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Surface reconstruction on Si(100) studied by the CNDO method

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Abstract. We have examined seven reasonable asymmetrical dimer configurations for a Si(100) surface using the CNDO method. In this work, all structures resulting from higher-order dimer reconstruction are named according to Pauling and Herman's terminology. Reconstructed 4×1 and 4×2 surfaces are found to be energetically more favourable, followed by $2 \times 2A$ and 2×1 . The total energies per dimer of these four structures are reasonably close to each other and a disordered mixture of them might appear at the Si(100) surface. The results agree well with previous theoretical work as well as with experimental results. However, the 4×1 configuration cannot be confirmed as it has not been observed experimentally. The results on the amount of charge transfer to the dimer atoms and the dimer lengths for each configurations are also presented.

1. Introduction

The study of clean Si(100) surfaces has been very active in the last two decades both experimentally and theoretically. The experimental techniques used include LEED [1–3], He atom diffraction [4], ion beam crystallography [5], photoemission spectroscopy [6] and scanning tunnelling microscopy [7]. The experimentally observed Si(100) reconstructions are 2×1 , 4×2 and 2×2 . However, the reconstructed structure observed may depend upon the methods of preparation and temperature.

Among recent theoretical investigations, the self-consistent pseudopotential calculation with a local density approach by Yin and Cohen (YC) [8] has been the most successful. In this calculation, the most stable geometry is obtained by calculating the total energy with Hellmann–Feynman forces as a guide. Since the fully self-consistent pseudopotential approach is based on a plane-wave expansion, YC used a large number of plane waves to describe the electronic state in Si; this makes the use of YC's method very expensive as far as computation time is concerned. Chadi [9] has proposed a simple tight-binding approach to calculate the minimum total energy of the Si(100) surface and hence to find the most stable reconstructed surface. This results in a Hamiltonian matrix at least an order of magnitude smaller than those employed in YC's method. Furthermore, the results obtained by Chadi's method agree well with YC's self-consistent pseudopotential calculation. However, one of the weaknesses of Chadi's method is that it is not a self-consistent method. To date, YC's method has only been applied to the 2×1 reconstructed surface while Chadi's has been extended to a few other possible reconstructed surfaces. Pauling and Herman [10] have investigated six reasonable recon-

structed surfaces by minimising the sum of the squares of the differences of the bond angles from the ideal value (109.47°). These bond angles are formed by the dimer silicon pairs with the atoms in the layer below. By using a modified Keating potential [11] to describe the interactions of Si atoms, Weber [12] used the steepest-descent method to locate the mechanically stable reconstructed surfaces. Nonetheless, this method involves the use of a pairwise potential in the spacious structure of silicon and the validity of using a bulk potential on the surface layer atoms [13] is questionable. More recently, Needels *et al* [14] have used an energy functional constructed by density functional and pseudopotential theories to describe the potential of the system in their molecular dynamics approach to study the structure of the Ge(100) surface. They have then overcome the uncertainty of the use of a pairwise potential in the molecular dynamics approach.

In this paper we explore the usefulness of the complete neglect of differential overlap (CNDO) method [15] to study the surface reconstruction of Si(100). We considered all the six 'superstructures' proposed by Pauling and Herman [10], as well as the $c(2 \times 2)$ structure proposed by Chadi. We shall follow Pauling and Herman's terminology closely and name the $c(2 \times 2)$ structure of Chadi as $2 \times 2D$. The CNDO method has a simplicity similar to Chadi's method and is able to yield the total energy of the system. It also has self-consistent features similar to YC's. We show that the CNDO method is able to supplement Chadi's and YC's methods in studying reconstructed surfaces.

2. Models and methods

We have used the semi-empirical self-consistent molecular method of CNDO to calculate the total energies associated with different reconstructed surfaces. Two major approximations have been made. Firstly, Hartree-Fock-Roothaan equations are approximated by neglecting the two electron overlap integrals on different atoms. Secondly, approximation on other elements in the order of overlap integrals are made by the following semi-empirical parameters which depend only on the atomic species: (i) orbital exponent ζ ; (ii) electronegativity E ; and (iii) bonding parameters β . Each valence electron orbital of an atom possesses these three parameters. For a given set of parameters, the CNDO method will yield self-consistent calculations similar to Hartree-Fock calculations. The energy eigenvalues and wavefunctions are thus obtained. The Harwell MOSES code [16] is used for the CNDO calculation in the present study.

We have used a molecular cluster as shown in figure 1 to simulate the crystalline Si(100) surface. The cluster is made of 35 Si atoms from the four top atomic layers of the Si(100) surface. Twenty eight pseudo-atoms, Si^* , consisting of sp^3 hybrid orbitals are also introduced to the external dangling bonds at the edges of the silicon cluster. The two outward dangling bonds attached to each of the Si atoms of the outermost layer are not saturated by pseudo-atoms. The numbers of atoms in the first, second, third and fourth layers of the cluster are 8, 12, 9 and 6, respectively. In order to minimise the edge effect, the silicon atoms at the outermost layer are connected to silicon atoms at the layer below and not to any pseudo-atoms.

The CNDO empirical parameters for Si are taken from values determined by Harker and Larkins [17] using 16-atom, periodically repeated large unit cells. The use of this set of parameters in the CNDO calculation leads to the reproduction of the experimental values for the cohesive energy, the valence band width and the equilibrium internuclear separation of a perfect Si crystal. The approximate valence band structure is also predicted in these calculations. In fact, the same set of parameters has been successfully

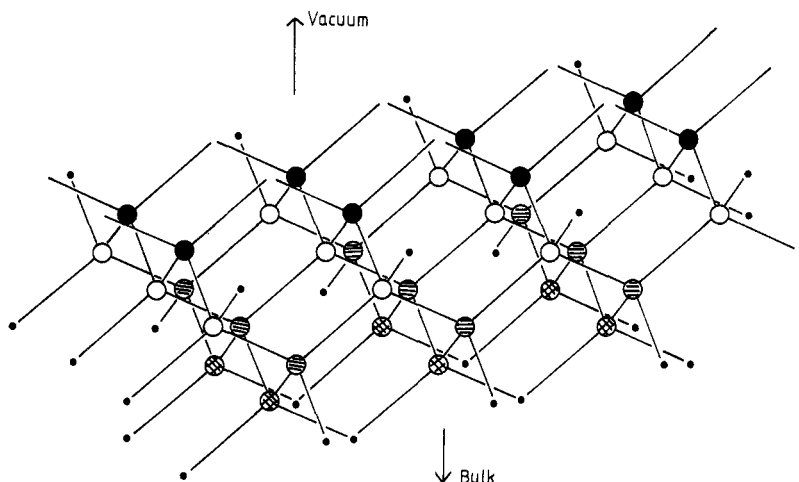


Figure 1. The 63-atom cluster used in the present work. Large full circles represent Si atoms at the outermost layer; open circles Si atoms at the second layer; hatched circles Si atoms at the third layer from the vacuum; cross hatched circles Si atoms at the fourth layer, and small full circles Si* pseudo-atoms.

Table 1. CNDO parameters for Si and Si*.

Atoms	Orbital exponents ζ (au)	Bonding parameters β (eV)	Electronegativity	
			E_s (eV)	E_p (eV)
Si	1.54	-6.4	6.3	4.5
Si*	1.54	0	6.3	4.5

tested in many defect studies [18, 19]. The parameters of Si* are similar to those of Si except that the bonding parameter is set to zero. This was found necessary by Mainwood and Stoneham [20] in order to give a constant charge on the inner atoms of the silicon cluster and reproduce the valence band width of the bulk silicon. Table 1 gives the values of the CNDO parameters used.

3. Surface reconstruction

In a Si(100) surface, each atom at the outermost layer is attached to the atoms in the layer below by two single bonds. Therefore, there remain two dangling bonds on each of these (100) surface atoms. Two adjacent atoms at the surface layer will bend toward one another to form a third covalent bond. This pair of atoms is said to form a dimer as indicated by 1 and 2 in figure 2. The strain energy caused by bond bending can be reduced by the relaxation of atoms [21–23] and the transfer of charge from one atom of the pair to the other or from subsurface atoms. In the present calculation, we allow only the atoms at the outermost layer to relax, as Pauling and Herman did, and the atoms at the second, third and fourth layers are fixed at the ideal bulk positions. The lengths of the bonds between the outermost layer atoms and the atoms at the layer below are kept

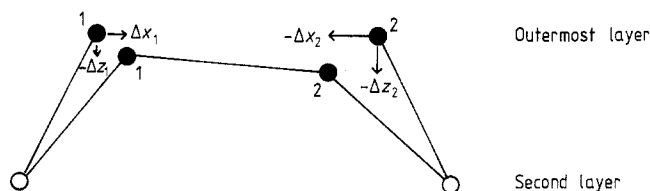


Figure 2. Side view of Chadi's dimer model of a reconstructed Si(100) surface. Surface atoms (1 and 2) are shown as full circles and second-layer atoms as open circles. The arrows refer to the direction of atomic displacements from ideal bulk positions. The atoms at the second, third and fourth layers are fixed at the ideal bulk positions. We have taken the (100) surface to be lying on the x - y plane and the surface normal in the z -direction.

constant and taken to be equal to bulk bond length in the present model. In figure 1 the surface lies on the x - y plane and the surface normal is in the z -direction. The displacements of the outermost layer atoms 1 and 2 in the x -directions are denoted as Δx_1 and Δx_2 , respectively. The displacements of atoms 1 and 2 towards the vacuum above the surface are denoted Δz_1 and Δz_2 , respectively. If Δz_1 and Δz_2 are equal and Δx_1 and Δx_2 are also equal, then the given reconstructed structure is termed a symmetric dimer; otherwise, it is called an asymmetric dimer [9].

There are many possible configurations for the Si(100) surface when it is constructed in terms of asymmetric dimers and we have considered seven of them. The atomic positions of the eight outermost atoms in our computation cluster are illustrated in figure 3(a)–(g) for each configuration considered. The aim of this paper is to determine which of the configurations gives the lowest total energy per dimer. Six of the configurations considered were proposed by Pauling and Herman [10]. The same structures were also studied by Ihm *et al* [24] named in the conventional nomenclature. Ihm *et al* divided these structures into two families of 2×1 and $c(2 \times 2)$ backbones as a great energy barrier was observed between these two families. The seventh configuration, $2 \times 2D$ (figure 3(e)), is equivalent to $c(2 \times 2)$ in Chadi's work and $p(4 \times 2)$ in the terminology of Ihm *et al*. In table 2 we compare Pauling and Herman's nomenclature with that of Ihm *et al* for the higher-order reconstructed structures on the (100) surface of semiconductors. We performed the CNDO calculation on each of these and obtained the total energy as a function of Δx_1 , Δx_2 , Δz_1 and Δz_2 . The minimum total energy and the corresponding optimum values for the displacements of the outermost atoms are then obtained for each dimer configuration. The calculated results of the total energy per dimer, together with the dimer length and the charge transfer to the dimer atoms for all seven dimer configurations investigated are summarised in table 3. We found that 4×1 , 4×2 are the most stable structures, followed by $2 \times 2A$ and 2×1 . In general, our results agree well with previous calculations [8–10, 12, 25]. Pauling and Herman found $2 \times 2A$, 2×1 and 4×2 to be the most stable geometries; however, they felt that the 4×1 structure could be ruled out. Chadi [26] found 4×2 , $2 \times 2A$ and $2 \times 2D$ to be more favourable than 2×1 . However, this was contradicted by Weber [12] who reported that the 2×1 structure had lower energy than the $2 \times 2D$. Verwoerd [25] performed a MINDO/3 cluster calculation of the Si(100) surface and found $2 \times 2A$ to be more stable than 2×1 . His models, methods and levels of approximation are similar to those of this study, but the nine Si atom cluster that he used to simulate the Si(100) surface is much smaller than the one used here. Furthermore, his use of hydrogen atoms to saturate the external bonds is less realistic and unsatisfactory. Our calculated dimer bond lengths are greater than the bulk bond length by 1.25% to 3.25%, similar to those obtained by Chadi [9] and

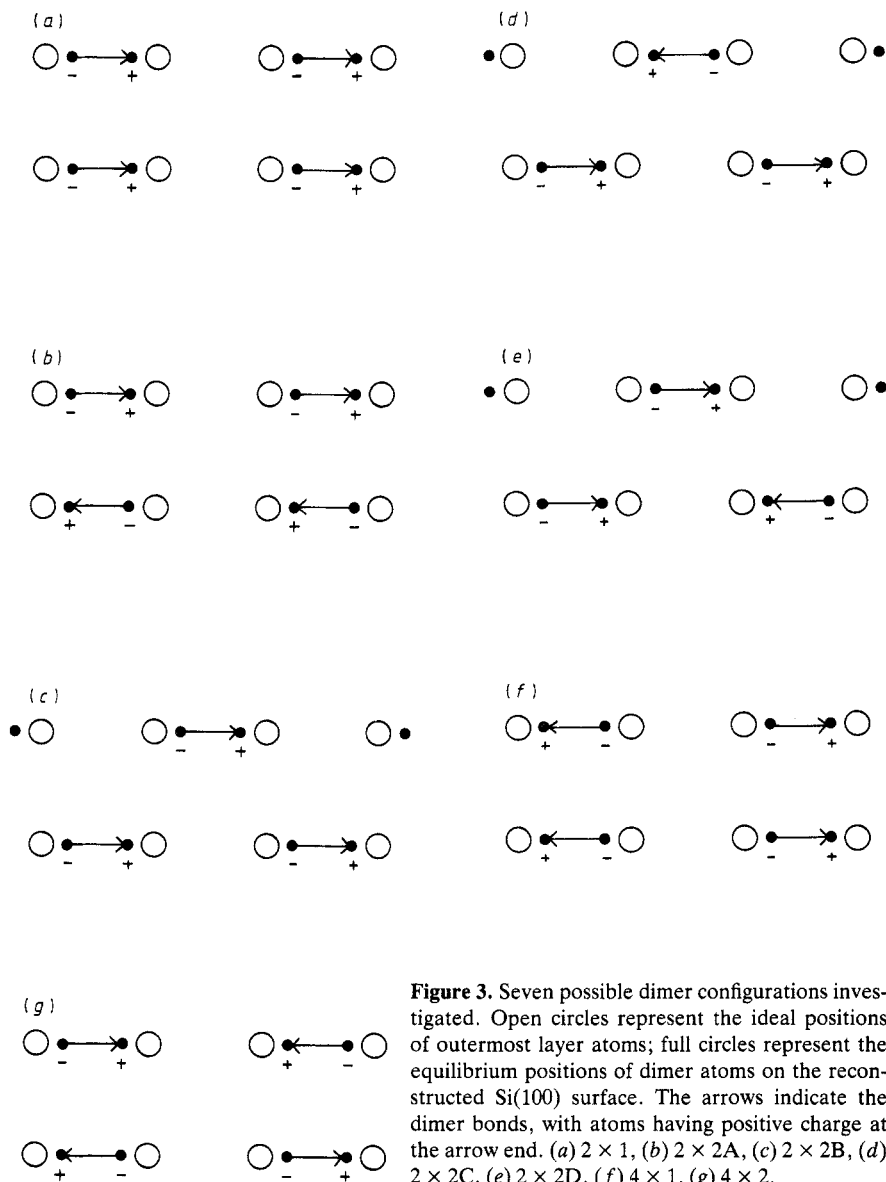


Figure 3. Seven possible dimer configurations investigated. Open circles represent the ideal positions of outermost layer atoms; full circles represent the equilibrium positions of dimer atoms on the reconstructed Si(100) surface. The arrows indicate the dimer bonds, with atoms having positive charge at the arrow end. (a) 2×1 , (b) $2 \times 2A$, (c) $2 \times 2B$, (d) $2 \times 2C$, (e) $2 \times 2D$, (f) 4×1 , (g) 4×2 .

Weber [12]. This result contradicts that obtained by YC, who found the dimer bond length to be shorter than the bulk bond length by 4.25% in their self-consistent pseudopotential calculation. Recently, Aono *et al* [27] used low-energy ion scattering spectroscopy to determine the intra-dimer atomic distance parallel to the surface and found it to be $2.4 \pm 0.1 \text{ \AA}$, which is the parallel component of the dimer bond length. This result indicates that the dimer bond length is most likely greater than the bulk bond length of 2.35 \AA .

These experimental data seem to support our results again. However, the differences in the various theoretical results may be explained by considering the following

Table 2. Pauling and Herman's terminology versus that of Ihm *et al* for the structures resulting from higher-order reconstruction on (100) surface of semiconductors. f1 and f2 in the second column indicate 2×1 and $c(2 \times 2)$ families, respectively, as explained in [24].

Pauling and Herman [10]	Ihm <i>et al</i> [24]
2×1	2×1 f1
$2 \times 2A$	$p(2 \times 2)$ f1
$2 \times 2B$	$c(2 \times 2)$ f2
$2 \times 2C$	$p(2 \times 2)$ f2
$2 \times 2D$	$p(4 \times 2)$ f2
4×1	4×1 f1
4×2	$c(4 \times 2)$ f1

Table 3. Calculated results of the total energy/dimer, dimer bond length in terms of % longer than bulk bond length and the charge transfer to the dimer atoms for all seven possible dimer reconstructed surfaces. The total energy of the ideal surface is set to 0.

Dimer reconstructed surface	Total energy/dimer (eV/dimer)	Dimer bond length (% longer than bulk bond length)	Charge transfer (electron)
2×1	-1.21	1.92	-0.13, 0.16
$2 \times 2A$	-1.22	1.25	-0.12, 0.14
$2 \times 2B$	-1.15	2.43	-0.11, 0.12
$2 \times 2C$	-1.05	3.25	-0.12, 0.14
$2 \times 2D$	-1.09	3.25	-0.11, 0.15
4×1	-1.27	1.25	-0.12, 0.16
4×2	-1.27	1.25	-0.11, 0.13

factors: (1) the dimer may be doubly bonded in order to saturate the bonds of the surface atoms; (2) the directional forces acting on the surface atoms due to its backbond tend to pull the surface atoms apart; and (3) since the dimer atoms have some ionic characteristics, they may be expected to move according to the electrostatic field arising from charge redistribution in the cluster as well as the long-range effects of charges, such as polarisation or distortion of the crystal beyond the finite cluster. Since different theoretical models have different degrees of accuracy in describing factors (2) and (3) above, it is therefore difficult to justify the validity of factor (1). In the present calculation, point (3) above has been taken into account fairly satisfactorily. This is because charge transfer polarisation is already treated in our self-consistent CNDO calculation. Therefore, the minimum total energy found will include terms which allow net charges on atoms, and will place these charge entities in the appropriate positions. However, the long-range effects of charges are neglected here. The validity of the approximation depends on the size of the cluster chosen. The restriction we made on the relaxation of atoms in the second, third, etc., layers may introduce some inaccuracies in the computation.

The charge transfer we obtained ranges from 0.11 to 0.16 electronic charge. It is much smaller than the value of 0.34 electronic charge quoted by Chadi. The calculated values of the relaxation of the surface layer atoms of the 2×1 asymmetric dimer structure together with other previous theoretical results are summarised in table 4. They are consistent with each other at least qualitatively. The values obtained by Weber using a cluster of ten layers with all 326 atoms undergoing relaxation are quite different from

Table 4. Calculated relaxations Δx_1 , Δx_2 , Δz_1 , Δz_2 of surface layer atoms for a (2×1) dimerised reconstructed surface, together with other theoretical results.

Displacement	Pauling and Herman [10]	Chadi ^a [9]	Yin and Cohen ^b [8]	Verwoerd [25]	Present work
Δx_1 (Å)	0.55	0.46	0.573	0.51	0.38
Δx_2 (Å)	-0.95	-1.08	-1.038	-0.97	-1.121
Δz_1 (Å)	-0.12	+0.04	-0.159	-0.07	-0.055
Δz_2 (Å)	-0.39	-0.44	-0.468	-0.55	-0.592

^a Atomic displacement up to fifth layer.

^b Atomic displacement up to fourth layer.

Table 5. Results of atomic relaxation of surface layer atoms for $2 \times 2A$, $2 \times 2B$, $2 \times 2C$ and $2 \times 2D$, 4×1 and 4×2 reconstructed surfaces.

Displacement	$2 \times 2A$	$2 \times 2B$	$2 \times 2C$	$2 \times 2D$	4×1	4×2
Δx_1 (Å)	0.38	0.46	0.38	0.38	0.38	0.38
Δx_2 (Å)	-1.152	-0.998	-1.075	-1.075	-1.152	-1.152
Δz_1 (Å)	-0.055	-0.081	-0.055	-0.055	-0.055	-0.055
Δz_2 (Å)	-0.65	-0.44	-0.527	-0.527	-0.65	-0.65

those presented here. We tabulate our calculated results of Δx_1 , Δx_2 , Δz_1 and Δz_2 of outermost layer atoms for $2 \times 2A$, $2 \times 2B$, $2 \times 2C$, $2 \times 2D$, 4×1 and 4×2 reconstructed surfaces in table 5. These results are in general agreement with the observation of ion channelling and blocking experiments [5] that the surface atoms are displaced more than 0.45 Å in the surface dimer direction. In general, there is a tendency for the most stable configuration to have a shortest dimer length. Since the dimer length and the amount of inward displacement toward the bulk (z -direction) are different, the strain energy induced by the reconstruction of the surface is different for different configurations.

4. Conclusion

Among the seven asymmetrical dimer configurations considered, 4×1 and 4×2 are energetically more favourable, followed by $2 \times 2A$ and 2×1 . The total energies per dimer of these four structures are reasonably close to each other and thus the appearance of a disorder mixture of these structures at the Si(100) surface is possible. Our findings agree well with other theoretical work and experimental results. Our results also show close similarity with those obtained by Needels *et al* [14] in their calculation for Ge(100) surface reconstruction using the *ab initio* molecular dynamics approach. They found that the 4×2 reconstructed structure is energetically more favourable than 2×1 by 0.05 eV per dimer. We also support the scanning tunnelling microscopic observations by Tromp *et al* [7] that more than one type of reconstruction occurs simultaneously on the same surface. However, in our calculation, the total energy per dimer of all the seven asymmetric dimer configurations considered is much lower than the value of -0.745 eV of the symmetric dimer. This disagrees with Tromp *et al*'s observation that both sym-

metric and asymmetric dimers were present in the Si(100) surface. This is probably due to the contribution of defects, which occur in rather large numbers in Tromp *et al*'s experimental sample, but which is not taken into account in our theoretical model. The reconstructed 4×1 configuration has not been observed experimentally. More experimental and theoretical work will be necessary for the confirmation of the 4×1 configuration result.

We have demonstrated that CNDO is a useful total energy algorithm for the determination of the stable reconstructed configurations. It may well be used to assist experimentalists for quick checking in their research planning.

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