

## Absence of double-bond formation on the Ge(111)3×1-Na surface studied by scanning tunneling microscopy

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The structure of the Na-induced 3×1 reconstruction of the Ge(111) surface has been examined using scanning tunneling microscopy (STM). The STM images reveal significant differences from those of the metal-induced Si(111)3×1 surfaces. Our interpretation of the images leads us to conclude that unlike the Si(111)3×1 surfaces, there exist no Ge=Ge double bonds on Ge(111)3×1-Na despite the similarity in structure. This raises a serious question about a recent proposal that the metal-induced 3×1 reconstruction of the Si(111) surface is stabilized by the formation of a Si=Si double bond. We propose that surface electrostatic energy due to the charge transfer accompanying the surface relaxation plays an important role in stabilizing the Ge(111)3×1-Na surface, and possibly the metal-induced Si(111)3×1 surfaces as well.

The reconstructions of semiconductor surfaces are driven by simple principles, reduction of the number of dangling bonds and relief of surface stress. Well-known elements reducing the number of dangling bonds are adatoms and dimers. Another way is to form  $\pi$  bonding, resulting in a covalent bond of higher order than that of a single bond.  $\pi$  bonding between surface atoms has been proposed in Si reconstructions as a double bond on Si(100)-(2×1),<sup>1</sup> and as a  $\pi$ -bonded chain on Si(111)-(2×1).<sup>2</sup> However, neither of them can be considered as multiple bonds stabilizing the reconstruction in a true sense, because significant polarization (i.e., charge transfer) as well as buckling occurs. Recently, the existence of a *true* Si=Si double bond at a surface has been proposed<sup>3</sup> as a result of theoretical calculations of the structure of metal-induced Si(111)-(3×1) surfaces.<sup>3,4</sup>

For more than a decade, the 3×1 reconstruction of the Si(111) surface induced by the adsorption of alkali metals [(AM) Li, Na, K] and Ag has drawn much attention (see Refs. 3 and 4, and references therein). However, the surface atomic structure has remained controversial, although it is believed to be a single common structure regardless of the metal species. Recently, a very promising geometrical model for Si(111)3×1 has been established based on experimental<sup>5,6</sup> and theoretical<sup>3,4</sup> work. The structure consists of an unusual topmost layer which is nearly planar and honeycombl-like, together with empty channels where the metal atoms locate. This model, referred to as a ‘‘honeycomb chain-channel’’ (HCC) model,<sup>3</sup> was found to be energetically more favorable than previously proposed  $\pi$ -bonded chain models.<sup>7–9</sup> In a calculation on Si(111)3×1-Li, Erwin and Weitering<sup>3</sup> found that a *true* Si double bond is formed between the atoms *b* and *c* in the top layer in the fully optimized HCC geometry of Fig. 1. As a consequence, the interlayer bonding between any of these atoms and the underlying first-layer atom *e* is broken. Charge transfer occurs from the atom *e* to the atom *d* as well as from the metal atom to the atom *a*. It was also proposed that the Si=Si double bond is

‘‘primarily responsible for the stability of the HCC model,’’ making this the first incidence of a stable Si=Si unit on a surface.<sup>3</sup> An independent theoretical calculation on Si(111)3×1-Na by Kang *et al.*<sup>4</sup> reached virtually the same conclusion.

While much existing experimental data can be accounted for within this HCC model,<sup>10–12</sup> one of the compelling argu-

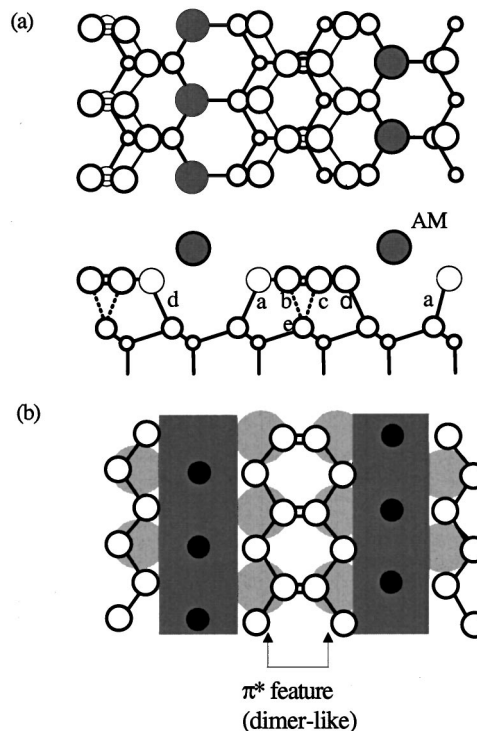


FIG. 1. (a) Schematic diagram of the fully relaxed honeycomb chain channel (HCC) model for Si(111)(3×1)-AM. There is no direct bonding between the Si atom *e* and any of the surface Si atoms *b* and *c*, as denoted by dashed lines. (b) Schematic of simulated empty state STM image (Refs. 3,4).

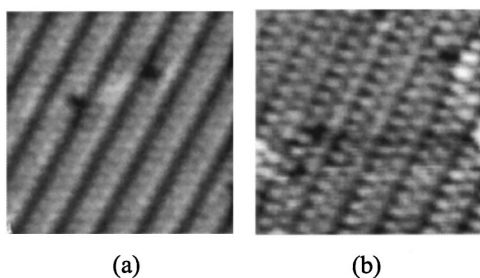


FIG. 2. High-resolution empty state STM images of (a) Si(111)(3×1)-Na and (b) Ge(111)(3×1)-Na acquired at sample biases of +2.0 V and +1.5 V, respectively.

ments favoring it is the interpretation of detailed features present in scanning tunneling microscopy (STM) images. In a simulated empty state image derived from this HCC model [Fig. 1(b)], an antibonding  $\pi^*$  orbital appears as a *dimerlike* feature (with a node in the middle) between bright rows due to the alkali metals. Weak “side spurs”<sup>13</sup> or “dimerized features”<sup>14</sup> observed in the empty state images of Si(111)3×1-Li and Si(111)3×1-Ag can be interpreted as originating from these antibonding  $\pi^*$  orbitals in the Si=Si double bonds.

The Ge(111) surface also undergoes a 3×1 reconstruction induced by alkali-metal adsorption.<sup>15</sup> Ge(111)3×1-AM is expected to have structural and electronic properties similar to those of Si.<sup>6</sup> Since a Si=Si double bond has been proposed as the stabilizing influence on the surface of Si(111)3×1, the question arises: “Does the Ge=Ge double bond also exist and stabilize the same HCC Ge(111) 3×1 structure?” It is questionable since a Ge double bond is expected to be weaker and unlikely to be the stabilizing factor in a Ge(111)3×1-AM structure. If a Ge double bond is not possible, then how is the HCC structure to be modified for Ge(111)3×1-AM and what stabilizes the structure?

In this work, we have examined the above questions by studying the Na-induced Ge(111)3×1 surface using STM and comparing its behavior with STM images of Si(111)3×1 surfaces. Unlike the cases of Si(111)3×1-Li and Si(111)3×1-Ag, the feature attributed to the antibonding  $\pi^*$  orbitals in a double bond is not observed in the empty state image of Ge(111)3×1-Na. In particular, the empty state image of Ge(111)3×1-Na is not compatible with formation of a Ge=Ge double bond. This suggests that the Ge=Ge double bond is not a stable unit on Ge(111)3×1, and some modifications are needed in the proposed model. It may raise a serious question as to the key role of the stabilizing influence of the double bond proposed for all the metal-induced 3×1 surface structures.

Experiments were performed in an ultrahigh vacuum chamber with base pressure of  $1.5 \times 10^{-10}$  mbar. The Na-induced 3×1 surface was prepared by exposing the clean Ge(111)c(2×8) surface at 350–450 °C to a high flux of Na from thoroughly outgassed dispensers (SAES getters Inc.). The STM images were taken at room temperature.

Figure 2 shows STM images of the Ge(111)(3×1)-Na

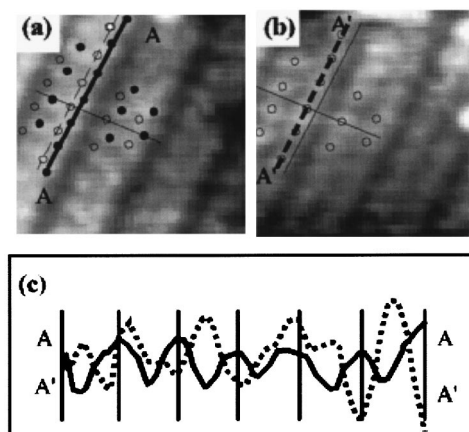
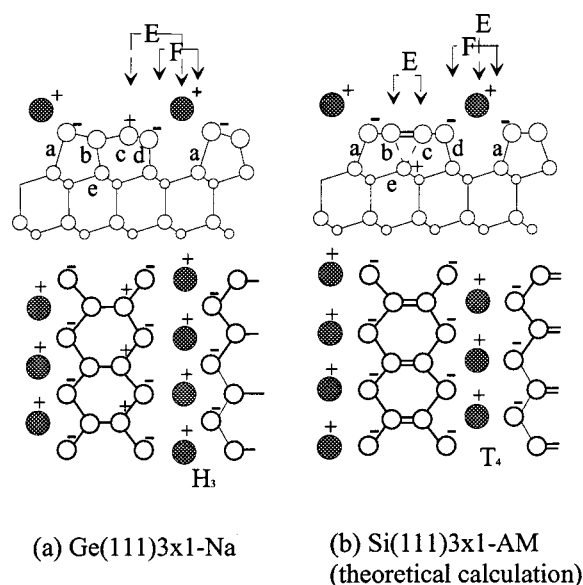


FIG. 3. Dual-polarity STM images of Ge(111)(3×1)-Na taken simultaneously at (a) −1.5 V and (b) +1.5 V sample biases. Maxima in the filled and the empty state images are marked by solid and open circles, respectively. The crosshairs are drawn in identical surface location in both images. (c) Surface height along the cross section AA (solid line) and A'A' (dashed line).

surface taken at opposite bias voltage polarities. Both filled state [Fig. 2(a)] and empty state [Fig. 2(b)] images (not taken simultaneously) show distinct atomic resolution. In particular, the atomic resolution along the row in the empty state is quite exceptional and unprecedented in that it has never been achieved for AM-induced Si(111)-(3×1) to our knowledge. The images show zigzag chains for both polarities. While the appearance of the zigzag rows in the filled state image is virtually identical to those of AM-induced Si(111)-(3×1), the zigzag chains in the empty state image are markedly different from the linear features reported for AM-induced Si(111)-(3×1).<sup>13,14,16</sup>

Comparison with any structural model requires that the STM images representing the occupied and the unoccupied states be taken simultaneously in order to determine the relative registry. For this purpose, dual-polarity tunneling images of Ge(111)3×1-Na are shown in more detail in Fig. 3. Between the zigzag chains in both images, there exists a lateral shift in the direction perpendicular to the rows [see the hairlines AA and A'A' in Figs. 3(a) and 3(b)]. Along the row, the corrugation maxima in one image correspond to the minima in the other image, and vice versa. That is, there exists a phase reversal between the filled and the empty state images, as clearly displayed by the cross-sectional profile in Fig. 3(c).

We interpret our experimental STM images within the HCC model because this structure is calculated to be the most stable for the Si(111)3×1 surface. The zigzag chains in the filled state images can be assigned to the electronic states associated with the negatively charged atoms *d* and *a* in Fig. 1(a). The triangular protrusions are nearly equilateral, while the atomic positions are not. The interpretation of the zigzag chain in the Ge(111)3×1-Na empty state image is difficult to reconcile with the double-bond configuration proposed for the HCC structure. The interpretation requires that some modifications of the bonding configuration occur. First, the observed phase reversal between the zigzag rows in the opposite-polarity images suggests that the ionized Na atoms



(a) Ge(111)3x1-Na

(b) Si(111)3x1-AM (theoretical calculation)

FIG. 4. Schematics of bonding configurations of (a) the Ge(111)(3×1)-Na surface in the modified HCC model and (b) the Si(111)(3×1) surface proposed from theoretical calculations (Refs. 3,4). *F* (filled) and *E* (empty) with arrows indicate the positions of the rows in the dual-polarity images, and + and − represent the charge states of the surface Ge (or Si) atoms and Na. Note that there is no double bond between the *b* and *c* Ge atoms, and the adsorption site of Na atoms is moved to the *H*<sub>3</sub> site for Ge(111)(3×1)-Na in (a).

are located at *H*<sub>3</sub> sites rather than at the *T*<sub>4</sub> sites proposed for Si(111)3×1-AM.<sup>3,4</sup> We can then interpret the zigzag chains in the empty state image as due to the electronic states associated with rows of positively charged Ge atoms *c* and Na atoms. This explains the lateral shift of the zigzag rows observed in the dual-bias images as well.

Based on our STM images, our interpretation of the bonding configuration of the Ge(111)3×1-Na reconstructed surface is presented in Fig. 4, and compared to that based on the theoretical calculations.<sup>3,4</sup> Our interpretation suggests that the Ge atoms *b* and *c* are no longer equivalent and the Ge atom at position *c* is now polarized with positive charge. This in turn implies that there is no Ge=Ge double covalent bond between the *b* and *c* atoms on the Ge(111)3×1-Na surface. Instead, a Ge-Ge single bond forms between atoms *b* and *c* and the remaining orbital of the atom *b* backbonds to the underlying atom *e* in the first layer. The charge in the dangling bond of the atom *c*, not that of the atom *e*, is now transferred to atom *d* to form a polarized bond at the surface. As a result, there is a relaxation of the surface layer from the flat planar geometry proposed for the original HCC silicon reconstruction.<sup>3,4</sup> The orbitals of the atoms *b* and *c* now have to some extent *sp*<sup>3</sup> character which introduces buckling of these atoms at the surface. The new bonding configuration is now very similar to that originally proposed by Lottermoser *et al.*<sup>6</sup>

These modifications of the HCC model not only explain nicely the STM images of Ge(111)3×1-Na but are also compatible with core-level photoemission data.<sup>17</sup> The surface core-level shifts observed for Ge(111)3×1-Na show two Ge 3*d* surface components with intensity ratio of 2:1. In our modified HCC model, Fig. 4(a), the oppositely charged

surface Ge atoms (now *a* and *d* vs *c*) agree well with this ratio (the atom *c* is now similar to the bulk Ge atoms). Without this modification, the originally proposed HCC model<sup>4</sup> would give a 1:1 ratio for the different kinds of surface Ge atoms (*a* and *d* vs *b* and *c*).

The straightforward interpretation of the STM images excludes the formation of Ge=Ge double bonds on the Ge(111)3×1-Na surface. It is evident that the 3×1 reconstruction of this surface must be stabilized by some other mechanism than the formation of a surface double bond. We propose that charge transfer from the atom *c* to the atom *d* accompanying a surface relaxation (buckling with respect to a flat geometry) is important in lowering the surface energy of the HCC structure of the Ge(111)3×1 surface.<sup>19</sup> This effect may be enhanced by the adsorption of ionized Na atoms at *H*<sub>3</sub> sites, and stabilized via electrostatic (Madelung) surface energy.<sup>18</sup> This electrostatic Madelung energy appears to play an important role in the relative stability of the modified HCC geometry for the Ge(111)3×1-Na surface.

Absence of evidence for a double bond for Ge(111)3×1-Na may contain some implications as to the Si(111)3×1 structure. The formation of double bonds between Si (or Ge) atoms is rare in nature, while it is frequently found for C.<sup>20</sup> The Si=Si and Ge=Ge double bonds are considerably weaker and can exist only when they are sterically stabilized by bulky ligands and so their reactivities are hindered.<sup>21</sup> The proposed formation of Si=Si double bond on the Si(111)-(3×1) surface may be possible because of its steric stability on the surface. But, considering the similarities between Si and Ge, we feel that the *stabilizing* role of the double bond in the Si(111)-(3×1) structure is questionable. It also seems to contradict the general chemical evidence that Si and Ge double bonds, unlike the C=C double bond, are much less stable than their respective single bonds.<sup>22</sup> We suggest that the Si(111)3×1 structure is also stabilized by the same mechanism as that for Ge(111)3×1-Na, rather than by the formation of Si=Si double bonds.

In summary, we have shown that empty state images of the Na-induced Ge(111)3×1 surface appear distinctly different from those of Si(111)3×1 surfaces, though their filled state images look alike. Based on the images, we argue that there is no evidence to support a Ge=Ge double bond stabilizing the Ge(111)3×1-Na structure. We propose a different mechanism to stabilize the Ge(111)3×1-Na reconstruction: stabilization via the charge transfer accompanying buckling as well as an electrostatic (Madelung) energy. We further suggest that the stability of the HCC structure of the Si(111)3×1-AM surface is also achieved by the same mechanism. New total-energy calculations are called for to investigate the electrostatic energy contribution, particularly as regards the Ge(111)3×1 surface, to further clarify this concept.

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<sup>18</sup>It may be considered that the Ge atoms of *c* and *d* form a  $\pi$ -bond chain. This  $\pi$ -bond chain must be buckled to gain its stability, as in the case of Si(111)2 $\times$ 1.  
<sup>19</sup>For Si(111)3 $\times$ 1-Na, the Na adsorption energy at the  $H_3$  site is only 0.03 eV/Na higher (Ref. 4) than that at the  $T_4$  site. This slight energy difference can be easily inverted by the electrostatic energy gain from the modified HCC structure of Ge(111)3 $\times$ 1-Na.  
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<sup>21</sup>Only a few (highly reactive) molecules containing double bonds of Si and Ge, disilenes  $R_2Si=SiR_2$  and digermenes  $R_2Ge=GeR_2$  (*R* is ligand), have been synthesized [R. West, M. J. Fink, and J. Michl, Science **214**, 1343 (1981); D. E. Goldberg *et al.*, J. Chem. Soc. Dalton Trans. **1986**, 2387]. To date, the simplest forms of these molecules,  $H_2Si=SiH_2$  and  $H_2Ge=GeH_2$ , have not been synthesized.  
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