

## Low-temperature reconstruction pathway to the Si(111)( $\sqrt{3} \times \sqrt{3}$ )R30°-Ag interface

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Using the spectroscopic capabilities of a scanning tunneling microscope, we identified and investigated a low-temperature *reconstruction pathway* for forming Si(111)( $\sqrt{3} \times \sqrt{3}$ )R30°-Ag from the Si(111)3×1-Ag interface. A metastable intermediate phase consisting of one-dimensional atom chains atop the Si(111)3×1-Ag reconstruction stabilizes *locally*. The density of states at the chains indicates a Ag-Si bonding configuration similar to that of the ( $\sqrt{3} \times \sqrt{3}$ )R30° reconstruction. We propose a mechanism for the (3×1) to ( $\sqrt{3} \times \sqrt{3}$ )R30° phase transformation at low temperature. [S0163-1829(96)06420-X]

Most semiconductor surfaces reconstruct to reduce their number of “broken bonds,” which are energetically unfavorable and chemically reactive. For instance, the cleaved Si(111) surface exhibits a metastable Si(111)2×1 reconstruction with a surface band gap of ~0.4 eV, which transforms into the metallic Si(111)7×7 structure upon annealing.<sup>1</sup> Experimentalists have characterized the equilibrium structural and electronic properties of both surfaces to a great extent. Nevertheless, experiments offer little information about the dynamics of the transition between these two reconstructions, i.e., how bonds are broken and how new bonds are formed. Theory, however, can address this issue. *Ab initio* molecular-dynamics calculations have suggested a dynamical path in the formation of the Si(111)2×1 reconstruction starting from the bulk truncated surface.<sup>2</sup> “Snapshots” at selected instants reveal how “bond switching” leads to the formation of fivefold and sevenfold rings of the Si(111)2×1 surface. This phase transformation takes place beyond the time resolution of conventional surface science techniques. With certain other systems, however, intermediate metastable structures can be *locally* “frozen in,” thereby becoming experimentally accessible. It will be shown that *spectroscopic* studies of such local intermediate structures provide key information about the *reconstruction pathway*.

In this paper, we report on the isolation and characterization of one such intermediate structure through which the well-known Si(111)( $\sqrt{3} \times \sqrt{3}$ )R30°-Ag or ( $\sqrt{3} \times \sqrt{3}$ ) surface reconstruction is formed from the Si(111)3×1-Ag or (3×1) reconstruction near *room temperature* (RT). The (3×1) reconstruction is formed by depositing  $\frac{1}{3}$  monolayer of Ag atoms onto the clean Si(111)7×7 surface at  $T \approx 500$  °C and is composed of  $\pi$ -bonded Si chains along the  $[1\bar{1}0]$  direction, separated by single rows of Ag atoms [Figs. 1(a) and 1(b)].<sup>3–5</sup> The ( $\sqrt{3} \times \sqrt{3}$ ) reconstruction incorporates 1.0 ML of Ag and is well described by the honeycomb-chained-trimer (HCT) model [Fig. 1(c)].<sup>6–9</sup> The formation of the ( $\sqrt{3} \times \sqrt{3}$ ) reconstruction from Si(111)7×7 requires an activation temperature of at least 250 °C,<sup>10</sup> but recent low-energy electron diffraction (LEED) studies revealed that the ( $\sqrt{3} \times \sqrt{3}$ ) reconstruction can also be formed by deposition of Ag onto the (3×1) surface at RT.<sup>3</sup> Using a scanning tunneling microscope (STM) we now find that the RT formation of the ( $\sqrt{3} \times \sqrt{3}$ ) reconstruction proceeds through a *metastable structure*. Low-density one-dimensional (1D) Ag atom rows form along the  $[1\bar{1}0]$  direction. The (3×1) underlayer appears to remain intact, but the *local electronic properties* alter dramatically. In fact, the 0.9-eV band gap of

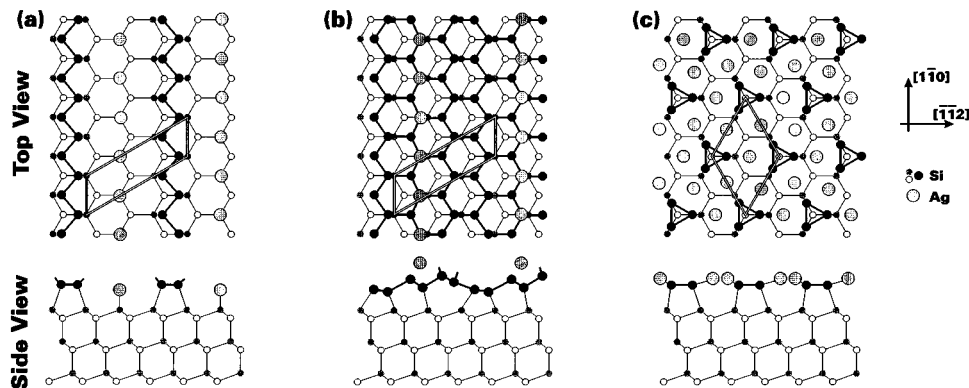


FIG. 1. (a) Seiwatz chain model of the Si(111)3×1-Ag reconstruction (Refs. 3–5); (b) extended Pandey model of the Si(111)3×1-Ag reconstruction (Ref. 5); (c) HCT model of the Si(111)( $\sqrt{3} \times \sqrt{3}$ )R30°-Ag reconstruction (Refs. 6–9). Based on total-energy considerations, models (a) and (b) are the most likely candidates for the (3×1) reconstruction. Other models have been proposed, but have significantly higher energies (Ref. 5).

the  $(3 \times 1)$  substrate closes and the spectral distribution of interface states becomes similar to that of the  $(\sqrt{3} \times \sqrt{3})$  reconstruction. In places,  $(\sqrt{3} \times \sqrt{3})$  domains nucleate at the chains. Based on these spectroscopic observations, we propose the following reconstruction scenario. At RT, Ag atoms initially bond to the  $\pi$ -bonded chains of the  $(3 \times 1)$  reconstruction. By increasing the Ag coverage, the  $\pi$ -bonded chains become unstable and break up, allowing the existing *fivefold* Si rings to rearrange and form trimers. Ag atoms then bond to the Si trimers, resulting in the  $(\sqrt{3} \times \sqrt{3})$  reconstruction.

Experiments were carried out in an ultrahigh vacuum system equipped with LEED, deposition source, and a variable temperature STM. Sample and tip parking capabilities allow for the direct heating of samples and electron bombardment heating of tips. Si(111) wafers were cut into  $(7 \times 1)$ -mm<sup>2</sup> samples, degreased in acetone, and degassed in vacuum overnight. Finally, the samples were flashed to  $\sim 1200$  °C while maintaining the pressure below  $1 \times 10^{-9}$  mbar. LEED and the STM consistently verified well-ordered  $(7 \times 7)$  structures. High-purity Ag was evaporated from a Ta filament. Careful selection of the deposition parameters resulted in a specimen with coexisting  $(7 \times 7)$ ,  $(3 \times 1)$ , and  $(\sqrt{3} \times \sqrt{3})$  reconstruction often visible in a single STM scan.

Images have been slightly filtered to remove dominant acoustic noise frequencies, to offset sample inclination, and to enhance contrast. Spectroscopy experiments have been repeated many times with different samples, tips, and at different tunneling parameters to ensure accuracy and reproducibility. By acquiring constant-current topographic data simultaneously with spectroscopic data, a method known as current imaging tunneling spectroscopy (CITS),<sup>11</sup> we can selectively obtain spectroscopic information from regions where different reconstruction coexist. Area-averaged spectra from the  $(3 \times 1)$  and  $(\sqrt{3} \times \sqrt{3})$  domains are acquired simultaneously with those of Si(111) $7 \times 7$ . Data sets that are at variance with the literature results for Si(111) $7 \times 7$  (Ref. 11) are deemed unreliable. The use of Si(111) $7 \times 7$  as a reference standard for the spectroscopy largely eliminates the threat of artifacts related to tip-induced distortions in the electronic structure.

Figure 2 (top) is an  $(\sim 390 \times \sim 290)$ -Å<sup>2</sup> topographic STM image of a surface region where several reconstructions coexist. On the right, one recognizes the clean Si(111) $7 \times 7$  surface *a*. The large “striped” region *b* represents the  $(3 \times 1)$  reconstruction. Detailed small-scale images of the  $(3 \times 1)$  surface have been published previously.<sup>12,13</sup> Typically, one resolves three rows of protrusions parallel to  $[1\bar{1}0]$  that, depending on the tunneling parameters, may have a different contrast.<sup>13</sup> On top of the  $(3 \times 1)$  domain, bright protrusions *c* form one-dimensional chains of variable length, parallel to  $[1\bar{1}0]$ . Some “chains” are as short as a single protrusion; others incorporate four or five protrusions. The longest chain ever observed had 26 protrusions. We inferred that the protrusions exist on top of the  $\pi$ -bonded chains of the  $(3 \times 1)$  reconstruction.<sup>13</sup> The protrusion spacing is  $\approx 7.7$  Å, twice the  $(3 \times 1)$  unit cell width along  $[1\bar{1}0]$ . Similar atop structures are observed at the zipperlike boundaries between neighboring  $(3 \times 1)$  domains (Fig. 3).

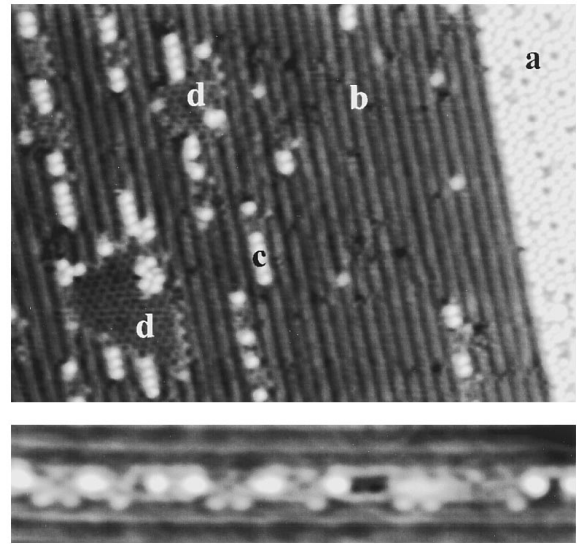


FIG. 2. Top:  $\sim 390 \times 290$  Å<sup>2</sup> topographic STM image of (+2-V empty state) of a region where the (a) Si(111) $7 \times 7$ , (b) Si(111) $3 \times 1$ -Ag, and (c) Si(111) $(\sqrt{3} \times \sqrt{3})R30^\circ$ -Ag reconstructions coexist. The protrusions labeled *c* are low-density 1D Ag chains atop the  $\pi$ -bonded chains of the Si(111) $3 \times 1$ -Ag reconstruction. Bottom: close-up of a low-density 1D chain, interrupted by several nuclei of the Si(111) $(\sqrt{3} \times \sqrt{3})R30^\circ$ -Ag reconstruction.

The presence of these chains critically depends on the preparation procedure of the  $(3 \times 1)$  structure. Best results are obtained if the sample remains exposed to the Ag source for a short while immediately after switching off the sample heating. The larger the flux, the more chains are seen. We therefore identify these protrusions as Ag atoms that still have substantial mobility on the cooling substrate surface. This identification is *tentative*, however, because STM imaging reflects the charge density distribution at a surface, not necessarily adsorption sites. RT deposition onto  $(3 \times 1)$  produces similar features, but those agglomerate more often into 2D clusters.

Quite often, small patches of the  $(\sqrt{3} \times \sqrt{3})$  reconstruction *d* have nucleated near the chains. Figure 2 (bottom) shows a precursor structure to such a region. A long chain of Ag adatoms appears interrupted *several times*. Where the atop Ag atoms are missing, the  $(3 \times 1)$  structure is locally

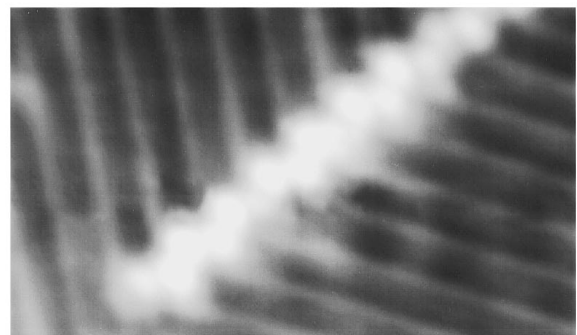


FIG. 3. Topographic image of a phase boundary between two  $(3 \times 1)$  domains making an angle of  $120^\circ$ . The bright protrusions atop the phase boundaries are assumed to be Ag atoms.

destroyed and the characteristic honeycomb structure of the  $(\sqrt{3} \times \sqrt{3})$  reconstruction can be seen. It is thus unlikely that the 1D structures merely represent diffusion channels for excess Ag needed to form a  $(\sqrt{3} \times \sqrt{3})$  patch. Instead, these observations indicate that *the Ag atoms on top of the  $(3 \times 1)$  surface represent an intermediate structure in a low-temperature pathway for forming the  $(\sqrt{3} \times \sqrt{3})$  structure.* These 1D structures are metastable because irrespective of their length, patches of the stable  $(\sqrt{3} \times \sqrt{3})$  reconstruction always nucleate at the chains without apparent activation barrier. These observations thus provide an *atomistic view* of the RT formation of the  $(\sqrt{3} \times \sqrt{3})$  reconstruction from  $(3 \times 1)$  as seen in LEED.<sup>3</sup> In a separate study using low-energy electron microscopy,<sup>14</sup> it was found that the  $(\sqrt{3} \times \sqrt{3})$  structure nucleates from the  $(3 \times 1)$  reconstruction under similar Ag flux but at  $T > 500^\circ\text{C}$ . Possibly, the pathway to form the  $(\sqrt{3} \times \sqrt{3})$  reconstruction at  $T > 500^\circ\text{C}$  employs the same intermediate metastable structure we observe at RT. However, such a structure would likely *not* be experimentally accessible at high temperature.

CITS data were taken from the above domains. Experimental  $I$ - $V$  data are plotted on a semilogarithmic scale in Fig. 4 (top). Figure 4 (bottom) shows the logarithmic derivatives  $(V/I)(dI/dV)$  as a function of tunneling bias. The logarithmic derivative reflects the local density of states (LDOS).<sup>15,16</sup> The tunneling spectrum of the Si(111) $7 \times 7$  surface (Fig. 4) is consistent with earlier reports and is characteristic of a metal, i.e., one can tunnel into states right at the Fermi edge ( $E_F$ ).<sup>17</sup> There are two states at 0.25 and 0.8 eV below  $E_F$  and one at 0.55 eV above  $E_F$ , consistent with previous CITS,<sup>11</sup> photoemission,<sup>18</sup> and inverse photoemission results.<sup>19</sup> The scanning tunneling spectroscopy (STS) curve of the  $(3 \times 1)$  interface exhibits a large gap of  $\sim 0.9$  eV. This is very close to the experimental gaps reported for the Si(111) $3 \times 1$ -Na and Si(111) $3 \times 1$ -K interfaces<sup>3,20,21</sup> and is qualitatively consistent with the fairly large theoretical gaps of the  $\pi$ -bonded chain models ( $\approx 0.4$  eV, Ref. 5).

Although tunneling spectra of the  $(\sqrt{3} \times \sqrt{3})$  reconstruction are also characteristic of a metal [Fig. 4(d)], the gap resistance near  $E_F$  is about a factor of 2 larger than that of the Si(111) $7 \times 7$  surface (at identical tunneling conditions). This shows that the density of states (DOS) near  $E_F$  is very small on the  $(\sqrt{3} \times \sqrt{3})$  surface, consistent with the first-principles pseudopotential calculations by Ding, Chan, and Ho.<sup>7</sup> However, the experimental DOS does not resemble their theoretical DOS. In particular, we do not see the  $\sim 1$ -eV pseudogap above  $E_F$ . Rather, the experimental observation of a metallic ground state is consistent with a very recent *ab initio* augmented spherical wave calculation by van Roosmalen, van Leuken, Flipse, and de Groot.<sup>22</sup> The STS data reveal the presence of a prominent surface state at  $\sim 0.85$  eV below  $E_F$ . This matches the photoemission data by Johansson *et al.* and Yokotsuka *et al.*<sup>23</sup> We also find a shoulder near 0.4 eV below  $E_F$ .<sup>24</sup>

The most fascinating observation, however, is the *closing* of the 0.9-eV tunneling gap on the 1D Ag rows atop the  $(3 \times 1)$  substrate [Fig. 4 (top)]. Note the low DOS at the chains made data acquisition unreliable within 0.15 eV of  $E_F$ ; this structure probably does not possess a band gap. At distances larger than  $\sim 10$  Å away from the Ag chains in

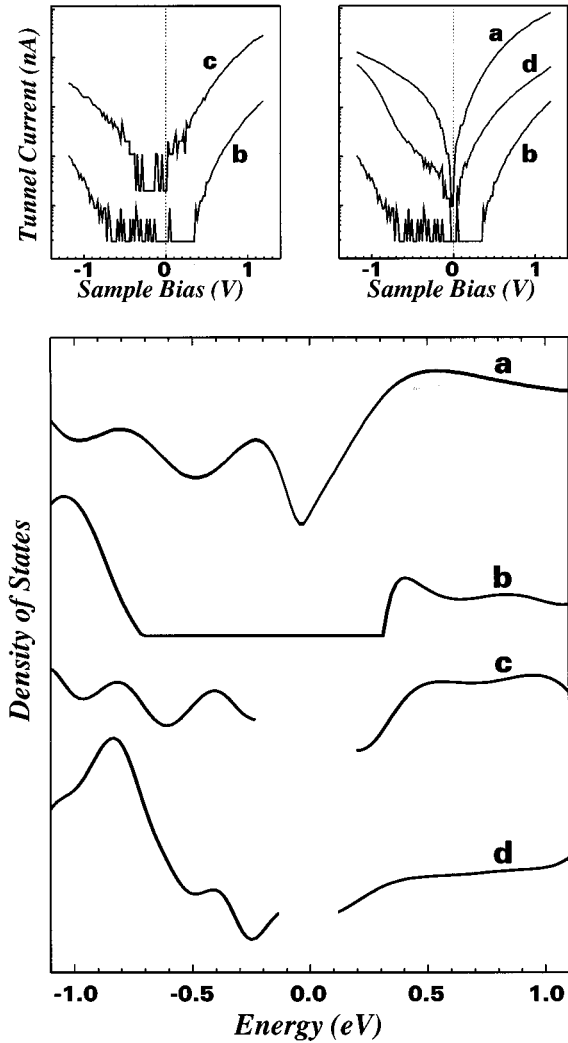


FIG. 4. Semilogarithmic plots (top) and logarithmic derivatives (bottom) of the  $I$ - $V$  spectra. The  $I$ - $V$  data were taken from the selective areas of the top section of Fig. 2. Spectra are labeled according to the annotations in Fig. 2. To produce the LDOS spectra (bottom), raw data were fitted with a polynomial, which was subsequently differentiated *analytically*.

any direction, however, the spectroscopy is essentially that of the clean reconstruction, i.e.,  $(3 \times 1)$  or  $(\sqrt{3} \times \sqrt{3})$ . This *proves* that the gap states associated with the excess Ag atoms are *spatially localized*. In addition, the STS data from the chains appear independent of chain length. A similar closing of the gap is also observed with excess Ag atoms on top of the “zipperlike” boundaries between the different  $(3 \times 1)$  domains (Fig. 3). Here the Ag atoms form a *zigzag chain* that does *not* run parallel to the  $\pi$ -bonded chains of the substrate. The apparent insensitivity of STS data on the adatom environment (e.g., short chain, long chain, “zipper”) also indicates that the gap states are localized. This excludes several speculative scenarios that in principle could explain the absence of a tunneling gap but would require a delocalized (i.e., dispersive) state at  $E_F$ : (i) the Ag atom chains are not 1D metals or “quantum wires,” probably because the spacing between the individual atoms is too large (7.7 Å), and (ii) the Ag atoms do not donate their valence electron to the empty surface state bands of the  $(3 \times 1)$  substrate. Theo-

retical calculations<sup>5</sup> have indicated that the empty states have significant dispersion and, accordingly, the excess valence charge should have been delocalized along the  $[1\bar{1}0]$  direction. Moreover, the *closing* of the 0.9-eV gap is incompatible with such a rigid band scenario. Most interestingly, the LDOS of the 1D chains exhibits striking similarities to the DOS of another reconstruction with a very *different symmetry*, namely,  $(\sqrt{3}\times\sqrt{3})$ . Both filled state spectra exhibit a prominent electronic state at  $\sim 0.85$  and  $\sim 0.4$  eV [Fig. 4 (bottom)]. Even though the 0.85-eV state appears less pronounced at the 1D chains, it evolves as  $(\sqrt{3}\times\sqrt{3})$  patches start to nucleate from the chains. These observations indicate that both reconstructions exhibit similar *local bonding geometries*.

In the HCT model of the  $(\sqrt{3}\times\sqrt{3})$  reconstruction,<sup>6-9</sup> Si surface atoms form *fivefold rings* that are tied together to form Si trimers, centered above the  $T_4$  sites. Each trimer atoms has one dangling bond that is satisfied by one Ag atom. Thus the basic building block of the  $(\sqrt{3}\times\sqrt{3})$  reconstruction is a single Ag atom attached to a fivefold Si ring. A similar configuration would exist for Ag atoms adsorbed *on top* of the  $\pi$ -bonded Si chains in the Seiwatz chain model [Fig. 1(a)]. The experimental observation that these 1D chains convert spontaneously into the HCT reconstruction without apparent activation barrier is consistent with this proposition and lends some credibility to the Seiwatz model.<sup>3</sup> It is not clear why the protrusions only appear in every other unit cell along  $[1\bar{1}0]$ , but we speculate that at higher Ag density, the  $\sigma$  bonds *between* the fivefold rings of the *silicon*

chains break up rapidly, allowing the fivefold rings to rearrange and form trimers resulting in the  $(\sqrt{3}\times\sqrt{3})$  reconstruction. However, this would require an additional  $\frac{1}{3}$  ML of *silicon* atoms because the Seiwatz reconstruction incorporates only  $\frac{2}{3}$  ML of top-layer Si atoms. At present, it is not clear how the extra  $\frac{1}{3}$  ML of Si atoms is incorporated into the HCT reconstruction.<sup>25,26</sup>

In conclusion, we have investigated a reconstruction pathway in the formation of the metallic  $(\sqrt{3}\times\sqrt{3})$  surface, starting from the nonmetallic  $(3\times 1)$  reconstruction. An intermediate metastable phase stabilizes *locally*, consisting of 1D atom chains atop the  $\pi$ -bonded Si chains of the  $(3\times 1)$  reconstruction. The on top adsorption of Ag atoms leaves the channel structure of the underlying  $(3\times 1)$  substrate reconstruction intact. However, the LDOS at the atop sites changes dramatically and strongly reflects the DOS of the  $(\sqrt{3}\times\sqrt{3})$  reconstruction. Thus, even though the  $(3\times 1)$  and  $(\sqrt{3}\times\sqrt{3})$  reconstructions are very different in symmetry and electronic properties, local spectroscopy indicates that their building blocks are essentially the same.

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<sup>24</sup>This state does not match any of the reported surface states (Refs. 7-9). It could be the valence-band maximum (VBM). Core-level studies indicated that  $E_F$  is located between  $\sim 0.2$  and  $\sim 0.5$  eV above the VBM; see G. Le Lay *et al.*, Surf. Sci. **307-309**, 280 (1994).

<sup>25</sup>We have not seen evidence of Si diffusion at RT. Although Si is believed to be immobile at RT, this study reveals that Si bonds can be broken at RT. Hence the additional  $\frac{1}{3}$  ML of Si possibly diffuses in from the bulk or step edges.

<sup>26</sup>The phase transformation from the extended Pandey reconstruction to the HCT reconstruction would require *one full monolayer* of Si atoms to diffuse *away* from the  $(\sqrt{3}\times\sqrt{3})$  patches at RT.