PHYSICAL REVIEW B VOLUME 50, NUMBER 4 15 JULY 1994-II

Large-scale *ab initio* study of the binding and diffusion of a Ge adatom on the Si(100) surface

V. Milman, D. E. Jesson, and S. J. Pennycook
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

M. C. Payne, M. H. Lee, and I. Stich
Department of Physics, Cambridge University, Cambridge CB3 0HE, United Kingdom

(Received 15 April 1994)

We identify the binding sites for adsorption of a single Ge atom on the Si(100) surface using *ab initio* total-energy calculations. The theoretical diffusion barriers are in excellent agreement with experimental estimates. Using a large supercell we resolve the controversy regarding the binding geometry and migration path for the adatom, and investigate its influence on the buckling of Si dimers. We find that the adatom induces a buckling defect that is frequently observed using scanning tunneling microscopy, indicating that the study of a single adatom may be experimentally accessible.

The study of fundamental atomistic processes that govern the surface kinetics of the epitaxial growth of Si-Ge materials is of considerable scientific and technological interest. In particular, a number of important problems related, for example, to interface sharpness[1] or ordering during alloy growth[2] have yet to be understood on the atomistic level. One of the most fundamental questions underlying several of these issues[3,4] is the identification of binding sites for Ge adatoms on the Si(100) surface, and the determination of the activation energy for surface diffusion. Recent scanning tunneling microscope (STM) observations suggest that the behavior of a Ge adatom is essentially similar to that of a Si adatom. Ge islands have the same anisotropy of 1000:1 at typical growth temperatures as Si islands, and the diffusion barrier in the fast direction is estimated to be 0.62 eV (Ref. 3) compared to 0.67 eV reported for Si surface diffusion.[5]

Measurements such as these provide an excellent starting point for theoretical investigation, although it is certainly desirable to study Ge adsorption from first principles rather than using semiempirical schemes. Previous studies of the Si adatom on the Si(100) surface revealed that the *ab initio* calculated bonding and diffusion characteristics[6,7] differ significantly from the predictions made using empirical interatomic potentials.[8-11] For example, the diffusion barrier in the fast direction (along the dimer rows) is found from *ab initio* calculations to be 0.6 eV.[6,7] The best empirical potentials available for the covalent semiconductors are of the Stillinger-Weber (SW) (Ref. 12) or Tersoff (T) (Ref. 13) type, which have produced a variety of results for the Si adatom diffusion barrier including 0.67 eV (SW),[8] 0.75 eV (T),[9] 0.24 eV (SW),[10] and 1.2 eV (SW).[11] Furthermore, these studies predict different binding sites for the Si adatom, different migration paths (on top of the dimers, in the interdimer trough, or a zigzag path), and different degrees of the surface diffusion anisotropy.

The empirical description of covalent bonding on the Si surface has a number of fundamental difficulties. None of the potentials mentioned above can reproduce even the correct sign of the energy difference between the asymmetric (buckled) dimers and symmetric reconstructions of the Si(100) surface.[14,3,4] *Ab initio* calculations show that the alternating buckling in $p(2\times2)$ domains reduces the energy of the surface by approximately 0.10 eV per dimer,[15,16] and the $c(4\times2)$ structure is found to be a true ground state with the energy gain of 0.14 eV/dimer compared to the symmetric structure.[17] One can expect that the Si-Ge interaction is described by empirical potentials even less accurately. These potentials predict the barrier for fast migration of Ge on Si to be 0.73 eV (T) (Ref. 18) or 0.64 eV (SW).[19] The barrier for diffusion across the dimer rows is calculated to be 1.17 and 0.80 eV, respectively. These barriers correspond to the anisotropy of the surface diffusion at 500 K of either 20 000:1 (Ref. 18) or 50:1 (Ref. 19) if we assume that the preexponential coefficient is the same in both directions. The experimentally observed anisotropy is of the order of 1000:1 (Ref. 3) at this temperature, and is not reproduced correctly by either of the empirical potentials.

In this Brief Report we present a large-scale *ab initio* study of Ge binding and diffusion on the Si(100) surface. For the electronic structure calculation we applied the pseudopotential total-energy method,[20] employing density-functional theory in the local-density approximation (LDA), Perdew and Zunger's parametrization[21] of the exchange-correlation energy, norm-conserving pseudopotentials of the Kerker type[22] in the Kleinman-Bylander form,[23] supercells, and a plane-wave basis set. We use s-only nonlocal pseudopotentials for both elements and treat them according to a real-space method.[24] Convergence properties of the Ge potential were improved by using the three-term optimization scheme.[25] A supercell with (100) slab geometry contained 12 layers of Si with the inversion symmetry imposed and eight layers of vacuum. This supercell with the $p(4\times4)$ surface cell contained 192 Si atoms and two Ge adatoms (one on each side of the slab). Only the atoms in the two innermost layers were kept fixed, the coordinates of the rest of the atoms were optimized during the structural relaxation. A single k point (Γ) was used for the Brillouin-zone sampling, and the energy cutoff for the plane wave expansion of the wave functions was 10 Ry. Calculations were performed using the Intel parallel computers iPSC/860 and XP/S 5 Paragon at the ORNL Center for Computa-

0163-1829/94/50(4)/2663(4)/$06.00

tional Science. Technical details of the parallel implementation of the CETEP code (Cambridge-Edinburgh Total-Energy Package) are given in Ref. 26.

The accuracy of the computational scheme was tested by performing calculations for the clean Si(100) surface. We found that the symmetric dimer configuration is lower in energy compared to the unreconstructed surface by 2.18 eV/dimer, and asymmetric dimer buckling further reduces the energy by 0.09 eV/dimer, in good agreement with the previous results.[14–17] The symmetric reconstruction was used as the starting geometry for the Ge adsorption since, at the typical deposition temperatures, asymmetric buckling is effectively destroyed by thermal fluctuations.[3,4,14] The equilibrium dimer bond length for the symmetric reconstruction is 2.30 Å, which is close to that of 2.31 Å from the work of Brocks, Kelly, and Car[6] and to that of 2.23 Å from the work of Roberts and Needs.[15]

The energy surface was mapped out by calculating the total energy for positions (x,y) of the adatom in the irreducible quarter of the $p(2\times1)$ surface cell shown in Fig. 1. These positions form an equidistant grid with a spacing between the grid points of 0.96 Å in either direction. We start by placing the adatom 2.5 Å above the surface, and proceed with the simultaneous total-energy minimization in the space of atomic coordinates (including the adatom's z coordinate) and wave-function expansion coefficients. The local minima were found by allowing the (x,y) coordinates of the adatom to relax starting from the nearby grid point. The energy surface was further refined by mapping out the regions around the local minima on a finer grid. We also used the force on the adatom which represents the gradient of the energy surface to obtain the final energy surface, Fig. 2.[27]

We found only two binding positions for the adatom. The global minimum is located at point M on top of the second-layer atom, while the pedestal site H is only 0.06 eV higher in energy. However, we do not expect a high occupancy for the pedestal site due to the small volume of the configuration space associated with it. Contrary to the case of Si adsorption, the point C that was found to be a local minimum[6] is now only a saddle point. No binding site was found in the channel between the dimer rows, similar to *ab initio* results for the Si adsorption[6] and contrary to the predictions of the empirical potential simulations.[18,19] The long-bridge site B corresponds to the absolute maximum and is 1.90 eV higher in energy than the binding site M. The cave site A represents another maximum with a height of 1.21 eV. These results contrast sharply with empirical simulations where the long-bridge site is the absolute minimum[18,19,28] and the fast diffusion path is in the middle of the interdimer channel B-A-B. The same discrepancy exists between *ab initio*[6] and empirical simulation results[8–11] for the Si adatom.

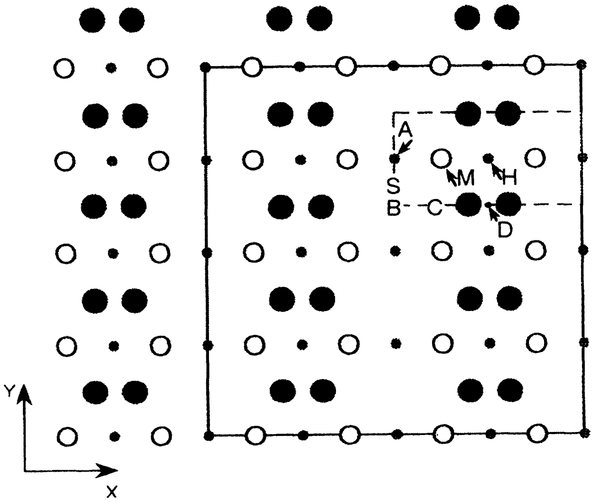


FIG. 1. Top view of the reconstructed Si(100) surface. The actual $p(4\times4)$ surface unit cell is indicated by the solid line, and the $p(2\times1)$ cell by the dashed line. The red circles represent the top-layer Si atoms, the yellow circles represent the second-layer atoms, the blue circles represent the third-layer atoms. Letters correspond to the critical points on the energy surface (see text).

We find that the diffusion path in the direction along the dimer rows is a zigzag between point M and the dimer bridge site D which is the saddle point of the trajectory, and no visit to the H point is necessary, a fundamental difference from the case of the Si adatom.[6] The barrier height is 0.62 eV, in excellent agreement with the experimental estimate.[3] There are two consecutive inequivalent saddle points on the trajectory for the slow diffusion across the dimer rows, as can be seen from Fig. 2. The experimentally observed barrier is determined by the higher of the two which corresponds to the hopping across the channel at point S and has a height of 0.95 eV. These results lead to a diffusional anisotropy of 2000:1 at 500 K, in excellent agreement with STM observations.[3] Thus we conclude that the experimental data are consistent with Ge adatom diffusion that takes place on top of the dimers and not in the interdimer channel.

We now consider the bonding geometry, which seems to be the most controversial issue in the comparison of *ab initio* and empirical results. Our data indicate that the bond length between the Ge adatom and the surface Si atoms is normally close to the Si dimer bond length. In the equilibrium adsorption geometry, the Ge adatom at site M is bonded to two dimers from the same row, and all bond lengths are about 2.39 Å. The distance from the adatom to the second-layer Si atom is only 2.46 Å, but there is no directional bond to this atom according to the charge-density distribution [Fig. 3(b)]. This explains why empirical potentials do not recognize site M as the absolute minimum. Both SW and T potentials give strong repulsive three-body interactions for this configuration, while in fact there is no third bond involved. Adsorption at the pedestal site H is characterized by the formation of four long bonds of 2.48 Å and by the dimer bond stretching to 2.52 Å. The latter effect is more pronounced than for the Si adsorption[6] due to the larger size of the adatom.

We find that the adatom causes maximum strain on the dimer bond when it is located at the saddle point for the hopping across the trough S or in its vicinity. In this configuration the distance between the dimer atoms becomes 3.3 Å, which is already closer to the bulk distance of 3.84 Å than to the dimer bond at the clean surface,

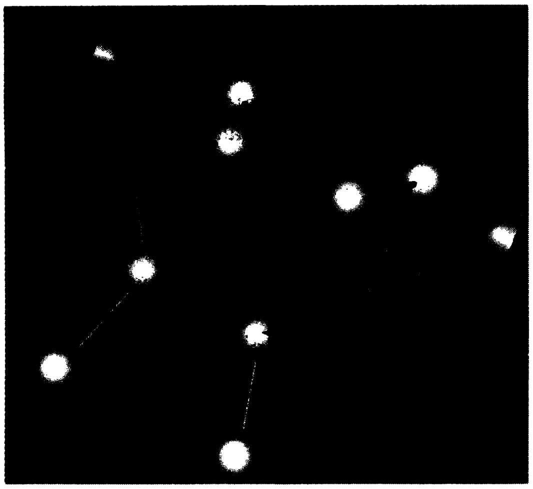
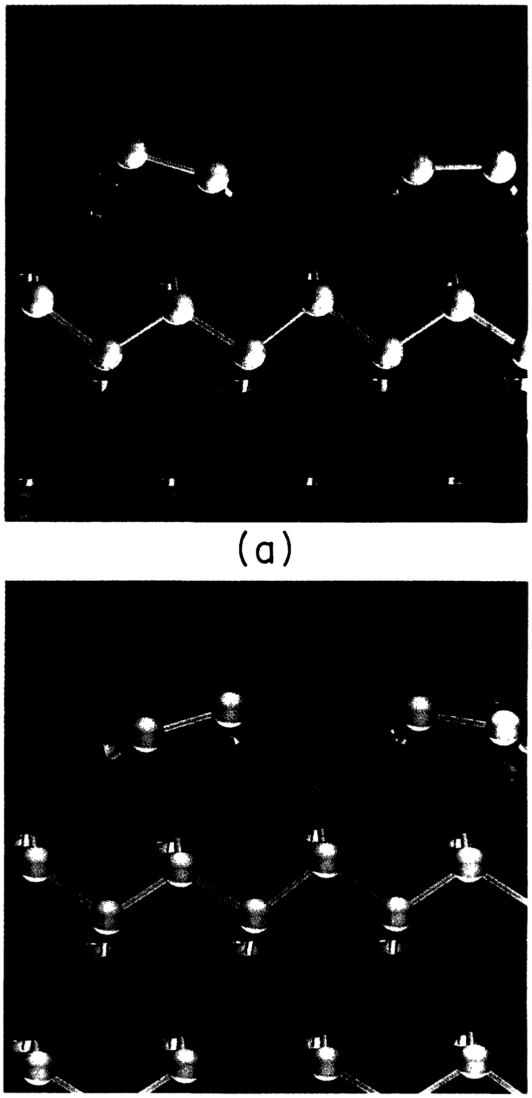


FIG. 2. The energy surface for the Ge adatom (magenta). The first- and second-layer Si atoms from the $p(2\times1)$ cell are shown (yellow spheres). The central minimum corresponds to site *H*, two equivalent side minima correspond to binding site *M*.

2.30 Å. According to the charge-density distribution we consider this configuration as a broken dimer. No such effect caused by the Si adatom was reported by Brocks, Kelly, and Car.[6] The empirical potential simulations predict the adatom-induced dimer opening for either adatom located along the *H-D* line (except at the *H* site itself).[9,10,18] We have seen no signs of the dimer opening for this configuration.

Finally we consider the role of the dimer buckling on the energetics of adsorption and surface diffusion. In *ab initio* investigations this problem was dismissed mainly because of the small energy effect involved, but also because of the prohibitively large size of the corresponding supercell. Empirical simulations, on the other hand, cannot approach this problem as they predict symmetric reconstruction as the ground state of the Si(100) surface. Our surface cell is sufficiently large to shed some light on this issue.

As discussed earlier, symmetric dimers are the starting point for the energy surface calculations. However, during atomic relaxation we always observe spontaneous dimer buckling initiated by numerical noise in the calculated atomic forces. The character of this buckling depends on the adatom position (Fig. 3). With the adatom at point *H* the second dimer row in the unit cell is only slightly perturbed compared to the clean asymmetric (2×1) reconstructed surface. The dimer bond length in that row is 2.28 Å and the buckling amplitude is 0.70 Å. These values may be compared with the recent *ab initio* results of 2.29 and 0.69 Å obtained by Northrup[17] for the clean Si(100) surface. Buckling is entirely absent within the four dimers of the row that contains the adatom [Fig. 3(a)], although we have no doubt that with the longer cell one would observe a buckled dimer row with a localized symmetric part around the adatom. The picture is qualitatively different in the vicinity of the Ge adatom at the binding site *M*, Fig. 3(b). In this case both rows are affected. The dimers bonded to the adatom are slightly tilted [as is the case for the Si adatom[6]] by 0.16 Å. The buckling amplitude grows to 0.43 Å for the next dimers in the same row, so we can be certain that the influence of the single adatom on buckling is localized within approximately four dimers. An additional effect can be seen as a result of the relative proximity of the Ge adatom to the next dimer row. Strong in-phase buckling (0.62 Å) is induced in the two dimers nearest to the adatom. Obviously, there is no direct bonding between these dimers and the Ge atom, and the driving force for this configuration should come from the second-layer atom displacements. In this case elastic strain caused by the presence of the adatom prevails over the energy gain related to the ferroelectric ordering of asymmetric dimers. The resulting configuration of two adjacent dimers buckled in the same direction has indeed been observed on Si(100) at low temperatures.[14] Since it would be expected that a Si adatom at site *M* should produce qualitatively the same structure as a Ge adatom, we suggest that the buckle-inducing defects observed by Wolkow[14] might correspond to single Si



(a)

(b)

FIG. 3. The equilibrium structure and the isosurface of the electron density distribution for the adatom at sites *H* (a) and *M* (b). The surface cell is oriented as in Fig. 1.

adatoms. Their imaging gives the only experimental information available about the binding site of the adatom.

In conclusion, a large-scale *ab initio* study of Ge bonding and adsorption on the Si(100) surface has been performed. We have identified the binding site and the probable diffusion paths in the directions along and across the dimer rows. The activation barriers for diffusion in fast and slow directions are 0.62 and 0.95 eV, respectively, and are in excellent agreement with the experimental STM results. Because of the large supercell employed, we identify the localized buckling defects observed in STM as being due to the adatom bonded at the equilibrium site, implying that the study of single adatoms is experimentally accessible.

We are grateful to T. Kaplan and M. Mostoller for useful discussions about empirical methods, and to A. Cline for providing a "Faultpack" package. This research was sponsored by the Division of Materials Sciences, U.S. Department of Energy, under Contract No. DE-AC05-84OR21400 and Martin Marietta Energy Systems, Inc., and in part by the Oak Ridge National Laboratory. This research is part of the Grand Challenge project on first principles simulation of materials properties, funded under the High-Performance Computing and Communications Initiative.

---

[1] D. E. Jesson, S. J. Pennycook, and J.-M. Baribeau, Phys. Rev. Lett. **66**, 750 (1991).

[2] D. E. Jesson, S. J. Pennycook, J.-M. Baribeau, and D. C. Houghton, Phys. Rev. Lett. **68**, 2062 (1992).

[3] M. G. Lagally, Jpn. J. Appl. Phys. **32**, 1493 (1993); Y.-W. Mo and M. G. Lagally, Surf. Sci. **248**, 313 (1991); M. G. Lagally (private communication).

[4] J. Knall and J. B. Pethica, Surf. Sci. **265**, 156 (1992); F. Iwawaki, M. Tomitori, and O. Nishikawa, Ultramicroscopy **42-44**, 902 (1992).

[5] Y. W. Mo, J. Kleiner, M. B. Webb, and M. G. Lagally, Phys. Rev. Lett. **66**, 1998 (1991).

[6] G. Brocks, P. J. Kelly, and R. Car, Phys. Rev. Lett. **66**, 1729 (1991).

[7] T. Miyazaki, H. Hiramoto, and M. Okazaki, Jpn. J. Appl. Phys. **29**, L1165 (1990). These results correspond to 50% coverage rather than to the isolated adatom case.

[8] C. Roland and G. H. Gilmer, Phys. Rev. B **46**, 13 428 (1992).

[9] D. Srivastava and B. J. Garrison, J. Chem. Phys. **95**, 6885 (1991).

[10] Y.-T. Lu, Z. Y. Zhang, and H. Metiu, Surf. Sci. **257**, 199 (1991).

[11] Z.-H. Huang and R. E. Allen, J. Vac. Sci. Technol. A **9**, 876 (1991).

[12] F. Stillinger and T. A. Weber, Phys. Rev. B **36**, 1208 (1987).

[13] J. Tersoff, Phys. Rev. Lett. **56**, 632 (1986).

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

[15] N. Roberts and R. J. Needs, Surf. Sci. **236**, 112 (1991).

[16] J. Dabrowski and M. Scheffler, Appl. Surf. Sci. **56-58**, 15 (1992).

[17] J. E. Northrup, Phys. Rev. B **47**, 10 032 (1993).

[18] D. Srivastava and B. J. Garrison, Phys. Rev. B **46**, 1472 (1992).

[19] C. Roland and G. H. Gilmer, Phys. Rev. B **47**, 16 286 (1993).

[20] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, Rev. Mod. Phys. **64**, 1045 (1992).

[21] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[22] G. P. Kerker, J. Phys. C **13**, L189 (1980).

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

[24] R. D. King-Smith, M. C. Payne, and J. S. Lin, Phys. Rev. B **44**, 13 063 (1991).

[25] J. S. Lin, A. Qteish, M. C. Payne, and V. Heine, Phys. Rev. B **47**, 4174 (1993).

[26] L. J. Clarke, I. Stich, and M. C. Payne, Comp. Phys. Commun. **72**, 14 (1992).

[27] We used the "Faultpack" package by A. Cline and R. Renka to perform triangulation on an irregular grid using the values of the gradient.

[28] We also found two possible *B*-site configurations with the adatom 0.5 Å higher than the dimers, B^*, or 0.9 Å below the dimers level B_0. The B_0 configuration is more stable by 0.18 eV. A similar double-well energy profile was reported in the SW simulations of the Si adsorption at the *B* site (Refs. 8 and 10).

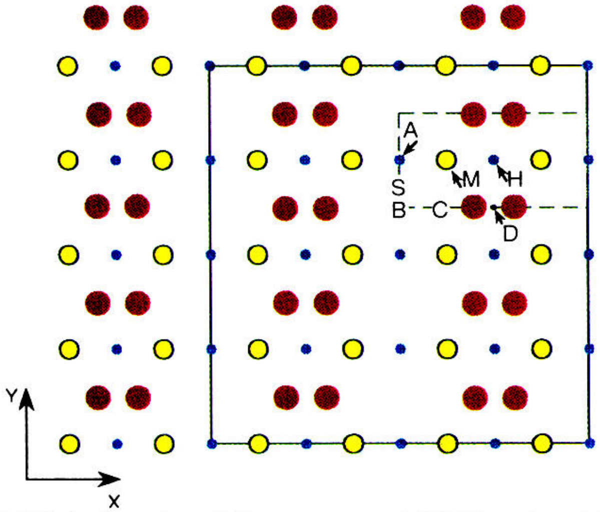


FIG. 1. Top view of the reconstructed Si(100) surface. The actual $p(4\times4)$ surface unit cell is indicated by the solid line, and the $p(2\times1)$ cell by the dashed line. The red circles represent the top-layer Si atoms, the yellow circles represent the second-layer atoms, the blue circles represent the third-layer atoms. Letters correspond to the critical points on the energy surface (see text).

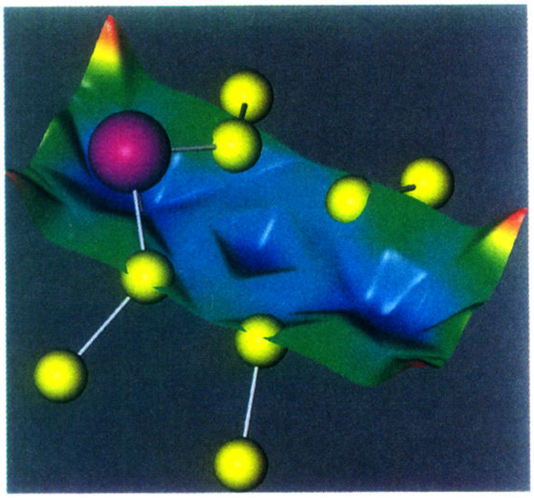


FIG. 2. The energy surface for the Ge adatom (magenta). The first- and second-layer Si atoms from the $p(2\times1)$ cell are shown (yellow spheres). The central minimum corresponds to site *H*, two equivalent side minima correspond to binding site *M*.

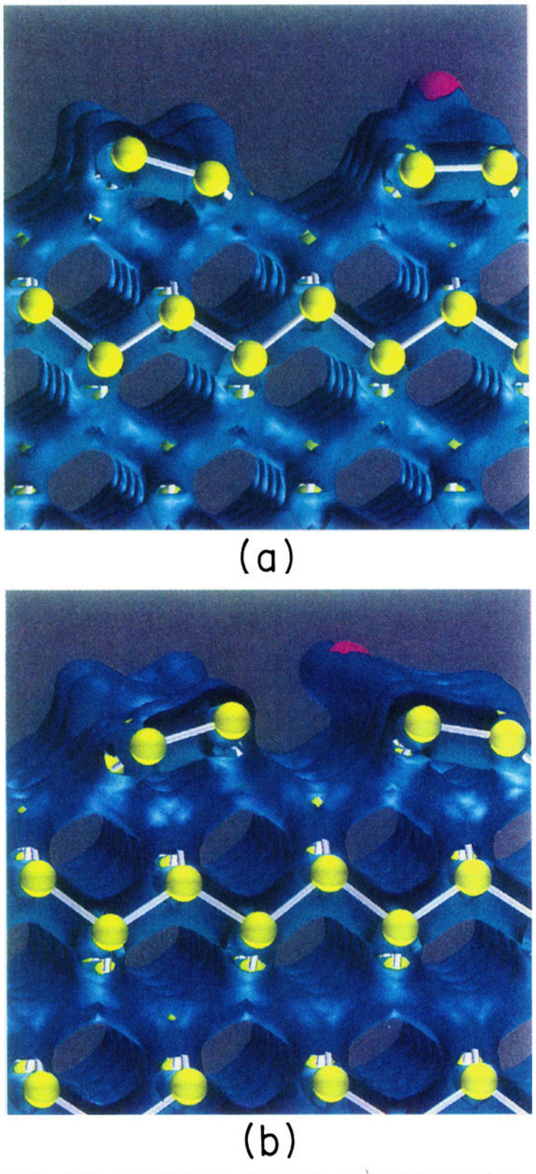


FIG. 3. The equilibrium structure and the isosurface of the electron density distribution for the adatom at sites *H* (a) and *M* (b). The surface cell is oriented as in Fig. 1.