STM Images Apparently Corresponding to a Stable Structure: Considerable Fluctuation of a Phase Boundary of the Si(111)-($\sqrt{3} \times \sqrt{3}$)-Ag Surface

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We study scanning tunneling microscopy (STM) images near a phase boundary of the Si(111)-($\sqrt{3} \times \sqrt{3}$)-Ag surface by using Monte Carlo simulations based on results of first-principles calculations. The boundary is found to fluctuate from snapshot to snapshot, and the feature of the simulated STM images differs distinctly from the observed one with a straightly extending honeycomb pattern of bright spots. Remarkably, statistical averages of the simulated images reproduce the observed feature. This study gives a warning of our tendency to relate STM images revealing clear arrangement of bright spots with some stable structure.

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Scanning tunneling microscopy (STM) is an excellent tool to examine local structures of solid surfaces on the atomic scale. However, when topmost atoms of a surface move drastically, they are often observed as noisy images. In some cases, they do not even leave any traces of themselves [1] or are observed as the images with an extending protrusion in a confined area [2]. A common tendency of all the above is that the STM images do not reveal a clear arrangement of bright spots corresponding to the moving topmost atoms.

Remarkable exceptions are clean Si(001) and Ge(001)-(2×1) surfaces. On these surfaces, neighboring topmost atoms form asymmetric tilting dimers [3] and repeat rapid flip-flop motion, resulting in the filled-state STM images with a (2×1) symmetric arrangement of bright spots [4]. This picture was substantiated by an *ab initio* estimate of the flipping frequency [5]. The average feature of the images is rather straightforward, because the dangling bond orbital of the upper atom in each dimer mainly contributes to the intensity of the images [6], and the flip-flop motion is confined along the vertical direction.

Recently, another remarkable exception, the Si(111)-($\sqrt{3} \times \sqrt{3}$)-Ag surface, was found. Until a few years ago, the most stable structure of this surface had been believed to be the "honeycomb-chained triangle (HCT)" model [7–9], which seemingly explains the feature of the observed STM images with a honeycomb pattern of bright spots at room temperature [10–12]. However, the latest model, the "inequivalent triangle (IET)" one [13], has been shown to be more stable. Both models are compared in Fig. 1. Looking into the topmost Ag atoms, the IET model is obtained by a little rotational displacement from the HCT one [13]. It has two equivalent phases in accordance with the rotation, which are accessible to each other via the HCT one. Soon after the finding of the IET model, STM images were examined by using Monte Carlo simulation (MCS) [14] based on results of first-principles calculations (FPC) [15]. The surface was confirmed to undergo an order-disorder phase transition [14,16], and the observed STM images at room temperature were well understood as an average in a disordered state [14].

In this Letter, we report a more interesting exception, the low-temperature STM images near the phase boundary of two different IET domains of the Si(111)-($\sqrt{3} \times \sqrt{3}$)-Ag surface. We show that the observed STM images seemingly corresponding to a straightly extending HCT domain come from the boundary fluctuation. This study gives a warning of our tendency to relate STM images revealing a clear arrangement of bright spots with some stable structure.

We consider thermal motion of Ag atoms explicitly and all the rest implicitly [14,16]. The position of the mth Ag

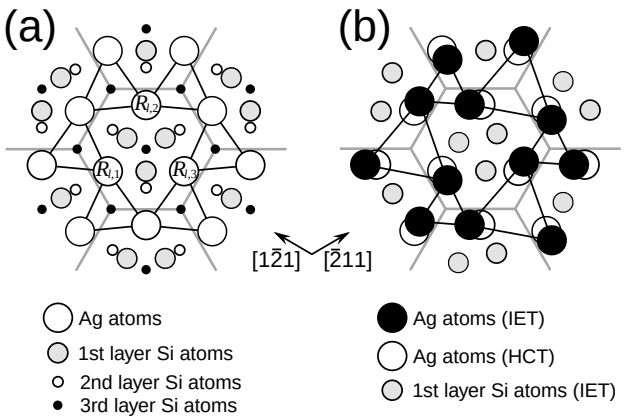

FIG. 1. Schematic illustration of (a) the honeycomb-chained triangle (HCT) model and (b) the inequivalent triangle (IET) model of the Si(111)-($\sqrt{3} \times \sqrt{3}$)-Ag surface. Gray and black lines denote boundaries of $\sqrt{3} \times \sqrt{3}$ unit cells and chained triangles of Ag atoms, respectively. In (b), Ag atoms of the HCT model are also shown for comparison.

atom in the lth unit cell of the HCT structure is represented by $\boldsymbol{R}_{l,m}$ $(m = 1, 2, 3)$. The displacement $u_{l,m}$ of each Ag atom from $\boldsymbol{R}_{l,m}$ is allowed only on the tangent touching the circle on which $\boldsymbol{R}_{l,1}$, $\boldsymbol{R}_{l,2}$, and $\boldsymbol{R}_{l,3}$ lie [14,16]. The $\pm$ phase of the IET structure is represented by $u_{l,m} = \pm 1$ according to the direction of the rotation, respectively. We use the adiabatic potential for the Ag atoms developed in our previous study [14].

We perform MCS for the system consisting of 50 rows of the unit cell arranged along the $[1\bar{2}1]$ direction, each of which has 50 unit cells along the $[\bar{2}11]$ direction (7500 Ag atoms). The displacement from the HCT position u is allowed to take 0, ± 0.5, ± 1, ± 1.5, ± 2, ± 2.5, and ± 3 [14]. As the initial condition, the system is divided equally into two different IET domains along the $[\bar{2}11]$ direction, in the temperature region below the transition temperature (about 260 K) [14] on the basis of the STM observations [13,17]. Both edges of the system along the $[\bar{2}11]$ direction are kept fixed to the initial configuration during MCS, and the periodic boundary condition is imposed on those along the $[1\bar{2}1]$ direction. The Metropolis algorithm is used to update the configuration of the Ag atoms. Each snapshot obtained after a set of updating over the system in the thermal equilibrium is used for thermodynamic averages.

STM images for negative bias voltages reflect the characteristic of the local density of states for unoccupied states [18]. We represent the images by the density plots, which are approximated by the superposition of the two-dimensional Gaussian functions centered at the centroid of each chained triangle of Ag atoms [14] on the basis of the results of FPC [13].

Figures 2(a) and 2(b) show results of typical examples of snapshots near the IET phase boundary in the same area at 100 K. Open, filled, and meshed circles represent Ag atom positions with $u \geq 0.5$, $u \leq -0.5$, and $u = 0$, respectively. We find that the boundary region is dominated by the atoms with $|u| \geq 0.5$, most of which with $|u| = 1$, and that those with $u = 0$ hardly appear. That is, the boundary structure is sharp and HCT domains do not exist practically.

Figures 2(c) and 2(d) show corresponding STM images of snapshots (a) and (b), respectively. In accordance with the two different IET domains extending over both sides of the boundary, the two different phases of hexagonal lattice pattern are seen in Figs. 2(c) and 2(d). We find that the boundary region does not reveal a honeycomb pattern. It should be noted that both shape and positions of the boundary fluctuate from snapshot to snapshot as seen in Figs. 2(a) and 2(b). Correspondingly, the feature of the simulated STM images differs from each other as seen in Figs. 2(c) and 2(d), both of which are also quite different from the observed one [13,17]. However, after we take a statistical average over snapshots (10^5 snapshots), the resultant image comes to reveal a clear honeycomb pattern in the boundary region as seen in Fig. 3. This reproduces well the feature of the observed STM images near the IET phase boundary at 62 K [13,17].

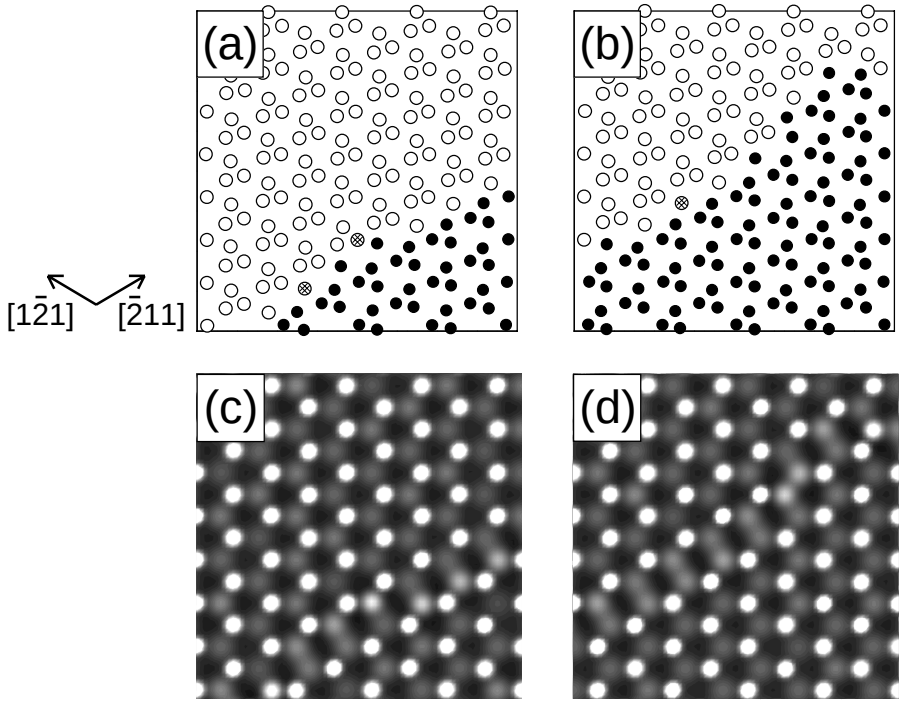

FIG. 2. (a), (b) Examples of snapshots of the same area at 100 K. Open, closed, and meshed circles represent positions of Ag atoms with displacement from HCT position $u \geq 0.5$, $u \leq -0.5$, and $u = 0$, respectively. (c), (d) Corresponding STM images of snapshots (a) and (b), respectively.

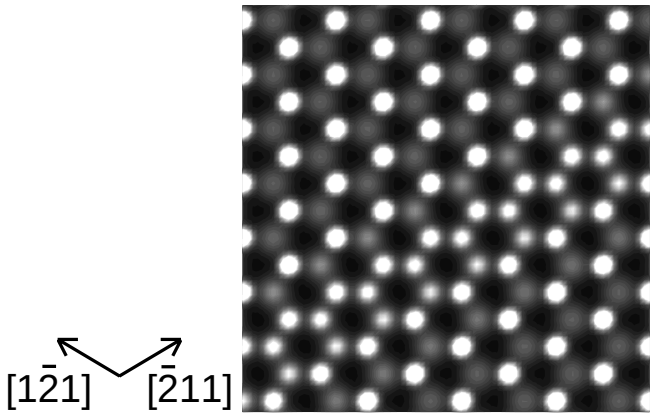

FIG. 3. STM image averaged over 10^5 snapshots at 100 K.

Further, the present MCS explains qualitatively the following puzzling features observed in the low-temperature STM experiments [13,17]: while defects are hardly seen on the surface, the width of the boundary is observed differently even at the same temperature, and the position fluctuates from one observation to the other. We show the STM images averaged over the first 10^5 and the last 10^5 snapshots in the sequence of 5×10^5 snapshots of the same area in the thermal equilibrium at 100 K in Figs. 4(a) and 4(b), respectively. A honeycomb pattern extends widely in the upper left region in Fig. 4(a), while it becomes narrower and moves to the central part in Fig. 4(b). These are caused by the boundary fluctuation similar to the Brownian motion: a honeycomb pattern appears in the region where the ratio of each site being on one side of the boundary to the other is nearly the same on average, and the position and the width of such a region are able to be observed differently.

As for the dynamics of the boundary fluctuation, it is considered that the Ag atoms in one of the two different IET domains change into those in the other via the HCT positions. Then, the energy barrier for this motion ΔE_B concerns the time scale of the fluctuation of Ag atoms near the boundary. Assuming that the transition rate t is expressed as $f \exp(-\Delta E_B/k_B T)$ together with roughly estimated values of $\Delta E_B \approx 20$ meV and $f \sim 10^{12}$ [sec^{-1}], we obtain t to be of the order of 10^{11} [sec^{-1}] at $T = 100$ K, where k_B and T are the Boltzmann constant and the temperature, respectively. Therefore, the boundary fluctuates more than enough to reveal the averaged feature during the STM observation (of the order of 1–10 [msec/pixel]) at such a low temperature.

It has been well known that a clear arrangement of bright spots of STM images does not directly reflect the atomic configurations [12,18–20]. In addition to this, the present study gives another important message: a warning of our tendency to relate STM images revealing a clear arrangement of bright spots with some stable structure. This tendency becomes stronger at a lower temperature, because the thermal fluctuation seems to be hardly expected. Consequently, we hardly expect the possibility of surface fluctuation, which may lead to a wrong interpretation of STM images as we have demonstrated in the present Letter. This is expected to be a serious problem common to the scanning probe microscopy observations as a whole [21,22]. On the clean Si(001) and Ge(001) surfaces, direct detection of the flip-flop motion has been experimentally achieved using the STM tip [23,24] by keeping the tip over a preselected atom of the dimer and measuring time variation of the tunneling current. However, the fluctuation of the Si(111)-($\sqrt{3} \times \sqrt{3}$)-Ag surface is considered to be too fast to defect due to the limitation of the dynamic characteristics of the STM amplifier. Therefore, new alternative methods to detect such rapid fluctuation are highly desired.

Local freezing and its influence on the surface domain structures are other interesting issues, as we see in the

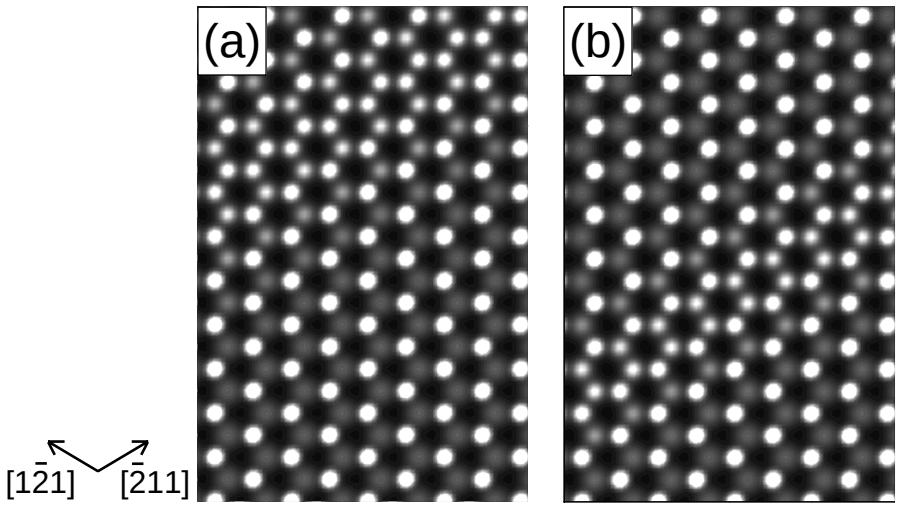

FIG. 4. STM images averaged over (a) the first 10^5 and (b) the last 10^5 snapshots in the sequence of 5×10^5 snapshots of the same area at 100 K.

recent intriguing STM observation of Ge(001) [25], for example. Studies on this kind of issue for Si(111)-($\sqrt{3} \times \sqrt{3}$)-Ag are now in progress.

In conclusion, we performed Monte Carlo simulations based on results of first-principles calculations to study STM images near the IET phase boundary of the Si(111)-($\sqrt{3} \times \sqrt{3}$)-Ag surface. It was found that the boundary fluctuates from snapshot to snapshot at low temperatures ($\sim$100 K) and that the feature of the simulated STM images differs distinctly from the observed one with a straightly extending honeycomb pattern of bright spots. Remarkably, statistical averages of the simulated images reproduce the observed feature well. The present study not only contributes to a unified understanding of the observed images of this surface but also gives a warning of our tendency to relate STM images revealing a clear arrangement of bright spots with some stable structure.

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