Bi-induced reconstructions on Si(100)

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Two reconstruction structures are proposed for Bi adsorption on Si(100) based on a first-principles local-density-functional molecular-cluster study employing total energies and atomic forces. Bi dimers, rather than monomers, are predicted to form the basic structure on the Si(100) surface. At high coverage, Bi adsorption leads to the breaking of Si dimers, which in turn removes the reconstruction of Si(100)2×1. Our results appear to explain recent results of scanning tunneling microscopy experiments.

I. INTRODUCTION

The clean Si(100) surface, which is known to reconstruct into a 2×1 structure by forming Si dimers that are arranged in parallel rows,[1] is still chemically reactive since there is a dangling bond associated with each surface Si atom. There are many applications that require the Si surface to be less reactive and stable against contamination, oxidation, etc.[2,3] Thus, the search for adsorbates that can passivate the surface is an attractive and interesting subject of surface physics. Experiments[3-5] have shown that group-V elements such as As and Sb can be used to passivate Si(100) by saturating the Si dangling bonds. In addition, these metal elements can break the Si dimers and form metal dimers on Si(100),[3,5,6] resulting in a metal-induced 1×2 structure at a coverage above 0.5 monolayer (ML). In the last few years, As and Sb have been frequently used as a surfactant to force layer growth of some non-lattice-matching materials.[7] Other metals, such as group-III (Ref. 8) and group-VI (Ref. 9) elements, have also been studied as possible candidates to passivate Si(100).

Bismuth, another group-V metal that may have behavior similar to that of As and Sb on the Si(100) surface, was recently found to be an ideal surfactant for the molecular-beam epitaxy of Si/Ge heterostructures.[10] Surprisingly, the basic structure of the Bi overlayer on Si(100) is still unclear. This will certainly hinder the understanding of the Bi-mediated growth mechanism of the Si/Ge system and future studies of related systems. Here we report a theoretical study of the atomic structure of Bi on Si(100) at low and high coverage. We found that Bi tends to form dimers on both the 2×1 and 1×1 Si(100) surfaces. At low coverage, Bi adsorbs on the modified bridge site of Si(100)2×1. Deposition of more Bi between nearest Bi-occupied bridge sites induces a large relaxation of the Si substrate that leads to the breaking of the underlying Si dimers. As a result, Bi forms a 1×2 structure on the recovered Si(100)1×1 surface.

There are a few experimental studies on the Bi/Si(100) system, and yet they provide results that are far from consistent. Earlier experiments[11] using quadrupole mass spectrometry, low-energy electron diffraction (LEED), and Auger electron spectroscopy showed that there are two adsorption phases for Bi on Si(100). Below 0.5 ML, a 2×1 structure is observed, while at coverage above 1 ML, both 1×1 and 2×1 structures appear. From their reflection high-energy electron diffraction (RHEED) study, Hanada and Kawai[12] reported Bi:n×2 surface structure with n ranging from 5 to 13 depending on Bi coverage. They proposed a missing-row dimer model corresponding to $(n-1)/n$ ML coverage. This model assumed that Bi dimers line up on the cave sites of Si(100)2×1 and that the Si atoms just below the missing Bi dimer remain dimerized, while other Si dimers under the adsorbed Bi dimers are broken. Later, Fan and co-workers[13] found a 1×1 structure in their LEED experiment at 1 ML coverage, apparently due to the recovered Si(100)1×1 structure, and that Bi atoms form a disordered phase but serve to stabilize the 1×1 structure. No Bi dimer structure is mentioned in their work. Recently, Park *et al.*,[14] using LEED and scanning tunneling microscopy (STM), also observed Bi:n×2 surface structures on Si(100) with n ranging from 5 to 12 at about 1 ML. The most recent study using STM and LEED by Noh *et al.*[15] reported a local 2×2 structure up to 0.5 ML and a 1×2 structure beyond 0.5 ML. They did not find the 1×1 structure reported in the previous LEED experiment.[13] In addition, they suggested that Bi forms dimers on the surface and that the underlying Si dimers may be broken above 0.5 ML. Thus, these studies differed mainly in two aspects: the reconstruction structures below and above 0.5 ML and the nature of the Bi adsorption, i.e., dimer or monomer.

II. METHODOLOGY

Our approach is the first-principles molecular-cluster [DMol (Refs. 16,17)] total-energy and atomic-force method, which is based on the local-density approximation to density-functional theory. We used the Hedin-Lundqvist exchange-correlation potential.[18] The frozen-core approximation was made for Si and Bi except that the semicore Bi 5d electrons were treated fully in the self-consistent iterations. An extended basis set was chosen for Si and Bi, which contains a double set of valence functions plus a single d polarization function. This basis set has been proven to be successful in studying the As and Sb/Si(100) systems.[6,19] As to the simulation of the bare Si(100)2×1 surface, a symmetric dimer

arrangement was chosen in which the first-layer Si atoms relax inward by 0.38 Å and the dimer bond length is 2.23 Å.[20] Atomic-cluster models ranging from 22 to 62 atoms were employed to simulate the Si(100)2×1 and 1×1 surface. Hydrogen atoms were used to saturate the Si dangling bonds at the cluster boundary and the Si-H bond length was taken to be 1.48 Å. The binding energy for a given geometry and the forces on selected atoms were calculated. In cases where relaxation of certain atoms was needed, those atoms were further displaced according to the forces acting on them. An optimized structure was obtained for the geometry that gives the lowest binding energy and has residual forces that are sufficiently small.

III. RESULTS AND DISCUSSION

We first studied the optimal chemisorption geometry of a single Bi atom (i.e., monomer) on Si(100)2×1. There are four possible adsorption sites shown in Fig. 1, which can be simulated by four appropriate clusters having a number of atoms ranging from 22 to 26.[19] Since experiments[3,5] showed that group-V metals such as As and Sb adsorbed on Si(100) are bonded with two surface Si atoms, the bridge and cave sites may seem to be more favorable adsorption sites also for Bi. Indeed, we found that the bridge site has the lowest adsorption energy among the four sites studied and thus is the most stable position. The calculated adsorption energies are bridge: −3.00 eV; cave: −2.60 eV; pedestal: −2.38 eV; valley bridge: −2.05 eV. The adsorption energy of the cave site is the second lowest but is still 0.40 eV higher than the bridge site. This result is consistent with results for As and Sb on Si(100)2×1, which show that a single As or Sb atom is adsorbed on the bridge site.[19]

It must be pointed out that the cave site is generally considered as the favored chemisorption site where two dangling bonds of the underlying Si atoms can be saturated.[12,21] Thus, the adsorption of group-V metals on bridge sites demonstrates a unique feature for this group. In our previous studies, As and Sb were shown to be able to passivate the dangling-bond states of the underlying Si dimer atoms[6] and to form stronger covalent bonding with the
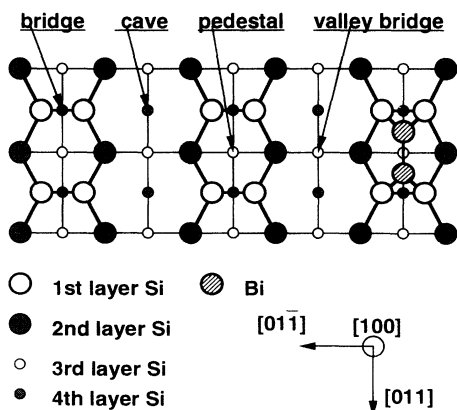
first-layer Si.[19] Although they could also passivate the dangling-bond states at cave sites, in this case they form π-like bonding with the first-layer Si which is much weaker than that at the bridge site.[19]

We now turn to the case where more Bi atoms are adsorbed on the Si(100)2×1 surface. The main purpose here is to study whether the Si dimer is broken when more Bi is present. Since the lowest-energy position for single Bi is the bridge site, it should be occupied first before going to the second-lowest-energy site, namely, the cave site. We used a cluster shown in Fig. 2 which consists of 62 atoms simulating the combination of two bridge sites and one cave site occupied by Bi. Initially, the three Bi atoms are placed at the height calculated from single-atom adsorption. The binding energy of this cluster is −206.39 eV. This structure is extremely unstable; there is a large unbalanced force exerted on the first three Si layers, indicating that extensive relaxation of the Si substrate is necessary to release the strain. The calculated force direction showed that Si atoms tend to move toward their positions in the ideal 1×1 surface. Using the same cluster displayed in Fig. 2, but breaking the Si dimers as if there is no reconstruction and relaxation of the Si substrate, Bi adsorption on the ideal 1×1 Si(100) surface can be studied. Three Bi atoms are put on bridge sites at a height calculated from a separate study of single-atom adsorption on the ideal Si(100)1×1 surface. Now the binding energy is −207.40 eV. This gives a net energy lowering of 0.51 eV/dimer over the previous 3Bi/Si(100)2×1 system. The calculated forces on the first three Si layers show that there is need for a small relaxation of the substrate. The final optimized structure gives an extra 0.03 eV lower energy than the nonoptimized one and presses the first-layer Si down by 0.05 Å. These results show clearly that breaking the Si dimer leads to a more stabilized structure.

To evaluate the effect of Bi at the cave site on the underlying Si dimer, we also performed the calculation using the cluster given in Fig. 2 but placing only two Bi atoms on the bridge sites and leaving the cave site empty. The energy of this structure is then compared to that with all Si atoms in the ideal 1×1 surface. It turns out that the former structure is 0.62 eV/atom lower than the latter. In other words, without Bi at the cave site, the Si substrate remains dimerized even if the nearest bridge sites are occupied by Bi.
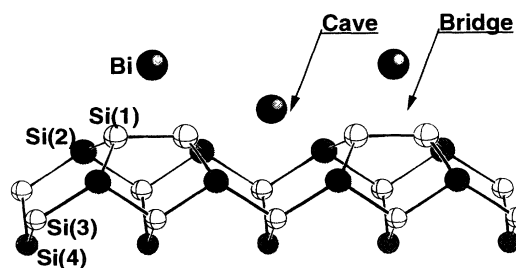

FIG. 1. Top view of the Si(100)2×1 structure. The various adsorption sites are indicated by arrows.

○ 1st layer Si   ⊘ Bi

● 2nd layer Si   [01$\bar{1}$]   [100]

○ 3rd layer Si

• 4th layer Si   [011]

FIG. 2. The $Bi_3Si_{27}H_{32}$ cluster model simulating three Bi atoms adsorbed on two bridge sites and one cave site. Numbers in parentheses indicate the Si layer. Hydrogen atoms are not shown in the figure.

The importance of breaking the Si dimer is that, in principle, Bi could form an ordered structure up to 1 ML. In an ideal situation, all surface Si dimers are broken and their dangling bonds are saturated by Bi. This would lead to a Bi:1×1 structure on the surface that was not detected in recent experiments.[12,14,15] Although Fan and co-workers' LEED study[13] did see a 1×1 structure, they showed from their I-V curve calculation that it is from the recovered Si(100)1×1 surface, rather than from Bi. The STM and LEED investigations[15] found a 1×2 reconstruction at 1 ML. Previous studies[3,6,19] of As and Sb on Si(100) all suggest that metal dimers are formed on Si(100). The 1×2 structure seen in STM and LEED (Ref. 15) could be attributed to Bi dimer formation. To find out, we used a 33-atom cluster to simulate two Bi atoms adsorbed on neighboring bridge sites in the same dimer row.[22] Initially, we kept the Si substrate dimerized and placed Bi on the two bridge sites which are separated (by 3.84 Å) as if they are in monomer adsorption. The calculated force on Bi indicates a large attractive force between the two Bi atoms so that they tend to move toward each other, as shown in Fig. 1. When the distance between two Bi atoms reaches 3.14 Å, the energy gained by forming the dimer is 0.30 eV per Bi atom compared to that when two Bi atoms are 3.84 Å apart, which is a strong signal of a stabilized dimer structure. When we then change the Si substrate to the ideal 1×1 structure, the same Bi dimerization is observed with an energy gain of 0.23 eV per Bi atom compared to monomer adsorption. Table I lists the calculated Bi-Bi bond length and the binding-energy results for a Bi dimer adsorbed on the Si(100) surface with and without breaking the underlying Si dimer. It can be seen that a Bi dimer adsorbed on the Si(100)2×1 reconstructed surface is more stable than that on the ideal Si(100) surface by 1.54 eV, which confirms that Bi adsorption does not break the Si dimer at low coverage. However, as discussed above, bringing more Bi onto Si(100)2×1 can break the Si dimers if these Bi atoms are at cave sites between the two nearest bridge sites.

It is now clear that, since the dimerized Bi structure has the advantage of lowering the energy, it is more favorable than monomer adsorption. It has to be emphasized that Bi atoms form dimers on both the Si(100)2×1 reconstructed and Si(100)1×1 nonreconstructed surfaces; this again shows a similar phenomenon to that of As and Sb adsorbed on Si(100).[6,19] With the above results in mind, two structure models of Bi adsorption on Si(100) can be naturally introduced. Given in Fig. 3(a) is a 2×2 structure for low coverage. Here the Si dimer is not broken; each Bi atom adsorbs on a modified
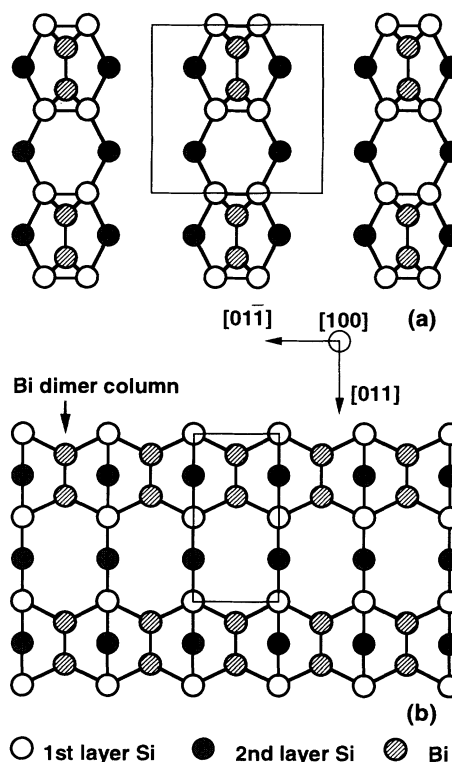

FIG. 3. Two structural models representing Bi adsorption on Si(100)2×1 and 1×1 surfaces. Si dimer rows and Bi dimer rows are along [011] and [01$\bar{1}$] directions, respectively. (a) Bi:2×2 dimer structure at low coverage; (b) Bi:1×2 dimer structure at high coverage.

bridge (MB) site, which is shifted from the bridge site along the [011] direction, and forms a dimer with another Bi in the nearest MB site. In an ideal situation, each MB site of Si(100)2×1 is occupied and Bi dimers form rows that are perpendicular to the Si dimer rows, resulting in a Bi:2×2 reconstruction pattern at 0.5 ML. At high coverage, Bi atoms begin to adsorb on the cave sites, which will induce large relaxations of the Si substrate and lead eventually to the breaking of Si dimers. The structure model given in Fig. 3(b) shows that all surface Si dangling bonds are saturated by Bi and a 1×2 reconstruction pattern appears due to the dimerized Bi structure. This is just like the structure of the clean Si(100)2×1 surface but replacing the first-layer Si dimers with Bi dimers and rotating the surface by 90°. Here Bi atoms serve to passivate the Si surface. The two structures presented can explain the 2×2 and 1×2 structures found in recent STM and LEED experiments[15] at low and high coverage, respectively.

The Bi:2×2 structure proposed is more likely to be seen in local areas of Si(100), because any Bi adsorption on a cave site between two Bi-occupied bridge sites will destroy the 2×2 structure. This may be the reason why only a very faint 2×2 spot was observed in a LEED study at 0.5 ML.[15] Due to the relatively large atomic size of Bi compared to As and Sb, it can be expected that Bi may induce larger strains on the surface. While the strain-relieving mechanism is still unclear, the formation

TABLE I. The Bi-Bi bond length $L_{Bi\text{-}Bi}$ and binding energy E_b for a Bi dimer adsorbed on Si(100)2×1 and Si(100)1×1 surfaces calculated from a 33-atom cluster.

	Bi_2/Si(100)2×1	Bi_2/Si(100)1×1
$L_{Bi\text{-}Bi}$ (Å)	3.14	3.21
E_b (eV)	−112.33	−110.79

of defects, missing dimers, and antiphase boundaries on Si(100) will certainly help relieve the strain, as was indeed observed in several experiments[12,14,15] for Bi/Si(100). Accordingly, in the STM study of Sb on Si(100),[5] the Sb overlayer was also found to have more defects than the As/Si(100) system. These defects will also reduce the adsorbate saturation coverage, which is assumed to be 1 ML for the ideal situation. Finally, the missing-dimer model proposed in Ref. 12 can be slightly modified to explain the Si(100)$n \times 2$:Bi series surface structures found in RHEED, LEED, and STM experiments.[12,14] Since these structures are found at a coverage near 1 ML, Si dimers are unlikely to remain as proposed previously.[12] Assuming a recovered Si(100)1×1 surface, if there is a missing Bi dimer column for every successive $n - 1$ Bi dimer columns, it will show $n \times 2$ surface structure.

IV. CONCLUSION

In conclusion, our first-principles DMol molecular-cluster study of Bi adsorption on Si(100) reveals that the Si dimer is broken when Bi adsorbs on the cave site between two Bi-occupied bridge sites along the Si dimer rows, leading to a recovery of the 1×1 structure. We found that the Bi dimerized structure is so energetically stable that it exists regardless of the geometry of the Si substrate (i.e., 2×1 or 1×1). These Bi dimers form rows that are perpendicular to the underlying Si dimer rows. We proposed two surface structure models, namely, Bi:2×2 at low coverage and Bi:1×2 at high coverage, which are found to be fully compatible with recent STM and LEED experimental results. The Bi behavior on Si(100) at high coverage is shown to be in line with other group-V metals on Si(100). However, since a 2×2 structure has not yet been reported for As and Sb at low coverage, further experimental studies are needed.

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[22] The cluster model can be found in Ref. 19. We also studied several other dimer geometries adsorbed on different sites and oriented either perpendicular or parallel to Si dimer rows. The dimer geometry presented here has the lowest energy.
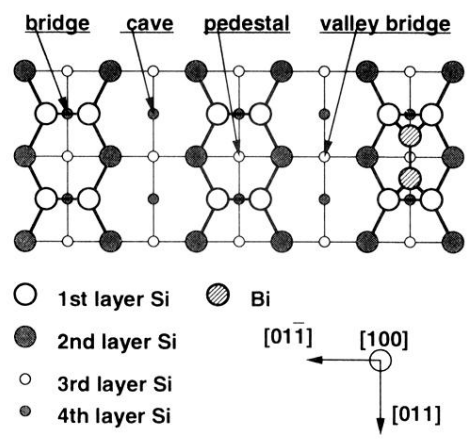
bridge   cave   pedestal   valley bridge

○ 1st layer Si   ◍ Bi

● 2nd layer Si

○ 3rd layer Si   [01$\bar{1}$]   [100]

● 4th layer Si   ← ○

                                                      ↓ [011]

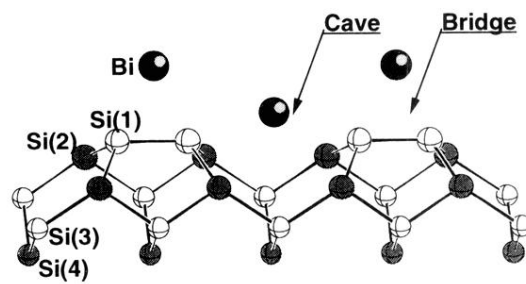FIG. 1. Top view of the Si(100)2×1 structure. The various
adsorption sites are indicated by arrows.

FIG. 2. The $Bi_3Si_{27}H_{32}$ cluster model simulating three Bi atoms adsorbed on two bridge sites and one cave site. Numbers in parentheses indicate the Si layer. Hydrogen atoms are not shown in the figure.
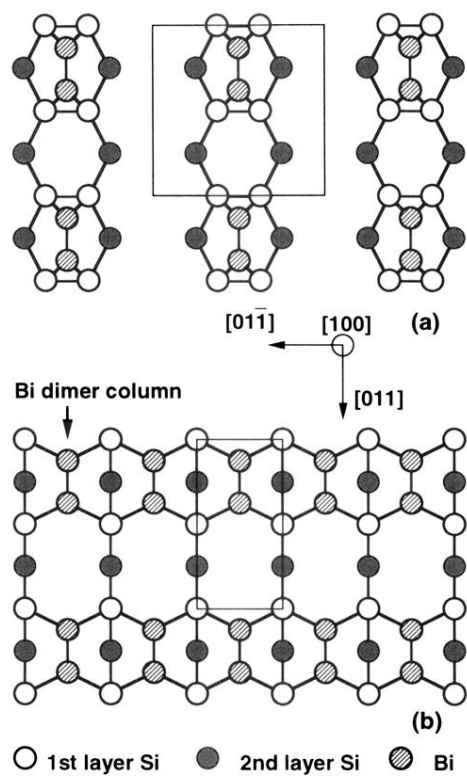
[01$\bar{1}$]   [100]   **(a)**

[011]

Bi dimer column

(b)

○ 1st layer Si   ● 2nd layer Si   ⊘ Bi

FIG. 3. Two structural models representing Bi adsorption on Si(100)2×1 and 1×1 surfaces. Si dimer rows and Bi dimer rows are along [011] and [01$\bar{1}$] directions, respectively. (a) Bi:2×2 dimer structure at low coverage; (b) Bi:1×2 dimer structure at high coverage.