreconstructed surface occurs here. This is a logical consequence of missing out the rings from terraces in our calculations. Forming a π-like bond requires a specific coordination of the surface atoms, therefore including the correct structure for the rings would be necessary. All previously proposed models of the rings try to saturate all surface dangling bonds in this area and therefore leave no space to explain existence of the U3/L3 states.

Structures with fewer than seven atoms removed from the surface were modeled but failed to match STM images. Our model of the step edge also sheds light on the observations of Ge deposition on the Si(110)-(16×2) reconstruction.[10] The deposition of up to 0.6 ML of Ge results in no change to the pentagons in the middle of terraces. The obvious conclusion is that the Ge is being adsorbed at the step edges. The holes created by removing the Si atoms can explain this, and underline the importance of understanding the step-edge structure.

IV. CONCLUSIONS

We have presented STM images of the Si(110)-(16×2) surface, concentrating on the step edges. Our images show a number of states associated with the steps which have not been observed previously. We have studied these states using differential conductance and adsorption of water molecules as well as variable bias STM, and find a striking symmetry between upper and lower terraces.

Using the experimental data, we have constructed a number of models of the step edges and tested their appearance using DFT. The structure which reproduces the STM images has seven atoms missing from the step edge, when compared to a perfect step (illustrated in Fig. 4). However, our model may not be exact as we have omitted the ring structures on the terraces. A key finding of this work is that all suggestions for the ring structures on the terraces are incompatible with the states observed in STM. New ideas are needed for this fascinating reconstruction.

We have also observed that water molecules form a perfectly ordered array on the upper terrace of the reconstruction because there is only one type of adsorption position located on the step edge. An equivalent adsorption position exists on the lower terrace but water also reacts with lower terrace pentagons which prevents formation of an ordered array. As far as we know this is the first case of self-assembly on Si(110)-(16×2) surface.

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