Bi on Si(111): Two phases of the $\sqrt{3}\times\sqrt{3}$ surface reconstruction

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Scanning tunneling microscopy (STM) has been used to determine the surface structure of the $\sqrt{3}\times\sqrt{3}$ reconstruction induced by Bi on the Si(111) surface. The STM images show that there are two distinct ordered surfaces with $\sqrt{3}\times\sqrt{3}$ periodicity. At $\frac{1}{3}$-monolayer Bi coverage, the $\sqrt{3}\times\sqrt{3}$ phase consists of one Bi adatom per unit cell adsorbed at T_4 sites on a Si(111) bilayer. At nearly one monolayer of Bi coverage, STM images show protrusions with a complex shape dependent on bias voltage. These STM images are discussed and compared with structural models derived from previous experimental studies.

The characterization of metal-induced reconstructions of semiconductor surfaces is a significant subject that pertains to the understanding of both metal-semiconductor interface formation and general growth processes on semiconductor surfaces. Ordered surface structures with $\sqrt{3}\times\sqrt{3}$ periodicity are commonly seen for metal-deposited Si(111) surfaces, including group-III metals,[1] noble metals,[2] and some group-V elements (Sb, Bi).[3] Column III metals [Al,[4] Ga,[5] In (Ref. 6)] in the $\sqrt{3}\times\sqrt{3}$ structure have been well studied and consist of $\frac{1}{3}$ of a monolayer (ML) of metal adatoms bonded at T_4 sites directly above second-layer Si atoms. However, the column V metals [Sb,[7] Bi (Ref. 8)] are known to make another $\sqrt{3}\times\sqrt{3}$ structure with 1 ML of metal atoms forming trimers on the surface. The currently accepted model, called the milkstool model, is derived from analysis of photoelectron and x-ray-diffraction data,[8,9] as well as electronic structure calculations.[10]

A recent dynamical low-energy electron-diffraction (LEED) study has shown that there are two different $\sqrt{3}\times\sqrt{3}$ structures induced by Bi.[11] At less than $\frac{1}{3}$-ML coverage, Bi atoms adsorb as adatom monomers at the T_4 site. This is basically the same structure as for the column III metals. At nearly 1 ML, Bi atoms form trimer clusters centered over the T_4 site. The Bi atoms in the trimer are each bonded to the two other metal atoms in the trimer, and have one remaining bond to an underlying Si atom, forming milkstool structures.

Scanning tunneling microscopy (STM) is a direct tool for studying both surface geometric and electronic structure. We have taken STM images of Bi deposited on the Si(111) surface at metal coverages up to 1 ML. We have imaged both the low coverage and high coverage $\sqrt{3}\times\sqrt{3}$ reconstructions. The appearance of the STM images is discussed in terms of previously proposed structural models for these surfaces,[8,11] and the bias dependence of the images is explained in terms of what is known about the surface electronic structure.[10]

All sample preparation and measurements were performed in an ultrahigh-vacuum (UHV) system having base pressure better than 5×10^{-11} Torr. The Si(111) surfaces were cleaned by chemical cleaning, UV pretreatment, and annealing at 1150 °C in vacuum better than 2×10^{-10} Torr. Bi was deposited from a heated tungsten filament and metal coverages were determined by timed exposure to an evaporant flux previously calibrated by a quartz crystal microbalance. All samples were prepared by depositing Bi at room temperature, annealing 10 min at 650 °C, and then cooling down to room temperature. All STM and LEED measurements were done at room temperature.

Figure 1 shows a pair of images of a surface with 0.1-ML Bi coverage. This pair is composed of images taken at positive and negative tip bias over the same area of the surface. Both STM and LEED at this coverage indicate a

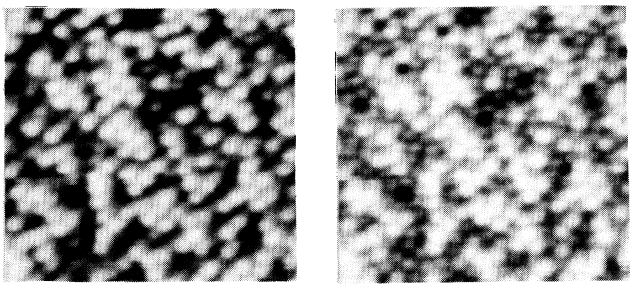

FIG. 1. Two STM images of the Si(111) 7×7 surface with 0.1-ML Bi deposited. These images were acquired over the same (130 Å)^2 area of the surface, with tip voltages of (a) $V_t=+2.5$ V and (b) $V_t=-2.3$ V. Some of the adatoms differ in brightness due to substitution of a Bi adatom for a Si adatom.

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7×7 surface structure. However, different adatoms in the 7×7 structure are seen to have different brightness in the STM images. The density of brighter adatoms in the filled state image shown in Fig. 1(a) is about 5.4 per 7×7 unit cell which agrees with the nominal Bi coverage of 0.1 ML. It appears that Bi atoms substitute for Si adatoms in the original 7×7 structure. A similar behavior is seen for low coverages of Sb and group-III metals on the Si(111) 7×7 surface.[6,12]

It is straightforward to understand why a group-V adatom might be brighter in a filled state image since the extra electron would reside in a lone-pair state whereas a Si adatom would have only a partially occupied dangling bond extending above the adatom. By the same token, it would be expected that the group-V adatom would be less bright than a Si adatom in the empty states. However, the same adatoms that are bright in the filled states [Fig. 1(a)] are also bright in the empty states [Fig. 1(b)]. The reason for this is not clear. Sb adatoms substituted for Si in the 7×7 structure are bright in the filled states, and darker in the empty states.[12]

One other point can be made about these 7×7 images: there is very little height difference between the faulted and unfaulted halves of the unit cell in the filled state image [Fig. 1(a)], in contrast to images of the clean surface under the same bias conditions. At the same time, there is a slight asymmetry in the distribution of Bi adatoms, with about 60% residing in the faulted half of the unit cell, which in these images correspond to a downward-pointed triangle. The additional charge introduced by the Bi might in some way account for the reduced asymmetry in tunneling between the faulted and unfaulted sides of the unit cell.

When the Bi coverage is raised to 0.3 ML, the surface shows a mixture of $\sqrt{3}\times\sqrt{3}$ and 7×7 structure. Figure 2(a) shows a STM image of an area with both surface phases. First, the $\sqrt{3}\times\sqrt{3}$ phase appears as a centered hexagonal array of bright dots whose general appearance at all bias voltages is characteristic of a $\frac{1}{3}$-ML array of adatoms. This particular image shows two terraces of the $\sqrt{3}$ phase. The lower one which adjoins the 7×7 is at the same height as the 7×7, whereas the second terrace is raised one double height step. The data in this image have been high pass filtered to reduce the relative contrast of this step edge.

Figure 2(b) is a diagram of the adatom arrangement seen in Fig. 2(a). The triangular grid of 7×7 unit-cell boundaries corresponds to the overlaid dark lines in the STM image. The $7\times7/\sqrt{3}\times\sqrt{3}$ phase boundary is shown as a dark solid line. One missing $\sqrt{3}$ adatom is marked as a reference point in both panels. Examination of the registry between the two phases shows that the adatoms in the $\sqrt{3}$ phase lie over the T_4 site, i.e., in the threefold site that is above a second-layer Si atom in the underlying Si bilayer. This is the same bonding site that is observed for the low coverage Sb $\sqrt{3}\times\sqrt{3}$ phase,[12] as well as the $\frac{1}{3}$-ML $\sqrt{3}$ phases for all group-III elements on Si(111).[5,6] A larger scan of the same general area shows the entire island of the $\sqrt{3}$ phase surrounded by the 7×7.

When the Bi coverage is raised to between 0.6 and 0.9 ML, LEED and STM both show a $\sqrt{3}\times\sqrt{3}$ surface periodicity. The appearance of this $\sqrt{3}$ phase in the STM images is different than that seen at the lower coverages. Figure 3 shows three images of this higher coverage $\sqrt{3}$ phase, taken at different tunneling voltages. It is immediately apparent that the appearance of this phase is highly bias dependent. In Fig. 3(a), the $\sqrt{3}$ phase consists of triplets of bright dots arranged one per $\sqrt{3}\times\sqrt{3}$ unit cell. This image is in qualitative agreement with images for the Sb $\sqrt{3}\times\sqrt{3}$ phase reported previously.[7,12] It appears to support models of the $\sqrt{3}$ structure involving trimers of Bi adatoms in a milkstool arrangement, consistent with the model of the high coverage phase seen in LEED analysis.[11]

At other bias voltages, there can be a single round protrusion per unit cell [Fig. 3(b)], or even a honeycomb arrangement [Fig. 3(c)]. Figure 4 shows an antiphase boundary in the $\sqrt{3}$ structure, taken under the same bias conditions as Fig. 3(c). This image demonstrates that the honeycomb arrangement of the $\sqrt{3}$ structure is not due to a tip artifact. An empty state with this honeycomb-shaped spatial distribution has been calculated for As

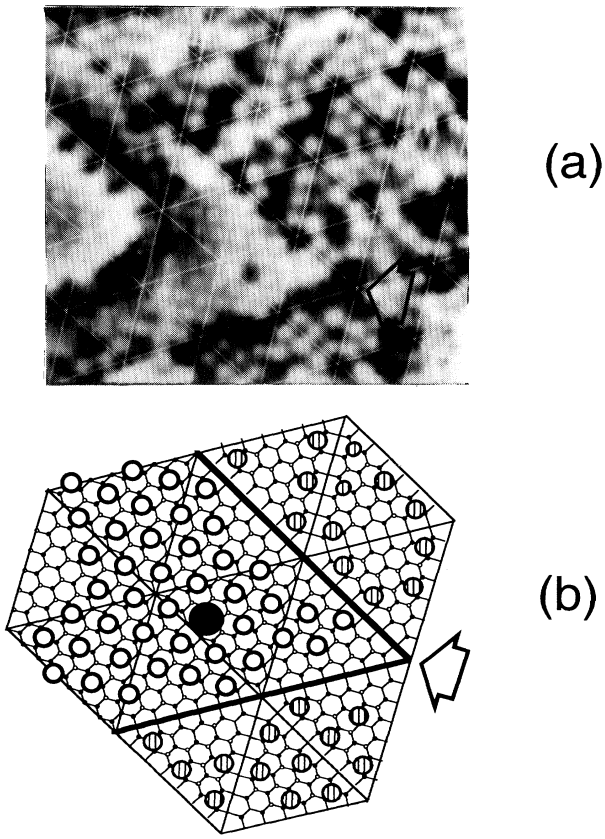

FIG. 2. A phase boundary between an area of the low coverage $\sqrt{3}\times\sqrt{3}$ phase and an adjacent area of 7×7. (a) A 275-Å^2 STM image with a superimposed grid along 7×7 unit-cell boundaries. (b) A schematic representation of the adatom positions in the 7×7 (hatched circles) and the monomer $\sqrt{3}\times\sqrt{3}$ (open circles) reconstructions as seen in (a). The heavy black line indicates the step edge along the phase boundary, and the black circle indicates an adatom vacancy in the $\sqrt{3}$ area. The arrows indicate the same point in both panels.

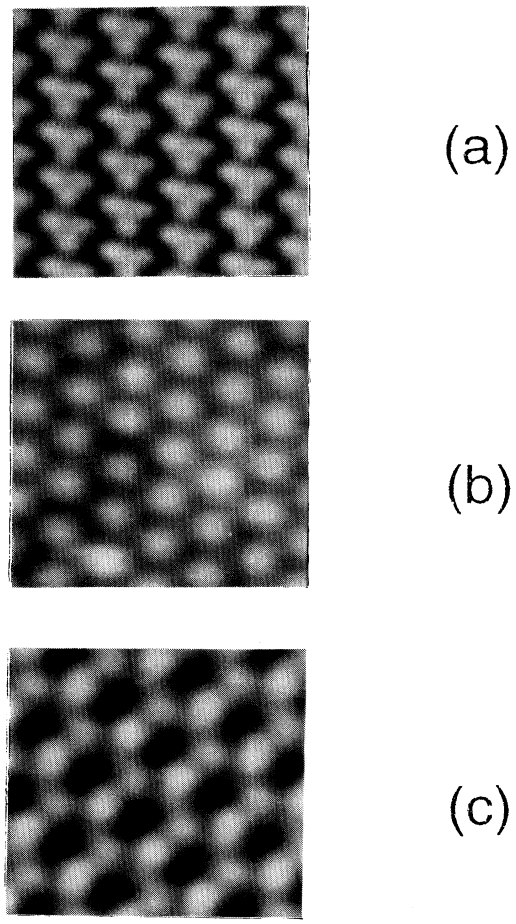

FIG. 3. Typical images of the high coverage $\sqrt{3}\times\sqrt{3}$ phase at bias voltages and currents of (a) $V_t=-0.41$ V, $I_t=0.52$ nA; (b) $V_t=-0.47$ V, $I_t=1.62$ nA; (c) $V_t=-1.02$ V, $I_t=0.78$ nA. Each image is approximately (30 Å^2).

milkstools on Si(111).[10] A more recent cluster calculation shows similar results.[13] Understanding the details of the bias-dependent appearance of these images in order to verify the detailed atomic structure of the surface will require a comparison with calculations specific to the Bi-induced $\sqrt{3}\times\sqrt{3}$ structure.

One other point should be made about the appearance of the trimers in Fig. 3(a). The orientation of the trimers with respect to the substrate can indicate whether the trimers are bonded over an H_3 or a T_4 site in the underlying Si bilayer. Our data show the appropriate orientation for placing the trimer over the H_3 site which is contrary to some previous studies of the Sb $\sqrt{3}$ phase which favor placing the adatom trimer over a T_4 site. On the other hand, these data show the same trimer orientation seen in previous STM images of the Sb $\sqrt{3}$ phase.[12] Thus the bonding site of the trimers remains an open point at this time.

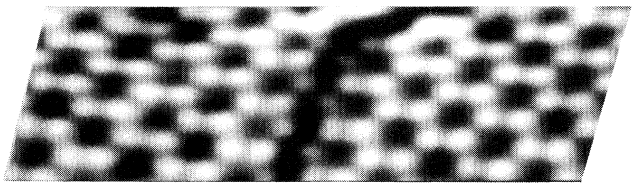

FIG. 4. STM image of an antiphase boundary in the trimer $\sqrt{3}\times\sqrt{3}$ phase. This image is about 20 Å$\times$50 Å and has been corrected for thermal drift. $V_t=-0.82$ V, $I_t=0.11$ nA.

Finally, Figs. 5(a)–5(c) show some interesting defects in the high coverage $\sqrt{3}$ structure. These three images were taken under bias conditions such that the $\sqrt{3}$ phase has the same appearance as in Figs. 3(a)–3(c), respectively. These defects have a bias-dependent height, being dark and bright at opposite bias voltage polarities. The spatial extent of each defect appears to be larger than one $\sqrt{3}$ unit cell in all directions. This effect might be due to a localized band-bending effect similar to that seen for O on GaAs(110).[14] Similar extended areas of raised or

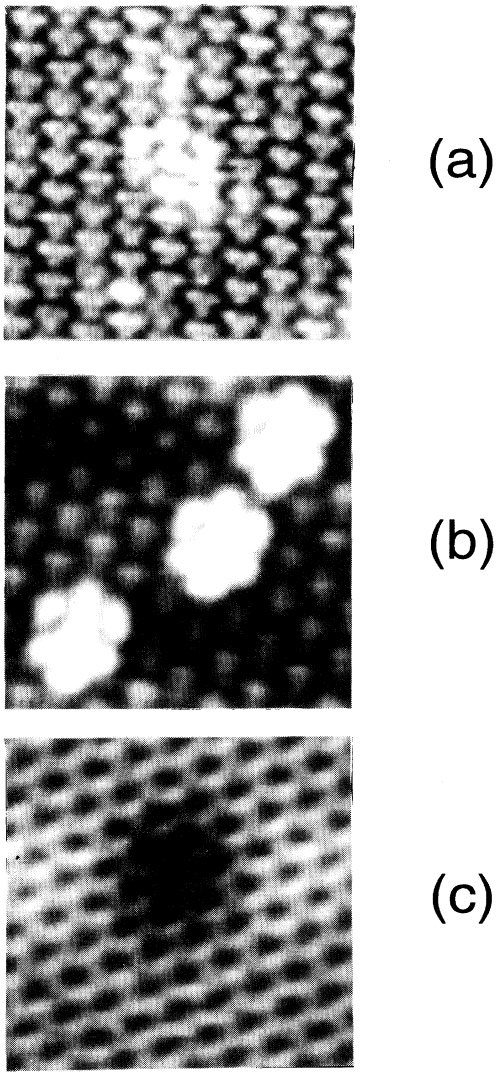

FIG. 5. STM images of defects in the high coverage $\sqrt{3}\times\sqrt{3}$ phase, under the same tunneling conditions as in Figs. 3(a)–3(c): (a) $V_t=-0.41$ V, $I_t=0.52$ nA; (b) $V_t=-0.47$ V, $I_t=1.62$ nA; (c) $V_t=-1.12$ V, $I_t=0.94$ nA.

lowered topography are seen in the Sb $\sqrt{3}$ data of Mårtensson *et al.*, although in those data the defects are clearly centered on missing trimers.[7] The images in Fig. 5 do not show similar holes in the array of $\sqrt{3}$ maxima so that the interpretation is not straightforward. These defects are seen in the data at 0.6 ML and are much rarer in the 0.9-ML data. Since the high coverage $\sqrt{3}$ phase corresponds to 1-ML Bi coverage, these defects might be due to a local Bi deficiency. Once again, detailed interpretation of this type of image is not possible without a comparison to appropriate theoretical calculations.

In summary, we have presented STM images of the Si(111) surface after deposition and annealing of Bi at coverages up to 0.9 ML. At low coverages, Bi atoms substitute for Si adatoms in the original 7×7 structure. At higher Bi coverages, two different $\sqrt{3}\times\sqrt{3}$ structures are seen, in accordance with a recent LEED analysis of this system. The low coverage $\sqrt{3}\times\sqrt{3}$ structure corresponds to $\frac{1}{3}$ ML of Bi adatoms lying on T_4 sites of an otherwise unreconstructed Si bilayer. This bonding site was determined from the registration of the 7×7 and the $\sqrt{3}\times\sqrt{3}$ phases. Images of the higher coverage $\sqrt{3}\times\sqrt{3}$ phase show a strong dependence on bias voltage. However, some of the images are suggestive of Bi trimers which have appeared in previous models of this surface and the analogous structure seen for Sb on Si(111).

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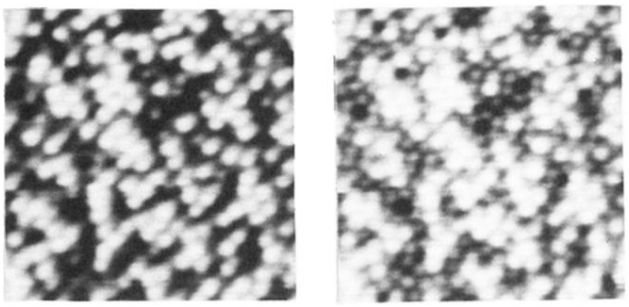

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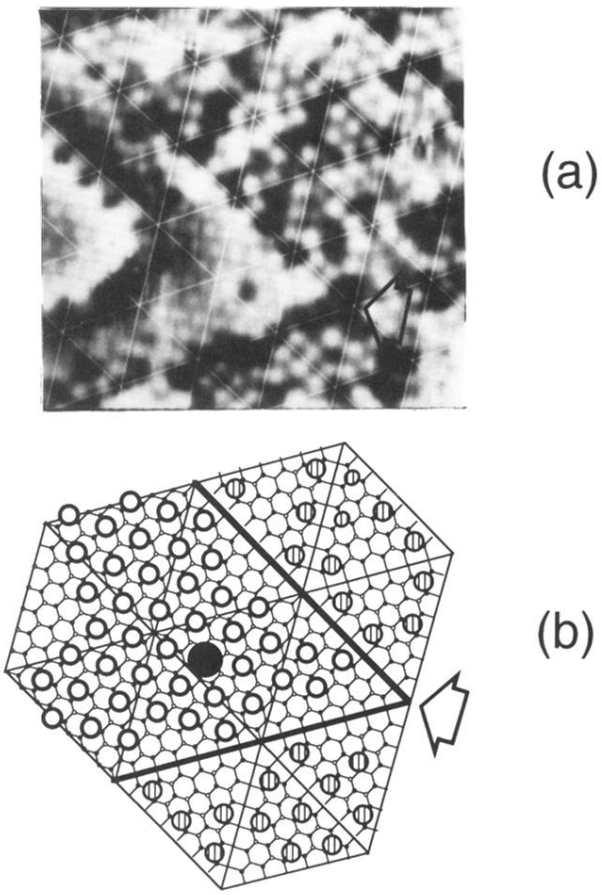

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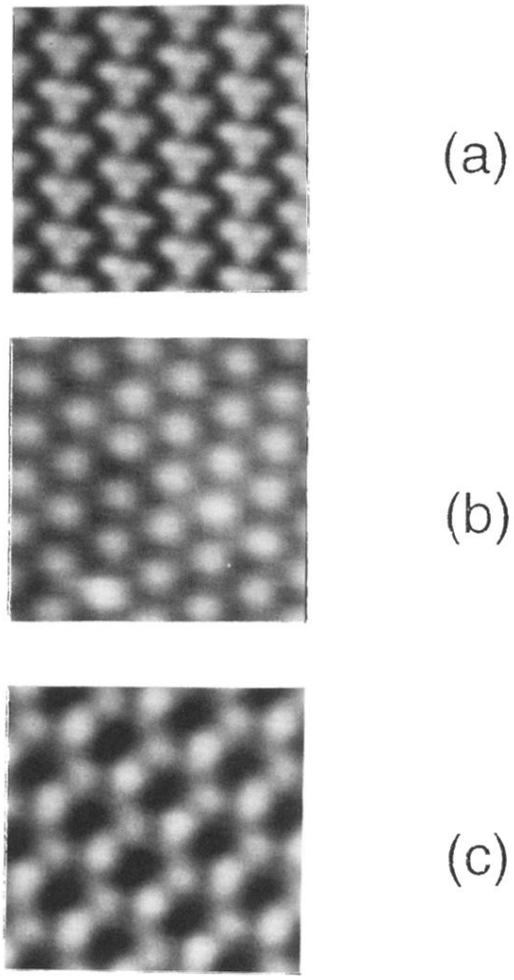

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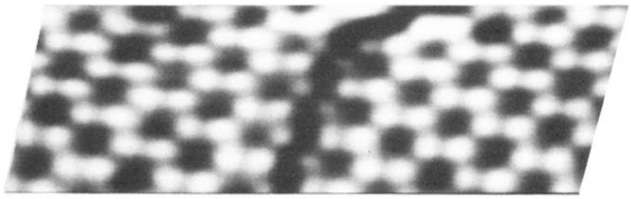

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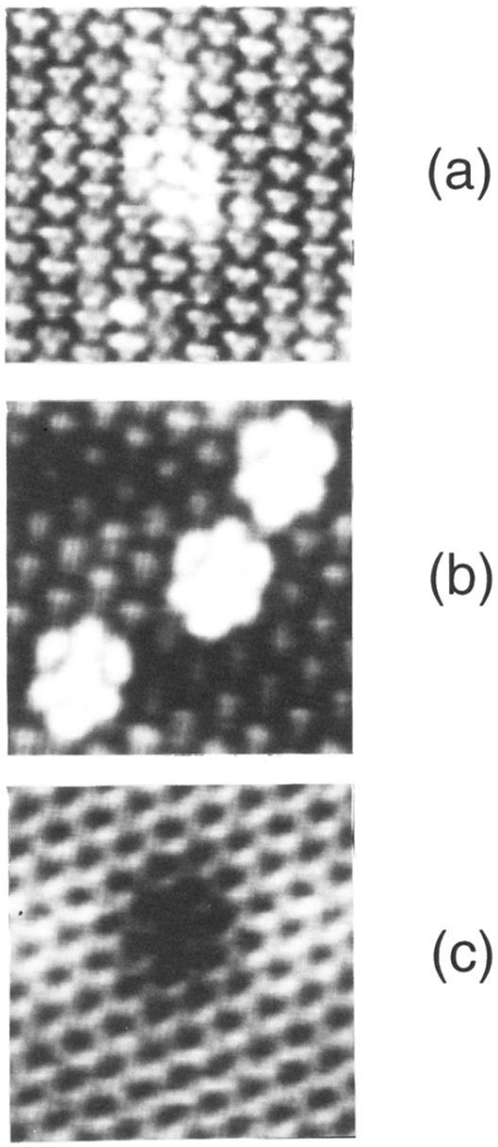

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