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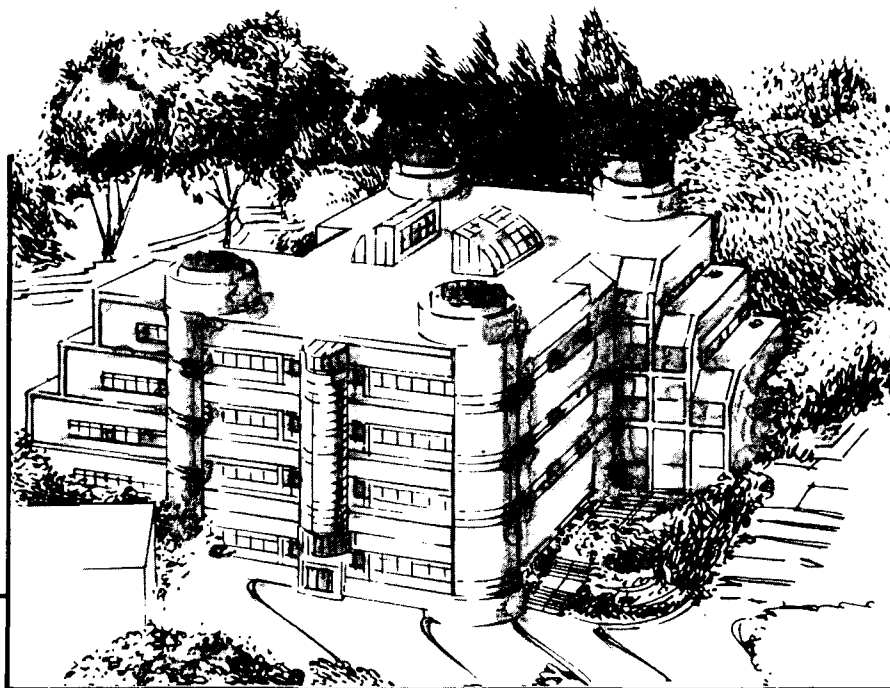
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## Prediction of the Effect of the Sample Biasing in Scanning Tunneling Microscopy and of Surface Defects on the Observed Character of the Dimers in the Si(001) (2x1) Surface

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**PREDICTION OF THE EFFECT OF THE SAMPLE BIASING  
IN SCANNING TUNNELING MICROSCOPY  
AND OF SURFACE DEFECTS  
ON THE OBSERVED CHARACTER OF THE DIMERS  
IN THE Si(001) (2x1) SURFACE**

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**Abstract.**

Self-consistent quantum chemical cluster calculations are reported which address the controversy about the presence or absence of dimer buckling in the Si(001)-(2x1) reconstructed surface. The results indicate that biasing the surface, as in the scanning tunneling microscopy (STM) experiment, is likely to produce a relatively symmetric STM image even if dimers in the unbiased surface are buckled, as deduced from scattering experiments. We have also investigated a dimer close to a surface defect, such as a step, and propose a mechanism which makes the dimer there appear buckled to STM.

After the experimental observation of a (2x1) surface structure by low-energy electron diffraction (LEED) on Si(001), the suggestion was first made by Schlier and Farnsworth and then rediscovered by Levine [1] that the pairing of surface atoms brought about by the linking up of dangling bonds to create surface dimers is responsible for the reconstruction. Starting from this simple idea, a great deal of effort, both experimental and theoretical, has been spent on attempts to obtain a clear picture of the character of these dimers [2]. The results are nevertheless not conclusive. Scattering experiments like LEED [3-7] and ion beam channeling and blocking [8] are strongly in favour of buckled dimers. More recent scanning tunneling microscopy (STM) images [9], however, revealed patterns which were identified as due to symmetric dimers in the regions away from the surface defects such as steps and due to buckled dimers close to the defects. Finally, core level shift measurements [10,11] interpreted according to the STM images indicate that surface dimer atoms from both symmetric and asymmetric dimers have to contribute to the underlying peak. However, the fact that only one relevant peak is seen in the experiment suggests that the core level shifts do not really distinguish between the two types of dimers.

The theoretical calculations are not conclusive either. Apart from the first calculations which assumed symmetry [12], until recently most calculations [13-17] were mainly in favour of asymmetric dimers. Nevertheless, already several years ago [14,18] it was pointed out that this result could be connected with the type of many-electron wave function used in the calculations. The connection was fully discussed by Verwoerd [13,14] who showed that a triplet wave function (which mimics the spin correlation of a full open shell wave function) results in a symmetric dimer with a slightly lower energy than that calculated

for the closed shell asymmetric dimer. At the time, the significance of this was unclear since the relevant energy difference was within the limits of a systematic underestimation of the energy of open shell states by the MINDO/3 [19] calculation method employed. A basically similar conclusion regarding ordering of the two types of dimers on the energy scale was recently obtained from a first-principle pseudopotential total energy study [20]. On the other hand, an ab initio Hartree-Fock (H-F) cluster calculation by Artacho and Yndurain [21] of a triplet state similar to the one used in ref. 14 gave a symmetric state 1.3 eV below the asymmetric (buckled) closed shell state. This large difference in energy that favours the symmetric dimer structure does not agree with the experimental findings. Scattering experiments favour buckled dimers, while STM finds both symmetric and asymmetric dimers in comparable numbers. Instead the near degeneracy found in the MINDO/3 calculation [13,14], in the tight binding calculations [22] and in the very recent first-principle pseudopotential total energy study [20] appears more plausible. The reason for the discrepancy was fully discussed in ref. 14: pure H-F calculations overestimate the Coulomb repulsion in the doubly occupied orbital of the asymmetric dimer because of the neglect of the intra-atomic correlation. In the MINDO/3 method this is taken care of by a suitable parametrization. Similarly, the pseudopotential calculations use an exchange term which, although local, represents not only exchange but also dynamical correlations which are here responsible for the reduction of the relevant intra-atomic Coulomb repulsion energy.

Bearing the above in mind, we believe that the present theoretical total energy studies cannot conclusively decide in favour of either type of dimers in the (2x1) reconstructed Si(001) surface. On the other hand, the strong sup-

port of LEED and ion scattering results makes us believe that the asymmetric (buckled) dimer model is the correct structural model of the Si(001)-(2x1) reconstructed surface. However, a very small energy difference between the two dimer configurations obtained in most total-energy studies indicates that experimental artifacts as well as slight imperfections in the surface itself can easily influence the resulting experimental image of the surface. This situation leads to interesting questions: What makes scattering results disagree with the STM images of the Si(001)-(2x1) surface? Why do the STM topographs show symmetric dimers in most parts of the surface, but not everywhere? The aim of this paper is to propose answers to the above questions, rather than to make yet another attempt to theoretically determine the character of the dimers.

In principle the symmetric STM image can be caused by the thermally activated random flipping of buckled dimers, with the underlying phonon frequency sufficiently high that the STM averages over the two configurations. One can then expect that near defects the two bucklings have different energies due to stress and flipping is suppressed. This dynamical aspect of the surface image has been recently addressed by Weakliem, Smith and Carter [23]. Nevertheless we believe that the simple mechanical model is here not quite sufficient. For instance, according to its reasoning one should not expect observed large buckling in the STM images of dimers which are close to and in the same dimer row as a missing dimer type defect. Moreover, the existing total energy calculations strongly suggest that there is at least a local minimum in total energy realised by symmetric dimers. This in turn indicates that in the presence of flipping a substantial fraction of the dimers should indeed be symmetric. The presence of (metastable) symmetric dimers in the surface should then influence



the dynamical LEED results.

In view of the above, we believe that an investigation which takes into account possible interaction between the surface and the tip should be of interest. We approached the issue by investigating how the character of the dimer can be influenced by the presence of an STM tip close to the sample and by the sample biasing. To this end, we performed a set of self-consistent quantum chemical MINDO/3 [19] cluster calculations modelling a Si(001) surface dimer as well as the dimer in the vicinity of a carbon whisker imitating the end of an STM tip.

MINDO/3 cluster calculations have been proven to produce particularly good results when modelling Si surfaces [13,14,24-26]. From the point of view of the present work, MINDO/3 is also particularly useful in that, in the geometry optimization performed within this method, both symmetric and buckled dimers represent local minima of the surface energy. This allows for the comparative analysis of the two types of dimers in the presence of a cluster of atoms representing the end of an STM tip as well as in the case when there is an external biasing voltage applied to the surface. As both closed-shell and open-shell electronic states of the substrate-tip system could be relevant for the results, in the electronic structure calculations the two types of states had to be treated equally. In order to do so we used unrestricted Hartree-Fock calculations throughout.

To model the surface dimer interacting with an unbiased tip we chose the  $\text{Si}_9\text{H}_{12}$  cluster described earlier [13]. When investigating a biased surface we also used a larger  $\text{Si}_{15}\text{H}_{16}$  cluster which contains two surface dimers.

First, we looked at the interaction energies between the approaching un-

biased tip and the dimer. Knowing that the atomic-resolution tips are often terminated by graphitic protrusions [27] we tried several predominantly carbon clusters as models of a tip interacting with the surface. The results were independent of the particulars of the tip and showed that without biasing, the tip – surface interaction does not differentiate between the two ends of the dimer (different if the dimer is buckled) and therefore cannot affect the character of the dimer significantly enough to produce symmetric STM images of otherwise buckled dimers.

Having ruled out the direct influence of the tip, we further investigated how biasing the surface can influence the character of the dimer. To do so we compared the results for electrically neutral and electrically charged  $\text{Si}_9\text{H}_{12}$  clusters (modelling one surface dimer) and, bearing in mind that charging a small cluster may produce an unrealistic model of surface biasing, we also investigated the larger  $\text{Si}_{15}\text{H}_{16}$  cluster (modelling two parallel surface dimers). The conclusions which we subsequently make about the surface refer only to those results which were found independent of the cluster size.

Charging the  $\text{Si}_9\text{H}_{12}$  cluster by  $\pm e$  changed the energy of the highest occupied molecular orbital (HOMO) by about  $\mp 4.3$  eV. The charging of the cluster and the associated HOMO energy change can be regarded as resulting from biasing the sample by an external potential of  $\pm 4.3$  V. The same argument applied to the larger cluster indicates that charging it by  $\pm e$  can be associated with biasing by  $\pm 3.4$  eV.

Our calculations are confined to these particular values of the biasing poten-

tial. Nevertheless, the results are expected to be meaningful since our values are close to a typical biasing voltage used to obtain the STM images on Si surfaces [9].

At this point one could still argue that biasing the sample might lead to charging by only a minuscule fraction of an electron per surface atom. Therefore small clusters charged by a full electron charge would be unrealistic. Somewhat surprisingly, our results suggest otherwise, at least for biasing of the Si(100) surface. The calculated electronic structure of the charged cluster  $\text{Si}_{15}\text{H}_{16}$  indicates that, instead of occupying a delocalized surface state, the additional electron (or its absence) influences mainly the local electronic structure of a single dimer. In the cluster containing two dimers one dimer changes its character due to cluster charging, while the other dimer is to a large extent unaffected. The results listed in tables 1 and 2 further show that the change in the affected dimer (the one below the tip) is fairly independent of the biasing potential and that it corresponds to substantial decreases of both buckling and charge asymmetry within the affected dimer.

When the sample is negatively biased (tunneling from the sample), the additional electron generates a single occupation of a molecular orbital which is to a large degree localized on the lower atom in the buckled dimer. As this orbital is now the HOMO, the relative probability of tunneling to the tip from the lower atom in the dimer is increased, a feature which together with the reduced buckling is likely to produce an STM image with relatively symmetric dimers, even if the dimers in an unbiased surface are buckled. With a positive bias (tunneling towards the sample), the lowest unoccupied molecular orbital (LUMO) stays lo-

calized mainly on the lower atom in the dimer which is again likely to produce a symmetric STM image.

At this point one could still raise the objection that a well localized additional electron (or its absence) is a source of Coulomb repulsion and therefore should be energetically unfavourable. In our calculations this effect is reduced by the suitable adjustment of the polarization of the back bonds. The net result is such that even though the additional electron is predominantly localized on one atom, the net charges on this and the surrounding atoms are affected by only a small fraction of the electron charge. As one would expect, a relatively large portion of the additional charge (about  $0.4e$  in total) can be found on the hydrogen atoms saturating the clusters.

The calculated result is in fact not as unexpected as it may seem at first. It is basically consistent with the observed tendency in Si to lower the energy of dangling bonds by the asymmetrical reordering of the electronic structure, the phenomenon which leads for example to buckled chains in the  $(2\times 1)$  reconstructed Si(111) surface or to buckled dimers in the (100) surface.

The way in which biasing affects the dimers changes considerably when the second-layer Si atoms are not 4-fold (bulk-like) coordinated, a situation which one expects in the vicinity of surface steps and defects of the missing-dimer type. We modelled this case by removing hydrogen atoms which imitate first-layer atoms and saturate Si atoms A and B (cf. fig. 1) in the  $\text{Si}_9\text{H}_{12}$  cluster. In this respect we also investigated  $\text{Si}_{15}\text{H}_{16}$  clusters similarly depleted of two H atoms.

The results presented in table 3 show that, even though the contrary is true for the unbiased and for the positively biased surfaces, the negative biasing of the sample should substantially increase buckling next to a missing dimer defect as well as next to a step.

In addition to the isolated charged clusters we also investigated charged clusters about  $10\text{\AA}$  below oppositely charged ions. This arrangement could be regarded as a crude model of a polarized tip interacting with the sample. The results were basically the same as for the isolated clusters, with the addition that in the  $\text{Si}_{15}\text{H}_{16}$  cluster the affected dimer was the one nearer to the ion. This was however not the case for the  $\text{Si}_{15}\text{H}_{14}$  cluster (modelling two dimers in the vicinity of a missing dimer). Here we found that for the ion above either of the two dimers, the affected dimer was always the one next to the defect, which in turn left the other dimer considerably buckled (as in the unbiased surface). These results can then explain why the STM images show symmetric dimers on the flat parts of the  $\text{Si}(001)$  surface and a row of few buckled dimers close to each surface step and defect.

In summary, we have shown that even though the mere presence of an STM tip in the vicinity of the dimers is not likely to influence the character of the dimers, biasing a sample, like in an STM experiment, can visibly influence the resulting surface image. In the case of the  $(2\times 1)$  reconstruction of the  $\text{Si}(001)$  surface this means that one can expect STM images to show symmetric dimers even if the dimers in the unbiased surface are buckled.

We have also presented a possible explanation of why the STM images show

buckled dimers in the vicinity of defects and simultaneously symmetric dimers on the flat parts of the surface. The result is associated with the presence of the dangling bonds on the second-layer atoms, which together with negative sample biasing contribute to the substantial enhancement of the buckling of the neighbouring surface dimers. This mechanism is independent of the possible subsurface stress, which can be expected at the vicinity of the double steps (due to asymmetry caused by dimerization at the lower/upper terrace), but should not appear close to an isolated missing-dimer defect.

The analysis presented here concentrates on the particular Si(001) surface. The results are however of more general relevance. They show that while analysing surface images one should be aware of the fact that biasing the surface can locally influence the surface electronic structure to an extent observable in the resulting geometry. Moreover, a particular surface feature can be influenced in qualitatively different ways depending on its local environment. Further work which aims at self-consistent calculations of the patterns of STM currents is in progress.

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**Table 1.** Buckling  $\Delta h$  in Å and net charges on dimer atoms in charged  $\text{Si}_9\text{H}_{12}$  clusters.  $Q(\text{high})$  and  $Q(\text{low})$  denote net charges on the two surface atoms forming a buckled dimer.

Charge	$Q=0$	$Q=-1$	$Q=+1$
$\Delta h$	0.48	0.24	0.23
$Q(\text{high})$	-0.11	-0.15	0.11
$Q(\text{low})$	0.34	-0.04	0.34

**Table 2.** Buckling  $\Delta h$  in Å and net charges on dimer atoms in charged  $\text{Si}_{15}\text{H}_{16}$  clusters.  $Q(\text{high})$  and  $Q(\text{low})$  denote net charges on the two surface atoms forming a buckled dimer.

Charge	$Q=0$	$Q=-1$	$Q=+1$
$\Delta h^\dagger$	0.49	0.23	0.24
$Q(\text{high})^\dagger$	-0.11	-0.13	0.10
$Q(\text{low})^\dagger$	0.34	-0.01	0.31
$\Delta h^\ddagger$	0.49	0.49	0.49
$Q(\text{high})^\ddagger$	-0.11	-0.16	0.04
$Q(\text{low})^\ddagger$	0.34	0.30	0.33

† Dimer affected by charging the cluster.

‡ The other dimer in the cluster.

**Table 3.** Buckling  $\delta h$  in Å and net charges on dimer atoms in charged  $\text{Si}_{15}\text{H}_{14}$  clusters modelling two dimers at a step. Q(high) and Q(low) denote net charges on the two surface atoms forming a buckled dimer.

Charge	Q= 0	Q=-1	Q=+1
$\Delta h^\dagger$	0.00	0.60	0.23
Q(high) <sup>‡</sup>	0.04	-0.19	0.05
Q(low) <sup>‡</sup>	0.03	0.26	0.28
$\Delta h^\dagger$	0.49	0.50	0.48
Q(high) <sup>‡</sup>	-0.09	-0.16	-0.04
Q(low) <sup>‡</sup>	0.31	0.29	0.33

† Dimer next to the step.

‡ The other dimer, separated from the step by the first one.

## FIGURE CAPTION

**Figure 1.** Clusters  $\text{Si}_9\text{H}_{12}$  (a) and  $\text{Si}_{15}\text{H}_{16}$  (b) modelling one and two surface dimers, respectively. Hydrogen atoms saturating the silicon are not shown. The second-layer atoms referred to in table 3 are represented by the full circles.

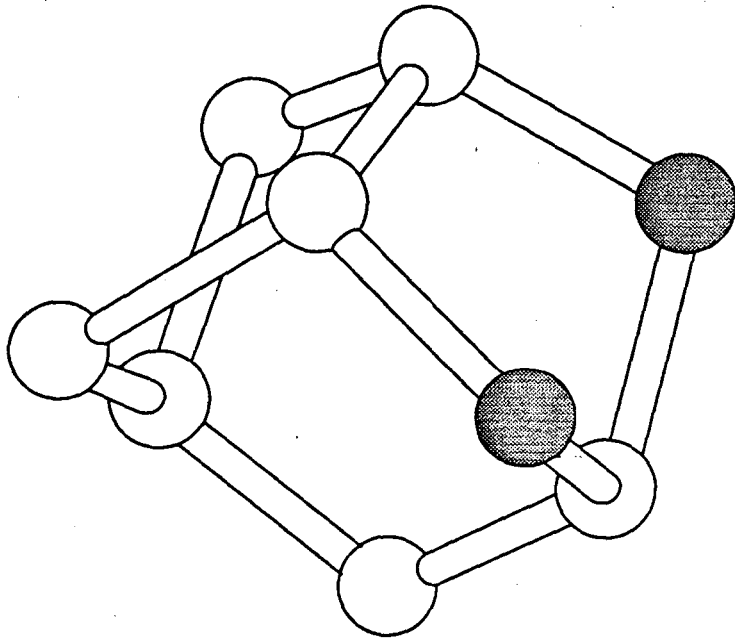


Figure 1(a)

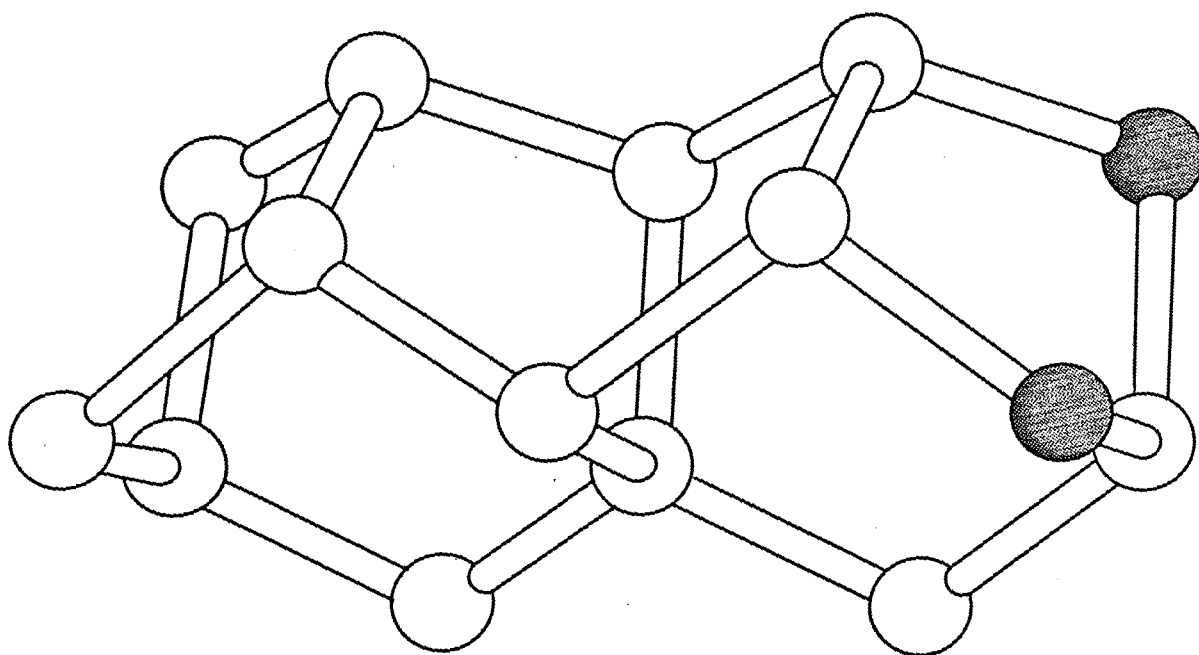


Figure 1(b)

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