

First-Principles Molecular Dynamics Simulation for Scanning Tunneling Microscopy Image of Si(001) Surface

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We have simulated scanning tunneling microscopy (STM) images of buckled dimer on Si(001) reconstructed surface by first-principles calculation. STM images reflect the spatial distribution of electronic states rather than the geometric structure on the sample surface. To compare between the experimental STM images and the simulated STM images allow us to clarify relationship between the electronic spatial distribution and the geometric structure. We clarify sample-bias-dependence on the buckled dimer structure of Si(001) surface and relationship between the surface atomic geometry and the spatial distribution of the electronic states of it.

Key words: STM, silicon surface, first-principles molecular dynamics, simulation

1. INTRODUCTION

Many studies of the atomic structure and electronic states on the solid surface at the atomic level are performed by using scanning tunneling microscopy (STM). Although STM images reflect the atomic geometry in a sense, they do the electronic spatial structure on the sample surface. As depending also on the energies of the surface electronic states, STM image changes with varying the sample bias voltage. We must, accordingly, pay attention to interpret STM images. For example, in the Si(111) $\sqrt{3} \times \sqrt{3}$ -Ag surface structure, the realistic atomic geometry is different from the STM image, i.e., the electronic spatial structure on the surface[1,2].

In order to analyze the surface electronic states, a lot of first-principles calculations have been attempting, and theoretical understanding such as reconstructed surface and first-stage of reaction have been studied by first-principle molecular dynamics simulation. STM image simulation is one of these applications[3-5]. Tsukada and co-workers clarified the Si(111) $\sqrt{3} \times \sqrt{3}$ -Ag surface structure mentioned above by theoretical simulation[2].

In this paper, a method for tunneling current of STM is proposed and is applied STM images simulation for the buckled dimer row on Si(001) surface under various biasing conditions. As comparing these simulated STM images with bias-dependent changes in experimental STM images for buckled dimer row of SA step edge on Si(001) surface at room temperature, relationship between the surface atomic geometry and the spatial distribution of the filled or empty electronic states of Si(001) buckled dimer is examined.

2. SIMULATION AND EXPERIMENTAL

2.1 Method of electronic states calculation

The electronic states calculation is performed within the density-functional theory in the local-density approximation[6]. Only valence electronic states at the Γ point of the surface Brillouin zone are treated explicitly using a plane-wave expansion with a kinetic energy cutoff of 74 Ry, while electron-ion interactions are described in terms of the norm-conserving pseudopotential. Our calculation model is the Si(001)p(2 \times 2) asymmetric dimer surface. The supercell has twice of silicon lattice constant (=5.428 Å) in horizontal dimensions and four times of that in perpendicular direction. It contains a slab of silicon five layers thick, the lowest layer of which is terminated by hydrogen atoms, and a vacuum region of three times of lattice constant. The positions of the four topmost Si layers are fully optimized using a quenched molecular-dynamics algorithm in the Car-Parrinello scheme[7].

2.2 Method for STM image simulation

We propose the following method for tunneling current of STM and apply it to the STM image simulations. The STM system is separated into the electrodes of the sample surface and the tip as Bardeen's perturbation approach in Fig.1 [8]. It is, however, important that the tunneling current of STM is contributed sums of convolution of the each local density-of-states (LDOS) between the sample surface and the point atom of the STM probe tip (cross mark in Fig.1). The tunneling current, $I(x,y)$, is simply expressed as

$$I(x,y) \propto \int_{-eV}^{eV} \rho_s(x,y,z, E_F - eV + \epsilon) \cdot \rho_t(z, E_F + \epsilon) d\epsilon dz, \quad (1)$$

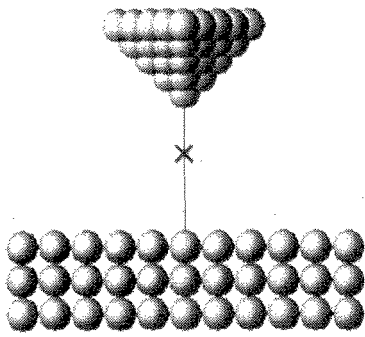


Fig.1. Schematic of a theoretical STM system that is separated two electrodes. The tunneling current contains all cross point from the sample to the tip.

where $\rho_s(x,y,z,E_F - eV + \epsilon)$ and $\rho_t(z,E_F + \epsilon)$ are the LDOS of the sample and the tip, respectively, d is the tip-sample distance and V is the bias voltage of the sample. It is, however, not consider that the effect of electric field in STM system, the tunneling probability for energy.

In this report, we assume that the LDOS of the tip is constant for the energy level and the charge density damps exponentially from the point atom of the tip to the sample surface. The position of the tip locates $\sim 6 \text{ \AA}$ from the sample surface and the simulated STM images imply constant-height mode.

2.3 The experimental method of STM

The STM used in this study was mounted in ultrahigh-vacuum (UHV) with a background pressure 1×10^{-10} Torr. The sample was a Si(001) (B-doped, $0.2\text{-}0.5 \text{ \Omega cm}$). The clean Si(001) 2×1 surface was prepared by annealing to $\sim 1450\text{K}$ for about 30sec after overnight degassing at $\sim 700\text{K}$ and then cooling to room temperature. The tips were prepared by the electrochemical etching of polycrystalline W wire. It was treated prior to use in UHV with electron bombardment. The STM topographic images of Si(001) surface were taken at room temperature.

3. RESULTS AND DISCUSSION

3.1 Geometry on Si(001) $p(2 \times 2)$ surface obtained by first-principles molecular dynamics

The results of optimized geometry on Si(001) $p(2 \times 2)$ surface by first-principles molecular dynamics simulation are explained. Fig.2 shows two types of dimer structures [(A) and (B)], standing mutually in a row, are obtained in the calculation model above. For dimer(A), the dimer bond length is 2.43 \AA and the buckling angle is 18.2° in Fig.2(b). For dimer(B), the dimer bond length is 2.41 \AA and the buckling angle is 17.6° in Fig.2(c).

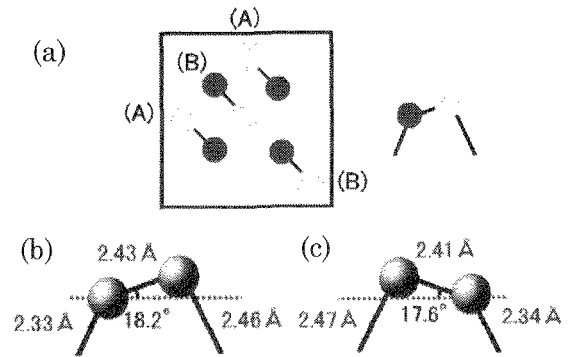


Fig.2. Optimized geometry of Si(001) $p(2 \times 2)$ surface. (a) Schematic is top and side view of buckled dimers, in which drawing upper (large ball) and lower (small ball) atom. Schematics of (b) and (c) are geometry of dimer (A) and (B) in (a), respectively.

3.2 Simulated STM images

We show simulated STM images for Si(001) $p(2 \times 2)$ surface in Fig.3 at filled-state [Fig.3(a), -2.0V ; 3(b), -1.0V] and empty-state [Fig.3(c), $+0.6\text{V}$; 3(d), $+1.2\text{V}$; 3(e), $+2.0\text{V}$]. As is shown in Fig.3(a) and 3(b), The dimer row is reproduced zigzag structure in both simulated STM images at filled-state. The large electron density localizes around the upper silicon atom of dimer, on the other hand, the low electron density is not revealed around the lower atom of dimer.

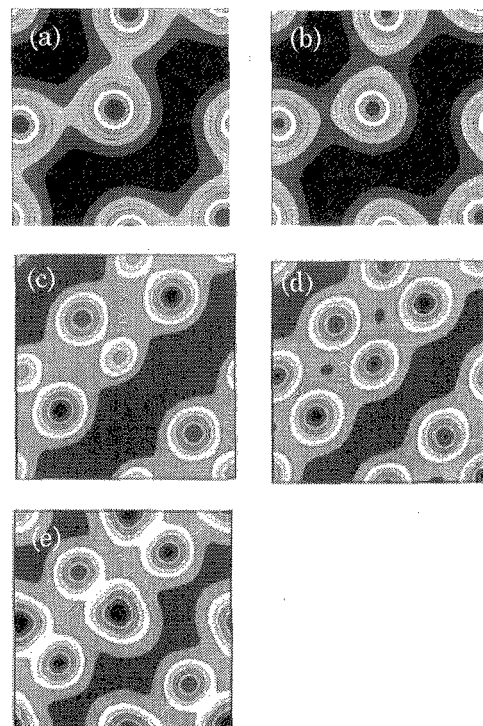


Fig.3. Contour maps of simulated STM images on Si(001) $p(2 \times 2)$ under various sample biasing conditions. Images are calculated at -2.0 , -1.0 , $+0.6$, $+1.2$ and $+2.0\text{V}$ bias for (a), (b), (c), (d) and (e), respectively. Position of dimer atoms roughly corresponds to schematic as shown in Fig.2(a).

The dimer row is observed zigzag structure at +0.6V sample bias, as shown in Fig.3(c). The zigzag dimer row reverses its bright site, as compared with that of filled-state results. Although the lower silicon atom of dimer at filled-state is no appearance, we can find both atoms of dimer at +0.6V bias. That is, the lower atom of dimer is bright and the upper atom is dim. As shown in Fig.3(d), zigzag dimer changes symmetry dimer at +1.2V bias. In Fig.3(e), the dimer changes zigzag dimer again. The zigzag pattern at +2.0V bias, however, reverses that at +0.6V bias. The electronic distribution of the upper atom becomes larger than that of the lower atom in simulated STM image at +2.0V bias.

3.2 Experimental STM images

Fig.4(a) and 4(b) show filled-state and empty-state STM image of clean Si(001) 2×1 surface at room temperature, respectively. Filled-state and empty-state STM topograph are observed symmetric bean-shaped and symmetric splitting dimer structures on the terrace, which reflect the bonding (π b) and antibonding (π a*) states, respectively[10]. In contrast, STM images of Si(001) in Fig.4(a) and 4(b) reveal buckled dimer row at the SA step edge. At room temperature, dimer flip-flop motion cause on the terrace[11,12], but it is limited at the step edge.

We notice buckled dimer row at the SA step edge and examine, in detail, sample-bias-dependent changes in STM images. In Fig.5, we show STM image of the SA step edge at filled-state [Fig.5(a), -2.0V; 5(b), -1.0V] and empty-state [Fig.5(c), +0.6V; 5(d), +1.2V; 5(e), +2.0V].

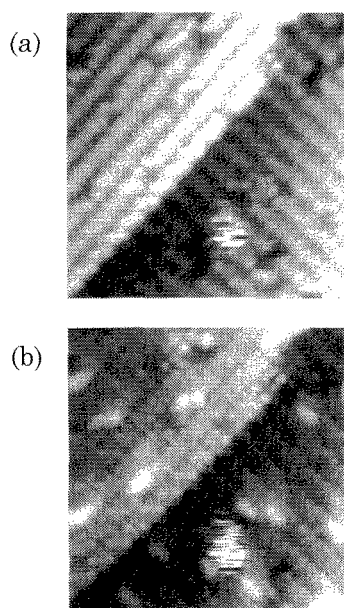


Fig.4. (a) Filled-state and (b) empty-state STM images ($10 \times 10 \text{ nm}^2$) of a monatomic SA step on Si(001) at room temperature. Images are taken at -1.0 and $+1.0 \text{ V}$ sample bias for (a) and (b), respectively.

The dimer row at the SA step edge is observed zigzag structure in both STM images at filled-state, as shown in Fig.5(a) and 5(b). The feature of SA step dimer is that one atom of it is brightly founded and the other is no appearance.

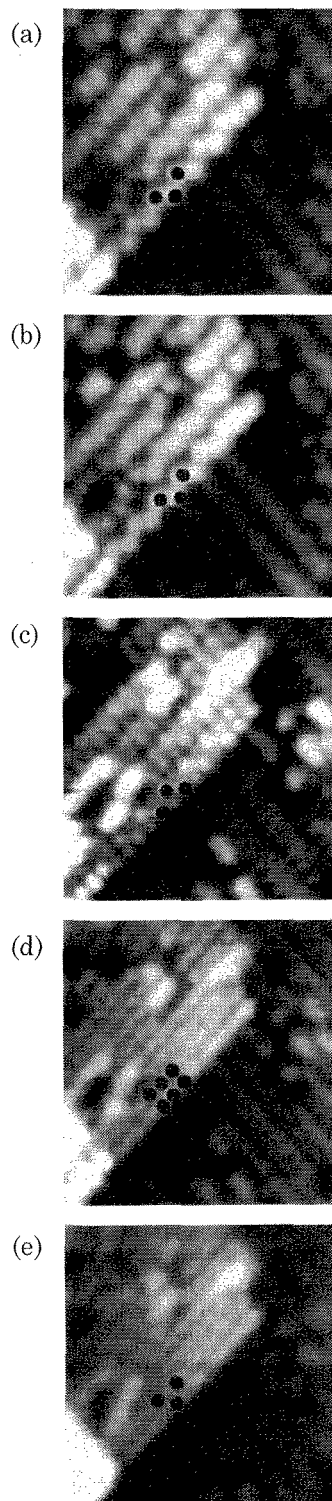


Fig.5 STM images ($7 \times 7 \text{ nm}^2$) of SA step on Si(001) under various sample biasing conditions. Images are taken at -2.0 , -1.0 , $+0.6$, $+1.2$ and $+2.0 \text{ V}$ bias for (a), (b), (c), (d) and (e), respectively. Filled-circles indicate brighter atoms of dimers.

As seen in Fig.5(c), at +0.6V sample bias the dimer row at SA step edge is observed zigzag structure. It should be noted that the bright atoms of zigzag dimer row at +0.6V bias reverses, as compared with filled-state STM images. Although one atom of dimer at negative bias is revealed, we can, in addition, find both atoms of dimer. That is, one atom of dimer is bright and the other is dim. As is shown in Fig.5(d), the zigzag dimer changes symmetry-appearing dimer at +1.2V sample bias. Moreover, in Fig.5(e), dimer of SA step edge changes zigzag dimer again. The zigzag pattern at +2.0V bias, however, reverses that at +0.6V bias, which differs from the zigzag image at negative bias.

Thus STM images depend on sample bias, that is, they reflect the spatial distribution of electronic states on the sample surface. So we cannot exactly understand geometry structure on surface, as only seeing STM images. Those results, therefore, have to be compared with the simulated STM images.

3.3 Comparison the experimental results with the simulated results

As comparing the results of STM simulation in Fig.5 with those of STM observation in Fig.3, we clarify relation between the atomic geometry and the electronic distribution of the buckled dimer row. In filled-state case, the both simulated images at $-1.0V$ sample bias and $-2.0V$ sample bias agree with experimental STM images, respectively, in points of finding only one atom of silicon dimer, not finding the other. This result suggests that the bright silicon atom in filled-state STM images is the dangling-bond of upper atom of silicon dimer. The filled-state electron density localizes largely on the upper atom of silicon dimer. In empty-state case, the result of the simulated images at +0.6V sample bias shows agreement with the experiment result regarding to find the both atoms of silicon dimer, one of which is brighter than the other, and to reverse its bright atom position of dimer for the filled-state bias case. Thus the brighter atom in STM image at +0.6V sample bias is the lower atom of silicon dimer. Accordingly, the amplitude of the electron density at the lower atom is larger than that at the upper atom around +0.6V sample bias. As the sample bias is applied to +1.2V, the both results show that two atoms of dimer become symmetric. Moreover, as it is applied to +2.0V, the darker atom of dimer becomes gradually brighter than the other in both results and the dimer row changes zigzag structure again. Thus it is effective to simulate the surface electronic states by first-principles method.

4. CONCLUSION

We have simulated the STM image reconstructed of buckled dimer on Si(001) surface. As compared the experimental STM images with the

simulated images, relationship between the atomic geometry and the spatial distribution the electronic states, i.e. STM image, on Si(001) surface has been clarified.

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