Dimer Exchange Mechanism for Substitutional As Adsorption on Si(100)

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We present first-principles calculations which support a dimer exchange mechanism for substitutional As adsorption on Si(100) surfaces. In contrast to the prevailing picture, we find that the origin of the substitution of the underlying Si atoms by As is the flexible reconstructions of the Si atoms in the resulting geometries, including the newly discovered π-bonded reconstruction between the top-layer and the second-layer Si atoms. Calculated scanning tunneling microscopy images of the resulting As-Si heterodimer and the As dimer differ prominently from that of the Si dimer.

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Adsorption of As on the Si(100) surface offers interesting phenomena which are fundamental to the understanding of the initial stage of heteroepitaxial growth. The vicinal Si(100) surface with sufficiently large miscut angles exhibits a single-domain 2×1 reconstruction: Si atoms on a terrace form dimers and each terrace is bordered to adjacent ones by bilayer step edges to which the Si dimers are parallel [1-3]. Arsenic atoms on this surface are expected to adsorb on top, breaking the existing Si dimers and forming new As dimers, which leads to a rotation of the dimer orientation on the 2×1 terrace to 1×2. This was indeed observed at low adsorption temperature (less than 400 °C) [4,5]. At higher temperature ($400 \le T \le 600$ °C), however, the single-domain 2×1 orientation was found to remain unrotated even after As adsorption [4,5].

To explain this surprising phenomenon Alerhand *et al.* have performed total energy calculations for the two types of bilayer steps for the As-covered Si(100) [6]. They have found that one type where the As dimers are parallel to the step edges has lower energy than the other where the dimers are perpendicular to the edges. This implies that the dimer-rotated 1×2 structure made by the As adsorption is metastable. A counterargument that substitutional As adsorption occurs on a terrace has come from Tromp, Denier van der Gon, and Reuter based on low-energy electron microscopy and scanning tunneling microscopy (STM) measurements [7]. They consider that the As atoms on top replace the underlying Si atoms, leading to a 2×1 reconstruction of the As-covered surface. In both arguments, the relaxation of the surface stress is the only driving force for the phenomenon: It is considered to be relaxed at the step edges in the former, and on the terrace in the latter. Further, little is known about reaction pathways toward the lower energy states.

In this Letter we present total-energy electronic-structure calculations within the local density approximation (LDA) for the dimer-exchange and the subsequent dimer-diffusion reactions on a terrace of the As-covered Si(100) surface. We find that the substitutional As adsorption occurs by the exchange of the As dimer with the underlying Si atoms and by subsequent diffusion of the two Si atoms: The total energy gained is more than 0.7 eV during this exchange reaction. In contrast to the prevailing picture, the driving force for the exchange is *not relaxation of the surface stress but π bonding of the displaced Si atoms.* We also calculate STM images of the resulting As dimer and the As-Si heterodimer which would be the fingerprints of the exchange mechanism proposed here.

In the calculation the surface is simulated by a repeating slab model in which typically eight atomic layers and an 8.14 Å vacuum region are included, and the periodicity in the lateral directions is set to be 2×2. We use norm-conserving pseudopotentials [8], Ceperley-Alder [9] exchange-correlation energy in the LDA, the plane-wave basis set with the cutoff energy of typically 8 Ry, and the $4k$ points in a wedge in the surface Brillouin zone (BZ) integration. The nonlocal part of the pseudopotential is treated by the Kleinman-Bylander procedure [10] with the real space partitioning [11], if necessary, to avoid the deviations in the logarithmic derivatives [12]. Both the electronic and the geometric degrees of freedom are optimized by the highly efficient conjugate gradient minimization technique [13]. The symmetry-unrestricted geometry optimization has been performed for all atoms except for the ones in the innermost two atomic layers in the slab. In the optimized geometries the remaining forces acting on the atoms are less than 0.01 Ry/Å. Most calculations in this paper have been performed with the above set of calculational parameters. Yet the key results are confirmed by using a more extensive set of parameters such as the twelve-atomic-layer slab, the 10.9 Å vacuum region, the 10 Ry cutoff energy, and the $9k$ points in the wedge in the BZ. We have found that the values in the total-energy difference presented here are accurate to 0.1 eV.

We start with the energetics of an exchange process for substitutional As adsorption. The initial geometry is the As dimer on the Si(100) surface shown in Fig. 1(a). In the optimized geometry, the As dimer is symmetric in accord with the previous experiment and the calculation [14]. The surface energy bands are metallic due to the presence of dangling bonds from the second-layer Si atoms. We have examined the possibility that these two As atoms replace underlying Si atoms and lead to the

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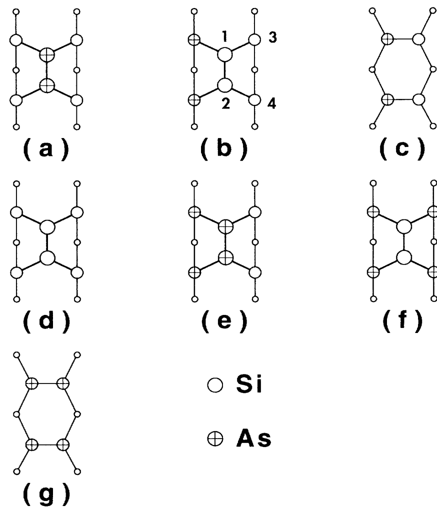

FIG. 1. Schematic top views of several geometries in the exchange mechanism for substitutional As adsorption on Si(100). The open and crossed circles represent Si and As atoms, respectively. (a) As dimer on Si(100), (b) Si dimer on underlying As (the numbered Si atoms are referred to in text), (c) As-Si heterodimer on Si(100), (d) Si dimer on Si(100), (e) As dimer on underlying As and Si atoms, (f) Si dimer on underlying four As atoms, and (g) As dimers on Si(100). Each figure depicts a half of the 2×2 periodic unit cell which is used in the present calculations.

geometry with a Si dimer above the As atoms [Fig. 1(b)]. We have indeed found that the total energy of the geometry shown in Fig. 1(b) is lower than that of Fig. 1(a) by 0.7 eV per dimer. This energy gain from the exchange of the As dimer and the Si dimer is not a consequence of the relaxation of the surface stress. The π bonding between the top-layer and the second-layer Si atoms, presented below, is the microscopic reason for this large energy gain. Figure 2 is the optimized geometry after the exchange of the dimers. The Si dimer is found to be buckled and remarkably flattened, in sharp contrast with the As dimer and with the asymmetric Si dimer on clean Si(100). The distance between the top-layer and second-layer Si atoms [2.27 Å for Si(1)-Si(3) and 2.22 Å for Si(2)-Si(4), respectively] is thus shorter than the distance between the top-layer Si atoms [2.34 Å for Si(1)-Si(2)] which is close to the bulk bond length of 2.35 Å. This results in a new π-bonded structure between the top-layer and the second-layer Si atoms. Figure 3 is a contour plot of the charge density of an occupied state near the Fermi level, which clearly shows the π-bonded structure. Of note is that this occupied state consists of an antibonding combination of the top-layer Si orbitals. We have also found partial electron transfer from the top-layer to the second-layer Si atoms. Hence, the surface energy bands change from metallic [Fig. 1(a)] to semiconducting [Fig. 1(b)] upon exchange between the As and Si dimers. This charge transfer is due to the flattening of the top-layer atoms and their larger bond angles

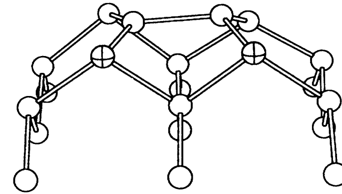

FIG. 2. Stable geometry after substitutional As adsorption on Si(100), corresponding to the schematic illustration of Fig. 1(b). The open and crossed spheres denote the Si and As atoms, respectively.

(ranging from 105° to 139°) compared with the angles for the second-layer Si atoms (ranging from 75° to 118°).

The next stage in the exchange mechanism is the dissociation of the top-layer Si dimer [Fig. 1(b)] from the As site and its diffusion to another site on the terrace or the step edges. Only by this dissociation and the subsequent diffusion does the As site recover its reactivity. A possible product configuration is an As-Si heterodimer [Fig. 1(c)] plus a Si dimer on the terrace [Fig. 1(d)]. We have computed the total energies of the optimized geometries including the asymmetric Si dimer and the As-Si heterodimer and found that the reaction of the dissociation and the diffusion is exothermic: The calculated heat of formation for the reaction from Figs. 1(b) to 1(c) plus 1(d) is 0.4 eV. The reason for the exothermicity is presumably the relaxation of the stress energy in the geometry shown in Fig. 2.

Additional As atoms approach the surface and may form an As dimer on the As-Si heterodimer [Fig. 1(e)]. In the optimized geometry, the As dimer is almost symmetric, but the second-layer Si and As are dislodged considerably from the ideal sites. We have compared the total energy of the geometry of Fig. 1(e) with that of the

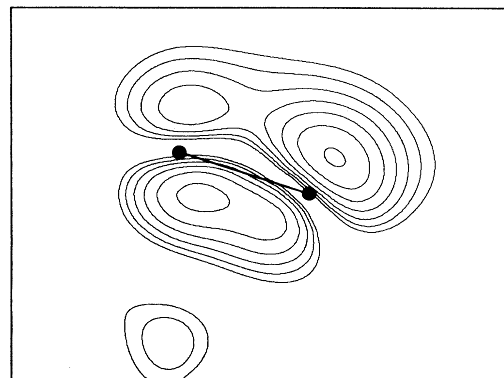

FIG. 3. Charge density of an occupied state near the surface BZ boundary [$\mathbf{k}=\pi/2a_0(\frac{3}{8},\frac{3}{8},0)$]. A π bond between Si(2) and Si(4) denoted by the solid circles is shown on the vertical plane cutting the two Si atoms. The value of the highest contour is 3.5×10^{-3} $e/(\mathrm{a.u.})^3$, and the subsequent contours differ by a factor of 1.65.

geometry of Fig. 1(f), which is obtained by displacing the second-layer Si atoms to form a top-layer Si dimer. The total energy of the converted geometry (f) is lower than that of (e) by 0.8 eV. In the optimized product geometry (Fig. 4), the top-layer Si dimer has similar local geometry to that of the buckled Si dimer on clean Si(100). An unusual feature is the reduction of the bond lengths between the As atom and the lower Si atom of the top-layer buckled dimer by 0.13 Å compared with the usual As-Si bond length (2.44 Å). Consequently, the bond lengths between the lower Si of the top-layer dimer and its three neighbors are almost identical to each other, causing partial electron transfer to the upper Si of the buckled dimer. Hence, the surface energy bands change from metallic to semiconducting upon dimer exchange. The subsequent dissociation and diffusion of the Si dimer is also favorable. The calculated heat of formation for the reaction from the geometry of a Si dimer on four As atoms [Fig. 1(f)] to the geometry of two As dimers [Fig. 1(g)] plus a Si dimer on the terrace [Fig. 1(d)] is 0.6 eV.

The present total-energy calculations provide a natural explanation for the mysterious phenomenon that the single-domain 2×1 orientation of Si(100) remains unrotated even after As adsorption: The adsorbed As atoms form a dimer on top of Si(100) and substitute for the underlying Si atoms; the Si atoms are, in turn, displaced to the top layer and then diffuse to another site on the terrace or the step edges, leaving the As-Si heterodimer; further As adsorption on the heterodimer site again leads to the displacement and diffusion of the underlying Si atoms with the As dimers forming not the 1×2 but the 2×1 structure. All these reactions are found to be exothermic. Although the activation energies for the above reactions are still unknown, the driving force for the dimer exchange is clear, i.e., the π-bonded reconstruction which reduces the number of dangling bonds in the resulting geometry (Fig. 2). A process of As diffusion may compete with the above dimer exchange process: When the As diffusion is so fast that another As dimer attaches to the first As dimer, the driving force for the dimer exchange would be diminished. We speculate that the activation energy for the dimer exchange E_{ex} is less than or comparable to the energy E_d for As diffusion. In that case, diffusion length during the exchange reaction is an order of bond length [15] which is much smaller than the terrace width in the usual experimental situation, and the dimer exchange process is dominant. At higher temperatures ($T > 600\,^\circ$C), the As diffusion becomes important and the dimer exchange and consequently the formation of the 2×1 structure on the 2×1 terrace are suppressed. This is indeed what Bringans, Biegelsen, and Swartz have observed [5].

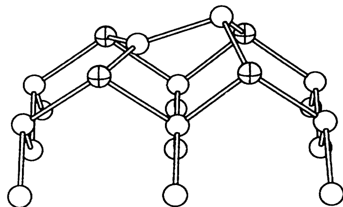

FIG. 4. Stable geometry corresponding to the schematic illustration of Fig. 1(f).

We now present calculated STM images for the As-Si heterodimer and the As dimer along with the Si dimer. The image, tunneling current density $j(\mathbf{r},V)$, is calculated using the simple expression [16] $j(\mathbf{r},V)=\int_{E_F+V}^{E_F} \times \sum_{n\mathbf{k}}|\psi_{n\mathbf{k}}(\mathbf{r})|^2\delta(\varepsilon_{n\mathbf{k}}-\varepsilon)d\varepsilon$ [17]. We have found prominent differences between the STM images of the As-Si heterodimer, the As dimer, and the Si dimer (Fig. 5). Hence the observation of the different images as shown in Fig. 5 would be a direct experimental evidence supporting the exchange mechanism. The assignment in Ref. [7] of the dark patch observed with the bias voltage of -1.5 eV (the occupied state) as the As dimer is consistent with the present calculation. Further, when the bias voltage is changed, the images exhibit a rich variation. For instance, the Si site of the As-Si heterodimer is bright when the bias voltage is $V=-1$ eV, whereas the As site becomes bright when $V=-2$ eV. This is a consequence of the fact that the lower occupied states consist of more As-orbital components. Moreover, we find that the image

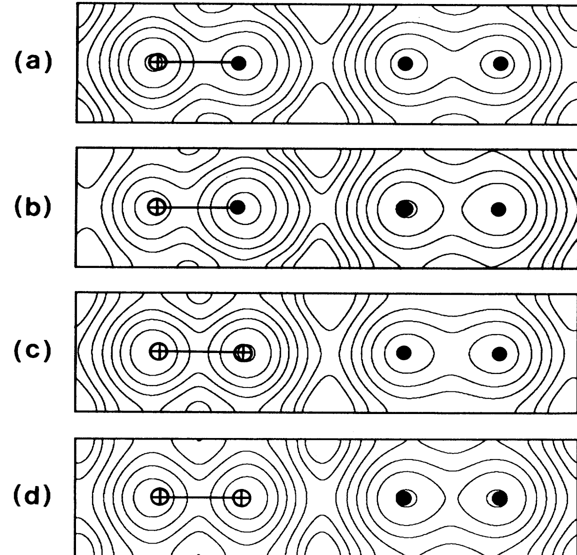

FIG. 5. Calculated tunneling current density for the As-Si heterodimer with bias voltage (a) $V=-2$ eV, (b) $V=-1$ eV, and the As dimer with (c) $V=-2$ eV, and (d) $V=-1$ eV. In the right half of each figure, the current density for the averaged Si asymmetric dimer is shown. The crossed circles denote the position of As atoms. The values of the highest contour are 3.10×10^{-4} $e/(\mathrm{a.u.})^3$ in (a), 1.85×10^{-4} $e/(\mathrm{a.u.})^3$ in (b), 3.88×10^{-4} $e/(\mathrm{a.u.})^3$ in (c), and 1.70×10^{-4} $e/(\mathrm{a.u.})^3$ in (d), respectively. The subsequent contours differ by a factor of 1.5.

of the symmetric Si dimer is considerably darker than the averaged image of the two equivalent asymmetric Si dimers buckled oppositely. Thus comparing the brightness of the Si dimer image with those of the As-Si and As dimers could be an evidence of the existence of the asymmetric Si dimer which has been observed by STM only at low temperature [18].

Finally we would like to comment on the surfactant epitaxy in which the As or Sb surfactant atoms segregate from the interface to the surface in the heteroepitaxial, e.g., Si/Ge epitaxial, growth [19]. This segregation seems to contradict the substitutional As adsorption discussed in this paper. The stable adsorption site, however, is quite different for the two cases. In the case of substitutional As adsorption, the As dimer sits on the (meta)stable site on the Si dimer and eventually substitutes for the underlying Si atoms which, in turn, form the π-bonded structure. On the other hand, in the case of the surfactant epitaxy, the Si dimer is unlikely to be adsorbed above the As or Sb dimer, as is assumed in the two-dimer correlated-exchange mechanism proposed by Tromp and Reuter [20]. Instead, our calculation shows that the most stable adsorption site for an additional Si atom on As-covered Si(100) is the site between the As-dimer rows. It is thus plausible that another Si atom diffuses to the first Si atom and forms a dimer at the site between the As-dimer rows. For this adsorption site, the displacement of the underlying As atoms by the Si dimer may be favorable.

In summary, we have presented the LDA calculations which naturally lead to the dimer exchange mechanism for substitutional As adsorption on the Si(100) surfaces. The substitution of the underlying Si atoms by the As atoms and the subsequent diffusion of the displaced Si atoms are found to be energetically favorable. The microscopic origin of this exothermicity is the flexible reconstruction of the Si atoms, including the π-bonded reconstruction of the top-layer and the second-layer Si atoms. This finding is in sharp contrast with the stress-relaxation mechanism suggested previously. The electronic energy gain during the heteroepitaxial growth demonstrated in the present paper depends on the initial adsorption site of the additional atom on the growing surface. This implies the importance of the initial stage of heteroepitaxy to the resulting surface morphology.

[1] D. J. Chadi, Phys. Rev. Lett. **59**, 1691 (1987).

[2] O. L. Alerhand, D. Vanderbilt, R. D. Meade, and J. D. Joannopoulos, Phys. Rev. Lett. **61**, 1973 (1988); O. L. Alerhand *et al.*, Phys. Rev. Lett. **64**, 2406 (1990).

[3] T.-W. Poon, S. Yip, P. S. Ho, and F. F. Abraham, Phys. Rev. Lett. **65**, 2161 (1990).

[4] R. S. Becker, T. Klitsner, and J. S. Vickers, J. Microsc. (Oxford) **152**, 157 (1988).

[5] R. D. Bringans, D. K. Biegelsen, and L.-E. Swartz, Phys. Rev. B **44**, 3054 (1991), and references therein.

[6] O. L. Alerhand, J. Wang, J. D. Joannopoulos, E. Kaxiras, and R. S. Becker, Phys. Rev. B **44**, 6534 (1991).

[7] R. M. Tromp, A. W. Denier van der Gon, and M. C. Reuter, Phys. Rev. Lett. **68**, 2313 (1992).

[8] D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).

[9] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[10] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

[11] M. Saito, O. Sugino, and A. Oshiyama, Phys. Rev. B **46**, 2606 (1992).

[12] X. Gonze, P. Käckell, and M. Scheffler, Phys. Rev. B **41**, 12264 (1990).

[13] O. Sugino and A. Oshiyama, Phys. Rev. Lett. **68**, 1858 (1992); Phys. Rev. B **46**, 12335 (1992).

[14] R. I. G. Uhrberg, R. D. Bringans, R. Z. Bachrach, and J. E. Northrup, Phys. Rev. Lett. **56**, 520 (1986).

[15] By using a diffusion coefficient $D=l^2\nu_d\exp(-E_d/k_BT)$ and the time $t_{ex}=[\nu_{ex}\exp(-E_{ex}/k_BT)]^{-1}$ during the exchange reaction, where ν_d, ν_{ex} are appropriate frequencies and l is the jump length for the diffusion, and by assuming $\nu_d\sim\nu_{ex}$, $E_d\sim E_{ex}$, and $l\sim$bond length, the diffusion length $\sqrt{Dt_{ex}}$ is estimated to be an order of the bond length.

[16] J. Tersoff and D. R. Hamann, Phys. Rev. Lett. **50**, 1998 (1983); Phys. Rev. B **31**, 805 (1985); A. Selloni, P. Carnevali, E. Tossati, and C. D. Chen, Phys. Rev. B **31**, 2602 (1985); Y. Miyamoto, Phys. Rev. B **46**, 1247 (1992).

[17] The tunneling current density $j(\mathbf{r},V)$ depends on the distance from the surface. We have found that the current density picture converges when the distance is more than 2.7 Å.

[18] R. A. Wolkow, Phys. Rev. Lett. **68**, 2636 (1992).

[19] M. Copel, M. C. Reuter, E. Kaxiras, and R. M. Tromp, Phys. Rev. Lett. **63**, 632 (1989).

[20] R. M. Tromp and M. C. Reuter, Phys. Rev. Lett. **68**, 954 (1992).