Simulations of constant-height atomic force microscope images of a H-terminated Si(100)2×1 surface with a CH₃ impurity *

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We have investigated constant-height atomic force microscope images of a hydrogen-terminated silicon (100) 2×1 surface including a methyl observed by a silicon tip with and without a hydrogen atom at the apex, using a density-functional-based tight-binding method. Using silicon-tip without hydrogen at the apex, we obtain good images with anisotropic spots reflecting the symmetry of methyl when observing with large tip-sample distance. Using silicon-tip with hydrogen at the apex, we expect to obtain better images showing internal hydrogen and carbon atoms of methyl if the forces can be measured precisely: they have atomic resolution for the image of adsorbed methyl.

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I. INTRODUCTION

Scanning probe microscopes (SPMs) make it possible to observe surfaces with the atomic or molecular resolution as well as to manipulate individual atoms or molecules.[1] Namely, we can say that the SPMs are our new eyes and hands in the nano(bio)technology area. Atomic force microscope (AFM) among SPMs has an advantage that it can observe not only conductive materials but also non-conductive ones. The resolution of AFM has been improved recently up to nearly the same as that of scanning tunneling microscope (STM).[2] However, little AFM observation with the atomic resolution has been reported on the non-conductive samples, such as self-assembled monolayer (SAM) of organic molecules. For example, a methyl on Si(111) surfaces is observed as spots with three- and six-fold symmetry in a STM image,[3] while the AFM image of the same surface has vague spots.[4] Some of images obtained by SPM are so complex that we cannot determine the atomic structures of the observed samples straightforwardly from the images. In fact, it is reported that a STM image obtained under a certain condition is quite different from images obtained under different conditions.[5] Because AFM usually has stronger tip-sample interaction than STM, this tendency seems to be stronger in AFM than in STM.

Keeping the above in minds, we have examined AFM images of a methyl impurity on the H-terminated Si(100) surface and the behavior of the methyl in the presence of the tip, using density-functional-based tight-binding (DFTB) method.[6]

II. METHOD

We consider H-terminated Si(100)2×1 surface including a CH₃ impurity (CH₃/H-SAM) and a Si-tip with or without a hydrogen atom at the apex. The Si-tip without hydrogen atom is modeled by a cluster of Si₄H₄ molecule which has a dangling bond toward the surface. The validity of this cluster tip has been confirmed in a previous study by Pérez et al.[7] The Si(100) surface is modeled by a slab of six Si layers, whose lateral size is 4×4. The periodic boundary conditions are imposed only in the lateral directions. The Si atoms of both surfaces are terminated by H atoms, but only the front surface is reconstructed to the 2×1 structure. The models of tip and sample is shown in Fig. 1.

In the calculation, we employ DFTB method, which can reproduce the reconstruction of Si surfaces.[8, 9] All the atoms in the surface slab model except two bottom layers are relaxed, and all the atoms of a tip except an apex Si atom (and a hydrogen atom terminating the apex Si atom) is fixed. We adopt the conjugated-gradient method for structural relaxation, and do not consider the effect of phonon. This procedure can be justified because the tip motion is assumed to be very slow compared with the atomic relaxation processes. Finally, we simulate AFM images by evaluating the forces acting on the tip with scanning the tip in planes of constant tip-sample distance; we will discuss conditions to obtain good images. Here, the tip-sample distance is defined as the shortest vertical distance between the tip and the surface in the initial structure.

III. RESULTS

A. Si-tip without hydrogen at the apex

First, we observe forces when the Si tip without a hydrogen at the apex approaches CH₃ and H. From the ver-
FIG. 1: Calculation model of the H-terminated Si(100)2×1 surface including a CH$_3$ impurity and a Si-tip without a hydrogen at the apex. Small black circles, large black circles and a gray circle denote H, Si and C atoms, respectively.

FIG. 2: Calculated vertical components of forces as a function of the tip-sample distance obtained using a Si-tip without the hydrogen at the apex. Solid and dashed lines denote the cases where the tip is located just above the CH$_3$ and H, respectively.

vertical components of the forces shown in Fig. 2, we can see that the tip first feels weak attractive forces and then repulsive ones as the tip approaches CH$_3$, while strong attractive forces and then repulsive ones as the tip approaches H. Considering this marked difference between the forces of the CH$_3$ and H site seen in Fig 2, we can speculate that the two sites can be easily distinguished in the constant height AFM image of the tip-sample distance of 0.2 nm, while we cannot in the cases of 0.1 and 0.3 nm: in the latter cases, images may have weak contrast between the CH$_3$ and H site.

In the case of the tip-sample distance of 0.1 nm, the constant height AFM image is shown in the left hand of Fig. 3. Obviously, this image is not like what we expect from the force curves of Fig. 2. The image has a "shaggy spot" of alternate intensities along its column, which is perpendicular to the direction of tip motion. This shaggy spot is mainly caused by a relation between the direction of tip motion and the direction where the CH$_3$ tilts easily. Another origin is the fact that the CH$_3$ relaxes flexibly with the tip position, which can be seen from the lateral components of forces acting on the tip shown in the right hand of Fig. 3, showing considerable change with the tip position. Consequently, the image is so complex that we cannot understand a surface structure and a CH$_3$ internal structure straightforward from it.

In the case of 0.1 nm, we found the flexible relaxation of CH$_3$ again, but the relaxation is less significant than in the case of 0.1 nm. The obtained image shown in Fig. 4 has regions of attractive forces around the H sites and regions of repulsive forces around the CH$_3$ sites, as we expect from the force curves of Fig. 2. We observe the CH$_3$ as a round spot in the image, and cannot observe an internal structure of CH$_3$, because the CH$_3$ relaxes flexibly with the tip moving as mentioned before.

In the case of 0.3 nm, we observe small forces for the CH$_3$ and no forces for the H. Therefore, the CH$_3$ hardly changes. It is hard to see the existence of H-C bonds in the CH$_3$ from the obtained image shown in Fig. 5, but we can recognize the heart-like anisotropic spot around the CH$_3$. The heart-like spot is actually caused by the fact that the height of one of the three H atoms in CH$_3$ differs from those of the other two H atoms.

B. Si-tip with hydrogen at the apex

Figure 6 shows the calculated vertical components of forces as a function of the tip-sample distance in the case
FIG. 4: Constant height AFM image (left) and lateral components of forces acting on the tip (right) at the tip-sample distance of 0.2 nm, calculated using a Si-tip without the hydrogen at the apex. Solid line and black (gray) circles denote the initial structure of the first layer of the CH$_3$/H-SAM.

FIG. 5: Constant height AFM image (left) and horizontal components of forces acting on the tip (right) at the tip-sample distance is 0.3 nm, calculated using a Si-tip without the hydrogen at the apex. Solid line and black (gray) circles denote the initial structure of the first layer of the CH$_3$/H-SAM.

FIG. 6: Calculated vertical components of the forces as a function of the tip-sample distances obtained using a Si-tip with hydrogen at the apex. Solid and dashed lines denote the cases where the tip is located just above the CH$_3$ and H, respectively.

IV. DISCUSSION

From the results presented in the previous section, we can say that the tip-sample distance is more important than the tip type. When the tip-sample distance is small, to obtain good images is difficult regardless of the tip apex type, because flexible relaxation of the CH$_3$ due to the tip makes AFM images complex. At the distance including a region where the tip-sample interaction is weak, good images can be obtained more easily, in the sense that the flexibility of CH$_3$ is small.

When the tip-sample distance is set to be a suitable one for the tip type, we can see the considerable difference between images of different tip types. Although we can observed anisotropic spots of the CH$_3$ reflecting its symmetry in both tip types, the images obtained with the apex hydrogen are clearer showing the internal H and C atoms in the CH$_3$. However, the magnitude of the forces is much smaller in the case of the tip with hydrogen than that without hydrogen. Therefore, more precise measurement of forces is needed.

Lastly, we note that the calculated force curves are not smooth. This may be due to the existence of many local
FIG. 7: Constant height AFM image (left) and lateral components of forces acting on the tip (right) at the tip-sample distance of 0.2 nm, calculated using a Si-tip with hydrogen at the apex.

minima in the adiabatic potential surface at least partly caused by the flexibility of the CH$_3$. Especially, this makes it difficult to obtain the images with good resolution when a tip-sample distance is less than the distance where the maximum repulsive force is observed. Furthermore, existence of many delicate local minima in total energy may make the assumption of zero phonon in the present calculation invalid for the small tip-sample distance: The AFM images may change drastically by considering phonons at finite temperatures.

V. CONCLUDING REMARKS

We have investigated constant-height AFM images of the H-terminated Si(100)2×1 surfaces including a CH$_3$ impurity, using density-functional-based tight-binding method. Using Si-tip without hydrogen at the apex, the obtained images are observed as a shaggy spot when the tip-sample distance is small, a round spot when it is middle, and a symmetric spot when it is large. When observing with large tip-sample distance, we obtain good images showing anisotropic spots reflecting the symmetry of CH$_3$. If atomic resolution is needed for the image of adsorbed CH$_3$ and the force can be measured precisely, we expect to obtain better images showing internal H and C atoms of CH$_3$ using Si-tip with hydrogen at the apex.

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