

## Energetics and bias-dependent scanning tunneling microscopy images of Si ad-dimers on Ge(001)

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We report an *ab initio* study of the energetics and scanning tunneling microscopy (STM) images of Si ad-dimers on Ge(001) and energetics of Ge ad-dimers on Si(001). As in the case of Si dimers on Si(001), we find for both systems that the *D* dimer configuration, lying between the substrate dimer rows and parallel to them, is highest in energy. Conversely, recent STM experiments for Si ad-dimers on Ge(001) deduce the *D* configuration to be most stable. Our theoretical STM images for this system find that both the *D* and *C* configurations (the latter also between the rows) have similar STM images for the experimental voltages. We propose an experimental test (low-bias STM imaging) which would unambiguously distinguish between the *D* and *C* configurations. [S0163-1829(99)04631-7]

The growth of Si (or Ge) on Si(001) and Ge(001) surfaces has recently been extensively studied, spurred by interest in GeSi superlattices.<sup>1-11</sup> Despite numerous studies of film growth in these systems, the initial stages of submonolayer growth are not well understood.<sup>9-11</sup> Most studies, both theoretical and experimental, have been carried out on the system of Si on Si(001).<sup>2-10</sup> They may be summarized as follows. In the earliest growth stage, no isolated adatoms are observed at room temperature; the smallest stable adsorbed unit is a dimer.<sup>3,4</sup> Figure 1 shows the four plausible local energy minima available for these ad-dimers, three of which (*A*, *B*, and *C*) have been experimentally detected.<sup>9,10</sup> Two of these (*A* and *B* configurations) consist of isolated dimers directly adsorbed on top of the substrate dimer rows; of these, the *B* dimer is found to be the most stable.<sup>6-10</sup> In addition to these, *C* dimers are also detected, both in isolation and in the form of diluted dimer rows. Multiatom structures oriented along the  $\langle 130 \rangle$  surface direction are also observed.<sup>4,10</sup> These structures are thought to be composed either of *C* dimers or of pairs of adatoms.<sup>10,11</sup> The fourth possible (*D*) configuration for isolated dimers has not been observed experimentally in isolation.<sup>10</sup> This is consistent with the results of *ab initio* calculations for isolated ad-dimers which find that the *D* dimer is highest in energy.<sup>5-7</sup> Experimental observations of Ge on Si(001) exhibit similar features.<sup>11</sup>

Recently, Wulfhekel *et al.*<sup>12</sup> (WHZRP) carried out a quantitative analysis of structures formed by deposition of 0.01 monolayer at 300 K of Si on Ge(001). Just as in the growth of Si and Ge on Si(001), they found no stable isolated adatoms but only stable ad-dimers. They also observed multiatom structures oriented along the  $\langle 130 \rangle$  direction. However, in contrast to growth on Si(001), they found *no* isolated ad-dimers in the *C* configuration. They found that *D* dimers are the most commonly observed dimers on the surface, and that they become even more numerous on annealing. By contrast, they found that dimers in the *A* and *B* configurations, which lie atop the substrate dimer rows, are less common and become even rarer on annealing. These features are quite different from the results on Si(001) mentioned above.<sup>4-11</sup>

In this paper, we describe *ab initio* simulations of Si ad-dimers on the Ge(001) surface. The goal of these calculations

is to understand the surprising contrasts between the results of Wulfhekel *et al.*<sup>12</sup> and those found for adsorption of Si or Ge on Si(001). For comparison, we have also carried out analogous studies of Ge dimers on Si(001). Our results show that the *D* dimer is the highest in energy for Si on Ge(001), contrary to the experimental deduction of WHZRP, but in keeping with the trend seen in theoretical and experimental results for Si (or Ge) growth on Si(001). We suggest two possible ways of reconciling our result with experimental observations. We then propose an experimental test which will unambiguously distinguish between these two possibilities.

Our total-energy calculations for the various surface structures were carried out using density-functional theory in the local-density approximation (LDA). We used generalized norm-conserving pseudopotentials<sup>13</sup> with a plane-wave basis set and the Ceperley-Alder exchange-correlation potential in the form parametrized by Perdew and Zunger.<sup>14</sup> Our supercell consists of a  $4 \times 4$  surface unit cell with six Si (or Ge) layers and six vacuum layers. Of the six layers, the bottom two layers were held fixed at their bulk lattice positions with the theoretical lattice constant of 5.58 Å for Ge and 5.38 Å for Si, while the remaining four layers were allowed to relax fully. The clean surface was taken to have the  $c(4 \times 2)$  reconstruction. The dangling bonds of the bottom layer were saturated by H atoms. We used an energy cutoff of 10 Ry in our planewave expansion and two special *k* points in the irreducible part of the surface Brillouin zone. The calculated

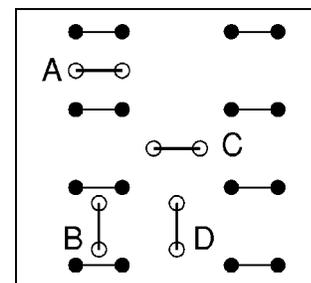


FIG. 1. Schematic diagram of the various adsorption sites for Si or Ge ad-dimers on Si or Ge (001) substrates. Filled dumbbells: substrate dimers; open dumbbells: adsorbed ad-dimers.

TABLE I. Energies in eV of the dimer configurations of Fig. 1 on Si and Ge substrates, relative to the stable  $B$  dimer. In each case the isolated  $D$  dimer is theoretically found to be the highest in energy. On the Si(001) substrate this isolated dimer is not observed experimentally (Refs. 10 and 11). On Ge(001) WHZRP (Ref. 12) report the existence of this dimer in isolation and also identify it to be the most stable.

Ad-dimer	Si/Si(001)		Si/Ge(001)	Ge/Si(001)
$D$	1.11 <sup>a</sup>	0.7 <sup>b</sup>	0.18	0.84
$C$	0.3	0.18	0.06 <sup>c</sup>	0.03
$B$	0	0	0	0
$A$	-0.01	0.07	0.06 <sup>c</sup>	0.03

<sup>a</sup>Theoretical values from Ref. 5.

<sup>b</sup>Theoretical values from Ref. 6.

<sup>c</sup>Experimental values from Refs. 8 and 9 (in italics).

forces on the atoms were converged to less than 0.0005 hartree/bohr. By varying parameters such as Brillouin-zone sampling and energy cutoff, we estimate that our calculated energy differences are converged to better than 0.05 eV. The computations were performed using the *ab initio* code FHI96MD.<sup>15</sup>

The calculated energies of the different ad-dimers relative to the  $B$  dimer are shown in Table I. From these results we make the following observations: (1) In all three systems, i.e., Si/Si(001), Si/Ge(001), and Ge/Si(001), we notice that the  $D$  ad-dimer has the highest energy. Our results for Ge/Si(001) are consistent with the experimental observation that no isolated  $D$  dimers are seen.<sup>11</sup> Previous *ab initio* calculations<sup>5-7</sup> for the Si/Si(001) system also indicate that the  $D$  dimer has the highest energy, consistent with experimental observations.<sup>7,10</sup> By contrast, WHZRP conclude that in Si/Ge(001) the  $D$  dimer is energetically the most favored among the different dimer types. (2) The energies of the  $B$  and  $C$  dimers for Si/Ge(001) are nearly degenerate, whereas for adsorbates on Si(001) the energies of these dimers are calculated to differ substantially. (3) Finally, we observe that the calculated energy of the  $D$  dimer relative to the  $B$  dimer is much smaller in the Si/Ge(001) system than in the Ge/Si(001) and Si/Si(001) systems.

We now discuss the experimental results of WHZRP,<sup>12</sup> in light of these calculations. As mentioned before, WHZRP found that isolated  $D$  ad-dimers are the most common species found in the Si/Ge(001) system at low coverage, making up 39% of the deposited material when 0.01 monolayer of Si was grown on Ge(001) at 300 K and 50% of the material when that same surface was annealed for five minutes at 350 K. Furthermore the predominant species when Si is deposited at 350 K are the  $D$  dimers. From these and related results, WHZRP conclude that the  $D$  dimer is the isolated dimer of lowest energy on this surface. While we compute the  $C$  dimer to be considerably lower in energy than the  $D$  dimer (cf. Table I) they observed *no* isolated  $C$  dimers. Despite the absence of isolated  $C$  dimers, WHZRP do report metastable multiatom (“ $CC$ ”) structures lying along  $\langle 130 \rangle$ , comprised of several  $C$  dimers. The experimental observation of stable  $D$  dimers, the absence of isolated  $C$  dimers, and the presence of  $CC$  structures, seems somewhat puzzling. Not only does it seem inconsistent with the calculated energy

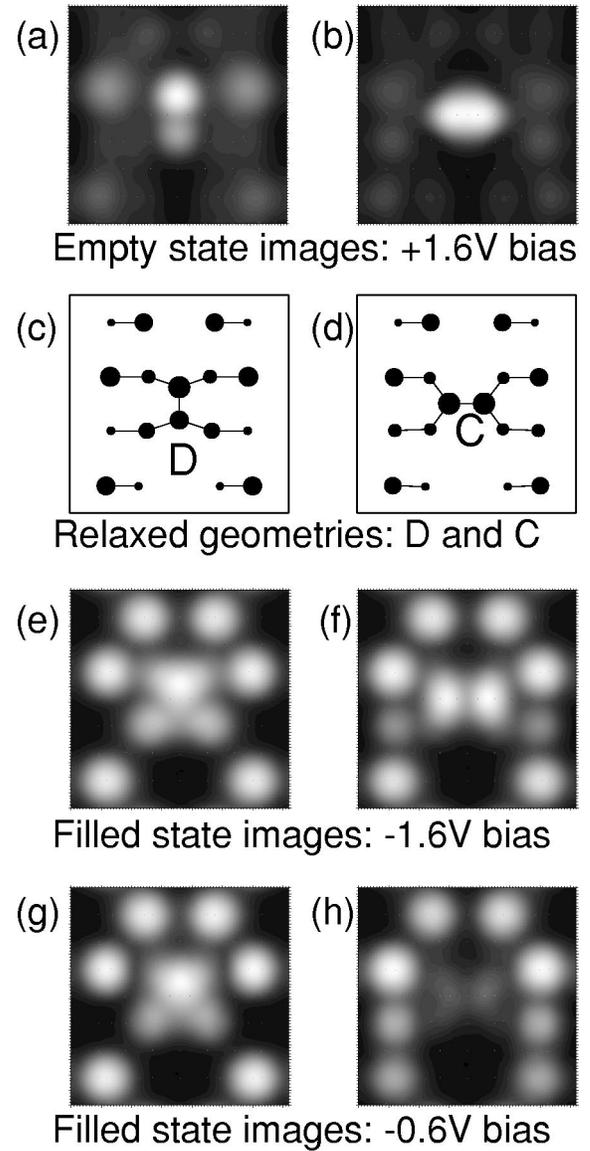


FIG. 2. STM images and fully relaxed geometries for Si dimers on the Ge(001) surface. Relaxed configurations of the ad-dimer and top layer atoms are shown for (c) the  $D$  dimer and (d) the  $C$  dimer. The height is represented by the size of the filled circles. Above the respective geometries are shown the empty state images in (a) and (b). Below the relaxed geometries are shown the respective filled state images at high bias [(e) and (f)] and low bias [(g) and (h)]. The images were generated at a distance of 3 Å from the uppermost substrate atom. The maximum (minimum) charge densities are 15(1), 14(0.9), 4(0.2), 4(0.2), 3(0.2), 2(0.1) for the images (a), (b), (e), (f), (g), and (h), respectively, in units of  $10^{-4} e/\text{Å}^3$ . Notice that the charge densities for the empty state images are significantly larger than for the corresponding filled state images, consistent with experiment (Ref.12).

sequences of Table I for Si/Ge(001); it also contrasts with the behavior of Si (or Ge) dimers on Si(001), where experimentally no isolated  $D$  dimers are found,<sup>10,11</sup> in agreement with calculated dimer energies.<sup>5-7</sup>

In an effort to resolve this puzzle, we generated scanning tunneling microscopy (STM) images of our relaxed geometries for the  $D$  and  $C$  dimers [cf. Figs. 2(c) and 2(d)]. Figure 2 shows the calculated STM images at constant height for

the Si/Ge(001) system. These images were generated in the Tersoff-Hamann approximation.<sup>16,17</sup> In this scheme, the tunneling current is proportional to the local density of states at the tip position integrated over the energy range allowed by the applied bias voltage.

Figures 2(e) and 2(a) show the computed filled and empty state STM images, respectively, for the *D* dimer. Note that the empty state image of the *D* dimer [Fig. 2(a)] shows buckling consistent with the relaxed atomic geometry [Fig. 2(c)]. Comparing with experiment we notice that the STM images of *D* dimers, as observed in Refs. 12 and 18, have four distinguishing characteristics: (i) in empty-state images, the ad-dimers lie in the troughs between dimer rows; (ii) they appear much brighter in empty state images than in filled state images; (iii) in filled-state images, they show a ringlike feature with a faint intensity in the middle; and (iv) in empty state images, they appear elongated along the dimer rows. All four of these characteristics are seen in our theoretical images. Hence these results are consistent with the fact that the most frequently occurring dimer reported by WHZRP in Si/Ge(001) is indeed the *D* dimer.

On the other hand, Table I indicates that the *D* configuration is theoretically always found to be energetically the *least* favored ad-dimer. One possible resolution of this apparent discrepancy is that the *D* dimer, although not the most stable energetically, is favored to form kinetically. This would be similar to the case of Si/Si(001), where the *C* dimer, though higher in energy than the *A* and *B* dimers, is argued to be favored kinetically.<sup>7,10</sup> Such a resolution would be consistent with the energetics of Table I, since then the *D* dimer need not be the dimer of lowest energy. This would also be in accordance with the agreement between our theoretical STM images of the *D* dimer and the experimental ones of WHZRP. However, we should note that experimental STM images probe only the local electronic density of states, and care must be exercised when inferring the corresponding atomic geometry.<sup>19</sup> Consider, as an example, the conclusion drawn earlier from the experimental STM images<sup>12</sup> that all four substrate atoms nearest to the *D* dimer recede into the Ge(001) surface. On the contrary, our *ab initio* computation for the *D* dimer shows that two of these four Ge atoms rise *upwards* by about 0.5 Å compared to their positions in clean Ge(001).

Keeping such considerations in mind, we now examine an alternate possibility: that the isolated ad-dimers identified by WHZRP (Ref. 12) as *D* dimers are actually dimers in the *C* configuration. Figures 2(f) and 2(b) show our computed filled and empty state STM images for the *C* dimer which, consistent with the underlying relaxed atomic geometry [cf. Fig. 2(d)], show no buckling. These images of the *C* dimer clearly exhibit the same first three characteristic features of the experimental dimer images. Only the fourth characteristic (i.e., elongation of the ad-dimer image along the dimer rows in empty state images) distinguishes the two types of dimer images, since the *C* dimer empty state image shows that it extends perpendicular to the substrate dimer rows. This distinction is clear in our theoretical STM images, which are generated assuming a perfectly sharp tip. However as Fig. 2(b) suggests, a slight distortion in this empty state image of the *C* dimer can make it appear extended along the direction parallel to the dimer rows. In practice such distor-

tions could arise from real finite-size effects of the STM tip. Thus the *C* and *D* dimer images could well be confused, since they share three common characteristics and differ only in the fourth. It is therefore possible that the dimer in the trough observed by WHZRP is the *C* dimer. If so, this result would be consistent not only with our calculated results for the Ge(001) substrate (cf. Table I), but also with the theoretical and experimental trend observed for Si and Ge grown on Si(001).<sup>5-7,9-11</sup>

To distinguish further between these two possibilities we generated theoretical STM images of these two dimers at varying biases. We found the main features of the *C* and *D* dimer empty state images to be nearly independent of bias in the range of +0.5 to +2.0 V. Furthermore, the filled-state images of the *D* dimer do not change much in the bias range from -0.5 to 2.0 V. This is seen in Figs. 2(e) and 2(g), which show nearly identical filled state images generated at biases of -1.6 and -0.6 V. However, the filled state image of the *C* dimer at low bias shows a dramatic change. The *C* dimer, which is very visible at a bias of -1.6 V [cf. Fig. 2(f)], shows a distinct reduction in intensity below a bias of -0.8 V and nearly *disappears* at the low bias of -0.6 V [cf. Fig. 2(h)].

We now propose an experimental test based on this difference. If such low-bias filled state images of the Si/Ge(001) system show that the dimer lying in the trough between the substrate dimer rows almost disappears at low bias, then it is a *C* dimer. If, on the other hand, the image remains principally unchanged in character, then this result indicates that it is a *D* dimer. Thus a low-bias imaging of this system should serve as a test to indicate unambiguously whether it is a *C* or a *D* dimer which has been observed. Such low-bias STM imaging can now be carried out, with a sufficiently sharp tip.<sup>20</sup>

If the proposed test detects a *D* dimer, then its formation would presumably be due to some kinetic mechanism. This would suggest a rather different growth mechanism for the Si/Ge(001) system than that found for Si/Si(001), where isolated *C* dimers have been argued to play a crucial role in the initial stages of growth.<sup>5,6,10</sup> Otherwise, if the test detects a *C* configuration, then the behavior of Si/Ge(001) would be consistent with our results in Table I for Si/Ge(001) and would suggest that Si/Ge(001) and Si (or Ge) on Si(001) have similar growth patterns.

To summarize, we have calculated the energies of Si dimers on Ge(001) and Ge dimers on Si(001), in various configurations. The *D* dimer is found to have the highest energy in both systems. This result is consistent with STM observations in the Ge/Si(001) system and Si/Si(001) system, in both of which no *D* dimers were seen. In the Si/Ge(001) system, STM experiments have identified *D* dimers as the most stable.<sup>12</sup> To account for this apparent discrepancy, we generated theoretical STM images for both the *C* and *D* dimers for Si/Ge(001). Our results suggest that the images of these two dimer types can be difficult to distinguish. Thus the existing experiments may be consistent with either *C* or *D* dimers. We also propose an experimental test (low-bias STM imaging) which, if carried out, should permit the two configurations to be unambiguously distinguished.

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