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Structure of the Si(100)2 × 1 surface: Total-energy and force analysis of the dimer models

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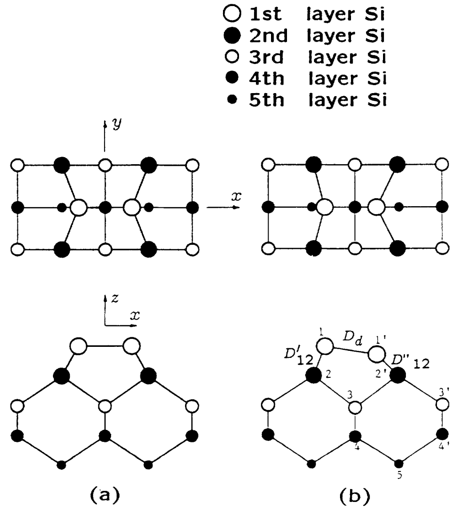
Results of extensive studies of the dimer model of the reconstructed Si(100)2 × 1 surface with molecular clusters containing up to 63 atoms are reported. An all-electron numerical method based on the local-density-functional approach for molecules with analytic energy gradients is applied to both symmetric and asymmetric dimer models. By calculating the force on the first four silicon layers and minimizing the total energy of the cluster, the optimized atomic geometry with minimum energy is obtained. The first-layer Si atoms are found to relax inward by about 0.38 Å for the symmetric dimers, and 0.16 and 0.55 Å for the asymmetric dimer. The dimer bond length is 2.23 and 2.27 Å for the symmetric and the asymmetric dimer, respectively. Further, the calculated energy difference between the symmetric and the asymmetric dimers is very small ($\sim$0.02 eV); thus it is quite possible that both dimers could coexist on the surface.

I. INTRODUCTION

The structural and electronic properties of the clean reconstructed Si(100)2 × 1 surface remain of considerable interest for both fundamental scientific and technological reasons. Although several models have been proposed for the Si(100)2 × 1 reconstructed surface,[1-3] such as the dimer model,[1] the vacancy model,[2] and the conjugated-chain-type model,[3] the early studies by Appelbaum, Baraff, and Hamann[4] and later calculations[5-20] all showed that the dimer model is the most favored model for the Si(100)2 × 1 surface reconstruction. However, the question of whether the surface dimer is symmetric or asymmetric (e.g., buckled dimer) [cf. Figs. 1(a) and 1(b)] remains open despite the large number of experimental and theoretical studies that have been performed. Early energy-minimization calculations suggested an asymmetric dimerized structure on the surface.[8] Later studies[9-15] also favored the asymmetric dimer result with some modifications of the Si coordinates. The asymmetric dimer model was, however, questioned by some other theoretical works.[16-20] Redondo and Goddard[16] found from Hartree-Fock cluster calculations that the ground state of the symmetric dimer is 1.0 eV lower than the buckled dimer. Pandey[17] found a substantial decrease in the surface total energy by introducing a π-bonded defect model based on the symmetric dimer and that an optimized symmetric dimer structure has an energy of 0.36 eV/dimer lower than the asymmetric dimer structure obtained by Yin and Cohen.[10] More recently, Artacho and Ynduráin[18] found, using a total-energy and core-level-shift cluster model calculation, that an antiferromagnetic spin arrangement with the symmetric dimer lowers the total energy by 1.3 eV/dimer below the asymmetric dimer. The symmetric dimer model was also supported by calculations of Abraham and Batra[19] and very recently by Batra.[20] These various calculations were done by utilizing tight binding,[8,11,12,14] pseudopotential,[9,10,15,17,20] Green's function,[13] and Hartree-Fock[16] methods with either slab[8-10,13-15,17,20] or cluster models[11,12,16,18] and with molecular-dynamics simulations.[19] Some results were obtained with more elaborate slab models by optimizing the coordinates of several Si layers using total-energy or force calculations,[10,14,15,20] since it was found experimentally[21,22] and theoretically[6,10] that the surface dimerization is accompanied by a large relaxation of the substrate atoms. Finally, previous cluster calculations



(a) (b)

FIG. 1. Schematic diagram showing the dimer's atomic geometry on the Si(100)2 × 1 reconstructed surface. Each figure is given in top view from the [100] direction and side view from the [011] direction. The Cartesian coordinates x, y, and z refer to the [01$\bar{1}$], [011], and [100] directions, respectively. (a) Symmetric dimer reconstruction, and (b) asymmetric dimer model.

employed a relatively small cluster, which contains only 9 silicon atoms and 12 saturating hydrogen atoms [e.g., a Si_9H_{12} cluster, cf. Fig. 2(a)]. The results of these cluster calculations differ, however, with some favoring the symmetric dimer[16,18] and others finding the asymmetric dimer to be more stable.[11,12]

On the experimental side, low[23] and medium[24,25] energy ion-scattering experiments supported the buckled dimer model. In addition, Yang, Jona, and Marcus[21] proposed a dimer model based on low-energy electron-diffraction (LEED) data in which the dimer can twist along the *y* direction. However, this conclusion was questioned by Holland, Duke, and Paton[22] who fitted their LEED data to yield an asymmetric dimer structure without a *y* twist. Recently, scanning-tunneling-microscopy (STM) studies by Tromp, Hamers, and Demuth[26] showed that symmetric and asymmetric dimers could be present on the surface in roughly equal amounts. Using the same technique, Samsavar *et al.*[27] found that most of the dimers on the Si(100) surface are nonbuckled and that the buckling of the dimer occurs mainly near defects or steps. It has been suggested by Soukiassian[28] that the existence of nonbuckled or buckled dimer surfaces is strongly dependent on the way the surface is prepared and especially on the temperature. Their STM studies have shown that a symmetric dimer is formed on the clean Si(100) surface.[29]

As a result of these conflicting results, it appears to be of value to perform a detailed theoretical study including substrate relaxation. In what follows, we report results of first-principles all-electron local-density calculations on finite cluster models of a dimer on the Si(100)2×1 reconstructed surface. We use large clusters (up to 63 atoms) to reduce the effect of the boundary and present results for optimized structural models based on both total-energy and force calculations. The short dimer bond length obtained by other authors[10,15,17,20] was confirmed. It was found that the energy difference between the symmetric and asymmetric dimer is very small. This result is consistent for all three cluster models chosen [cf. Figs. 2(a)–2(c)]. Therefore, it may be concluded that symmetric and asymmetric dimer structures may well coexist on the surface. In the next section, calculational details are described; Section III gives results for three cluster models, and the results obtained using the $Si_{17}H_{20}$ cluster are compared with recent experimental and theoretical data by other authors Finally, some general conclusions are presented.

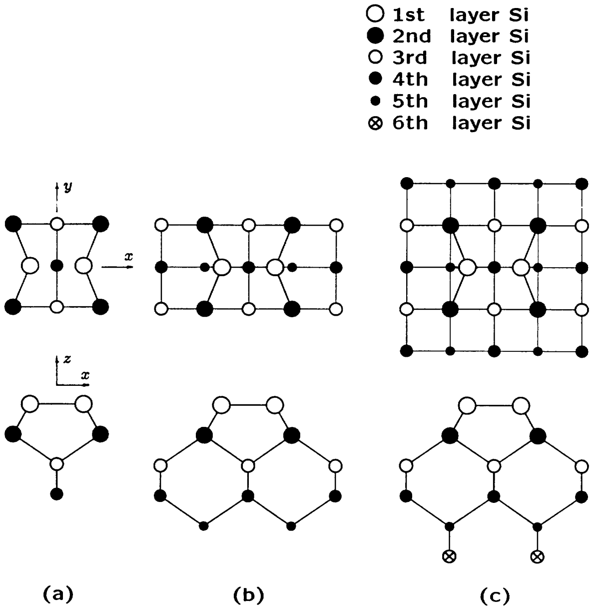


FIG. 2. Three cluster models used in the calculation. (a) Si_9H_{12} cluster, (b) $Si_{17}H_{20}$ cluster, and (c) $Si_{31}H_{32}$ cluster. The four sixth-layer Si atoms, which are not shown in the top view of the $Si_{31}H_{32}$ cluster model, are directly under the four second-layer atoms. Hydrogen atoms are not shown in the figures.

II. METHODOLOGY AND COMPUTATIONAL DETAILS

In this work, an all-electron numerical method[30] for solving the local-density-functional equations (DMOL) with analytic energy gradients[31] is applied to study dimer models of the Si(100)2×1 reconstructed surface. The DMOL method and its predecessors have been successfully applied to calculating various systems such as molecules,[30,32] chemisorption,[33] and the ground state of highly correlated transition and metal clusters.[34] We give here only some technical points relating to the calculation. The Hedin-Lundqvist exchange correlation potential[35] is employed with the core electrons treated fully in the self-consistent iterations. Before performing extensive calculations, the various basis functions set provided by the DMOL program have been tested. In this paper, we use MIN to represent a minimum basis referring to a single set of valence and core functions which consists of five functions for Si and one for H. DN stands for a double numerical basis set, which includes a double set of valence functions and a single set of core functions (seven functions for Si and two for H). DND is a DN basis plus a single *d* polarization function for Si and a single *p* function for H (eight functions for Si and three for H). DNP represents a more elaborate basis which contains 11 functions for Si and five for H. D9 and D10 stand for the basis containing three functions for H, and nine and ten functions for Si, respectively.

Table I gives the energy eigenvalues, the binding energy, and the bond length of the Si_2 molecule with C_{6h} symmetry calculated from a total-energy minimization. The DN and DND basis sets give a Si—Si bond length that differs by 3.0% and 0.1% and a binding energy that differs by 17.0% and 0.2% from that predicted by the more accurate DNP basis set, respectively. Thus, it can be seen that the DND basis set gives a consistently good set of results compared with those of the DNP. A DN basis set gives results which overestimate the binding energy and bond length in the second decimal figure of the DNP results. This is relatively consistent with a previous paper[30] which demonstrated that a DN basis gives binding energies that are uniformly higher than those from extended basis sets and also give slightly too long bond

TABLE I. Energy eigenvalues, binding energies (E_b), and Si—Si bond length ($d_{\mathrm{Si-Si}}$) for the Si_2 molecule as obtained with different basis sets (cf. text). Energies are in Hartree units, distance in Å.

	MIN	DN	DND	D9	D10	DNP
a_u	−65.2091	−65.1634	−65.1530	−65.1527	−65.1543	−65.1551
a_g	−65.2091	−65.1634	−65.1530	−65.1527	−65.1543	−65.1551
a_g	−5.1013	−5.0655	−5.0536	−5.0534	−5.0538	−5.0539
a_u	−5.1012	−5.0653	−5.0534	−5.0533	−5.0536	−5.0537
e_{1u}	−3.5424	−3.5053	−3.4942	−3.4940	−3.4945	−3.4945
e_{1g}	−3.5424	−3.5052	−3.4941	−3.4939	−3.4944	−3.4944
a_g	−3.5385	−3.5038	−3.4910	−3.4909	−3.4913	−3.4914
a_u	−3.5383	−3.5030	−3.4899	−3.4898	−3.4902	−3.4902
a_g	−0.4868	−0.4966	−0.4811	−0.4812	−0.4813	−0.4813
a_u	−0.3733	−0.3457	−0.3390	−0.3389	−0.3389	−0.3389
a_g	−0.2104	−0.2061	−0.2018	−0.2018	−0.2018	−0.2018
e_{1u}	−0.2080	−0.2062	−0.2015	−0.2016	−0.2016	−0.2016
e_{1g}	−0.1341	−0.1088	−0.1019	−0.1018	−0.1017	−0.1017
a_u	−0.0269	−0.0008	0.0043	0.0043	0.0043	0.0040
$d_{\mathrm{Si-Si}}$	2.524	2.276	2.220	2.219	2.218	2.218
E_b	−0.0812	−0.1016	−0.1217	−0.1218	−0.1219	−0.1220

lengths. It is worthwhile mentioning that a DNP basis uses 130% more CPU time than the DN basis, while a DND basis uses only 50% more CPU time.

In this paper, the DN basis set is used in first step of the calculations, and analysis and discussions will be based on the results thus computed. The final optimized results are given with the DND basis.

The binding energy of a cluster is defined as $E_b = E_t - E_a$, where E_t is the total energy of the cluster and E_a is the sum of each atomic energy. For a given atomic geometry, the binding energy of the system and the forces on each atom are calculated. To find the optimized geometry, the atoms are further displaced according to the forces acting on them. An optimized structure is obtained when all the forces acting on the atom are sufficiently small. In this work, the degree of convergence is measured by root-mean-square (rms) changes in the charge density which is set to be 10^{-5}, which allows the total energy to converge to 10^{-5} Ry. The force convergence criterion is 4.0×10^{-3} (Ry/a.u.). In determining the optimum geometry of the symmetric dimer, we restricted ourselves to those geometries which preserve C_{2v} symmetry. For the purpose of testing, we started the calculations by inputting the data on the symmetric dimer but without any restrictions on the symmetry. The optimized results turns out to be a symmetric dimer.

Figure 1 shows the dimer model (symmetric and asymmetric dimer) for the Si(100)2×1 surface. We include relaxation of the Si atoms down to the fourth layer, but do not consider the twisting of the dimer in the buckled dimer model in detail, A test calculation was performed: Moving the dimer along the y direction (e.g., perpendicular to the dimer) by 0.05 Å raised the energy by about 0.05 eV and gave force of 4.0×10^{-2} (Ry/a.u.) acting in the atom along the y direction, which is an order of magnitude larger than the optimized structure. Most of the theoretical and experimental work have also demonstrated that the twisting of the dimer is not possible.[10,12,15,19,20,22,24]

Three cluster models are chosen to simulate the dimer and the substrate, with H atoms used to saturate the dangling bonds. One is the Si_9H_{12} [Fig. 2(a)] cluster consisting of Si atoms ranging from the first to fourth layer, which is widely used in all previous cluster studies.[11,12,16,18] It is, however a small cluster with the boundary atoms quite near to the center atom of the cluster. The second, consisting of 37 atoms, $Si_{17}H_{20}$ [Fig. 2(b)], has five layers of silicon. The third, $Si_{31}H_{32}$ [Fig. 2(a)], which adds one shell of atoms to $Si_{17}H_{20}$ in the y direction, includes the sixth layer of silicon atoms. By assuming that the dimerization on the surface only affects four layers, the Si atoms below the fourth layer are kept in their ideal bulk position. The y coordinate of all Si atoms is also kept fixed. The Si—H bond length is set equal to 1.48 Å.

III. RESULTS AND DISCUSSION

A. Results for the small Si_9H_{12} cluster

First consider the Si_9H_{12} cluster which is used here mostly for testing the effect of the boundary. It is important to find out the effects of the boundary on substrate relaxation, since we need to compare small energy differences between the various models. For the symmetric dimer, we start with the simple dimer model where only the surface atoms form a symmetric dimer with the dimer bond length equal to the bulk bond length. The initial coordinates of the dimer atom are $x = \pm 0.75$ Å, $z = -0.22$ Å. For the asymmetric dimer, the Yin and Cohen[10] (YC) buckled dimer was used as a starting model.

The calculation was carried out by fixing the x component of the third and the fourth layer Si atoms and allowing these atoms to relax only along the z direction. Then the x component was freed and the structure was again optimized to see how much the coordinates and energy are affected. These calculations were done using the DN (double) basis set. For the calculation done by fixing the x coordinates of the Si atoms, the starting structure of the symmetric dimer has a binding energy of -61.87 eV. After relaxation, the energy is lowered by 1.71 eV (to -63.58 eV). The YC model gave a binding energy of -62.62 eV, which is 0.75 eV lower than the simple symmetric dimer model. The energy lowering after optimizing the coordinates is 0.94 eV (to -63.56 eV). These large energy gains indicate that the dimerization process in the Si(100) surface should be accompanied by the relaxation of silicon atoms near the surface. This is consistent with other existing theoretical and experimental results.[10,14,15,20–22,24] By relaxing the x component restriction for the third and the fourth layers, the symmetric dimer does not change because of the C_{2v} symmetry of the cluster. For the case of the asymmetric dimer, the x components of the third and fourth layer atoms change by about 0.025 a.u., whereas the coordinate change of other atoms is less than 0.01 a.u and the energy lowering is less than 0.005 eV. These small changes in coordinates and energy may be due to the fact that either the relaxation of the Si atoms below the third layer is mainly in the z direction or the cluster used is not big enough to tell the difference; it is difficult to choose which of these is the course at this level of the calculation. The dimer bond lengths, 2.24 and 2.25 Å for the symmetric and asymmetric dimers, respectively, are shorter than the Si—Si bond length in the bulk (2.35 Å). This indicates that a stronger interaction exists between the two dimer atoms than between the bulk atoms. The energy difference between the symmetric dimer and asymmetric dimer is very small (0.02 eV).

With the optimized coordinates obtained using the DN basis as an input, the optimization process was carried out again by using the DND basis and by fixing the x component of the third and the fourth Si layers. The dimer bond length obtained is 2.22 Å for both the symmetric and asymmetric dimers which is shorter than the results computed with the DN basis. The energy difference between the two systems is again very small (less than 0.01 eV) showing consistency with the results using the DN basis.

There exist two problems with the results calculated using the small Si_9H_{12} cluster: (1) The optimized silicon atom position may be affected by the nearby boundary since the cluster is small; (2) the dimer models used above are not completely optimized since there are only a few degrees of freedom in the cluster. It is obvious that larger cluster calculations are necessary for obtaining better results.

B. Results with larger clusters

Next, we use a 37-atom cluster, $Si_{17}H_{20}$, which extends the boundary of the model in Fig. 2(a) in the x direction and contains more atoms in the third and fourth layer; the nine atoms in the Si_9H_{12} cluster are all embedded in this large cluster. In order to assess possible effects of the boundary on the results for the small cluster calculation, we used the optimized atomic positions obtained for the Si_9H_{12} cluster for the corresponding nine silicon atoms coordinates in the $Si_{17}H_{20}$ cluster and calculated the forces acting on each atom. The results are shown in Table II where the forces between the optimized results in the Si_9H_{12} cluster (model I) and the nonoptimized results in the $Si_{17}H_{20}$ cluster (model II) are compared. It can be seen that the forces change a lot after embedding the small cluster into the larger one. The forces are an order of magnitude larger than the optimized results for the second layer Si atoms and thus demonstrate that the size of the cluster affects the geometrical configuration. Hence the results obtained with Si_9H_{12} are inadequate.

The same calculational procedure followed in the last section was then repeated. First we froze the x components of the third and fourth layers of Si atoms (i.e., atoms 3′ and 4′) near the boundary; there are then eight degrees of freedom for the symmetric dimer and 21 degrees of freedom for the asymmetric one. Next by releasing this restriction on the x components, two and six degrees of freedom will be added to the calculation for the symmetric and the asymmetric dimers, respectively. The optimized results for the binding energy and bond lengths shown in Table III were calculated with the DN basis set. It is found that the atoms move towards the center of the cluster if the atoms in the third and the fourth layer are allowed to move along the x direction. (This is reasonable since no forces are exerted on the cluster from the outside.) The relaxation along the x direction is about

TABLE II. The forces acting on the Si atoms in the Si_9H_{12} cluster (referred to as model I) and on the corresponding Si atoms in $Si_{17}H_{20}$ cluster (referred to as model II) using the DN basis. N is the atom number shown in Fig. 1(b). Forces are in 10^{-3} Ry/a.u.

	Symmetric dimer				Asymmetric dimer			
	Model I		Model II		Model I		Model II	
N	F_x	F_z	F_x	F_z	F_x	F_z	F_x	F_z
1	0.3	2.0	−8.2	−0.1	0.0	2.3	−9.7	−1.4
1′	−0.3	2.0	8.2	−0.1	3.8	0.4	10.5	−3.6
2	2.8	1.0	−53.7	−50.4	0.9	−0.6	−50.2	−50.9
2′	−2.8	1.0	53.7	−50.4	0.7	2.7	58.5	−46.9
3	0.0	0.6	0.0	10.4	0.0	−3.1	0.0	8.3
4	0.0	2.6	0.0	−17.6	0.0	0.0	0.0	−19.1

TABLE III. The binding energies (E_b) and dimer bond length (D_d) calculated from the $Si_{17}H_{20}$ cluster using the DN basis. Model III refers to the calculation without the x component restriction, model IV with this restriction. Energies are in eV, distance in Å.

	Model III		Model IV	
	Symmetric dimer	Asymmetric dimer	Symmetric dimer	Asymmetric dimer
E_b	−118.10	−118.08	−118.06	−118.04
D_d	2.26	2.30	2.27	2.31

0.05 a.u., and the energy gained is 0.04 eV for both the symmetric and the asymmetric dimers. The dimer bond length calculated with the x component restriction for both dimers is 0.01 Å longer than that without the restriction for the corresponding dimers. This can be regarded as an indication of part of the boundary effect. It is gratifying to see that the energy difference between the symmetric and the asymmetric dimers with and without the x component restriction remains almost the same (0.02 eV). Therefore further calculations with the x component restriction to reduce the boundary effect can be made without disturbing the comparison of the energy difference between the two dimer models. Recent studies by Batra[20] also showed that after relaxation the x component for atoms below the second layer only change a little for the asymmetric dimer and do not change for the symmetric dimer.

In the following, we shall only discuss the results obtained by freezing the x component of the atoms below the second layer. To check whether the cluster used can predict reasonable coordinate information, a larger cluster consisting of all the atoms in the model of Fig. 2(b) with the boundary enlarged by embedding this optimized cluster into a large one [Fig. 2(c)] was chosen. In this case, only those atoms that are the same as those in the $Si_{17}H_{20}$ cluster are allowed to relax and atoms in the third and the fourth layers are allowed to relax only in the z direction. If the effect of the boundary is significant, large forces acting on the atoms at the interface between the embedded cluster and the boundary atoms would be found. Indeed, it was found that there are some increased forces acting on the third and the fourth layer atoms and that the forces acting on the atoms in the first two layers do not change much. The largest force is 16.3×10^{-3} (Ry/a.u.) The energy difference between the optimized symmetric and asymmetric dimer models using $Si_{31}H_{32}$ is about 0.01 eV.

From the above results, it can be seen that (1) while the $Si_{17}H_{20}$ cluster may provide relatively reliable coordination information for the first two silicon layers, the larger cluster is necessary to get adequate coordinate information for the third and fourth silicon layers. (2) The energy difference between the symmetric and the asymmetric models is very small regardless of the size of cluster.

Using the DND basis, we performed the optimization again on $Si_{17}H_{20}$ and $Si_{31}H_{32}$ clusters, respectively. For $Si_{17}H_{20}$, the binding energy of the symmetric dimer is −127.98 eV as compared with −128.00 eV of the asymmetric dimer. In the calculation on $Si_{31}H_{32}$, we allow the fifth layer of silicon to relax along the z direction and fix the position of the sixth layer. The final optimized coordinates for the symmetric and the asymmetric dimers are shown in Tables IV and V. Since Bechstedt and Reichardt[14] have already compared all the optimized results for the asymmetric dimer obtained prior to 1986, only those results after 1986 and the result of Holland, Duke, and Paton[22] derived from the LEED data are listed in the tables for comparison. There are two basic features that are unanimously agreed upon in all these studies. (1) The dimerization of the Si(100) surface is accompanied by the relaxation of several silicon layers. The amplitude of the relaxation of the first Si layer varies from 0.1 to 0.6 Å in the different calculations. (2) The second-layer atoms move towards each other in the same direction as do the dimer atoms. For the symmetric dimer, the present calculation shows that the dimer atoms relax inward by 0.38 Å. This value lies between the two available results for the symmetric dimer, e.g., that of Abraham and of Batra[19] (0.10 Å) and of Batra[20] (0.44 Å). For the asymmetric dimer, almost all the theoretical and experimental results[36] show an inward relaxation of the top layer except for two.[14,24] The inward relaxations of the top layer in our calculation are 0.16 and 0.55 Å, which are close to the recent pseudopotential results.[20]

The binding energies of the symmetric and asymmetric dimers are −225.97 and −225.99 eV, respectively. The small difference of binding energy between the two dimer models (0.02 eV) indicates that the possibility of their presence on the surface is almost equal. The same conclusion was also reached by Bechstedt and Reichardt[14] who show that the energy difference of the two dimers is 0.04 eV with the asymmetric dimer having lower energy. Batra finds that the symmetric dimer is only 0.02 eV/dimer lower than the asymmetric dimer.[20] Therefore, these theoretical calculations agree with each other quite well.

The coexistence of the symmetric and asymmetric dimer on the surface is confirmed by a recent STM study[26] that found an almost equal amount of both dimers on the surface. The same phenomenon is seen in the photoemission study of the Ge(100)2×1 surface by Schnell *et al.*[37] who showed that the ratio of the symmetric and the

TABLE IV. The optimized atomic positions (given in Å) of the symmetric dimer model ($Si_{31}H_{32}$ cluster) calculated with the DND basis set compared with the results of Batra (Ref. 20).

	Ideal surface		Present work		Batra	
N	x	z	x	z	x	z
1	−1.921	0.000	−1.114	−0.376	−1.11	−0.44
1′	1.921	0.000	1.114	−0.376	1.11	−0.44
2	−1.921	−1.358	−1.892	−1.408	−1.83	−1.44
2′	1.921	−1.358	1.892	−1.408	1.83	−1.44
3	0.000	−2.716	0.000	−2.782	0.00	−2.90
3′	3.841	−2.716	3.841	−2.741	3.84	−2.65
4	0.000	−4.074	0.000	−4.104	0.00	−4.17
4′	3.841	−4.074	3.841	−4.056	3.84	−4.04

TABLE V. Optimized atomic positions (given in Å) of the asymmetric dimer model ($Si_{31}H_{32}$ cluster) calculated with the DND basis set. Also listed are results obtained by Batra (Ref. 20), Zhu, Shima, and Tsukada (ZHT) (Ref. 15), Bechstedt and Reichardt (BR) (Ref. 14), and results from LEED studies by Holland, Duke, and Paton (HDP) (Ref. 22).

	Present		Batra		ZHT		BR		HDP	
N	*x*	*z*	*x*	*z*	*x*	*z*	*x*	*z*	*x*	*z*
1	−1.310	−0.164	−1.32	−0.19	−1.330	−0.106	−1.247	0.038	−1.421	−0.250
1′	0.926	−0.550	0.85	−0.50	0.876	−0.471	1.211	0.028	1.021	−0.614
2	−1.881	−1.402	−1.83	−1.40	−1.806	−1.346	−1.872	−1.302	−1.827	−1.380
2′	1.902	−1.408	1.80	−1.33	1.781	−1.337	1.811	−1.304	1.816	−1.303
3	0.000	−2.782	−0.01	−2.90	−0.059	−2.912	0.002	−2.772	−0.016	−2.862
3′	3.841	−2.741	3.82	−2.59	3.836	−2.539	3.832	−2.575	3.839	−2.585
4	0.000	−4.106	0.00	−4.18	0.006	−4.229	−0.014	−4.093	0.026	−4.186
4′	3.841	−4.059	3.84	−4.04	3.834	−3.938	3.857	−3.999	3.809	−3.974

asymmetric dimers present on the surface is about 1:3. The simultaneous appearance of symmetric and asymmetric dimers on the surface can also explain somewhat conflicting results of photoemission studies on the Si(100)2×1 surface.[38–40]

Comparing the coordinates between the symmetric and the asymmetric dimers of our calculation and that of Batra[20] from Tables IV and V, it can be seen that the small energy difference between the two dimers is not too surprising since the symmetric and the asymmetric dimers have almost the same amount of substrate relaxation except for the dimer atom positions. Our results show good agreement with other calculations and with the LEED study on the first two layers of Si. The major difference lies in the fact that a smaller relaxation (about 0.07 Å with a 63-atom cluster) for third layer atoms is obtained in our calculation, whereas the others give 0.1 to 0.2 Å (Refs. 6, 10, 15, 20, 22) relaxation. This may be due to the limited cluster size, which restricts the relaxation of those atoms near the boundary. In Table VI we have collected the dimer bond lengths (D_d), the bond lengths between a dimer-forming atom and the second layer atoms (D_{12}, cf. Fig. 1) derived from different theoretical and experimental studies with the exception of that by Abraham and Batra,[19] which was recently modified by Batra.[20] Note that our calculation gives a little longer dimer bond length than that obtained by Yin and Cohen,[10] Zhu, Shima, and Tsukada,[15] Pandey (2.22 Å),[17] and Batra[20] who used the pseudopotential approach. This difference may be due to the fact that they use the frozen-core approximation.

Figure 3 shows the contour plots of the charge density of two dimer models. It is obvious that the dimer bond is covalent in nature. The symmetric dimer bond is a little stronger than the asymmetric dimer, since the symmetric dimer has a smaller bond length. It can be seen that after buckling of the dimer atoms, the bonding between the down dimer atom and the nearest second layer Si atoms is enhanced, and there is a small amount of charge accumulated on the dangling bond of the up dimer atom. From a Mulliken population analysis, the charge transfer from the down dimer atom to the up atom is about 0.1*e*, which is in agreement with estimates from high-resolution photoemission experiments.[41]

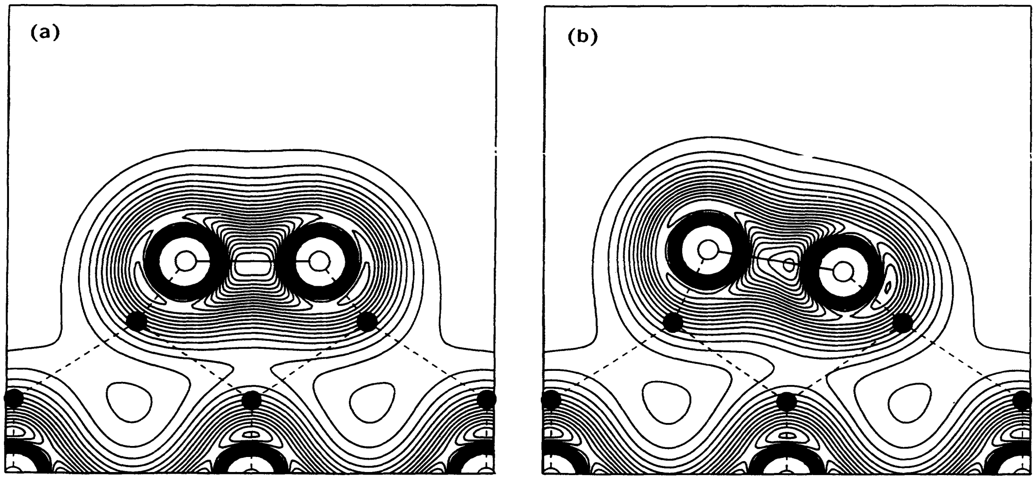


FIG. 3. Contour plots of the total charge density of the Si(100)2×1 surface. The plots are in a (011) plane cutting the surface at a right angle. The open circles represent the Si atoms lying on the plane and the solid circles represent those Si atoms not on the plane. The contour spacings are $0.004e/(\text{a.u.})^3$. (a) Symmetric dimer, and (b) asymmetric dimer.

TABLE VI. The dimer bond lengths (D_d), the bond length between the dimer forming atoms and the second layer atoms (D_{12}) derived from the optimized dimer model obtained by various authors. Bond lengths are given in Å.

		Present	Batra[a]	YC[b]	TSSC[c]	YJM[d]	HDP[e]	BR[f]	ZHT[g]
Symmetric	D_d	2.23	2.22						
dimer	D_{12}	2.31	2.28						
Asymmetric	D_d	2.27	2.19	2.25	2.36	2.54	2.47	2.46	2.24
dimer	D'_{12}	2.35	2.33	2.34	2.40	2.33	2.27	2.38	2.34
	D''_{12}	2.32	2.30	2.30	2.34	2.45	2.19	2.45	2.29

[a] Reference 20.
[b] Reference 10.
[c] Reference 24.
[d] Reference 21.
[e] Reference 22.
[f] Reference 14.
[g] Reference 15.

IV. CONCLUSION

We have made the first application of DMOL's force capability to study the dimer model of the Si(100)2×1 reconstructed surface. By combining force in the calculation, we have established a possible way to judge the cluster size for the system studied. We have shown that while the Si_9H_{12} cluster (used in all previous studies) is too small to give adequate coordinate information, the relative energy difference between the two dimers is less affected by the small size of the cluster. The structure of the dimer was optimized using a DND basis with a $Si_{31}H_{32}$ cluster, and it was found that the energy difference between the symmetric and asymmetric dimers is very small (~ 0.02 eV). Thus, the possibility that both dimers could coexist on the surface even at modest temperatures cannot be ruled out. The dimer bond lengths predicted from the present calculation are 2.23 and 2.27 Å for the symmetric and the asymmetric dimers, respectively. For the symmetric dimer, the dimer atoms relax inward by ~ 0.38 Å, and for the asymmetric dimer, the dimer atoms relax inward by ~ 0.16 and 0.55 Å, respectively.

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