

## The effect of the STM tip on Si(100) reconstructed surfaces

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Received 18 August 1992, in final form 23 December 1992

**Abstract.** We present a theoretical study of the effects of the STM tip on the geometry of Si(100) reconstructed surfaces. The energy barrier to switching between different reconstructions is also discussed. We use a molecular dynamics method and self-consistent forces to simulate the time-dependent behaviour of the surface atoms. The molecular orbital calculations are performed at the CNDO level using a cluster model. Our results indicate significant differences for positively and negatively biased tips. The thermally induced rocking of surface dimers is inhibited by the application of a positive bias to the tip and it is promoted by a negative bias. These bias-dependent effects may offer a plausible explanation for the bias dependence of STM images of this surface.

### 1. Introduction

The scanning tunnelling microscope (STM) has led to several developments in surface science. It has provided remarkable images of surfaces which contain structural information, and sometimes—as for the (100) surface of silicon—structural puzzles. The tunnelling microscope offers a means to manipulate the surface too: so-called nano-writing is one example; molecular switches are another. Clearly it is possible for the STM tip to affect the surface, for example the surface structure, in a way which means that it does not act as a totally benign observer. Such effects have been discussed by several authors [1–3]. Our present study shows a somewhat different effect, and one which may help to interpret some of the experimental results for Si(100) surfaces. The novel feature to emerge is the effect of the tip on the surface vibrational resonance whose existence was recognized over a decade ago [4]. This, in turn, relates the observations of dimers in the  $(2 \times 1)$  and related reconstructions, and the question of whether they are symmetric or not, and whether this depends on the tip. But there are more general implications too, and these are illustrated by our calculations. First, there is the question of when a static calculation of a reconstruction is adequate and when a dynamic calculation is needed. Secondly, the STM tip can be an active probe, applying a controlled, local, perturbation such that the system can be manipulated through interesting regions of its configuration space. The perturbation (as we have noted before) contains an important part of the electric field, in addition to short-range repulsions. Obviously, the extent to which that can yield quantitative information about an energy surface will depend on knowledge of the tip structure, and that is rarely available, but the opportunity exists in principle.

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Dimers (the bonding of surface silicon atoms in pairs) are key components of the reconstructions of the (100) surface. The simplest of such reconstructions is  $(2 \times 1)$ , with the dimers parallel to the surface. In this configuration the dimers are said to be symmetric. Experiments using low energy electron diffraction (LEED) [5, 6] and ion beam scattering [7] show the presence of  $p(2 \times 2)$  and  $c(4 \times 2)$  reconstructions as well as  $(2 \times 1)$ . The discovery of surface periodicities larger than  $(2 \times 1)$  strongly supports a buckled dimer structure. High-resolution photo-emission data [8] reveal two inequivalent types of surface atoms, also consistent with buckled dimers. In contrast, most of the dimers appear to be symmetric in STM images of Si(100) [9, 10] and it is only near isolated defects (generally believed to be dimer vacancies) that they appear to be tilted. A recent variable-temperature STM experiment [11] revealed a growing number of buckled dimers on cooling. The observed temperature-dependent growth of buckled-dimers domains suggests an asymmetric character for the Si(100) dimers. Their symmetric appearance in STM images at room temperature is probably due to a thermally-induced rocking, or flipping, between two equivalent buckled configuration as suggested by Hamers *et al* [10]. Nevertheless, the bias-dependent images obtained by Hashizume *et al* [12] remain a puzzle. Our discussion of tip-influenced dynamics may be a part of the explanation, but the situation remains complex.

A substantial theoretical study has emerged in parallel with experiment. In the earlier calculations the dimers were assumed to be symmetric [13, 14]. However, total energy calculations based on tight-binding [15], modified intermediate neglect of differential overlap (MINDO) [16], complete neglect of differential overlap (CNDO) [17] and pseudopotential [18–20] methods have shown that an asymmetric dimer structure is energetically more stable. However, *ab initio* calculations incorporating spin effects led Artacho and Yndurain to propose the symmetric dimer structure as the most stable [21]. Recent *ab initio* molecular dynamics simulations revealed the formation of symmetric and buckled dimers among other defects (e.g. interstitial dimers) [22].

The reason for these contradictory results is not clear, so it is hard to interpret STM images based on these results. Besides, they ignore the presence of a non-uniform electric field due to the STM tip, and this is likely to affect the atoms being imaged. This concept was first suggested by Badziag *et al* [23] and later used by Badziag and Verwoerd [24] in order to reproduce the experimental spectroscopy curves. The latter results suggest a dependence of buckling on imaging bias, and our present results address this point. Recent tight-binding calculations [25] suggest that asymmetric dimers might look symmetric in STM images, and this has refuelled the controversy regarding the dimer configuration and its STM image. The calculations mentioned show that the observed reconstructions correspond to local energy minima. If the magnitude of the energy barrier between different reconstructions is small, field-assisted interconversion is likely to occur at typical STM fields.

The aim of our work is to understand the way the STM tip affects the geometry of Si(100) surface and to assess the consequences for the STM image. One conclusion is that the effect of a negatively biased tip may be substantial, and especially through the way it influences the rocking mode of the surface dimers. This may explain in part their time-average symmetric appearance in STM experiments. There are at least three components to the interpretation of the images of tilted dimers. One concerns the several possible thermally-activated flips and their timescales relative to STM experiments. A second concerns the effects of long-range interactions between dimers, whether elastic or otherwise. We shall address a third issue here, namely the effect of the STM tip on dimer vibrational properties.

## 2. Models and methods

The approach we adopt, based on the Harwell CHEMOS code, combines self-consistent quantum chemistry and molecular dynamics. The quantum chemistry is embodied as the semi-empirical CNDO method, though we remark that our results using this relatively simple scheme agree with all other approaches (like the Car-Parrinello method [26] based on local density functional theory) where comparison can be made (e.g. our results are very similar to those of Ihara *et al* [22] so far as we can tell from published information; see also section 3.2). The relative ease of our approach means we can also exploit novel methods for finding energy surfaces and reaction paths between local energy minima, even though we cannot readily exploit symmetry. The economy of our method means that we can investigate complex situations and many different circumstances; one result is that we can also gain insight into some of the unexpected results of other calculations, e.g. the appearance of subsurface interstitials. There is a price to be paid for using simpler theories. As noted before, whilst the method we use gives good geometries, it tends to overestimate energies. We have noted before that such overestimates are systematic, so relative energies and energy barriers are reliable, but we must be cautious in comparing activation energies directly with those observed.

### 2.1. Surface model

The dimerized Si(100) surface is modelled by a cluster consisting of four layers containing 8, 12, 9 and 6 silicon atoms, respectively. The dangling bonds of the inner atoms were saturated by pseudo-hydrogen atoms. This cluster contains four surface dimers in two parallel dimer planes. The starting atomic coordinates for the experimentally observed  $(2 \times 1)$ , and  $p(2 \times 2)$  buckled dimer reconstructions were taken from the work of Ong and Chan [17], while those used to model a symmetric  $(2 \times 1)$  dimer structure were taken from the work of Roberts and Needs [20].

### 2.2. Technique

The calculations reported here represent an attempt to model quantitatively and self-consistently the effect of the STM probe on the reconstructed Si(100) surface. These calculations comprise two main steps. The first concerns the non-uniform electric field due to the STM tip. In the absence of the sample, our STM model consists of a charged spherical electrode at a given voltage, representing the tip, and an infinite, earthed, flat electrode representing the sample holder. The atoms of the sample are polarized by the electric field resulting from this configuration. The electric field experienced by each sample atom is then the sum of the applied field and that resulting from the interaction of the induced dipoles with each other and their images on both electrodes. Details of the electrostatic calculations are given elsewhere [27]. The second step consists of simulating the effect of such an inhomogeneous electric field on the surface configuration using a quantum-chemistry molecular dynamics method [28]. Here a molecular dynamical method uses self-consistent forces to simulate the time-dependent behaviour of the surface. The forces are obtained from CNDO molecular orbital calculations. This paper [28] discusses in detail the technical aspects of the program and its exploitation. For silicon we have used the CNDO parameters given by Pople and Beveridge [29] and no attempt has been made to reparametrize in order to fit particular molecular properties. The bonding parameters of the pseudo hydrogen atoms were reparametrized from those for hydrogen in order to avoid charge localization at the periphery of the cluster.

### 3. Results and discussion

#### 3.1. Surface reconstruction

Before we consider any interaction with the electric field, we have relaxed the cluster geometry, keeping only the pseudo hydrogen atoms at the edge of the cluster fixed at bulk equilibrium positions. These relaxed configurations were found by damped molecular dynamics on reducing the cluster temperature. Three dimerized structures were obtained (figure 1), corresponding to local energy minima. Asymmetric dimers were predicted for all these structures. The average dimer bond lengths are given in table 1. The values obtained by Ong and Chan [17], who used a similar cluster but only allowed the top layer of atoms to relax, are smaller than those presented here. Our results suggest dimer bond lengths larger than the bulk Si–Si spacing, in agreement with ion scattering data [30]. The interatomic spacings will not normally be the same as the separation of peaks in an STM image. As Molotkov *et al* [25] have shown, the apparent (STM) separation will normally be smaller, especially for a positive bias on the tip (negative on the sample in Molotkov *et al*'s convention).

**Table 1.** Dimer bond length and relative energies for  $(2 \times 1)$ ,  $p(2 \times 2)$  and  $p(4 \times 1)$  reconstructed Si(100) surface. The dimer bond lengths are about 6% stretched relative to bulk crystal Si–Si distance (2.35 Å). These values are longer than those given by Ong and Chang [17]. All energies are calculated relative to the energy of  $p(4 \times 1)$  reconstructed surface. These energies do not include the long-range Coulomb energies due to dimers outside the cluster considered.

Surface reconstruction	Dimer bond length (Å)	Relative energy (eV)
$(2 \times 1)$	2.512	0.84
$p(2 \times 2)$	2.520	0.73
$p(4 \times 1)$	2.491	0.0

A  $p(4 \times 1)$  buckled dimer structure was obtained spontaneously when the symmetric dimer reconstruction was allowed to relax. This result suggests that the symmetric dimer is unstable, in agreement with tight-binding calculations [31]. The formation of a  $p(4 \times 1)$  structure also suggests that this structure is energetically favourable for the cluster size used here, though it has never been observed experimentally. This is one case where cluster size is important. Taking into account the electrostatic energy due to dimers outside the cluster considered, Zandvliet [32] has shown that  $p(4 \times 1)$  is expected to be energetically unfavourable compared with  $c(4 \times 2)$  and  $p(2 \times 2)$  for real systems. Sawada's results [31] for a larger cluster confirm Zandvliet's findings.

#### 3.2. Effect of the STM electric field on surface dynamics

We have simulated the dynamical behaviour of the Si(100) reconstructed surface subject to the non-uniform electric field caused by an STM tip of 9 Å radius held 6 Å above the surface. We have considered the effects of both a positively and a negatively biased tip for a bias voltage typical of STM imaging ( $\leq 2$  V), with a few calculations at larger bias.

Our simulations were performed at constant temperature. At first we followed the same procedure as Ihara *et al* [22]. Initial atomic velocities were set by a Maxwell-Boltzmann distribution corresponding to the prescribed temperature (300 K), and the cluster temperature was maintained constant by re-scaling the atomic velocities every time-step. Our results for  $p(4 \times 1)$  buckled dimer structure suggest considerable effects on the first three layers when the tip is negatively biased (bias = 2 V). The most prominent effect predicted was

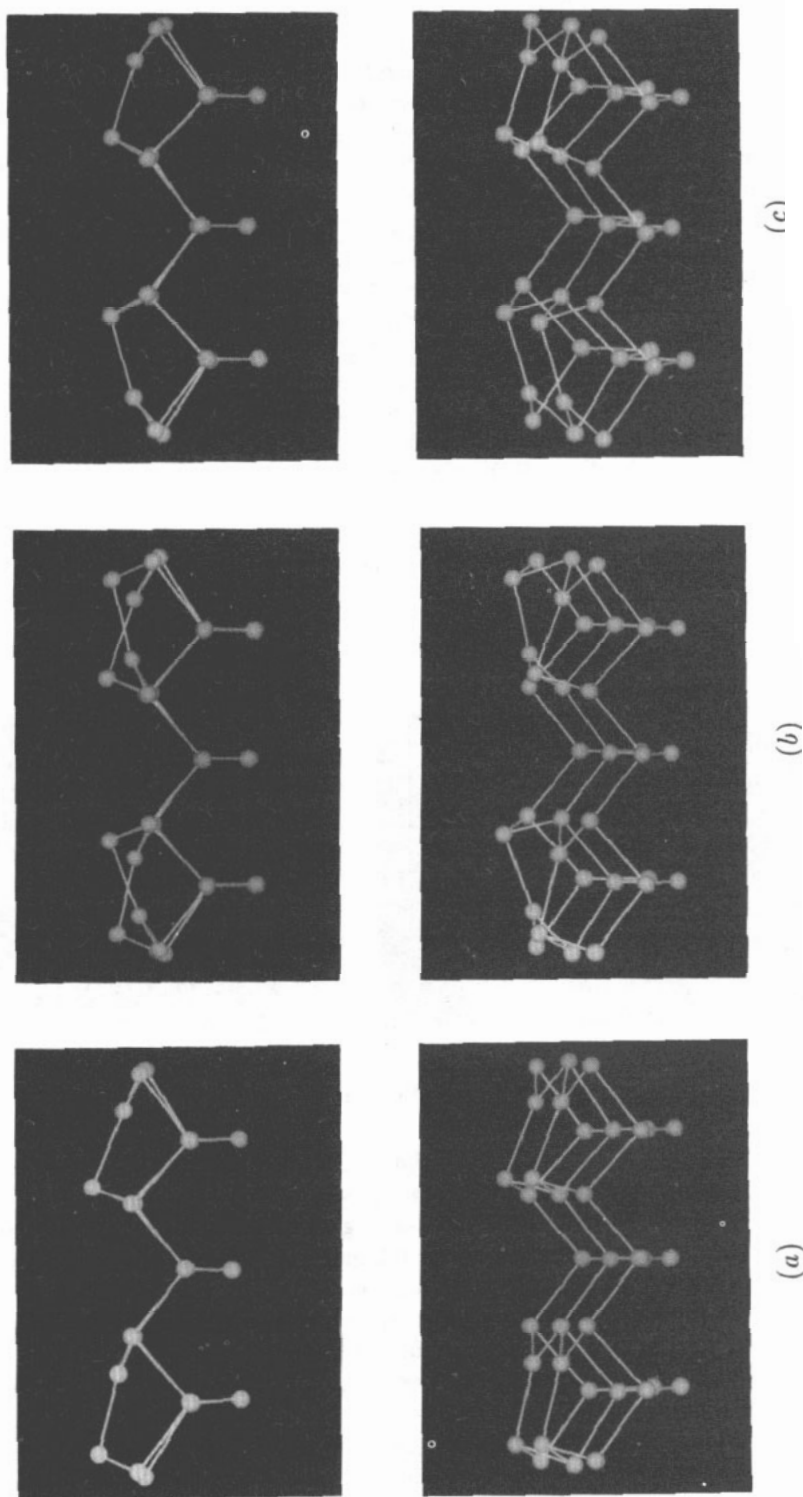


Figure 1. Si(100) surface containing (a)  $2 \times 1$ , (b)  $p(2 \times 2)$  and (c)  $p(4 \times 2)$ ; buckled dimer reconstructions

the formation of an interstitial dimer within 0.2 ps. Since Ihara *et al* [22] predicted the formation of a similar defect using an *ab initio* molecular dynamics in the absence of the STM probe, the formation of such a defect is unlikely to be either a real STM effect or an artifact of the quantum chemistry. Since the feature common to both calculations is the procedure used to maintain constant temperature, we decided to investigate the effect of initial velocities on constant temperature simulations. Setting the initial atomic velocities to zero and then scaling the velocities up to the required kinetic energies, no interstitial dimer was predicted in the absence of the STM tip. This result suggests that the ease of formation of the interstitial dimer predicted above is probably an artifact of the molecular dynamics rather than a real effect. Thus, one needs to be cautious when using any statistical distribution for atomic velocities in small systems.

Starting from zero Kelvin, our results suggest the formation of a  $p(2 \times 2)$  reconstruction (figure 2) in the presence of the STM tip. The surface dimers flip between two different buckling configurations ( $p(4 \times 1)$  and  $p(2 \times 2)$ ) while adjacent dimers swing in phase. The rocking frequency ( $\hbar\omega = 23.2$  meV for a bias of  $-2$  V) agrees qualitatively with that predicted by tight-binding [4] for the soft mode of Si(001) ( $2 \times 1$ ) ( $\hbar\omega = 25.7$  meV). The dimer reorientation produces subsurface strain propagating two layers deep. The subsurface atomic displacements give rise to strongly distorted bond angles. We suggest that the tip-induced dimer rocking motion may explain their (time-average) symmetric appearance in STM image.

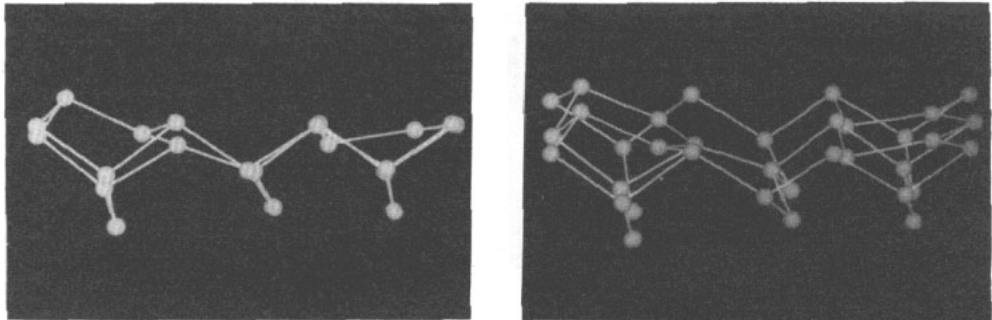


Figure 2. The  $p(2 \times 2)$  structure formed under the influence of a negatively biased STM tip (radius = 9 Å, bias = 2 V) on Si(100)  $p(4 \times 1)$  surface.

The negatively biased tip induces similar effects on  $(2 \times 1)$  and  $p(2 \times 2)$  reconstructed surfaces, although the formation of a  $p(4 \times 1)$  structure was predicted in this case (figure 3). No significant change is found in the rocking frequency. For a positively-biased tip, the main effect predicted is a change in the tilt angle; there is no change in the sign of tilt.

The reason for the different behaviour of the dimers under positive and negative bias may be traced to a small charge transfer between the dimer atoms in the absence of a bias. As we have already noted the ground state of the dimer, in the absence of a bias, is tilted. The hybridization state of the lower atom, which is in an almost planar configuration, is approximately  $sp^2$ . This forces the dangling bond on this atom to be an almost pure  $p$  state. The dangling bond on the upper atom of the dimer contains a greater  $s$  component because the three back bonds are not planar. Therefore, there is a small charge transfer from the partially occupied dangling bond on the lower atom to the partially occupied dangling

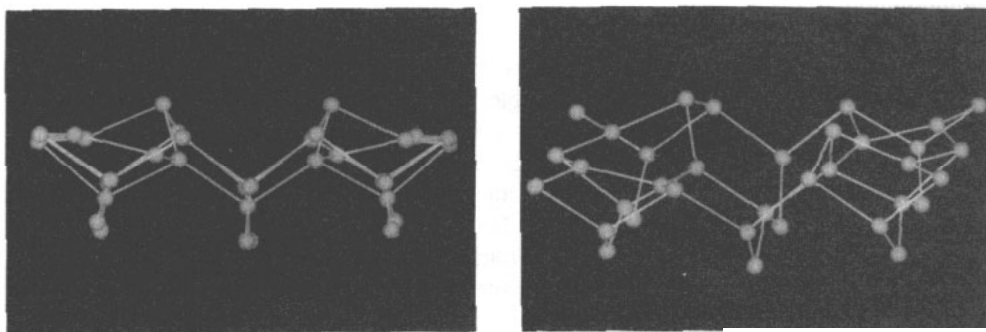


Figure 3. The  $p(4 \times 1)$  structure formed under the influence of a negatively biased STM tip (radius = 9 Å, bias = 2 V) on Si(100)  $p(2 \times 2)$  surface.

bond on the upper atom. Thus, the lower atom is positively charged and the upper atom is negatively charged. Under a positive bias the upper atom is attracted to the tip and lower atom is repelled. Thus a positive bias tends to stabilize the asymmetric dimer: it does not induce flipping of the dimer. Under a negative bias the upper atom is repelled by the tip and the lower atom is attracted to it. Therefore, a negative bias assists the thermal flipping of the tip, although the average angle of tilt is reduced by the repulsion between the upper atom and the tip.

Wilson [33] has given an argument for why the asymmetric dimers appear symmetric in the STM under a positive bias, which does not involve flipping of the dimers. Recall that the dangling bond on the lower atom of the dimer has a higher energy than that on the upper atom. Under a positive bias electrons tunnel from the specimen to the tip. Those electrons leaving the dangling bond state on the lower atom have further to tunnel than those leaving the dangling bond state on the upper atom. But it is argued that this is compensated by the greater decay length of the former states than the latter. However, the low temperature experiments [11] indicate that this mechanism may not apply.

Our most extensive results are for tips with negative biases ( $-1$  V,  $-2$  V) or with a positive bias of 1 V. The results (supported by less detailed studies for other voltages) show relatively modest effects of the tip for positive bias. The average tilt angle of the dimer (about  $20^\circ$  for 1 V bias) changes with voltage, and the dimer axis oscillates thermally with an amplitude of about  $\pm 9^\circ$ ; The sign of tilt does not change during the motion. For negative bias, the average tilt angle is smaller (about  $6^\circ$ – $7^\circ$  for  $-1$  V,  $-2$  V and  $-4$  V) but the amplitude is larger, roughly  $\pm 19^\circ$ . There is no significant dependence on bias, nor does the frequency change much (23 meV is typical). However, the amplitude of the tilt is sufficiently large that the sign of the tilt changes.

Our results show that the structure of the Si(100) surface is affected by the STM probe, the effect being strongest when the tip is negatively biased. The STM images are, of course, based on tunnelling currents, and these (as we and others have shown [1, 2, 34–37]) are not always easy to relate to atomic positions. In the present case it is clear that, irrespective of the detailed way time-averaging is done over the vibrational motion, the contrast between the two components of the dimer will be greater when the average tilt is greater (the amplitudes of tilt are similar in the two cases). The STM response will be too slow to detect the vibrational motion, but will follow slower thermally-activated processes (which themselves will be affected by the dynamical processes we describe). Our results also suggest bias-dependent effects, and these we believe to offer a partial but plausible explanation for the bias-dependent STM image.

### 3.3. Energy barrier for flipping

Within our cluster model (i.e. without correcting for the long-range electrostatic terms) we find the  $p(4 \times 1)$  structure the most stable. The  $p(2 \times 2)$  structure is higher in energy by 0.8 eV per four dimers and the  $(2 \times 1)$  structure higher in energy again by about 0.1 eV. Thus the  $(2 \times 1)$  and  $p(2 \times 2)$  structures are similar in energy. However, we need to know too the barriers to switching between these structures. This is not trivial because of the lack of symmetry at the saddle point. However, the CHEMOS code has a convenient feature for this class of problem. Starting from one configuration, we apply incrementally a generalized force whose effect is to push the system towards the desired final state. At each step, geometries are optimized and self-consistency achieved. The total energy rises (under the constraint of the generalized force) to a maximum corresponding to the saddle point. This approach is addressed in more detail elsewhere [27]. The energies found are given in table 2. These energies may well be too large by up to a factor of two (though this may depend on cluster size), but their relative sizes are likely to be realistic, except in so far as long-range electrostatic terms matter. The most interesting feature is that the barrier for both  $p(2 \times 2)$  and  $(2 \times 1)$  to go to  $p(4 \times 1)$  is lower than the rather large barrier between  $p(2 \times 2)$  and  $(2 \times 1)$ : the near degeneracy of reconstructions need not imply easy motion from one to the other.

Table 2. Energy barrier for flipping between different Si(100) reconstructions.

Interconversion	Energy barrier (eV)
$p(4 \times 1)$ to $p(2 \times 2)$	1.7
$p(2 \times 2)$ to $p(4 \times 1)$	0.9
$p(4 \times 1)$ to $(2 \times 1)$	2.0
$(2 \times 1)$ to $p(4 \times 1)$	1.1
$(2 \times 1)$ to $p(2 \times 2)$	1.4
$p(2 \times 2)$ to $(2 \times 1)$	1.5

## 4. Conclusions

Our calculations have implications of two types. First, we find that our relatively simple self-consistent molecular dynamics agrees in important features both with other approaches (from local density functional theory with molecular dynamics to tight-binding calculations) and with the main features from experiment. We verify that the dimers of  $2 \times 1$ -reconstructed (100) surface of Si are not symmetrical, and we also support previous views of surface vibrational resonances. Our results further suggest that dimers which appear symmetric in experiment do so through some sort of dynamic averaging, though just how this is achieved is unclear. However, the tip certainly affects the behaviour of the dimers: under a positive bias the tip inhibits the thermally induced rocking of the dimers, whereas under a negative bias it assists the thermally induced dimer rocking and the amplitude of the rocking increases.

The second set of implications arises because the STM is an intrusive probe. Whereas LEED, for instance, usually has no effect on the surface observed, the STM can indeed affect atomic configurations and rate processes. As we show here, it can also be an active probe, possibly driving instabilities. So, at least to the extent that the STM tips can be made in a controlled way, one might use this local probe to help map out energy surfaces and



reaction paths. In the present case, it would be helpful to understand whether particular dimer orientations make the dimer bond more vulnerable to attack by fluorine, oxygen or hydrogen or other species important in silicon processing. The reaction rate should depend on the presence of the tip and on the voltage bias, and a qualitative effect should be observed. If the STM tip were sufficiently well-defined and reproducible to yield quantitative information, then it (acting as an intrusive probe) could yield more significant information on silicon surface reactivity and reaction mechanisms.

## Acknowledgments

One of us (MMDR) is indebted to the European Community and UKAEA for financial support.

## References

- [1] Ramos M M D, Stoneham A M, Sutton A P and Pethica J B 1990 *J. Phys.: Condens. Matter* **2** 5913
- [2] Ramos M M D, Sutton A P and Stoneham A M 1991 *J. Phys.: Condens. Matter* **3** S127
- [3] Landman U, Luedtke and Nitzan A 1989 *Surf. Sci.* **210** L177
- [4] Allan D C and Mele E J 1984 *J. Chem. Phys.* **53** 826
- [5] Yang W S, Jona F and Marcus P M 1983 *Phys. Rev. B* **28** 2049
- [6] Tabata T, Aruga T and Murata Y 1986 *Surf. Sci.* **179** L63
- [7] Tromp R M, Smeenk R G, Saris F W and Chadi D J 1983 *Surf. Sci.* **133** 137
- [8] Wertheim G K, Riffe D M, Rowe J E and Citrin P H unpublished
- [9] Hamers R J, Tromp R M and Demuth J E 1986 *Phys. Rev. B* **34** 5343
- [10] Hamers R J, Avouris P and Bozso F 1988 *J. Vac. Sci. Technol. A* **6** 506
- [11] Wolkow R A 1992 *Phys. Rev. Lett.* **68** 2636
- [12] Hashizume T, Hamers R J, Demuth J E, Markert K and Sakurai T 1990 *J. Vac. Sci. Technol. A* **8** 249
- [13] Appelbaum J A, Baraff G A and Hamann D R 1977 *Phys. Rev. B* **15** 1408
- [14] Appelbaum J A and Hamann D R 1978 *Surf. Sci.* **74** 21
- [15] Chadi D J 1979 *Phys. Rev. Lett.* **43** 43
- [16] Verwoerd W S 1980 *Surf. Sci.* **99** 58
- [17] Ong C K and Chan B C 1989 *J. Phys.: Condens. Matter* **1** 3931
- [18] Yin M T and Cohen M L 1981 *Phys. Rev. B* **34** 2303
- [19] Payne M C, Roberts N, Needs R J, Needels M and Joannopoulos 1989 *Surf. Sci.* **211** 1
- [20] Roberts N and Needs R J 1990 *Surf. Sci.* **236** 236
- [21] Artacho E and Yndurain F 1989 *Phys. Rev. Lett.* **62** 2491
- [22] Ihara S, Ho S L, Uda T and Hirao M in 1991 *Computer Aided Innovation of New Materials* ed M Doyama, T Suzuki, J Kihara and R Yamamoto (Amsterdam: North-Holland-Elsevier)
- [23] Badziag P, Verwoerd W S and Van Hove M A 1991 *Phys. Rev. B* **43** 2058
- [24] Badziag P and Verwoerd W S 1993 *Surf. Sci.* submitted
- [25] Molotkov S N, Nazin S S, Smirnova I R and Tatarskii V V 1991 *Surf. Sci.* **259** 339
- [26] Car R and Parrinello M 1985 *Surf. Sci.* **55** 478
- [27] Ramos M M D 1992 *D Phil Thesis* University of Oxford
- [28] Wallace D S, Stoneham A M, Hayes W, Fisher A J and Harker A H 1991 *J. Phys.: Condens. Matter.* **3** 3879
- [29] Pople J A and Beveridge D L 1970 *Approximate Molecular Orbital Theory* (New York: McGraw-Hill)
- [30] Aono M, Oshima C and Ishizama Y 1982 *Phys. Rev. Lett.* **49** 567
- [31] Sawada S 1991 *Proceedings of the International Workshop on Computational Materials Science* (Japan: IRMS)
- [32] Zandvliet H J W 1989 *J. Phys.: Condens. Matter.* **1** 10603
- [33] Wilson J H 1992 *DPhil Thesis* University of Oxford
- [34] Ciraci S, Doyen G and Feenstra R M 1990 *STM and related methods* ed R J Behm, N Garcia and H Rohrer (Dordrecht: Kluwer)

- [35] Sautet P and Joachim C 1992 *Ultramicroscopy* **42-44**,115
- [36] Wilson J H, McInnes D A, Knall J, Sutton A P and Pethica J B 1992 *Ultramicroscopy* **42-44**, 801
- [37] Vigneron J P, Derycke I, Lambin P, Laloyaux T, Lucas A A, Libioulle L and Ronda A 1992 *Ultramicroscopy* **42-44**, 250