Tip-Surface Interactions in Scanning Tunneling Microscopy

K. Cho and J. D. Joannopoulos
Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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The tip-surface interactions in scanning tunneling microscopy (STM) of the Si(100) surface are investigated with *ab initio* total energy pseudopotential calculations. The results of the calculations lead to a new understanding of the microscopic STM measurement process. It is found that under typical conditions the influence of the tip is large enough to effectively flip a dimer on this surface. This leads to a reinterpretation of the "symmetric" dimer STM image as an asymmetric dimer configuration that flips as it follows the motion of the scanning tip.

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Scanning tunneling microscopy (STM) provides an image of the structure of a surface at atomic resolution [1]. This STM image is generated by an electron tunneling between the STM tip and a surface atom under the tip as a result of the overlap between the tip and surface wave functions. Consequently the tip and the surface may in certain cases interact significantly during the process of an STM measurement. The conventional theories of STM, however, are based on a first order perturbation approximation [2-4] which does not include the tip-surface interaction. STM images are then interpreted simply as a convolution of the tip wave function and the surface wave function. Although this interpretation is a very useful approximation for many applications, there may exist systems for which the tip-surface interaction and the surface dynamics play a crucial role in the STM measurement process.

In this Letter we use *ab initio* total energy pseudopotential calculations, with a conjugate gradient scheme, to demonstrate that the Si(100) surface is an example of a system for which STM does not provide a direct mapping of the surface atomic structure, and that a conventional interpretation of the STM images is not appropriate. Typically, a room temperature STM image of the Si(100) surface [5-7] shows the majority [8] of dimers in what appear to be unbuckled, symmetric configurations. Such configurations are in apparent disagreement with the theoretical predictions of buckled, *asymmetric* dimer configurations [9]. One might expect that this discrepancy could reasonably be resolved by arguing that thermal fluctuations in the asymmetric dimer configurations will create an averaged or "symmetric" image. Such thermal fluctuations have been predicted to be present on the surface *in the absence of a tip* [10-12]. In the presence of a tip, however, we propose that a different mechanism is operational. Specifically, we demonstrate that the tip-surface interactions are significant enough to flip and bind an asymmetric dimer to the tip. As the tip is then moved along the surface, dimers are flipped tracking the tip and create what appears to be a symmetric image in the scan.

Calculational details.—The *ab initio* total energy pseudopotential density functional calculations are performed using the preconditioned conjugate gradient scheme for the electronic energy minimization to the Born-Oppenheimer surface [13]. The minimum energy ion configuration on the Born-Oppenheimer surface is obtained by relaxing ions according to the Hellman-Feynman forces. Within the local density approximation (LDA), the total energy functional is calculated with the Perdew-Zunger parametrization of the exchange-correlation energy [14] and the Kleinman-Bylander separable form of the nonlocal ionic pseudopotentials [15]. The pseudopotentials for silicon and tungsten are generated by the kinetic energy optimization [16], and contain p and d nonlocal components and an s local component.

The convergence of the plane wave expansions and the transferability of the pseudopotentials are tested for bulk silicon crystal and bulk tungsten crystal. From the test calculations, the plane wave cutoff energy is chosen to be $E_c = 300$ eV, at which the total energy of the silicon crystal is converged to within 0.04% and that of the tungsten crystal to 0.07%. The transferability of the pseudopotentials is fairly good as shown in Table I for the calculations of the bulk lattice constants and the bulk moduli.

The STM tip-surface system is 0 by a supercell (15.35 Å×8.58 Å×16.00 Å) containing 52 atoms (4 tungsten atoms, 32 silicon atoms, and 16 hydrogen atoms). The corresponding Brillouin zone is sampled with one **k** point (Γ). The 32 silicon atoms form a four-layer slab with eight atoms in each layer (15.35 Å×8.58 Å) [17]. The four dimers in the top layer form a $c(4\times 2)$ surface reconstruction, and the slab is vertically separated from the periodic images by 10 Å vacuum regions. The bottom-layer silicon atoms are fixed at bulk positions, and all the dangling bonds are passivated by 16 hydrogen atoms. To model the STM tip we note that only the atoms at the very edge of the tip need to be adequately represented in order to address the questions raised in this work. Since W atoms on the surface form a close-packed structure, we have opted to represent the apex of the STM tip simply as a tetrahedron of four W atoms. The tungsten cluster is placed in the vacuum region with an apex atom pointing down to the surface. In the calcula-

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TABLE I. Calculated lattice constants and bulk moduli of tungsten crystal and silicon crystal are compared with experimental values.

	Experiment	Calculation	Difference
W lattice constant (Å)	3.16	3.13	0.9%
W bulk modulus (10^{12} dyn/cm^2)	3.23	3.47	7.4%
Si lattice constant (Å)	5.431	5.427	0.7%
Si bulk modulus (10^{12} dyn/cm^2)	0.988	1.013	2.5%

tions, the silicon atoms in the top three layers and the apex atom are allowed to relax according to the Hellman-Feynman forces.

To gauge the influence and relative importance of the tunneling current or bias voltage, we performed the following exercise. Typically the bias voltage is 2 V and the tip-surface separation is about 5 Å, so that the electrostatic force on a surface atom is approximately 0.6 eV/Å. This includes a conservative estimate of 1.5 for the enhancement factor caused by inhomogeneous field effects around the surface atoms as discussed by Kreuzer, Wang, and Lang [18]. The spring constant of a surface mode is roughly 5 eV/Å^2, so that the relaxation energy of the atom due to the applied bias voltage is less than 0.036 eV, which is consistent with *ab initio* calculations of the tip-induced polarization of the Si(100) surface by Huang *et al.* [19]. As we shall see in the results below, this energy is much smaller than our calculation of a tip-surface binding energy of 0.2 eV. We thus neglect the effects of the bias voltage in the forthcoming analysis.

In these calculations, we allowed the tip to vary in the range 4.5 to 5.2 Å above the atoms in the outermost surface layer. As shown in Fig. 1, even for the shortest tip-surface distance of 4.5 Å, the surface is not greatly perturbed by the presence of the tip, and no new bonds are formed between them. Nevertheless, as we discuss in the next section, there is enough interaction between tip and surface to significantly alter the dynamics of the surface dimers.

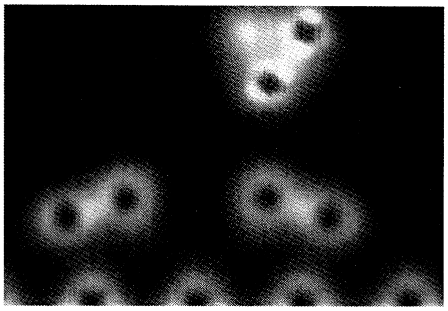

FIG. 1. This plot shows a cross section of the total charge density of the tip-surface system with the tip directly above an upper dimer atom. The buckling angle of the dimer, the position of the apex tip atom, and the charge density distributions of the tip and the dimer are not significantly changed by the tip-surface interaction, but the interaction energy is significant (−0.57 eV).

Interaction energies.— The tip-surface interaction energy is calculated by combining three separately calculated energies: E(tip), E(surface), and E(tip+surface). E(tip) is calculated by retaining the tip in the supercell and removing the Si slab. Similarly, E(surface) is calculated by retaining the slab and removing the tip. Finally, the energy of the tip-surface system E(tip+surface) is calculated with both the tip and the slab in the supercell. The tip-surface interaction energy is then simply

$$E_{\mathrm{int}} = E(\mathrm{tip+surface}) - E(\mathrm{tip}) - E(\mathrm{surface}) . \qquad (1)$$

The results of our calculations for a tip restricted to lie directly above a surface atom are summarized in Fig. 2. For the configuration shown on the left panel, the tip lies 5.2 Å above the lower dimer atom, and the interaction energy is −0.37 eV. The panel at the center of the figure refers to a symmetric dimer configuration that corresponds to the "saddle point" or static barrier configuration for flipping the buckled dimer. In the absence of the tip, the barrier is calculated to be 0.08 eV in good agreement with 0.09 eV as obtained by Dabrowski and Scheffler [12]. In the presence of the tip, the barrier for an *up flip* of the buckled dimer is found to be 0.1 eV. The opposite barrier, corresponding to a *down flip* of the buckled dimer, is obtained from the right panel of Fig. 2 and is found to be 0.3 eV. Note that the interaction energy in the latter case is correspondingly large at −0.57 eV and the distance between tip and dimer atom is 4.5 Å.

To determine how this barrier changes with respect to the position of the tip, we perform the calculations illustrated in Fig. 3. Now the tip is restricted to lie directly above a dimer *bond.* In this case, we find that the barrier decreases significantly to a value of about 0.05 eV.

Implications.— For a given value of energy barrier E_b the average time that a dimer spends in one asymmetric configuration before flipping to the other is simply

$$\tau_b = 10^{-13} e^{E_b/k_B T} , \qquad (2)$$

where the phonon frequency is estimated to be 10^{13} sec^{-1}. During an STM measurement, an STM tip typically stays 3×10^{-3} sec$\equiv t_{\mathrm{STM}}$ above a surface atom and therefore the relative values of τ_b and t_{STM} will determine the nature of the STM image. In the *absence of in-*

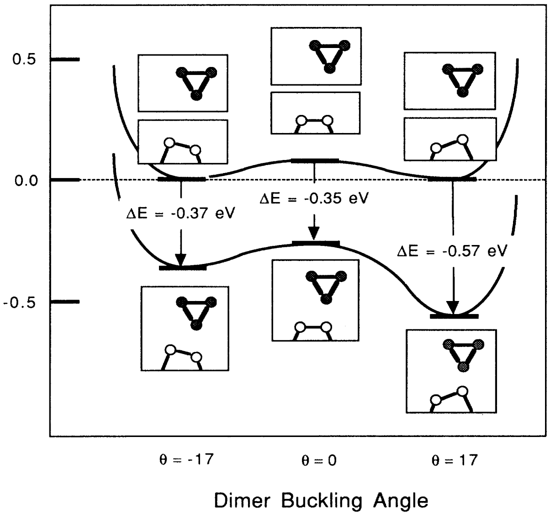

FIG. 2. Total energy (in eV) of a tip-surface system as a function of surface-dimer buckling angle. The tip (shown schematically as a triangle with filled circles) is situated directly above a surface-dimer atom (open circles). The results at and above the horizontal dashed line correspond to a tip-surface system in the *absence* of interactions. In this case the horizontal bars correspond to $E(\text{tip})+E(\text{surface})$. Note that the barrier for flipping from one asymmetric dimer configuration to the other is about 0.08 eV. The panels below the dashed line correspond to the fully interacting tip-surface system. In this case the horizontal bars correspond to $E(\text{tip}+\text{surface})$. Note that the barriers for up flip and down flip are 0.1 and 0.3 eV, respectively.

teractions between the STM tip and the surface, a buckled dimer is in a symmetric potential well as shown in the upper curve of Fig. 2, and the energy barrier for flipping (0.08–0.09 eV) is small enough that at room temperature the dimer can flip up and down very frequently ($\tau_b = 2\times10^{-12}$ sec). This would lead to a symmetric STM image that is the *average* of up-flip and down-flip configurations.

In the *presence of interactions* between the STM tip and surface, a buckled dimer is in an *asymmetric* potential well as shown in the lower curve of Fig. 2, and τ_b is different for the down-flip and the up-flip configurations. At room temperature, τ_b's are short enough ($\tau_{\text{down}} = 5\times10^{-12}$ sec and $\tau_{\text{up}} = 1.3\times10^{-8}$ sec) that, in principle, the dimer can flip up and down freely, and thermal equilibrium between two local energy minima of the asymmetric potential is reached during the STM imaging time. Therefore, the dimer spends different amounts of time in each local energy minimum, and the ratio of the times is given by the Boltzmann factor of the difference of two local minimum energies (4×10^{-4}). Consequently, the dimer stays *in the up-flip configuration* except for intermittent rapid *round trips* to the down-flip configuration. For all practical purposes, therefore, one is always measuring a dimer in the up-flip position as the tip moves along the surface. The resulting image is then deceptively that of a "symmetric" dimer.

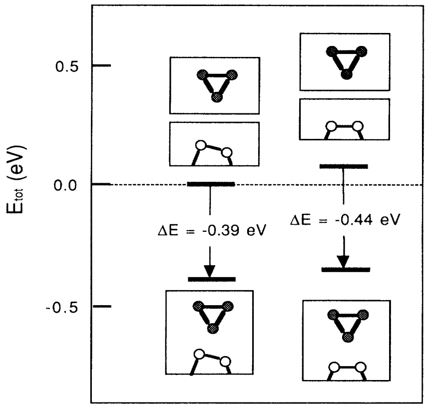

FIG. 3. Total energy (in eV) of a tip-surface system as a function of surface-dimer buckling angle for a tip situated directly above the dimer bond. Same convention as in Fig. 2. Note that the barrier for dimer flipping is now reduced to 0.05 eV.

As one decreases the temperature, τ_{down} and τ_{up} increase and eventually both become larger than t_{STM}. This occurs at and below a temperature $T_{\text{freeze}} = 48$ K for which the surface dynamics is so slow that a dimer cannot flip during the STM imaging time. Therefore, at this temperature range one can observe frozen buckled dimers in up-flip and down-flip positions from an STM image of the surface.

One possible experimental verification of our prediction regarding the room temperature "symmetric" dimer image would be to analyze the tunneling current while the tip remains above a dimer atom. If tip-surface interactions are *not* important the current should have the characteristics illustrated in the top panel of Fig. 4. The typical frequency at room temperature in this case should be around 10^{12} Hz. On the other hand, if tip-surface interactions are important and result in a "binding" of the up-flip configuration, one should observe a current as shown schematically in the bottom panel of Fig. 4. The frequency associated with these "glitches" should be in the neighborhood of 10^{8} Hz.

Finally, a special case can arise if the STM tip is constrained to move precisely along the dimer axis. Recall that in this case there exists a lower barrier when the tip is situated directly above a dimer bond (see Fig. 3). Consequently, as the STM tip moves along the dimer, the dimer can flip more easily which results in a lower freeze-in temperature of about 24 K.

Concluding remarks.— In all of this work we have specifically focused on the defect-free regions of the Si(100) surface. However, defects such as vacancies and step edges, for example, appear to occur frequently on such surfaces. STM images at room temperature reveal *asymmetric* dimer configurations in the vicinity of such

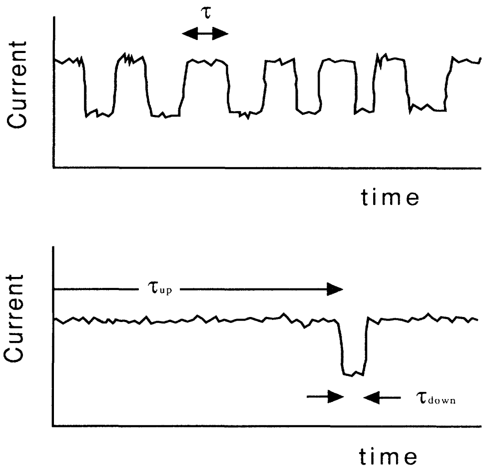

FIG. 4. Top panel shows a schematic tunneling current in the absence of tip-surface interactions. Bottom panel shows a schematic tunneling current in the presence of tip-surface interactions.

defects which would be consistent with a defect-pinning mechanism that leads to either a higher energy barrier for an up flip and down flip *or* a larger asymmetry between the barriers for up flip and down flip. We have recently begun attempts to investigate these differences but such *ab initio* calculations are beyond the scope of the present work.

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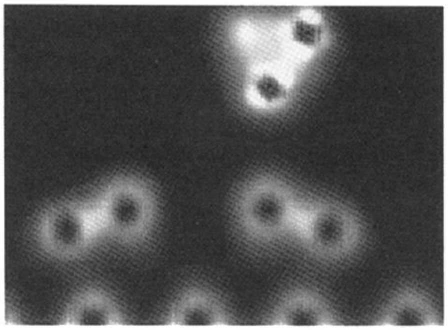
[1] G. Binnig and H. Rohrer, Phys. Rev. Lett. **49**, 57 (1982).
[2] J. Tersoff and D. R. Hamman, Phys. Rev. Lett. **50**, 1998 (1983).
[3] C. Julian Chen, Phys. Rev. Lett. **65**, 448 (1990).
[4] H. Kageshima and M. Tsukada, Phys. Rev. B **46**, 6928 (1992).
[5] R. M. Tromp, R. J. Hamers, and J. E. Demuth, Phys. Rev. Lett. **55**, 1303 (1985).
[6] R. J. Hamers, R. M. Tromp, and J. E. Demuth, Phys. Rev. B **34**, 5343 (1986).
[7] Robert A. Wolkow, Phys. Rev. Lett. **68**, 2636 (1992).
[8] The dimers that are in the vicinity of defects appear to be pinned in asymmetric configurations.
[9] D. J. Chadi, Phys. Rev. Lett. **43**, 43 (1979).
[10] J. Ihm, D. E. Lee, J. D. Joannopoulos, and J. J. Xiong, Phys. Rev. Lett. **51**, 1872 (1983).
[11] At room temperature for dimers not pinned directly to defects.
[12] Jaroslaw Dabrowski and Matthias Scheffler, Appl. Surf. Sci. **56-58**, 15 (1992).
[13] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, Rev. Mod. Phys. **64**, 1045 (1992).
[14] J. P. Perdew and Alex Zunger, Phys. Rev. B **23**, 5048 (1981).
[15] Leonard Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).
[16] Andrew M. Rappe, Karin M. Rabe, Efthimios Kaxiras, and J. D. Joannopoulos, Phys. Rev. B **41**, 1227 (1990).
[17] The interdimer interaction is stronger along the dimer rows (-0.026 eV) than across the dimer rows (0.010 eV), and the separation distances are chosen to avoid the correlated interaction of STM tips and the surface.
[18] H. J. Kreuzer, L. C. Wang, and N. D. Lang, Phys. Rev. B **45**, 12050 (1992).
[19] Z.-H. Huang, M. Weimer, R. E. Allen, and H. Lim, J. Vac. Sci. Technol. A **10**, 974 (1992).



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