

# Atomic and electronic structures of rebonded $B$ -type steps on the Si(001)- $2 \times 1$ surface

Takuji Komura and Takafumi Yao

*Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-Ku, Sendai 980, Japan*

Masamichi Yoshimura

*Toyota Technological Institute, Hisakata, Tenpaku-ku, Nagoya 468, Japan*

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Detailed atomic and electronic structures of rebonded  $B$ -type steps on the Si(001)- $2 \times 1$  surface are studied using scanning tunneling microscopy/spectroscopy (STM/STS). Both the step edge dimers on the upper atomic plane and the rebonded atoms in the lower atomic plane appear as bright protrusions in an empty-state STM image, indicating an enhancement in empty local density of states. A nonrebonded  $B$ -type step edge does not show these anomalous features. The differential conductance spectra on the bright protrusions indicate a strong enhancement in the local density of the empty state at the expense of the local density of the filled state. This change in the local density of states at the rebonded  $B$ -type step edge is tentatively interpreted in terms of the Haneman model, according to which rebonding-induced strain results in the rehybridization of the step edge atoms. Furthermore, we have found negative differential conductance (NDC) associated with the anomalous electronic states at the rebonded  $D_B$  step. The responsible localized states that induce NDC at the  $B$ -type step sites are caused by rebonding at the step. [S0163-1829(97)00832-1]

## I. INTRODUCTION

A surface step plays an important role in epitaxial growth processes. If the growth proceeds in a step flow mode, the surface steps act as incorporation sites for incoming atoms, and the step develops without forming islands on the surface. Surface steps are also important in the two-dimensional nucleation and growth mode, where two-dimensional islands are formed on the terrace. For instance, the surface islands observed at the beginning of Si epitaxy on the Si(001)- $2 \times 1$  surface are almost rectangular in shape with the longer side parallel to the surface dimer row.<sup>1,2</sup> Even a single dimer row forms a long dimer chain. The longer side of the island results in  $S_A$  steps, while the other side forms  $S_B$  steps.<sup>3</sup> The formation of the anisotropic surface islands has been discussed in terms of the enhanced incorporation of adatoms arriving at the  $S_B$  step edge.<sup>4</sup> During molecular-beam epitaxial growth of Si on the Si(001)- $2 \times 1$  surface, the formation of a single-domain surface with biatomic  $D_B$  steps was reported.<sup>5,6</sup> This single-domain surface reverts back to a two-domain surface after termination of growth at around 750 K.<sup>7</sup> It is obvious that atomistic mechanisms for the incorporation of adatoms at the  $S_B$  step or the formation of a single-domain surface with the  $D_B$  step during epitaxy are closely related to the atomistic and electronic structures at the  $B$ -type steps.

So far three types of  $S_B$  steps have been reported experimentally:  $S_B$  step with "rebonded" step edge,<sup>1,8</sup> "nonrebonded"  $S_B$  step,<sup>8</sup> "nonrebonded"  $S_B$  step with a missing dimer.<sup>1,3,9</sup> A theoretical calculation suggests that the "rebonded"  $S_B$  step is energetically more favorable than the "nonrebonded" one.<sup>3,10</sup> Although the local structure at  $S_B$  and  $D_B$  steps has been investigated by scanning tunneling microscopy (STM),<sup>8,9,11,12</sup> neither detailed local structure nor electronic structure at the  $B$ -type steps has been studied. This paper aims to study details of the local atomic arrangement

and electronic structures at rebonded  $B$ -type steps using scanning tunneling microscopy/spectroscopy (STM/STS).

## II. EXPERIMENT

We used an ultrahigh vacuum scanning tunneling microscopy (UHV-STM). The base pressure of the STM chamber is below  $1 \times 10^{-8}$  Pa. The tip used was a tungsten wire with a diameter of 0.5 nm that was sharpened by electrochemical etching. The specimens used were  $p$ -type Si(001) misoriented towards the [110] direction by  $0.5^\circ$ ,  $2^\circ$ , and  $4^\circ$ . It was prebaked at  $\sim 600^\circ\text{C}$  for 14 h, and cleaned by repeated flash heating to  $\sim 1200^\circ\text{C}$  below the pressure of  $1 \times 10^{-7}$  Pa to obtain a clean Si(001)- $2 \times 1$  surface. STM measurements were performed at room temperature.

## III. RESULTS AND DISCUSSION

Figure 1(a) shows a filled-state STM image of an  $S_B$  step edge on the Si(001)- $2 \times 1$  surface. The dimers on the lower terrace are clearly observed as well as those on the upper terrace. The distance from the first full dimer row in the lower plane to the first dimers in the upper plane is  $3a_0$  ( $a_0$  is surface lattice constant), which indicates that this step is rebonded. Most of the  $S_B$ -type steps observed in the present study are rebonded, while others are nonrebonded with an additional missing dimer adjacent to the step edge dimer. Only a few nonrebonded step structures were observed in the present study. Half-gray protrusions ( $A$ ) on the lower terrace at the step edge indicate rebonded atoms in the lower plane as previously discussed.<sup>8,13</sup> We note a deeper trench between the protrusion  $A$  and a dimer row in the lower atomic plane, which suggests a different charge distribution between the rebonded atom sites and the full dimers, despite that they are on the same atomic layer. No appreciable buckling of dimers on the upper terrace at the reb-

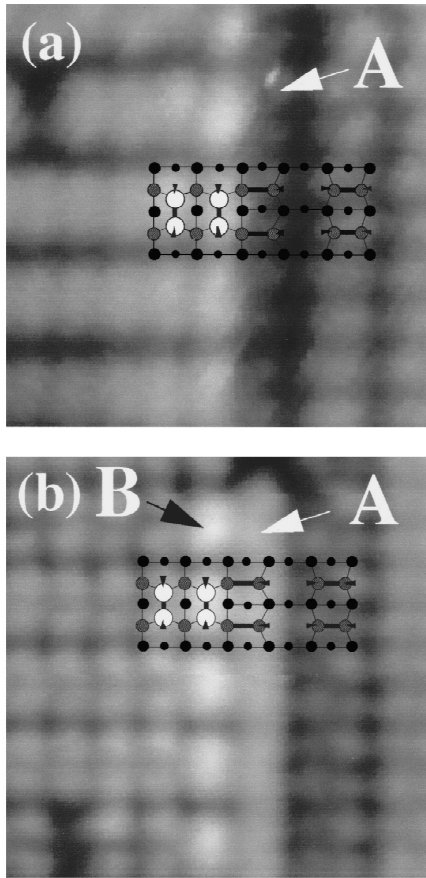


FIG. 1. (a) Filled-state ( $V_S = -2.0$  V,  $3.8 \times 3.8$  nm $^2$ ) and (b) empty-state ( $V_S = +1.0$  V,  $3.8 \times 3.8$  nm $^2$ ) STM images with schematics of a rebonded  $S_B$  step structure on the Si(001)- $2 \times 1$  surface. Open circles denote the topmost Si atoms on the upper terrace, while hatched circles represent Si atoms in the lower atomic plane.

oned  $S_B$  step is observed in the present experiment. This is in contrast to the  $D_B$  step edge, where buckling of dimers on the upper terrace was observed.<sup>11</sup>

Figure 1(b) shows an empty-state image of the rebonded  $S_B$  step, where the dimer splits reflecting the antibonding ( $\pi_a^*$ ) nature. Bright protrusions are observed at both the step edge dimer ( $B$ ) on the upper terrace and the rebonding atoms ( $A$ ). It should be noted that the protrusion  $A$  is brighter than the dimers on the lower terrace. These two types of protrusions do not show splitting in contrast to dimers on the terraces. However, a close look at protrusions  $B$  reveals slight splitting, which may reflect each rebonding dimer state. Another interesting feature, is that buckling of the dimers in the lower atomic plane close to the step edge can be seen in both filled- and empty-state images, resulting in  $p(2 \times 2)$  reconstruction. Recent *ab initio* calculations suggest preferential  $p(2 \times 2)$  reconstruction close to a rebonded  $S_B$  step,<sup>14</sup> which is consistent with the present observation.

Figure 2(b) shows a profile across a rebonded  $S_B$  step along the line labeled  $XX'$  in Fig. 2(a). Since this STM image was taken at a sample bias of  $+1.0$  V, the height value in this figure contains the information on the surface corrugation as well as the unoccupied electronic states. Note that the height between the dimers on the lower and upper terraces is  $1.24$  Å and in fair agreement with the monatomic step height of  $1.35$  Å. The rebonded atoms  $A$  are located

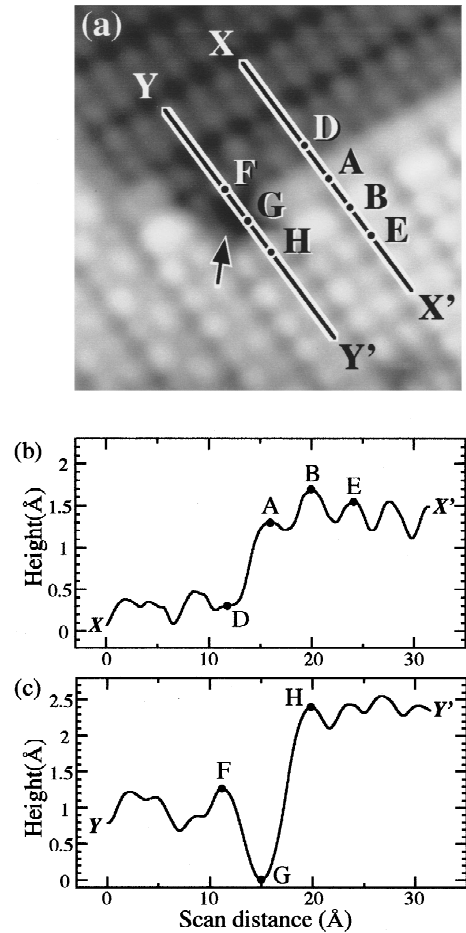


FIG. 2. (a) An empty-state STM image of the rebonded  $S_B$  step ( $V_S = +1.0$  V,  $4.0 \times 4.0$  nm $^2$ ). (b), (c) Step profiles across a rebonded  $S_B$  step along the line labeled (b)  $XX'$ , (c)  $YY'$  on (a). The height for ( $AD$ ) is  $0.97$  Å,  $BD = 1.38$  Å,  $BE = 0.14$  Å,  $FG = 1.27$  Å, and  $GH = 2.44$  Å.

higher than the dimers on the lower terrace by  $0.97$  Å. Since the rebonded atoms  $A$  are located on the lower atomic plane, the apparent height indicates that the rebonded atom has a larger local density of empty states than that of the full dimer on the same terrace. Protrusion  $B$  appears higher than the dimers on the upper terrace by  $0.14$  Å, indicating an enhancement in empty local-density of states at the step edge dimer.

In order to confirm that the observed protrusions such as  $A$  and  $B$  are associated with rebonding, we have closely investigated an  $S_B$  step with a missing dimer defect which contains no rebonded atoms. The arrow in Fig. 2(a) indicates two rebonded atom vacancies that have darker contrast compared to the dimers on the lower terrace. We note that the bright protrusions do not appear around the step edge. A step profile along line  $YY'$  is shown in Fig. 2(c). The depth of the defect is  $1.27$  Å, which suggests that the rebonded atoms are missing.

Figure 3(a) shows an empty-state image of a  $D_B$  step on the Si(001)- $2 \times 1$  surface misoriented by  $4^\circ$ . A stable structure of the  $D_B$  step has rebonded atoms as confirmed both experimentally<sup>9,11</sup> and theoretically.<sup>3,10</sup> Protrusions  $A$  denote rebonded atoms, while protrusions  $B$  denote step edge dimers. Again, both  $A$  and  $B$  show brighter protrusions than

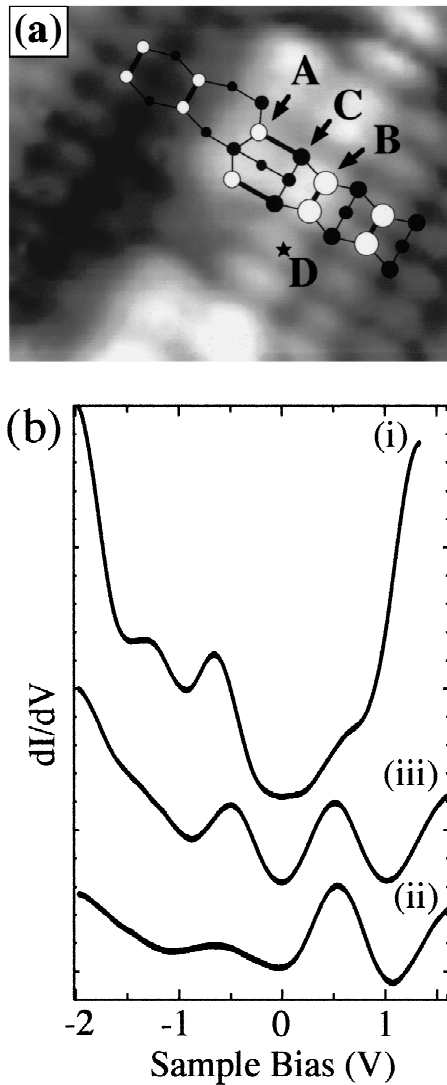


FIG. 3. (a) An empty-state STM image with a schematic of  $D_B$  step on the Si(001)- $2\times 1$  surface misoriented by  $4^\circ$  ( $V_s = +1.1$  V,  $2.8\times 2.0$  nm $^2$ ). Open circles denote the surface atoms. (b) Local differential conductance spectra recorded at (i) a normal dimer on the Si(001)- $2\times 1$  surface, (ii) bright protrusion (A), and (iii) bright protrusion (B), as shown in (a).

any other dimers in the same atomic planes.

These findings lead to the conclusion that the appearance of the bright protrusions in an empty-state image is a consequence of rebonding at the B-type steps and suggests that rebonding enhances the local density of state in the empty states at rebonded atoms and step edge dimers.

Local differential conductance ( $dI/dV$ ) for the  $D_B$  step was measured by the current imaging tunneling spectroscopy.<sup>15</sup> In the simplest case, the differential conductance is in proportion to the local density of states.<sup>16</sup> The differential conductance spectrum at a normal dimer on the Si(001)- $2\times 1$  terrace is shown as curve (i) in Fig. 3(b). A previous STS experiment showed peaks in the normalized differential conductance curve at  $-0.8$  and  $+0.35$  V.<sup>17</sup> These peaks have been assigned to the “dangling-bond” level and the corresponding antibonding level on the basis of theoretical work on the symmetric dimer model.<sup>18</sup> Recent photoemission<sup>19</sup> and inverse photoemission spectra<sup>20</sup> reveal states at  $-0.7$  and  $+0.3$  V. We tentatively assign the

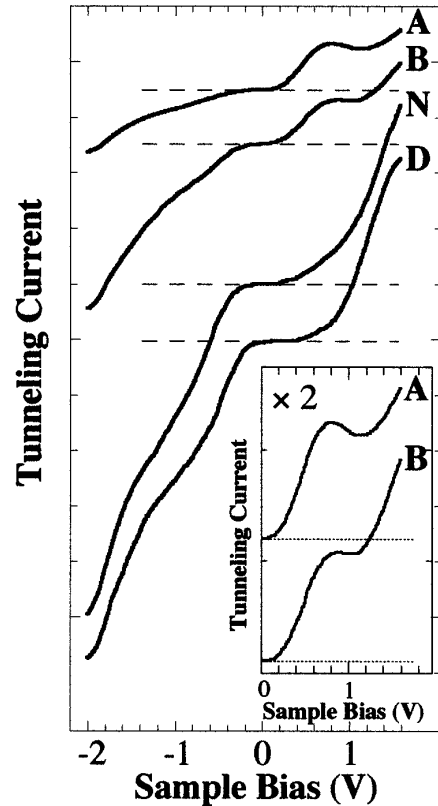


FIG. 4.  $I-V$  characteristics at several atomic sites around the  $D_B$  step. A, a rebonded atom site; B, step edge dimer site; N, normal surface dimer site; and D, step edge dimer at nonrebonded step, as shown in Fig. 3(a). The inset shows  $I-V$  characteristics whose scale of the tunneling current are two times as large as the other four curves.

$-0.8$  V peak to the bonding ( $\pi_b$ ) state and the  $+0.5$  V peak to the  $\pi_a^*$  state. Spectrum (ii) was taken at the rebonded atoms A in Fig. 3(a). We note a strong enhancement in the density of states for the empty state at around  $+0.5$  V with a reduction in the filled state. Spectrum (iii) taken at step edge dimers B also shows an enhanced state together with a reduced state. It is interesting to note that spectrum (iii) shows an intermediate feature of (i) and (ii). From this observation, it becomes clear that the bright protrusions (A and B) appear because of the enhanced empty state at around  $+0.5$  V.

The observed enhancement in the empty state and associated reduction in the filled state may invoke a charge-transfer mechanism due to strain as originally proposed by Haneman.<sup>21</sup> Here we attempt to explain the phenomena we have observed in a similar way. We suggest charge transfer due to the rehybridization induced by rebonding. Once atoms A in Fig. 3(a) are rebonded with atoms C, which are already bonded to dimers B, atoms A are pulled towards the bonded atoms C. It should be noted that dimers B are pulled down towards atoms C, since atoms C are pulled back by atoms A on rebonding. Consequently, the bond angles of rebonded atoms A and dimers B increase. Hence, the bonds of atoms A and those of dimers B are slightly mixed with  $sp^2$  nature and their dangling bonds are slightly mixed with  $p$  nature. This may cause charge transfer from the dangling bonds of atoms A and dimers B to the bonds associated with atoms C. We note that this explanation is analogous with Haneman’s explanation for charge transfer in buckled dimers,<sup>21</sup>

although in this case charge transfer is induced by rebonding.

We noted in the filled-state image [Fig. 1(a)] the presence of a deeper trench between protrusions *A* and the dimer row on the lower terrace, while in the empty-state image [Fig. 1(b)] no appreciable deep trench is observed. As discussed above, atoms *A* are pulled towards atoms *C* by rebonding, resulting in a reduction of the local density of filled states as well as an enhancement of the local density of empty states at atoms *A*. Both the displacement of the rebonded atoms *A* and the change of electronic structure at atoms *A* are responsible for the observed difference of the trench depth in the empty- and filled-states images.

Figure 4 shows tunneling current-voltage ( $I-V$ ) characteristics at several atomic sites (*A, B, D, N*) in Fig. 3(a).  $I-V$  characteristics at normal surface dimer sites (*N*) show semiconducting nature and agree with previous reports.<sup>17</sup>  $I-V$  characteristics greatly change at the edge dimer site (*B*) of the rebonding  $D_B$  step, where a slight negative differential conductance (NDC) is observed at around +1.0 V as shown in the inset. The NDC behavior is clearly observed at the rebonding atom sites (*A*) for +0.8–+1.1 V. In contrast, the step edge dimer (*D*) at the nonrebonding  $D_B$  step edge shows a semiconducting feature like a typical surface dimer (*N*).

These observations suggest that the observed NDC is caused by rebonding at the step edge. Rebonding at the step edge induces local bond strain, which in turn causes modification in local electronic states. In fact such modification has been theoretically suggested<sup>22</sup> and experimentally observed.<sup>23</sup> Local STS measurements indicated a consider-

able enhancement in the empty state at the rebonding sites and step edge dimer sites, while almost similar characteristics were not observed at the step edge dimer sites with nonrebonding steps.

It is well understood that the requisite for NDC is the presence of a localized state and in the present case, the enhanced empty state is responsible for NDC. If there is a localized state at the tip apex site, a resonant tunneling mechanism may occur to give rise to NDC. As suggested theoretically, both the intrinsic tips state<sup>24</sup> and extrinsic localized adsorbate state<sup>25</sup> can produce localized states. It is interesting to note that essentially the same characteristics were observed with two different STM systems (UHV-STM's by UNISOKU and by OMICRON) used in the present experiments.

In conclusion, we have studied the atomic and electronic structures of the *B*-type step on the Si(001)- $2\times 1$  surface, using STM and STS. We have found that most of the  $S_B$  steps are of rebonded type on a Si(001) surface with a miscut angle less than  $2^\circ$ . A rebonded step edge is characterized by bright protrusions in an empty-state STM image. These bright protrusions do not appear at nonrebonded step edges. The local differential conductance spectra for the rebonded *B*-type step show that these bright protrusions appear as a result of an enhanced empty state at around +0.5 V. We discuss the origin of the anomalous electronic structure in terms of the Haneman model. Furthermore, we have found NDC associated with the anomalous electronic states at around the rebonded  $D_B$  step. The responsible localized states at the step sites are caused by rebonding at the step.

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