Pairing of hydrogen atoms on the Si(100)-2 × 1 surface: The role of interactions among dimers

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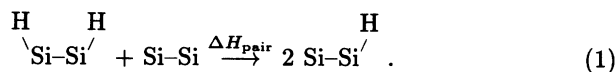
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Local-density-functional calculations of the pairing of H atoms on the (100)-2 × 1 surface of Si are presented. We find that significant interactions between neighboring dimers along a row are present, favoring configurations where H-unpaired dimers are in the same row and have the H atoms all on the same side. We discuss how these effects can contribute to the effective H-pairing energies determined experimentally.

The pairing of hydrogen atoms on Si(100)-2 × 1 has recently become the subject of considerable interest, due to its possible importance in the recombinative desorption of H_2 from this surface.[1] In fact, one of the most popular models proposed for this process is based on the so-called "prepairing mechanism," which requires that the H atoms should come to close sites, before the recombination/desorption takes place. The H pairing originates from the fact that the dangling bonds (DB's) on the silicon atoms belonging to the same surface dimer form a weak π bond,[2,3] which is disrupted when one hydrogen atom is adsorbed. Thus adsorption of two H atoms on the *same* dimer is favored over adsorption on *two distinct* dimers, since in the latter case two π bonds, instead of one, would be removed. Moreover, the π-bond energy should correspond approximately to the H-pairing energy (ΔH_{pair}), which is the energy necessary to separate two H atoms sitting on the same dimer and bring them on different dimers:

$$\overset{H}{\underset{\diagdown}{}}\text{Si-Si}\overset{H}{\underset{\diagup}{}} + \text{Si-Si} \xrightarrow{\Delta H_{Pair}} 2\,\text{Si-Si}\overset{H}{\underset{\diagup}{}} . \tag{1}$$

The H-pairing energy has been recently measured using different techniques,[1,4,5] with conflicting results. Analyzing the temperature-programmed desorption (TPD) data of Refs. 6 and 7, and assuming only intradimer interactions, D'Evelyn *et al.*[4] found a value of about 0.3 eV (7.5 kcal/mol). A similar value, 0.25 eV (5.8 kcal/mol), was obtained also by Höfer *et al.*,[5] by a numerical fitting of their laser-induced thermal desorption (LITD) data. By contrast, Boland,[1] using scanning tunneling spectroscopy (STS), has found a substantially larger value, i.e., ~ 0.8 eV (18 kcal/mol). Theoretical estimates of the pairing energy have been obtained on the basis of *ab initio* cluster calculations,[8–10] by computing the difference in energy required to remove the first and the second H atom adsorbed on a Si dimer. The resulting values (0.1–0.2 eV) are quite close to the LITD and TPD data.

It has been recently recognized[11] that an important difficulty with the present understanding of the H pairing on Si(100)-2×1—which is possibly at the origin of the discrepancies between different experimental estimates—concerns the effect of interdimer interactions, usually omitted in thermal desorption (TD) data modeling, as well as in cluster calculations. Evidence for interdimer interactions on H/Si(100)2 × 1 is provided by the scanning tunneling microscopy (STM) observation[1] that upon annealing doubly occupied dimers tend to form chain structures extending along the [011] dimer-row direction. The formation of these chain structures was originally attributed to the existence of a strong attractive interaction between H-paired units.[1] However recent Monte Carlo simulations incorporating effective nearest-neighbor attractive interactions between H-paired dimers[11] failed to reproduce the cluster size distribution observed by STM. To explain this discrepancy, a possibility is that interactions involving not only doubly occupied, but also singly occupied and unoccupied dimers play a role. As a matter of fact, important electronic interdimer interactions are present along the [011] dimer-row direction for the clean Si(100)-2 × 1 surface, as shown by the large dispersion of the surface valence bands along the $\bar{\Gamma}$-$\bar{J}'$ direction, found both in theoretical[3,12] and experimental[13] work. Similar interdimer interactions are likely to be active also between the dangling bonds of singly occupied dimers or between dangling bonds of unoccupied and singly occupied units.

In this paper we study the influence of interdimer interactions on the H-pairing energy on Si(100)-2×1 by means

of first-principles calculations for slab systems with different H coverages and various configurations of the H adatoms. We find that there is an effective attractive interaction of ~ 0.3 eV between singly occupied neighboring dimers in a *cis* configuration (i.e., with the H atoms on the same side of the dimers) along a row. As a result the H-pairing energy depends significantly on the spatial distribution and configuration of the two H-unpaired units on the right hand side of Eq. (1). On this basis, an explanation for the discrepancies among the available experimental H-pairing energy values is proposed.

Our calculations are based on local density functional (LDF) theory and have been carried out within the framework of the Car-Parrinello approach.[14] The Si(100) surface was represented by a periodically repeated slab of six layers of Si atoms, with eight atoms/layer forming a $p(\sqrt{8} \times \sqrt{8})R45°$ periodic supercell. This can accommodate four surface dimers along a dimer row of the 2×1 geometry, as shown in Fig. 1. One side of the slab has a bulklike termination and is saturated by hydrogens, while the other—the one representing the Si(100) surface—is covered with a variable number of H atoms. A vacuum region of ~ 9 Å is used to decouple the two surfaces. The experimental value of the bulk lattice constant is adopted. For the LDF exchange-correlation energy and potential we used the parametrization of the exact uniform electron-gas data[15] by Perdew and Zunger.[16] The interaction between Si ionic cores and valence electrons was described by a fully nonlocal[17] pseudopotential with *s*-only nonlocality.[18] Kohn-Sham orbitals were expanded in plane waves with kinetic energy cutoff $E_{\text{cut}} = 8$ Ry. Only the electronic states at $\bar{\Gamma}$ have been included. All the above approximations were extensively tested

and found adequate in a recent study of H diffusion on Si(100).[19] For the present study, selected calculations using a larger $p(4 \times 4)$ supercell with 16 atoms/layer (which can accommodate eight surface dimers belonging to two different rows; see Fig. 1) and $E_{\text{cut}} = 12$ Ry show that total-energy differences change by ~ 0.1 eV at most (see below). We have also performed a few calculations (including full geometry reoptimization) to test the effects of nonlocal corrections to the exchange and correlation energy and potential, as proposed by Becke[20] and Perdew.[21] As in the case of H diffusion on Si(100)-2×1,[22] we have found that these effects are very small or negligible, changes in total-energy differences being of the order 0.1 eV at most. This appears to be quite often the case when total energies of "isomeric" systems are compared (see, e.g., Ref. 23). We have not included zero-point energy (ZPE) in our results. Electron-energy-loss spectroscopy data show that even in the case of heavy structural modifications of H-covered Si(100) surfaces the ZPE per H atom varies by less than 3%.[24] Since in this work we consider total-energy differences between slabs with an equal number of adsorbed H's, we expect that the effect of the inclusion of ZPE corrections should be negligible.

All the calculations have been performed with the Si(100) surface in a "2×1"-type surface geometry, i.e., Si-Si dimer bonds were never broken.[25] The atomic structures that we have investigated are shown in Fig. 2, and include both low- and high-coverage configurations. At low-coverage we have considered the following cases: the clean surface (a); a single adsorbed H atom (b); two "paired" H atoms adsorbed on the same dimer (d), or on close dimers, both in a *cis* (e) and in a *trans* (f) configuration. Similarly, at high coverage we have considered the case in which all the DB's are saturated yielding a one-monolayer H coverage (g); a single DB on a H-saturated surface (h); two paired DB's on the same dimer (i); or on close dimers, both in a *cis* (j), and in a *trans* (k) arrangement. All structures were relaxed using a quenched-molecular-dynamics algorithm until residual forces were less than 0.03 eV/Å (for these structures secondary minima are not expected). The four topmost layers of Si as well as the H atoms adsorbed on them were left free to relax without constraints, while the lowest two Si layers were kept fixed in their bulk positions. Calculated geometrical parameters for the surface species of our slabs, i.e., clean, doubly occupied, and singly occupied dimers, are reported in Table I. Results relative to the first two species agree well with other recent high-quality calculations.[3,12,26] For singly occupied dimers we find that the buckling angle ($2° - 4°$, depending on whether the unit is on the H saturated or on the clean surface) is strongly reduced with respect to the unoccupied dimer case, the dimer Si atom to which the H atom is bonded being slightly higher than the other. As a whole, the geometry of singly occupied dimers is much closer to that of doubly occupied than of unoccupied units, suggesting that some strain energy should be associated with singly occupied units on the (otherwise) clean Si(100)-2×1 surface, as proposed in Ref. 1.

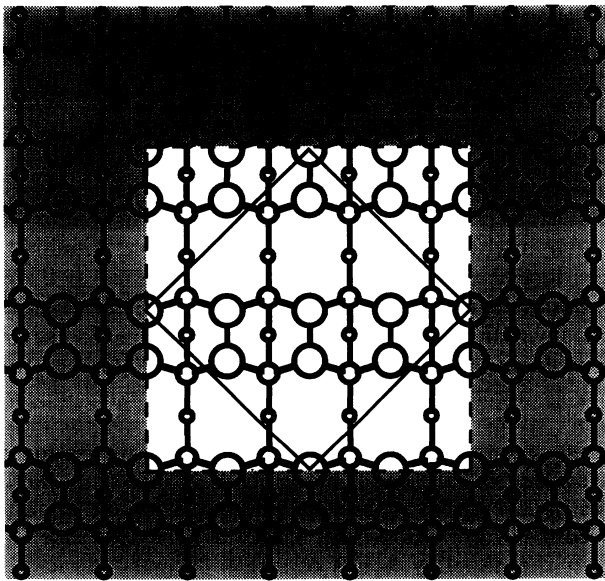The total energies obtained in our slab calculations are

FIG. 1. Top view of the Si(100)-2×1 surface: the $p(\sqrt{8} \times \sqrt{8})R45°$ and $p(4 \times 4)$ surface supercells are indicated, respectively, by the solid and broken lines within the nonshaded area. Only the atoms of the three topmost layers are shown. For simplicity, the Si-Si dimers are shown in a symmetric (unbuckled) configuration.
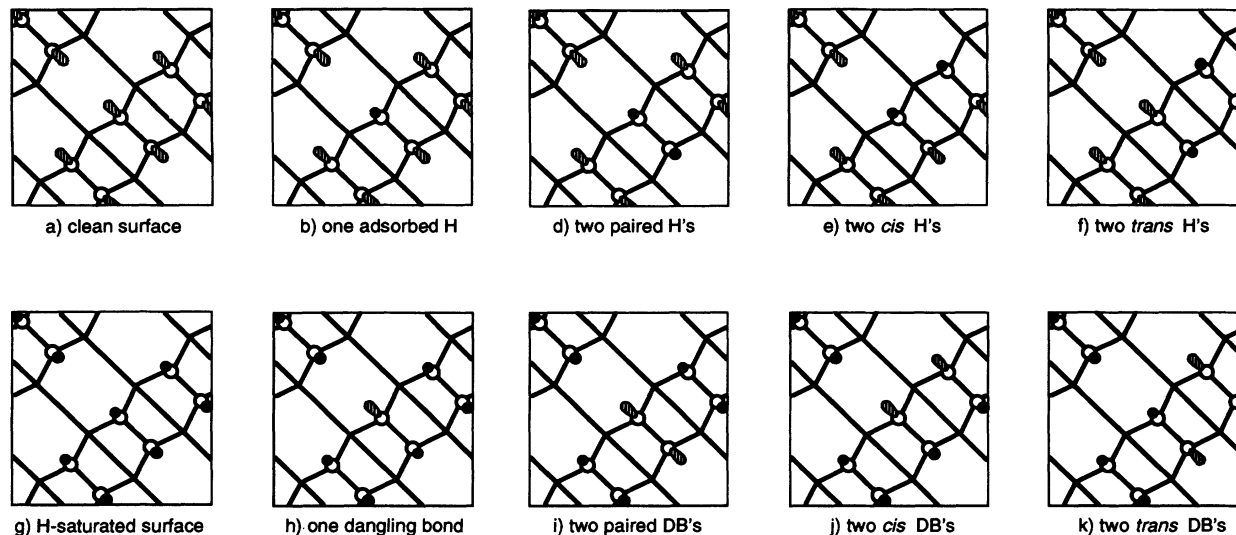
FIG. 2.   Top view of the atomic surface configurations considered in this work. Low- (high-) coverage configurations are grouped on top (bottom). Black dots and empty circles denote hydrogen and first-layer silicon atoms, respectively. DB's are hatched. The wireframe structure shows the bonds among the Si atoms belonging to the three topmost layers. Like in Fig. 1, all Si-Si dimers are shown in a symmetric configuration.

summarized in Table II. Low- (high-) coverage results are reported on the left (right) under the heading "thermodynamic," and are expressed relatively to the energy of the corresponding "paired" configuration. Thus, the second line gives the H-pairing energy relative to two isolated H-unpaired units,[27] while the third and fourth lines give the same quantity referred to adjacent[28] H-unpaired dimers in a cis and a trans configuration, respectively. Values in parentheses are calculations including the effects of gradient corrections to the LDF exchange and correlation. It is apparent that there is an effective attractive interaction of ∼ 0.3 eV between neighboring singly-occupied dimers in a cis configuration, while no attraction or even a repulsion (at low coverage) is present between adjacent H-unpaired units in a trans configuration. The origin of these interactions is largely electronic, as in the case of the interactions leading to the formation of π bands

on the clean surface. The effect which seems to play the main role is the possibility of delocalizing the DB charges along the dimer-row sides. Since the presence of adsorbed H atoms contrasts such a delocalization, configurations where H adatoms are clustered in the same row and on the same side of the row are energetically favored. This effect can also explain why singly occupied dimers, both

TABLE I.   Calculated geometrical parameters for unoccupied, doubly occupied, and singly occupied dimers. Buckling of unoccupied dimers close to singly or doubly occupied units is found to be slightly reduced with respect to that on the perfectly clean surface (reported below).

Dimer species	Buckling angle (degrees)	Si-Si distance (Å)	Si-H distance (Å)
Si–Si	15	2.27	
H H \Si–Si/	0	2.43	1.55
H Si–Si/	2–4	2.39	1.54

TABLE II.   Relative total energies (in eV) for the surface configurations of Fig. 2. The column "X=H" ("X=DB") refers to low (high) coverage. Thermodynamic values are computed as total-energy differences from various slab systems; spectroscopic values are obtained from energy eigenvalue differences. Values in parentheses refer to calculations including Becke-Perdew gradient corrections (Refs. 20 and 21). Bold vertical bars represent Si-Si dimers.

Configuration		Thermodynamic X=H	X=DB	Spectroscopic X=DB
X | | X		0.0	0.0(0.0)	0.0
X X | + |		0.5	0.7(0.7)	0.7
X X | |		0.2	0.4(0.3)	0.5
X | | X		0.8	0.6(0.6)	0.6

"isolated" and in a *cis* configuration, are more stable at low than at high coverage.[29]

While so far we have focused on a thermodynamic estimate of the pairing energy based on total-energy differences, it is also interesting to consider a spectroscopic estimate based on energy eigenvalue differences as in the STS experiment of Ref. 1. In the simplest approximation, tunnel spectra may be directly associated with the local density of states of the sample calculated in the absence of electric field.[30] Surface density of occupied states (SDOS) for some of the high-coverage configurations of Fig. 2 are reported in Fig. 3. They exhibit a remarkable similarity with the STS spectra of Boland.[1] The spectroscopic pairing energy values are reported in Table II for the high-coverage surface configurations (in the low-coverage case, band dispersion causes some uncertainty in defining the orbital energy of the π-bond state relative to that of a single DB). These values are quite close to the corresponding thermodynamic values, suggesting that differences between TD- and STS-derived pairing energies are not likely to originate from failures of STS in including attractive/repulsive effects among surface species, as proposed in Ref. 5.

In an attempt to understand the origin of the different experimental values for the pairing energy, we first notice some differences in the conditions of the STS and TD experiments. TD measurements of the pairing energy are generally obtained at low H coverages ($\sim$ 0.1–0.2 monolayer) and high temperatures ($T \sim$ 700–800 K), since they are indirectly derived from H_2 desorption measurements. In this case, because of the relatively low barrier for H diffusion,[19] a large fraction of the DB's (or adsorbed H atoms) should be paired, while singly occupied dimers are formed via thermal excitation. In the STS case, on the other hand, the pairing energy was estimated for a system prepared via room-temperature submonolayer adsorption of atomic hydrogen, and containing many unpaired DB's randomly sparse on the surface.

Our results in Table II show that the H-pairing energy relative to two *cis* H adatoms at low coverage is 0.2–0.3 eV,[29] which is very close to the TD values (0.25–0.30 eV). On the other hand, Table II shows also that the pairing energy measured relative to isolated (e.g., belonging to different dimer rows) H atoms is considerably higher [0.5– 0.6 eV (Ref. 29)], and rather close to the STS value (0.8 eV). This suggests that the pairing energies extracted from desorption experiments refer to a situation where the singly occupied dimers formed by thermal excitation tend to stay at close sites and in a *cis* configuration in order to benefit from favorable interdimer interactions. In the STS case, instead, the single H adatoms (or DB's) are really decoupled. Moreover also differences in the H coverage of the surfaces could play some role: we see
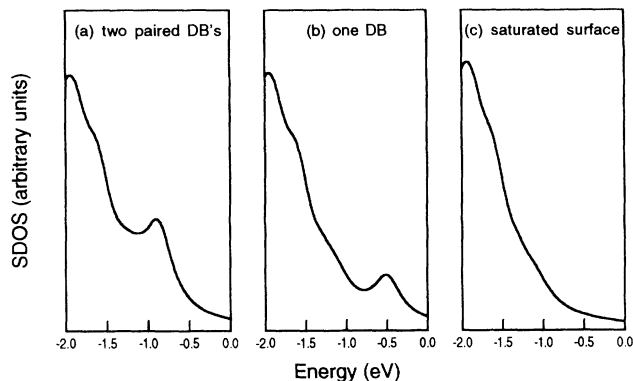

FIG. 3. SDOS relative to selected high-coverage configurations. This was obtained using a Lorentzian broadening of 0.2 eV and weighting each state with the value of the integrated charge density over a volume containing the two topmost layers. To facilitate the comparison with the STS spectra of Ref. 1, the energy scale has been shifted, so that the first peak of the SDOS in (b) falls at -0.5 eV.

from Table II that the pairing energy tends to increase from low to high coverage.[31] STS experiments performed on surfaces with different H coverages should be able to clarify this point.

The complex interdimer interaction pattern shown by Table II should provide an explanation also for the clustering tendency of doubly occupied units observed by STM.[1] A possibility is that this is an indirect kinetic effect arising from the attractive interactions between singly occupied units during H-thermal diffusion.[32] H atoms could give rise in a first stage to "*cis* clusters" of singly occupied dimers, which would be subsequently converted into the doubly occupied dimer clusters of the STM images.

In conclusion, on the basis of first-principle LDF supercell calculations we have found that a theory of H-H interactions on Si(100)-2 × 1 cannot be done on the basis of simple intradimer electronic interactions. Interdimer interactions originating mostly from electronic effects contribute to the effective pairing energy observed experimentally. Our results appear to provide a consistent explanation of the large differences found in experimental data.

[1] J. J. Boland, Phys. Rev. Lett. **67**, 1539 (1991); J. Vac. Sci. Technol. A **10**, 2458 (1992).

[2] M. T. Yin and M. L. Cohen, Phys. Rev. B **24**, 2303 (1981).

[3] Z. Zhu, N. Shima, and M. Tsukada, Phys. Rev. B **40**, 11 868

(1989); N. Roberts and R. J. Needs, Surf. Sci. **236**, 112 (1990).

[4] M. P. D'Evelyn, Y. L. Yang, and L. F. Sutcu, J. Chem. Phys. **96**, 6852 (1992).

[5] U. Höfer, L. Li, and T. F. Heinz, Phys. Rev. B **45**, 9485 (1992).

[6] K. S. Sinniah, M. G. Sherman, L. B. Lewis, W. H. Weimberg, J. T. Yates, Jr., and K. C. Janda, Phys. Rev. Lett. **62**, 567 (1989); J. Chem. Phys. **92**, 5700 (1990).

[7] M. L. Wise, B. G. Koehler, P. Gupta, P. A. Coon, and S. M. George, Surf. Sci. **258**, 166 (1991).

[8] C. J. Wu and E. A. Carter, Chem. Phys. Lett. **185**, 172 (1991).

[9] P. Nachtigall, K. D. Jordan, and K. C. Janda, J. Chem. Phys. **95**, 8652 (1991).

[10] P. Nachtigall, K. D. Jordan, and C. Sosa, J. Phys. Chem. **97**, 11 666 (1993).

[11] Y. L. Yang and M. P. D'Evelyn, J. Vac. Sci. Technol. A **11**, 2200 (1993).

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

[13] G. V. Hansson and R. I. G. Uhrberg, Surf. Sci. Rep. **9**, 197 (1988), and references therein; L. S. O. Johansson, R. I. G. Uhrberg, P. Mårtensson, and G. V. Hansson, Phys. Rev. B **42**, 1305 (1990); Y. Enta, S. Suzuki, and S. Kono, Phys. Rev. Lett. **65**, 2704 (1990); L. S. O. Johansson and B. Reihl, Surf. Sci. **269/270**, 810 (1992).

[14] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

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

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

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

[18] R. Car and U. VonBarth (unpublished). The pseudopotential parameters can be found, e.g., in W. Andreoni, G. Pastore, R. Car, M. Parrinello, and P. Giannozzi, in *Band Structure Engineering in Semiconductor Microstructures*, Vol. 189 of *NATO Advanced Study Institute, Series B: Physics*, edited by M.A. Abram and M. Jaros (Plenum, New York, 1989), pp. 129–135.

[19] See A. Vittadini, A. Selloni, and M. Casarin, Surf. Sci. Lett. **289**, L625 (1993), and references therein.

[20] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).

[21] J. P. Perdew, Phys. Rev. B **33**, 8822 (1986).

[22] A. Vittadini, A. Selloni, and M. Casarin, *Proceedings of the Fourth International Conference on the Formation of Semiconductor Interfaces, Jülich, Germany, 1993* (World Scientific, Singapore, 1994).

[23] L. Deng, T. Ziegler, and L. Fang, J. Chem. Phys. **99**, 3823 (1993).

[24] F. Stucki, J. A. Schaefer, J. R. Anderson, G. J. Lapeyre, and W. Gopel, Solid State Commun. **47**, 795 (1983).

[25] Under high atomic hydrogen exposures, the dimer bonds are broken, with the formation of SiH_2 units, giving 3×1 or 1×1 hydrogenated phases. See A. Vittadini, A. Selloni, R. Car, and M. Casarin, Phys. Rev. B **46**, 4348 (1992), and references therein.

[26] J. E. Northrup, Phys. Rev. B **44**, 1419 (1991).

[27] Energies of the "isolated" singly occupied units are obtained by suitable combinations of slab total energies E_{tot}^n [the superscript (n) denotes one of the configurations of Fig. 2], e.g., $\Delta E = 2E_{tot}^b - E_{tot}^a - E_{tot}^d$ at low coverage.

[28] Due to the relatively small size of our supercell, the possibile presence of interdimer interactions extending beyond nearest neighbors could not be investigated.

[29] We have repeated the calculations relative to the low-coverage case using the large $p(4 \times 4)$ surface supercell and larger cutoff. The largest difference with the results for the smaller $p(\sqrt{8} \times \sqrt{8})R45°$ cell refers to the relative total-energy of configuration (e), which increases from 0.18 eV (for the small supercell) to 0.31 eV (for the large supercell and higher cutoff), while the relative total energy of configuration (b) changes from 0.48 to 0.57 eV.

[30] J. Tersoff and D. R. Hamann, Phys. Rev. B **31**, 805 (1984); N. D. Lang, *ibid* **34**, 5947 (1986).

[31] While this coverage dependence causes a certain ambiguity in the definition of the H-pairing energy, it seems natural to refer the π-bond energy to the process where two decoupled singly occupied units are formed from an unoccupied dimer in a high-coverage surface, because here interdimer electronic interactions are removed. The corresponding value is 0.7 eV (see Table II).

[32] We have also performed total-energy calculations for two H-paired dimers placed either at close sites along a dimer row or at large separations on the surface, and found that the net interaction between adjacent doubly occupied dimers is negligible.
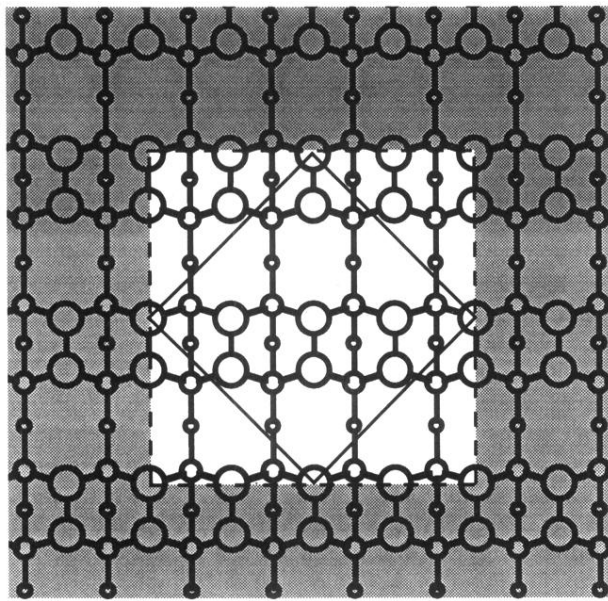
FIG. 1.   Top view of the Si(100)-2 × 1 surface: the $p(\sqrt{8} \times \sqrt{8})R45°$ and $p(4 \times 4)$ surface supercells are indicated, respectively, by the solid and broken lines within the nonshaded area. Only the atoms of the three topmost layers are shown. For simplicity, the Si-Si dimers are shown in a symmetric (unbuckled) configuration.