Visualization of Thermally Fluctuating Surface Structure in Noncontact Atomic-Force Microscopy and Tip Effects on Fluctuation: Theoretical Study of Si(111)-($\sqrt{3} \times \sqrt{3}$)-Ag Surface

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We investigated noncontact atomic-force microscopy (NC-AFM) images of a thermally fluctuating surface structure together with tip effects based on the first-principles electronic state calculation. As an example the Si(111)-($\sqrt{3} \times \sqrt{3}$)-Ag ($\sqrt{3}$-Ag) surface is studied. We have succeeded in theoretically visualizing the thermal fluctuation of the $\sqrt{3}$-Ag surface at room temperature, and in reproducing the observed NC-AFM image for the first time. Further, the pinning effect of the thermal fluctuation of the $\sqrt{3}$-Ag surface by the tip is clarified, which shows a novel ability of NC-AFM to modify the surface structure.

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Noncontact atomic-force microscopy (NC-AFM) [1] can image the surface in a true atomic resolution by scanning the nanoscale tip above the surface. In NC-AFM [Fig. 1(a)], the tip-surface interaction force F_z is detected as a frequency shift $\Delta\nu$ with the cantilever oscillated at the resonance frequency. Two-dimensional mapping of the frequency shift $\Delta\nu$ provides the images which exhibit various dynamical information of the surface.

However, as a tool for surface modification, the possibility of NC-AFM has not yet been well explored. The aim of this Letter is to clarify a unique ability of NC-AFM to modify the surface structure based on the first-principles calculation.

In this Letter, the Si(111)-($\sqrt{3} \times \sqrt{3}$)-Ag surface (referred to as the $\sqrt{3}$-Ag surface hereafter) is adopted as an example of sample surface for the following reasons: (i) Comparison with experiment is easy because there are several experimental results at room temperature [2,3]. (ii) Recent rapid progress of studies of the $\sqrt{3}$-Ag surface has revealed quite a new feature of the structure and dynamics of this surface, as described below.

As an energetically stable structure of the $\sqrt{3}$-Ag surface, the "inequivalent-triangle" (IET) structure [4] has been recently found and confirmed both theoretically and experimentally, although the "honeycomb-chained-triangle" (HCT) structure [5] had been firmly believed so far. As shown in Fig. 1(b), the HCT structure has dotted triangles of equivalent size within the $\sqrt{3} \times \sqrt{3}$ unit cell. On the other hand, there exist two different phases of IET structures (IETa and IETb), where dotted triangles of inequivalent size are located. As shown in Fig. 1(b), the IETa and IETb structures can be regarded as the structures obtained by rotating solid triangles of the HCT structure, by $-6°$ and $+6°$ around the fixed centers of the solid Ag triangles, respectively. The rotational angle of the triangle, θ_{Ag}, becomes 54°, 60°, and 66° for the IETa, HCT, and IETb structures, respectively. In the potential energy curve as a function of θ_{Ag} [Fig. 2(a)], the IETa and IETb structures correspond to the local minimum points, and the HCT corresponds to the saddle point [6]. Since the energy difference between the IET and HCT structures, ΔV, is about 0.1 eV, thermal fluctuation between the IETa and IETb becomes possible at room temperature. The thermal fluctuation of Ag atoms at room temperature has been theoretically predicted using the Monte Carlo simulation [7,8]. Experimental scanning tunneling microscopy (STM) images were reproduced well based on the assumption that the STM images at room temperature observe the time average of fluctuated structure of the $\sqrt{3}$-Ag surface [7].

However, experimental NC-AFM images could not be reproduced based on the assumption that the simple average of the fluctuating IET structures is observed [9]. The reason for that may be ascribed to the fact that the

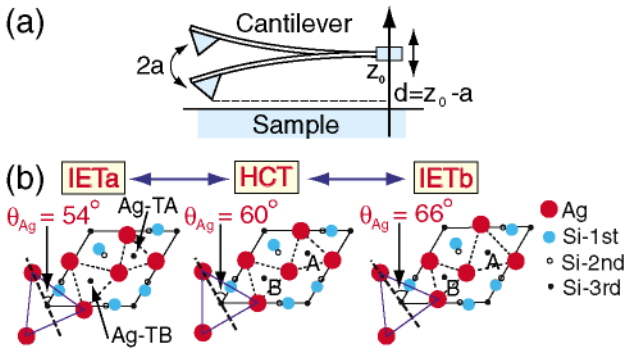

FIG. 1 (color). (a) The cantilever-surface system of NC-AFM. (b) The structures of Si(111)-($\sqrt{3} \times \sqrt{3}$)-Ag surface. HCT structure and two types of IET structures, IETa and IETb.

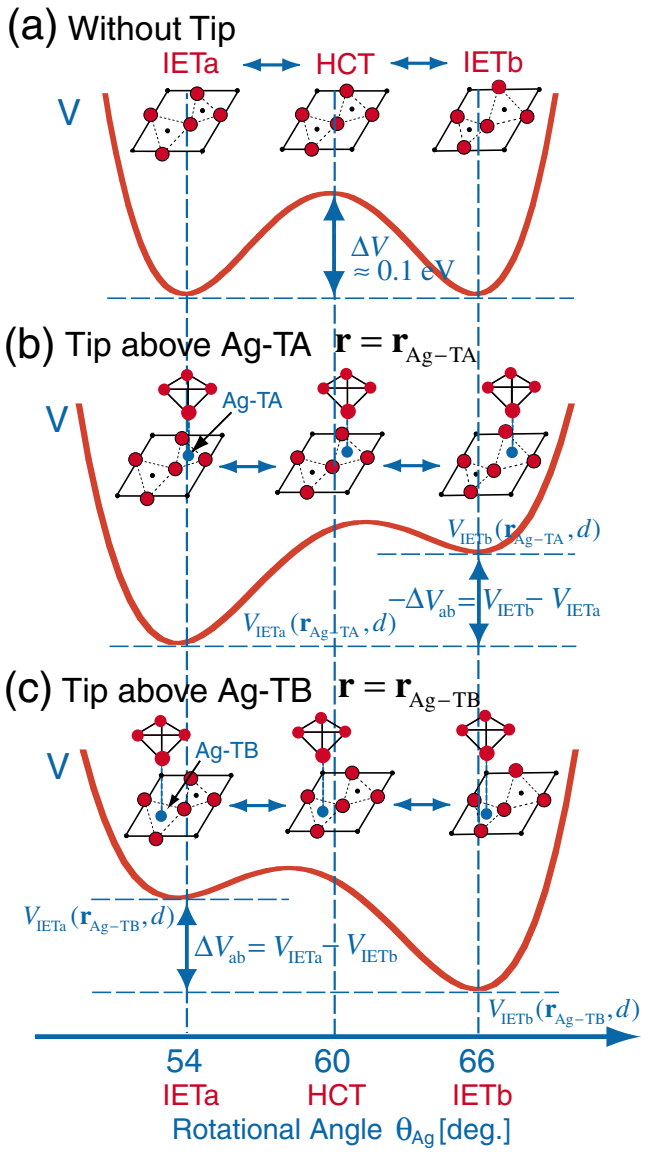

FIG. 2 (color). Potential energy curve as a function of the rotational angle θ_{Ag} for the $\sqrt{3}$-Ag surface (a) without tip, (b) with a tip above Ag-TA, and (c) with a tip above Ag-TB. $\Delta V_{\mathrm{ab}}(\mathbf{r}, d)$ is defined as $V_{\mathrm{IETa}}(\mathbf{r}, d) - V_{\mathrm{IETb}}(\mathbf{r}, d)$. Here, $V_{\mathrm{IETa}}(\mathbf{r}, d)$ and $V_{\mathrm{IETb}}(\mathbf{r}, d)$ denote the energies for IETa and IETb structures, respectively, when the tip is located at $(\mathbf{r}, d)$. In the case of (b) and (c), the symmetry of the potential is broken due to the tip-surface interaction.

tip-surface distance is much closer in the case of NC-AFM than in the case of STM, which means that the tip-surface interaction causes remarkable influence on the fluctuation in the former case.

Therefore in this Letter we describe the above effect by considering the weighted average of the IETa and IETb structures with the Boltzmann factor counting the difference of the interaction energies between both phases. As a result we have succeeded in visualizing thermal fluctuation and reproducing the experiment at room temperature. The most impressive success of our method is to clarify the pinning of the thermal fluctuation of $\sqrt{3}$-Ag surface by the tip position. This fact means that NC-AFM can not only observe but also control directly the fluctuating surface structures such as Si(001)-(2 × 1), Sn/Ge(111), and Si(111)-($\sqrt{3} \times \sqrt{3}$)-Ag surfaces. The unique ability of the NC-AFM should open a new research field in nanoscale science.

First, we should pay attention to the difference of the time scales between the fluctuation of the $\sqrt{3}$-Ag surface structure and the tip motion of NC-AFM operation. The typical interval of fluctuation time, τ_{fluc}, is estimated by $\tau_{\mathrm{fluc}} \simeq \nu^{-1} \exp(\frac{\Delta V}{k_B T})$, where ν, ΔV, k_B, and T are the frequency, barrier height, Boltzmann constant, and temperature, respectively. Here the frequency $\nu = 2.6 \times 10^{12}$ s and the barrier height $\Delta V \simeq 0.1$ eV are obtained using the previously calculated potential energy curve [6]. At room temperature ($T = 300$ K), τ_{fluc} is the order of 10^{-11} s, which is much smaller than that of the cantilever oscillation, $\tau^{z}_{\mathrm{AFM}} = 10^{-7}$–$10^{-8}$ s, and raster scan, $\tau^{xy}_{\mathrm{AFM}} = 10^{-3}$–$10^{-4}$ s. Therefore NC-AFM can observe the thermal fluctuated structure of the $\sqrt{3}$-Ag surface under the thermal equilibrium state at room temperature. Here, precisely, there exist two different types of τ_{fluc}, τ_{a} and τ_{b}, dependent on whether the surface takes an IETa structure or an IETb structure, which will be discussed later in this Letter.

Second, to calculate thermal fluctuated NC-AFM images with weighted average, we introduce a quantity p_{IETa}, the probability where the IETa structure is realized. As shown in Fig. 2(a), the total potential energy curve of the $\sqrt{3}$-Ag surface is symmetric. On the other hand, as shown in Figs. 2(b) and 2(c), when the tip is located on the $\sqrt{3}$-Ag surface, the potential energy curve becomes asymmetric due to the tip-surface interaction. Here the surface positions of Ag trimer center A (Ag-TA) and Ag trimer center B (Ag-TB) are defined as the centers of the smaller and larger dotted triangles of the IETa structure, respectively, as shown in Fig. 1(b). When the tip is located above the Ag-TA, the IETa structure is energetically more stable than the IETb structure, as shown in Fig. 2(b). This is because the tip-surface attractive interaction force becomes larger when the tip is located on the smaller dotted triangle than when it is located on the larger one. On the other hand, when the tip is located above the Ag-TB, the IETb structure similarly becomes more stable than the IETa structure, as shown in Fig. 2(c).

Since the thermal equilibrium state for the energy V at temperature T is realized with the probability proportional to the factor $p(V) \propto \exp(-\frac{V}{k_B T})$, the probability where the IETa structure is realized, when the tip is located at the position $(\mathbf{r}, d)$, can be obtained as

$$
\begin{aligned}
p_{\mathrm{IETa}}(\mathbf{r}, d) &= \frac{p[V_{\mathrm{IETa}}(\mathbf{r}, d)]}{p[V_{\mathrm{IETa}}(\mathbf{r}, d)] + p[V_{\mathrm{IETb}}(\mathbf{r}, d)]} \\
&= \frac{1}{1 + \exp(\frac{\Delta V_{\mathrm{ab}}(\mathbf{r}, d)}{k_B T})} : \Delta V_{\mathrm{ab}}(\mathbf{r}, d) \\
&= V_{\mathrm{IETa}} - V_{\mathrm{IETb}}\,, \qquad (1)
\end{aligned}
$$

where $\mathbf{r} = (x, y)$ and $d = z_0 - a$ denote a lateral and a closest approaching vertical tip position, respectively. Here z_0 and a denote the cantilever basal position and oscillation amplitude, respectively, as shown in Fig. 1(a). $\Delta V_{\mathrm{ab}}(\mathbf{r}, d)$ represents the difference between the energy for the IETa structure, $V_{\mathrm{IETa}}(\mathbf{r}, d)$, and that for the IETb structure, $V_{\mathrm{IETb}}(\mathbf{r}, d)$, when the tip is located at $(\mathbf{r}, d)$. To derive Eq. (1), the following three assumptions are adopted for simplicity. (*i*) Only two states corresponding to the IETa and IETb structures are considered. (*ii*) The energy $V(\mathbf{r}, d)$ for the closest approach of the tip to the surface is considered. (*iii*) Only the weak attractive interaction regime of the tip height of $d \geq 4.25$ Å is considered, because, for $d < 4.25$ Å, adhesion between the Si tip atom and Ag surface atom occurs, which causes a hysteresis in the force curve.

Equation (1) is of great importance, for it means that p_{IETa} is a function of the tip position through ΔV_{ab}. Note that p_{IETa} is a quantity which directly reflects the feature of the thermal fluctuation of the surface. Thus the thermally fluctuated NC-AFM image is obtained by calculating the weighted average of the frequency shift as

$$\Delta\nu(\mathbf{r}, d) = p_{\mathrm{IETa}}(\mathbf{r}, d)\Delta\nu_{\mathrm{IETa}}(\mathbf{r}, d) + p_{\mathrm{IETb}}(\mathbf{r}, d)\Delta\nu_{\mathrm{IETb}}(\mathbf{r}, d), \quad (2)$$

where $p_{\mathrm{IETb}} = 1 - p_{\mathrm{IETa}}$.

Here the total tip-surface interaction energy V and force F_z were calculated by the summation of the short- and long-range parts. The short-range part was obtained by the density functional theory with the local density approximation [10,11]. The SiH_3 tip and a surface slab comprised of a Ag layer, 5 silicon layer, and a terminating hydrogen layer, were used. The unit cell with a periodicity of $(\sqrt{3} \times \sqrt{3})R30°$ was employed. The long-range part was calculated by the continuous Hamaker model [12,13]. Thus the frequency shift $\Delta\nu(\mathbf{r}, d)$ was calculated utilizing the Fourier expansion method [13].

The first remarkable result we obtain is the direct visualization of the thermal fluctuation of $\sqrt{3}$-Ag surface. The probability p_{IETa} at room temperature, $T = 300$ K, is two dimensionally plotted for $d = 4.75$, 4.50, and 4.25 Å in Fig. 3(a). As the tip approaches close to the surface, above the Ag-TA, the IETa structure tends to appear in a larger probability p_{IETa} due to the increase of $|\Delta V_{\mathrm{ab}}| = -\Delta V_{\mathrm{ab}}$, that is to say, $p_{\mathrm{IETa}} \rightarrow 1$. On the other hand, above the Ag-TB, the IETb structure similarly tends to appear in a larger probability. Therefore the half of the unit cell including the Ag-TA and Ag-TB becomes brighter and darker, respectively [Fig. 3(a)]. Thus the image contrast between these bright and dark areas becomes more clear as the tip approaches closer to the surface. The increase of p_{IETa} (p_{IETb}) with the tip approach above Ag-TA (Ag-TB) can be regarded as a "pinning effect of the thermal fluctuation" induced by the increase of the attractive tip-surface interaction acting between the Si atom and the Ag atoms. This effect is clearly seen in the cross section of the p_{IETa} pattern along a long

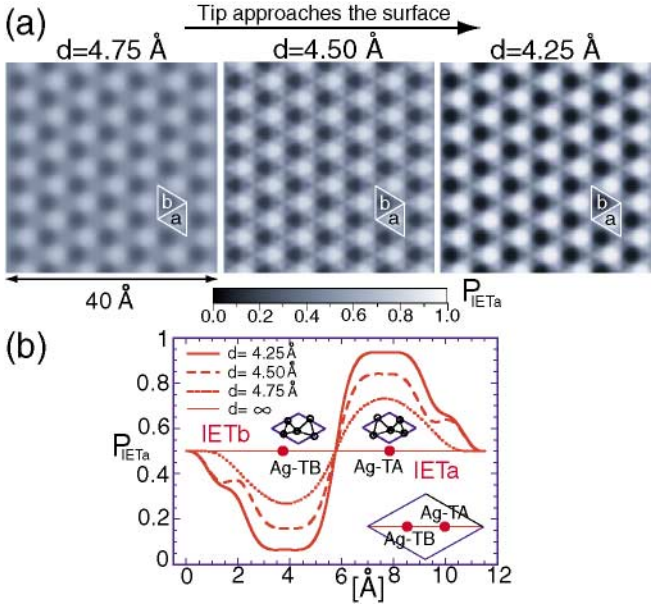

FIG. 3 (color). (a) The tip-height dependence of the two-dimensional plots of p_{IETa}, for $d = 4.75$, 4.50, and 4.25 Å, at $T = 300$ K. (b) Cross section of (a) along a long diagonal of a $\sqrt{3} \times \sqrt{3}$ unit cell.

diagonal of the $\sqrt{3} \times \sqrt{3}$ unit cell [Fig. 3(b)] and the tip-height dependence of τ_{fluc} (Fig. 4). In Fig. 4, as the tip approaches the surface above Ag-TB, τ_a and τ_b, the fluctuation times when the surface takes IETa and IETb structures, become shorter and longer, respectively, according to the relation $\tau \simeq \nu^{-1} \exp(\frac{\Delta V}{k_{\mathrm{B}}T})$. Because, the barrier heights for the IETa and IETb structures become smaller and larger, respectively. Figure 4 clearly exhibits a relation $\tau_a < 10^{-11}$ s $< \tau_b \ll \tau^{z}_{\mathrm{AFM}} \ll \tau^{xy}_{\mathrm{AFM}}$.

The second remarkable result we obtained is the simulation of NC-AFM images at room temperature by considering the weighted average. As seen in Fig. 5(a), the NC-AFM images for $T = 300$ K exhibit slightly deformed honeycomb structures ($d = 4.75$ Å), remarkably deformed honeycomb structures ($d = 4.50$ Å), and nearly triangular structures ($d = 4.25$ Å). These images exhibit network structures where the atom positions do

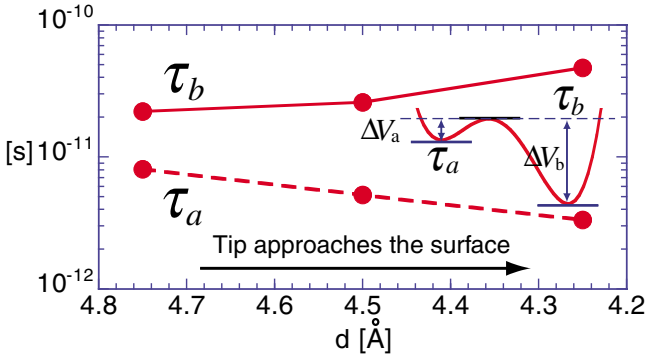

FIG. 4 (color). The intervals of the thermal fluctuation time, τ_a and τ_b, within which the surface takes an IETa and an IETb structure, respectively, as a function of the tip height. The tip is located above Ag-TB.

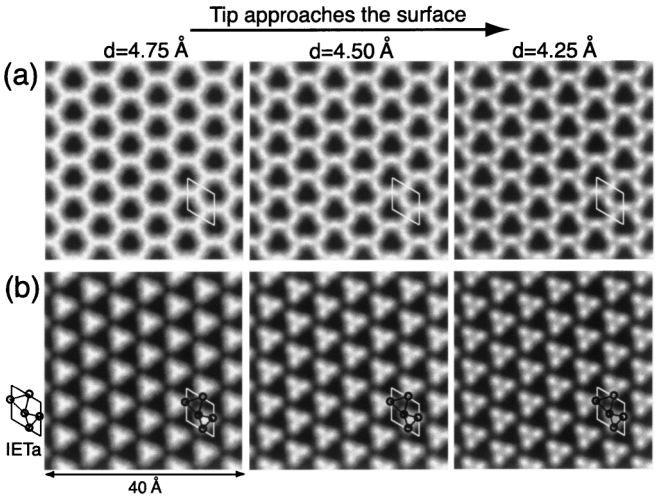

FIG. 5. NC-AFM images $|\Delta\nu(\mathbf{r}, d)|$ for (a) weighted average and (b) IETa structure with the tip height of $d = 4.75$, 4.50, and 4.25 Å.

not correspond to bright spots. This image transition is due to the following reasons: (I) pinning effect of the thermal fluctuation, (II) site dependence of the force curve, (III) change in the way the atomic orbitals of the tip and surface overlap, and (IV) deformation or structural change of the tip and surface. We have already reported the results of simulation when taking account of the factors (II), (III) and part of (IV) (deformation of sample surface) [6], but the agreement with experiments was not satisfactory. On the other hand, in the present results, including not only the above factors but also (I), the image for $d = 4.50$ Å reproduces quite well the reported experimental images [Fig. 2(a) in Refs. [2,3]]. Thus the description of the thermal fluctuation by the weighted average between the IETa and IETb structures can successfully explain experimental results. Here it should be noted that theoretical tip-height, $d = 4.50$ Å, is different from the experimental tip height, $z = 2.50$ Å, for Fig. 2(a) in Refs. [3,4], because the former and the latter are defined in different ways as follows: the theoretical one is defined as the distance between the Si tip atom and rigid Ag surface atom, while the experimental one is evaluated from the shape of the amplitude-distance curve.

Note also that the thermally fluctuated images are completely different from the original IET images. As seen in Fig. 5, thermally fluctuated images and IETa images exhibit $p31m$ symmetry of the HCT structure [Fig. 5(a)] and $p3$ symmetry of the IET structure [Fig. 5(b)], respectively. Therefore, if only information of images at room temperature [Fig. 5(a)] is used to interpret observed NC-AFM images, the HCT structure is naturally predicted as a $\sqrt{3}$-Ag surface. This result is consistent with the previous experimental results which showed that the images could be interpreted by the HCT structure [2,3]. Therefore we would like to emphasize that the information on the IET structure is "hidden" in NC-AFM images by the weighted average.

It should be noted that the tip apex structure can also affect the AFM image pattern as was discussed by Yokoyama *et al.* [14], and as has been known in the case of STM [15,16]. At present, we cannot deny the possibility that the difference between Figs. 2(a)–2(c) in Refs. [2,3] may be due to the tip apex structure, though this possibility is expected to be low judging from the experimental reproducibility. Detailed first-principles study must be necessary to reach the final and definite conclusion on this difference.

To summarize, we have succeeded in reproducing the observed NC-AFM image of $\sqrt{3}$-Ag surface at room temperature, and clarified the pinning effect of the thermal fluctuation by the NC-AFM tip, for the first time. The latter results exhibit the unique ability of NC-AFM to modify the surface, which should open a new research area of nanotechnology.

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