STM tip-induced diffusion of In atoms on the Si(111)$\sqrt{3}\times\sqrt{3}$-In surface

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Scanning tunneling microscopy (STM) tip-induced diffusion of In atoms was observed on the Si(111)$\sqrt{3}\times\sqrt{3}$-In surface. We found that In migration to the region beneath the tunneling tip results in the In coverage increase and spontaneous $\sqrt{3}\times\sqrt{3}$-In$\rightarrow$$2\times2$-In structural transformation at negative tip bias voltages. At positive tip bias voltage In diffusion from the region beneath the tunneling tip results in the In coverage decrease and 2×2-In$\rightarrow$$\sqrt{3}\times\sqrt{3}$-In structural transformation. Indium adatoms in our experiments show up as being positively charged. STM tip field-induced In-atom migration occurs at room temperature, at bias voltages typical for the STM observations, without additional tip movement toward the surface. [S0163-1829(97)06836-7]

I. INTRODUCTION

The scanning tunneling microscope has become one of the most important experimental techniques for surface science studies. It has provided images of surfaces and adsorbed atoms and molecules with atomic resolution. The scanning tunneling microscope has also been used to modify surfaces at the nanometer scale and to move single atoms.[1–8] Recently variable-temperature scanning tunneling microscopy (STM) has been used for *in situ* dynamic surface phenomena study such as diffusion, microscopic mechanisms of crystal growth, and surface ordering.[9–16] In this case the surface is imaged while keeping the sample at a temperature at which adsorbates move (diffuse) with a rate suitable for STM to track.[9,10] However, it was recognized, that the presence of the STM tip causes adatoms diffusion, especially for adsorbates with a large net charge or polarizability.[10,17,18] Nevertheless, the experimental study of STM tip-induced diffusion on semiconductor surfaces has not known a comparable development.

STM tip field-induced diffusion on semiconductor surfaces has been investigated in several works. By applying an appropriate voltage pulse between the sample and probe tip, Cs adatoms were induced to diffuse into the region beneath the tip, forming one-dimensional chains on the GaAs(110) surface.[19] Reversible displacement of Au on the Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface were observed when the tip was moved toward the surface in order to increase the field at the sample surface.[8] As a result, the edge of the $\sqrt{21}\times\sqrt{21}$-Au structure moved toward the tip or in the opposite direction depending on the tip bias.

In this paper, we report studies of STM tip-induced In-atom diffusion on the Si(111)$\sqrt{3}\times\sqrt{3}$-In surface at room temperature (RT). It is well known that electromigration of indium occurs on the Si(111) surface,[20] and its mass transport is driven by the electric field along the surface rather than a direct current through the sample. Thus one can expect a noticeable effect of the strong electric field under the STM tip on In-adatom diffusion. Furthermore, to reduce the surface corrugations of the Si(111)7×7 surface we formed a Si(111)$\sqrt{3}\times\sqrt{3}$-In structure. After that we formed a metastable ''low-temperature'' Si(111)2×2-In structure on it. This structure was formed during In adsorption onto the predeposited substrate, the Si(111)$\sqrt{3}\times\sqrt{3}$-In surface at around RT.[21,22] We found that a STM tip can repulse and attract In adatoms, resulting in 2×2-In$\rightarrow$$\sqrt{3}\times\sqrt{3}$-In and $\sqrt{3}\times\sqrt{3}$-In $\rightarrow$$2\times2$-In structural transformations at positive and negative tip bias voltages, respectively. The results were explained by STM tip-induced diffusion of In atoms on the $\sqrt{3}\times\sqrt{3}$-In and 2×2-In surfaces. We found that In atoms have high mobility on the $\sqrt{3}\times\sqrt{3}$-In and 2×2-In surfaces. Indium diffusion occurs truly reversibly, at RT, at bias voltages, typical of the STM observations, without additional tip movement toward the surface.

II. EXPERIMENT

A Si(111) sample (2×13 mm^2) was cut from Sb-doped n-type Si wafers (0.05 Ω cm) and mounted on a sample holder of a STM-LEED (low-energy electron diffraction) (''Omicron'') operated in an ultrahigh vacuum (UHV) of about 8×10^{-11} Torr and cleaned by repeated heating at 1250 °C in UHV better than 2×10^{-10} Torr to obtain a 7×7 surface. Electrochemically etched tungsten tips, cleaned by

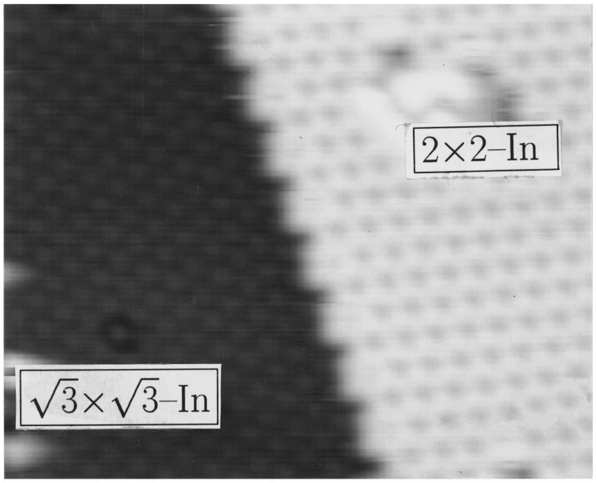


FIG. 1. Filled state STM images, 300×300 Å^2, of the surface coexisting domains of 2×2-In and $\sqrt{3}\times\sqrt{3}$-In structures. The image was taken with a tip voltage of $+1.3$ V and tunneling current of 0.05 nA.

in situ heating, were used. Indium was deposited from a Ta foil tube at the rate of about 0.1 ML/min. 2×2 reconstruction was formed by In deposition at temperatures $<100\ ^\circ$C on to the predeposited Si(111)$\sqrt{3}\times\sqrt{3}$-In surface. The latter structure was produced by the deposition of about 0.33 ML of In on the Si(111)7×7 surface held at $\approx550\ ^\circ$C. All STM images were taken with a tip voltage of $+2.0$ V, $I_t=0.07$ nA, and a scan speed of 1040 nm/s, unless otherwise stated.

III. RESULTS AND DISCUSSION

Surface modifications induced by STM were detected in term of changes in the STM image that result from the $2\times2\leftrightarrow\sqrt{3}\times\sqrt{3}$ structure transformation. It is well known that the Si(111)$\sqrt{3}\times\sqrt{3}$-In structure has a coverage of 0.33 ML,[23] while the Si(111)2×2-In structure has a saturation coverage of 0.75 ML.[22] Therefore, the $2\times2\rightarrow\sqrt{3}\times\sqrt{3}$ structure change during STM observation was associated with the decrease of In coverage in the region beneath the STM tip, and the $\sqrt{3}\times\sqrt{3}\rightarrow2\times2$ structure change with the increase of In coverage.

A high-resolution filled-state STM image of a $\sqrt{3}\times\sqrt{3}$-In surface partially covered by a 2×2-In structure is shown in Fig. 1. The area covered by 2×2-In reconstruction has a honeycomb arrangement of protrusions, and has an apparent height of 2.5 Å with respect to the $\sqrt{3}\times\sqrt{3}$-In one.[22] Thus it looks brighter in Fig. 1 and in all STM images presented below.

Prior to our experiments, we checked whether the STM tip can modify a $\sqrt{3}\times\sqrt{3}$-In surface, did not find any STM tip-induced modification of this surface at our experimental conditions. We observed STM tip-induced modification only after deposition of some additional In atoms on the $\sqrt{3}\times\sqrt{3}$-In surface at around RT. In our experiments, first, we imaged the surface, then the STM tip was held over the definite position of the sample (usually at the center of the imaged area), and the tip bias was pulsed to $+2$ or -2 V for some period of time. After that we imaged the same surface region again.

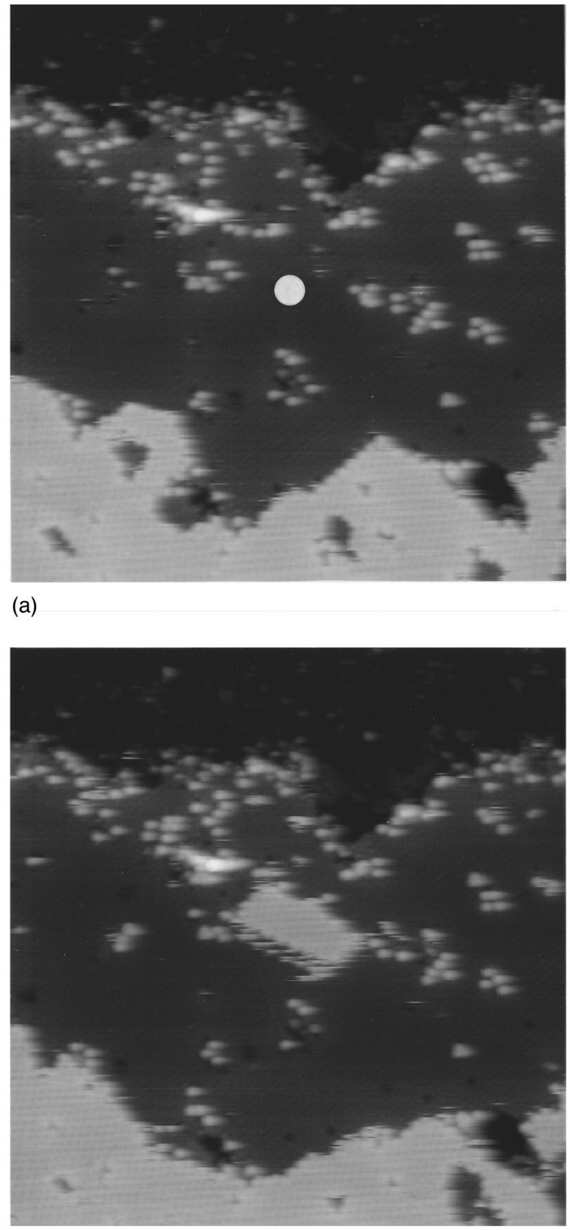
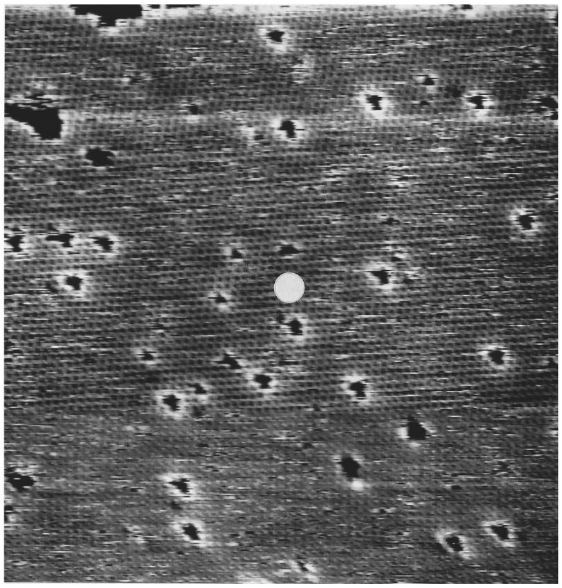


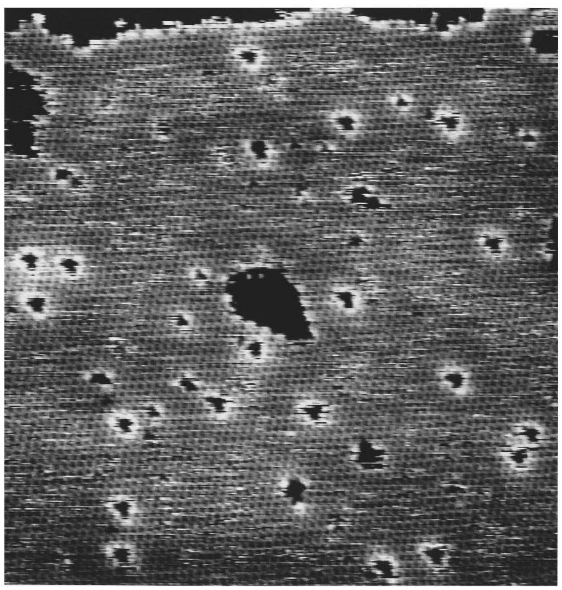
FIG. 2. Filled-state STM images, 500×500 Å^2, showing that the STM tip can induce 2×2-In structure formation in the region beneath the STM tip when the tip is negatively biased; before pulse (a), and after pulse (b). The tip was pulsed at $V_t=-2.0$ V, and $I_t=0.2$ nA for 5 s in the center of the imaged surface.

A STM image of $\sqrt{3}\times\sqrt{3}$-In surface partially covered by the 2×2-In structure (at the bottom) is shown in Fig. 2(a). In this case, an additional ~0.2 ML of indium was deposited on the $\sqrt{3}\times\sqrt{3}$-In surface. After this image was recorded, the STM tip was held over the position indicated by a white circle in Fig. 2(a), and the tip bias was pulsed to -2 V for 5 s. The image subsequently recorded [Fig. 2(b)] reveals the formation of the 2×2-In structure in the region beneath the tip and, thus, the increase of In coverage. It should be noted that there are two terraces on the surface shown in Fig. 2. The darkest area (the top of the image) corresponds to the lower terrace covered by the $\sqrt{3}\times\sqrt{3}$-In structure.

We repeated the experiment on the 2×2-In surface at the



(a)



(b)

FIG. 3. Filled-state STM images, 500×500 Å^2, showing that the STM tip can induce $\sqrt{3}\times\sqrt{3}$-In structure formation on the 2×2-In surface when the tip was positively biased; before pulse (a), after pulse (b). The tip was pulsed at $V_t=+2.0$ V, and $I_t=0.4$ nA for 10 s in the center of the imaged surface. Small holes are natural defects of the 2×2-In surface. These defects are stable with respect to the STM imaging. On the other hand, the domain boundary between $\sqrt{3}\times\sqrt{3}$-In and 2×2-In phases shown at the top of the images is unstable with respect to the STM imaging. Scanning at a positive tip bias voltage results in the repulsion of In atoms, 2×2-In $\rightarrow$ $\sqrt{3}\times\sqrt{3}$-In structural transformation and, finally, to the reduction of the area covered by the 2×2-In structure.

positive tip bias pulse. A STM image of the 2×2-In structure is shown in Fig. 3(a). After this image was recorded, the STM tip was held over the position, indicated by a white circle in Fig. 3(a), and the tip bias was pulsed to $+2$ V for 10 s. The image subsequently recorded [Fig. 3(b)] reveals that the positive voltage pulse-induced removal of In atoms beneath the tip, and $\sqrt{3}\times\sqrt{3}$-In structure formation in the region. As expected, we found that the amount of In added (removed) to (from) the region beneath the tip at negative (positive) tip bias increased with the pulse length. The amount of In also increased with the increase of the tunneling current. Thus one can see that the positive voltage pulse results in the removal of In atoms in the region beneath the STM tip, while the negative one results in the increase of In coverage in the region beneath the STM tip.

There are two possible explanations for the observed phenomena: First, extraction and deposition of In atoms induced by the STM tip, and second, STM tip-induced diffusion. That is, the decrease of In coverage at positive tip bias voltages can be explained by In-atom diffusion from the STM tip, or by extraction of In atoms by the STM tip; while the increase of In coverage at negative tip bias voltages can be explained by In-atom diffusion toward the STM tip or by deposition of In atoms from the STM tip. To elucidate the mechanism of STM tip-induced surface modifications, we carried out the following two experiments. In the first experiment we started from the surface with the patch of the $\sqrt{3}\times\sqrt{3}$-In structure which was produced by positive tip bias pulse. A STM image of this surface is shown in Fig. 4(a). After this image was recorded, the STM tip was held over the position, indicated by a white circle in Fig. 4(a), and the tip bias was pulsed to -2 V for 5 s. The image subsequently recorded [Fig. 4(b)] shows a dramatic redistribution of the the area covered by the 2×2-In structure. One can see that the negative voltage pulse-induced detachment of In atoms from the edge of the 2×2-In structure, diffusion towards the tip, and 2×2-In structure formation in the region. We estimated that the total area covered by 2×2-In (as well as by $\sqrt{3}\times\sqrt{3}$-In) structure in Figs. 4(a) and 4(b) is constant within the accuracy of our experiment. Thus this experiment definitely rules out In-atom deposition from the STM tip as, in this case, the increase of the total In coverage and so the increase of the total area covered by 2×2-In structure should occur.

In the second experiment we found the region with coexisting $\sqrt{3}\times\sqrt{3}$-In and 7×7-In structures. A STM image of this surface is shown in Fig. 5(a) (the 7×7-In structure at the center). After this image was recorded, the STM tip was held over the center, indicated by a circle in Fig. 5(a), and the tip bias was pulsed to -2 V for 360 s. The image subsequently recorded [Fig. 5(b)] reveals the formation of the 2×2-In structure around the 7×7-In structure. If this were the In deposition from the STM tip, one would expect the appearance of In atoms or clusters in the region beneath the STM tip on the 7×7-In surface, but this is not the case. The result of the experiment can be easily explained based on the fact that adatom mobility on the 7×7 surface essentially lower than that on the $\sqrt{3}\times\sqrt{3}$ one.[24] Adatoms were attracted by the STM tip and moved along $\sqrt{3}\times\sqrt{3}$ surface, but they were ''stopped'' by the presence of the 7×7 surface. Thus two these experiments make it apparent that we did observe STM tip-induced diffusion.

Indium atoms are weakly bonded in the 2×2-In structure. In our experiments we observed that the STM tip induces In-atom detachment from the edge of the 2×2-In structure at distances $<300-400$ Å. This is essentially larger than that for the Au adatoms on the Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface.[8]

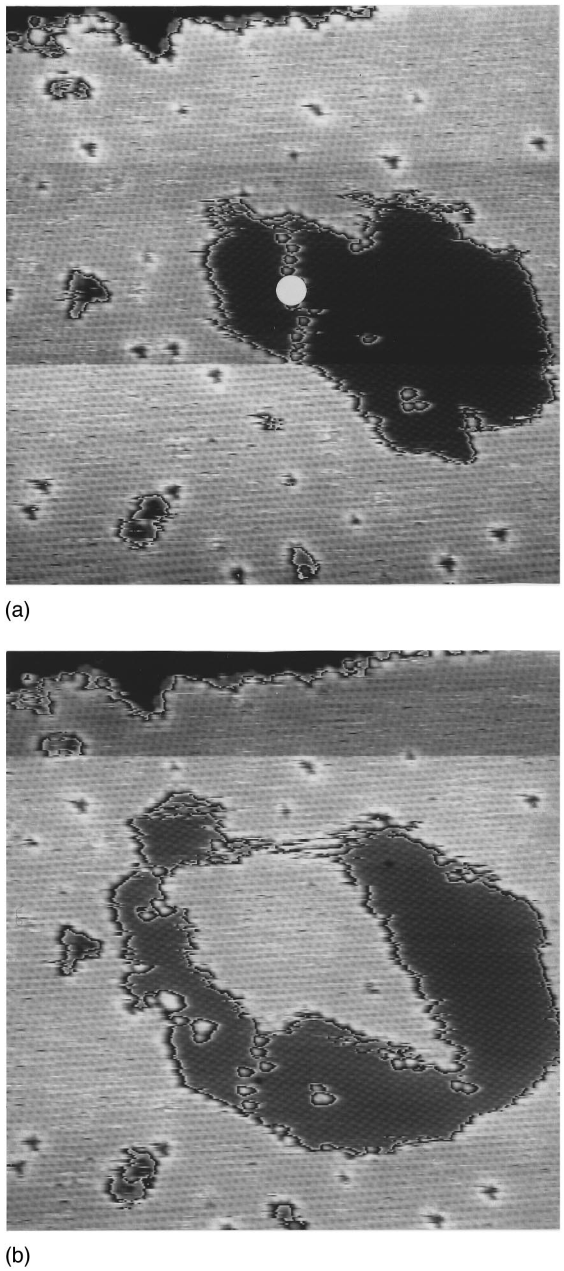


FIG. 4. Filled-state STM images, 500×500 Å^2, showing that the STM tip can induce In-atom detachment from the 2×2-In structure, and migration toward the STM tip when the tip was negatively biased; before pulse (a), after pulse (b). The tip was pulsed at $V_t=-2.0$ V, $I_t=0.2$ nA for 5 s in the center of the imaged surface. Two different full grey scales were used.

The authors observed a noticeable displacement of the edge of the Si(111)$\sqrt{21}\times\sqrt{21}$-Au structure only within a small region with a diameter of $\sim$20 Å around a tip in both attraction and repulsion modes.

Indium adatoms on the $\sqrt{3}\times\sqrt{3}$-In ''feel'' STM tip attraction at a distances of about several thousand Å. This is illustrated by the following experiment. We prepared a $\sqrt{3}\times\sqrt{3}$-In surface, and after that additionally $\sim$0.1 ML of indium was deposited on it at around RT. A large-scale STM image of this surface is shown in Fig. 6(a). The surface consists of several terraces covered by a $\sqrt{3}\times\sqrt{3}$-In structure. The upper part of left terrace is covered by 2×2-In. Defects

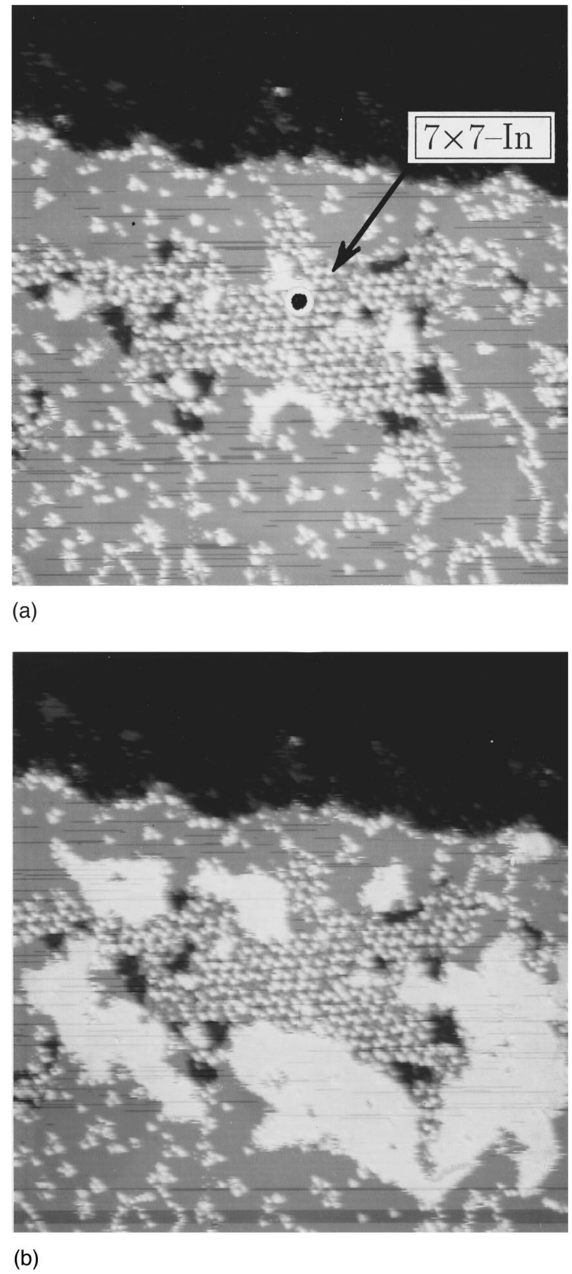
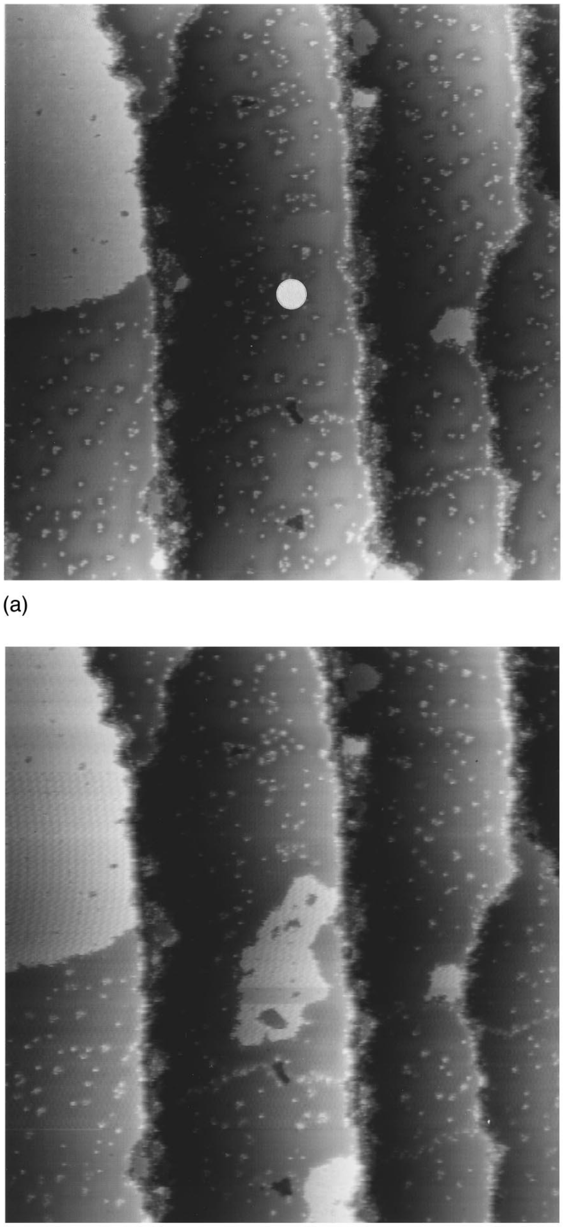


FIG. 5. Filled-state STM images, 1000×1000 Å^2, showing that the STM tip can induce In-adatom migration toward the STM tip over the 7×7 surface when the tip was negatively biased; before pulse (a), after pulse (b). The tip was pulsed at $V_t=-2.0$ V, $I_t=0.2$ nA for 360 s in the center of the imaged surface.

of the $\sqrt{3}\times\sqrt{3}$-In surface attracted additional In atoms (bright small spots on the $\sqrt{3}\times\sqrt{3}$-In surface), while In adatoms are not imaged on this surface, apparently due to their high mobility on this surface. Most likely they are repulsed by the STM tip during scanning. After this image was recorded, the STM tip was held over the center of Fig. 6(a), and the tip bias was pulsed to -2 V for 400 s. The image subsequently recorded, shown in Fig. 6(b), reveals the formation of the 2×2-In structure in the region beneath the STM tip and in another part of the same terrace (at the bottom part the image). The latter 2×2 structure was about 1000 Å apart from the STM tip during voltage pulse. Note that the shape of the area covered by the 2×2-In structure



(a)

(b)

FIG. 6. Large-scale, filled-state STM images, 2000×2000 Å^2, showing that the STM tip induces long-range In-adatom migration toward the STM tip when the tip is negatively biased; before pulse (a) and after pulse (b). The tip was pulsed at $V_t=-2.0$ V, $I_t=0.2$ nA for 400 s in the center of the imaged surface.

on another terrace (at the upper left part of the image) is not changed (the distance between it and STM tip was about 500 Å during the voltage pulse), and so only In adatoms on the $\sqrt{3}\times\sqrt{3}$-In surface could be attracted to the tip. Thus the formation of the 2×2-In structure at the bottom part of Fig. 6(b) indicates that In adatoms ''feel'' STM tip attraction at a distance of at least 1000 Å.

All our experimental results are consistent with a field-induced surface diffusion mechanism proposed by Nakayama, Huang and Aono.[8] This mechanism strongly implies that In adatoms should be ionized. Indium adatoms in our experiments show up as being positively charged. This is in agreement with the data for surface electromigration of indium on a Si(111) surface.[20]

All the experiments mentioned above were carried out with a tip held at a fixed position to induce In diffusion along the surface, and the surface was imaged before and after voltage pulse was applied. However, STM tip-induced diffusion occurs during the imaging itself. We observed that the area covered by the 2×2 structure reduced when we successively imaged the same area of the sample partially covered by the 2×2-In structure at positive tip bias voltages. In this case an increase of tunneling current or a reduction in scan speed resulted in an increasing tip-induced diffusion rate. Thus we have always used the lowest possible tunneling current and highest scan speed for the imaging of the surface during our experiments to minimize STM tip-induced diffusion rate. We found that the removal rate of the area covered by the 2×2-In structure from the scan area due to the the In-atom repulsion from the STM tip depends on the area covered by the 2×2-In structure, the size of this area, and their relative location on the $\sqrt{3}\times\sqrt{3}$-In surface.[25]

IV. CONCLUSION

We have shown that the STM tip induces In-atom diffusion on the Si(111) surface at room temperature, and this diffusion is the reason for the 2×2-In$\leftrightarrow\sqrt{3}\times\sqrt{3}$-In structural transformation on the Si(111) surface. We have found that In atoms have a high mobility on the $\sqrt{3}\times\sqrt{3}$-In and 2×2-In surfaces, and In atoms are weakly bonded in the 2×2-In structure. The STM tip induces In-atom detachment from the 2×2-In structure at a distance about 300–400 Å, while In adatoms on the $\sqrt{3}\times\sqrt{3}$-In ''feel'' STM tip attraction at distances of about several thousand Å. Indium adatoms in our experiments show up as being positively charged. Indium STM tip-induced diffusion occurs truly reversibly, at room temperature, at relatively low bias voltages, typical of the STM observations, without additional tip movement towards the surface. Our experimental results definitely show that STM tip-induced diffusion can strongly affect the surface processes during high-temperature, *in situ*, real-time STM observation. Although all our experiment were conducted at room temperature, nevertheless the mobility of In adatoms were high enough, and one can consider the In/Si(111) system as a good prototype for the observation of the results of STM tip field-induced atom migration on the initial growth stage and phase-transition process of crystal surfaces, as well as the atomic-level control of of materials.

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