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LETTER TO THE EDITOR

Total energy calculations of missing dimer reconstructions on the silicon (001) surface

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Abstract. Total energy pseudopotential calculations of missing dimer reconstructions on the Si(001) surface are presented. We have calculated the energy of the ideal unreconstructed surface and the energy of the (2×1) symmetric dimer, the (2×4) single missing dimer, the (2×2) single missing dimer and the (2×4) double missing dimer reconstructions. Our calculations give the (2×1) symmetric dimer reconstruction as the lowest energy surface of those considered. The double missing dimer reconstruction is very high in energy. The energy cost of removing one line of dimers in every four to form a (2×4) single missing dimer reconstruction is only 0.28 eV per dimer removed. Thus single missing dimer defects are either low-energy structural excitations or possibly a feature of the ground state of the silicon (001) surface.

The silicon (001) surface has been studied intensively for the past thirty years. Interest in this surface derives from its importance to device physics and the apparent simplicity of the reconstruction which has made it an ideal test case for theoretical and experimental work. Schlier and Farnsworth (1959) suggested that the basic unit of the reconstruction is a (2×1) unit cell formed by surface atoms moving together in pairs to form dimers. The driving force for the formation of dimers is the elimination of dangling bonds from the surface atoms. This structural feature has been broadly confirmed by scanning tunnelling microscopy (Tromp *et al* 1985). However, a number of experiments have indicated the presence of larger periodicities such as c(4×2) (Lander and Morrison 1962), c(4×4) (Kato *et al* 1988), c(8×8) (Muller *et al* 1984) and $(2 \times n)$ where n is between about 6 and 11 (Aruga and Murata 1986, Martin *et al* 1986, Rohlfing *et al* 1988).

It is important to understand what structural features of the surface give rise to these larger periodicities. It is also important to determine which, if any, of all these reconstructions is the true ground state of the surface. In this Letter we study a class of reconstructions that could give rise to some of these larger periodicities; the so-called missing dimer reconstructions.

Pandey (1985) suggested that it might be energetically favourable to remove some of the dimers from the surface. His idea was that the removal of a dimer would allow rebonding of the atoms below to eliminate two dangling bonds for every dimer removed. This rebonding introduces strain into the system which limits the number of dimers that can be removed to a small fraction of the total number. A repulsive interaction between the missing dimer defects along the rows of dimers arising from the strain energy could lead to an ordered array of defects that might explain the observed $(2 \times n)$ periodicities.
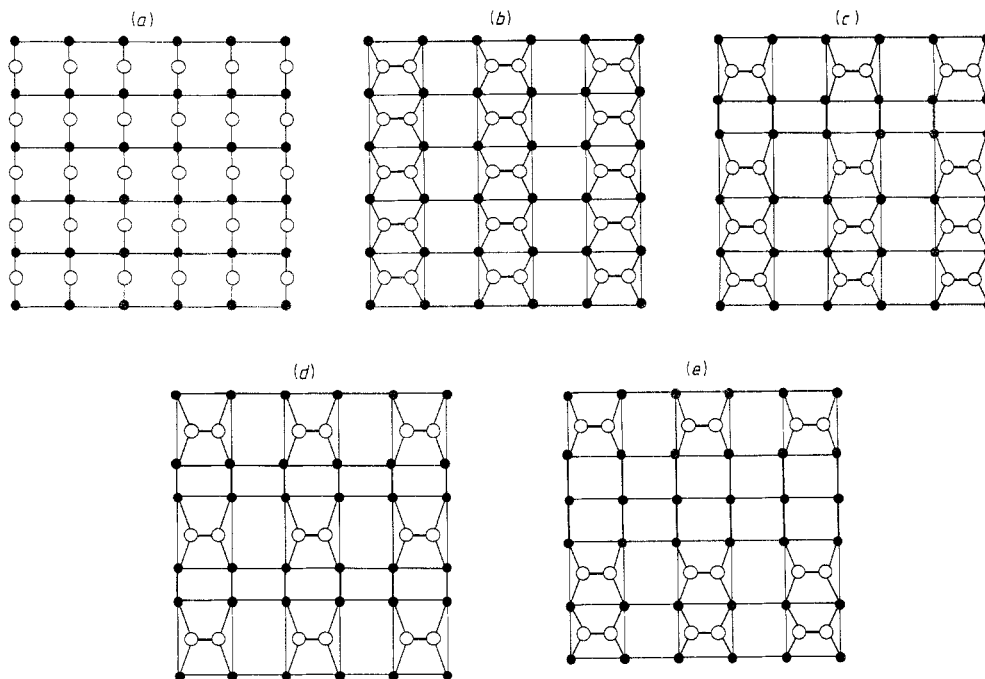
Figure 1. Plan views of the surfaces for which we have calculated the total energy. Open circles represent atoms in the surface layer and full circles represent atoms in the second layer. (*a*) The unreconstructed surface. (*b*) The (2×1) symmetric dimer reconstruction. (*c*) The (2×4) single missing dimer reconstruction. (*d*) The (2×2) single missing dimer reconstruction. (*e*) The (2×4) double missing dimer reconstruction.

Scanning tunnelling microscopy (STM) work has demonstrated that some of the dimers are missing from the (001) surfaces of silicon that have been studied (Tromp *et al* 1985, Nogami *et al* 1988).

In this Letter we present calculations of the total energy of ordered missing dimer reconstructions of the silicon (001) surface. For our calculations we have used the pseudopotential total energy technique, norm-conserving pseudopotentials and the local density approximation for the exchange–correlation energy. The calculations were performed in reciprocal space with a plane-wave basis set, including all waves with kinetic energies less than 6 Ryd. We used a super-cell geometry with ten layers of atoms separated by the equivalent of six atomic layers of vacuum. Brillouin zone integrations were performed with eight special k-points in the irreducible wedge for the (2×1) symmetric dimer surface. To ensure that the energies of all the structures could be compared, care was taken to use exactly equivalent sets of k-points for each of them. For instance, because of the lower symmetry and larger size of the unit cell, the exactly equivalent Brillouin zone integration for the (2×4) single missing dimer surface required four special k-points. The total energy and forces on the atoms were calculated and the structures were relaxed by moving the atoms in the direction of the forces. This relaxation process was repeated until the calculated forces on the atoms were negligible.

We have calculated the energy of the ideal unreconstructed surface, the (2×1) symmetric dimer, the (2×4) single missing dimer, the (2×2) single missing dimer and the (2×4) double missing dimer reconstructions. Figure 1 shows plan views of each of

Table 1. The energies of the five surfaces depicted in figure 1, taking the unreconstructed surface as the zero of energy. In each case the energies are in units of eV for a (2 × 4) cell.

Reconstruction	Energies of a (2 × 4) unit cell
(2 × 1) symmetric dimer	−8.08
(2 × 4) missing dimer	−7.80
(2 × 2) missing dimer	−5.88
(2 × 4) double missing dimer	−1.49
Unreconstructed	0.00

these surfaces and table 1 gives the energy of a (2 × 4) cell made up of them, using the unreconstructed surface as the zero of energy.

The starting atomic coordinates for the (2 × 1) symmetric dimer model (figure 1(*b*)) were taken from the work of Appelbaum and Hamann (1978) and included distortions of up to five layers into the bulk. When we relaxed this structure the final dimer bond length was 2.23 Å, about mid-way between single and double bond lengths. The back-bond lengths (between the dimer atoms and those in the layer below) were also slightly shortened from the bulk value of 2.35 Å to 2.29 Å and the vertical separation between these layers was reduced from the bulk value by 0.33 Å. We found that this reconstruction lowered the energy by 2.02 eV per dimer compared with the ideal unreconstructed surface. This can be compared with the value of 2.06 eV calculated by Pandey (1985).

In Pandey's missing dimer model, a dimer is removed from the surface; beneath this defect the second-layer atoms move together and form a weak bond. This removes two dangling bonds per defect at the expense of some strain energy. The neighbouring surface dimers in the row are pulled downwards into the surface, increasing the π-bonding between the atoms in these dimers, and further reducing the energy. Our starting coordinates were taken from the diagram in Pandey's paper (Pandey 1985) and we used a (2 × 4) geometry (figure 1(*c*)), following his suggestion that removing one dimer in four was likely to minimise the energy, trading off the advantages of removing dangling bonds against the cost of strain energy. This gives a unit cell of volume equivalent to 128 bulk silicon atoms. All the atomic positions were fully relaxed. To compare the energy of this reconstruction with that of a surface without missing dimers we considered that the atoms removed from the surface contributed the same energy as bulk atoms. The bulk energy per atom was determined by a separate total energy calculation. We found that it *cost* 0.28 eV per defect to create the missing dimer surface, as opposed to Pandey's estimate of at least 2 eV *gain* (Pandey did not perform energy calculations on this structure). In our optimal missing dimer structure the neighbouring dimers were pulled downwards (relative to their positions on the (2 × 1) symmetric dimer surface) and towards the defect, shortening these dimer bond lengths to about 2.19 Å and indicative of increased π-bonding between the atoms forming the dimer. The exposed second-layer atoms beneath the defect were depressed and pulled together until separated by only 2.71 Å indicating that a strained bond had been formed between them.

We have also calculated the energy of a relaxed surface in which one dimer in every two had been removed (figure 1(*d*)) to give a (2 × 2) unit cell. The energy of this structure was 2.20 eV per (2 × 4) unit cell higher in energy than the (2 × 1) symmetric dimer structure. Presumably this is because of the large strain energy of this structure.

The strain energy of the (2 × 4) single missing dimer structure may still be fairly large but our computational resources would not allow us to calculate the energy of larger unit

cells. Our results indicate that the strain energy of the (2×4) single missing dimer structure is considerably less than that of the (2×2) single missing dimer structure. The strain energy of the (2×4) structure may still be fairly large and it is likely that the removal of a still smaller fraction of dimers will cost even less energy or may even result in a lower energy than the (2×1) symmetric dimer surface. Other factors may also favour reconstructions involving the removal of dimers from the surface. STM images indicate that buckled dimers may be associated with missing dimer defects on the surface (Tromp *et al* 1985). In our calculations buckling of the dimers was not allowed, inclusion of buckling effects might further lower the energy of the missing dimer structures. Also there are other configurations of missing dimers that we have not investigated which may be low in energy. In our calculations complete lines of dimers were removed in the directions perpendicular to the rows, but there are many other possible missing dimer reconstructions where the dimers are removed in some other pattern. Indeed Kato *et al* (1988) have interpreted their LEED data to indicate a c(4×4) pattern of missing dimers where the dimers are removed in a more complicated way. However all this may turn out, we have clearly established that the removal of single dimers from the surface is either a low-energy structural excitation or possibly a feature of the ground state of the silicon (001) surface.

Our final calculations were for a double missing dimer defect. Recently it has been suggested (Rohlfing *et al* 1988) that the basic unit consists of a pair of adjacent missing dimers (figure 1(e)). We have calculated the energy of a (2×4) array of double missing dimer defects. In this structure the second-layer atoms were not able to rebond properly. Removing two adjacent dimers along the dimer row exposes three pairs of atoms in the layer below, but it does not seem possible to form two sets of symmetric bonds between these atoms as suggested by Rohlfing and co-workers because of the large strain energy involved. We found that symmetry was broken, the central pair of exposed second-layer atoms moving to one side of the defect to bond to the pair of second-layer atoms there, severing any connection with the second-layer atoms on the other side of the defect. We found that this structure was 6.59 eV per (2×4) unit cell higher in energy than the (2×1) symmetric dimer structure. It is possible that a lower density of double missing dimer defects will allow the second-layer atoms to rebond properly but this seems rather unlikely.

In summary, we have calculated the energy of a number of dimer reconstructions on the silicon (001) surface. The lowest in energy of these is the (2×1) symmetric dimer surface. The double missing dimer defect appears to be very high in energy, but single missing dimer defects are much lower in energy. The removal of half of the dimers from the (2×1) symmetric dimer surface in an ordered (2×2) array costs 2.20 eV per (2×4) unit cell. The energy cost to remove one quarter of the dimers in an ordered (2×4) array is only 0.28 eV per (2×4) unit cell. From this we conclude that it is possible that the true ground state of the surface consists of an ordered array of single missing dimers of density less than 0.25.

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