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Scanning Tunneling Microscopy of the GaN(000$\bar{1}$) Surface

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Abstract

In-situ scanning tunneling microscopy studies have been performed on the GaN(000$\bar{1}$) surface. Four dominant reconstructions have been observed: 1×1, 3×3, 6×6, and c(6×12). The 1×1 structure is formed by annealing the as-grown GaN surface to desorb excess Ga atoms. The higher order reconstructions are formed by depositing sub-monolayer quantities of Ga atoms onto this 1×1 surface. STM images showing the details of the reconstructions are presented, and results of quantitative measurements of the number of Ga atoms required to form the various reconstructions are reported. Structural models are compared with the STM data. Reversible order/disorder phase transitions and adatom motion on the GaN surface are discussed.

1 Introduction

Wurtzitic GaN surfaces have been under intensive investigation recently, since knowledge about the surface is vital for achieving high quality epitaxial growth.[1,2] Studies of the role played by surface reconstructions in growth processes has been studied in detail for many other semiconductor systems.[3-5] But so far the surface structures of GaN have been undetermined, although reflection high energy electron diffraction (RHEED) patterns having 1×1, 2×2, 2×3, 3×2, 3×3, 4×4, and 5×5 symmetries have been reported.[6] Complicating the situation, there exist two qualitatively different classes of surfaces for wurtzitic GaN, each with its own unique surface structures, depending on the surface stoichiometry. These two classes exist because the (0001) surface of GaN is inequivalent to the (000$\bar{1}$) surface. Thin films with (0001) surfaces are referred to as Ga-polar while those with (000$\bar{1}$) surfaces are N-polar; both polarities have been grown.[7] However, in most of the work done using RHEED, the film was either of unknown polarity or believed to have Ga-polarity.

In this paper, we discuss the surface reconstructions, observed using STM, which occur on

the $(000\bar{1})$ surface of GaN. Determination of the polarity of the film is discussed elsewhere.[8,9] We have found four dominant reconstructions for this surface. They are: 1×1, 3×3, 6×6, and c(6×12), listed in order of increasing surface Ga coverage. All of the reconstructions have been observed reproducibly many times and studied using not only STM but also RHEED, low energy electron diffraction (LEED), and Auger electron spectroscopy. Quantitative measurements have been done using these techniques to determine the number of Ga atoms involved in the various reconstructions and thereby to aid in determining structural models. Results for the 3×3 structure have recently been reported.[8] Here we report, in addition, the results for the 6×6 and c(6×12) and discuss these two structures in greater detail. Using RHEED, we also measure the order/disorder phase transition temperatures for the various reconstructions and discuss these in terms of relative bonding strengths and adatom motion on the GaN surface.

2 Experimental

The experiments are performed in a molecular beam epitaxy (MBE) system, having *in situ* surface analysis facilities. GaN films are grown on sapphire substrates using an RF plasma source to activate the nitrogen. Substrates are first solvent cleaned, then loaded into the growth chamber and heated to 1000° C for 30 minutes under an active nitrogen flux. GaN growth then begins at a substrate temperature of 685° C. During the first few hundred Å's of growth, the sample temperature is raised to about 775° C. The RHEED pattern at the growth temperature is always 1×1 and becomes streaky within the first ten minutes of growth. Growth proceeds at a rate of about 2000 Å per hour. After turning off the Ga and N fluxes, the sample temperature is increased to about 800° C for 15 min to remove excess Ga atoms which may have accumulated on the surface. After cooling the sample to room temperature, the RHEED pattern remains 1×1. STM and AFM imaging of this surface shows that it consists of a terrace-step morphology with terrace widths of up to one micron. Sub-monolayer deposition of Ga onto the 1×1 surface results in the other reconstructions. This deposition has been done with the sample temperature as high as 635° C and as low as 30° C, although the sticking coefficient is much smaller at the higher temperature, which then requires a longer deposition time. Either way, the reconstructions will appear when the surface is below the disordering temperatures. Samples are transfered directly from the MBE growth stage to the STM for imaging in UHV.

3 Results and Discussion

Figure 1 illustrates the evolution of the surface reconstructions with increasing Ga deposition. Although there are considerable ranges of Ga coverage over which a single reconstruction dominates the surface, images have been chosen at precise coverages where two of the reconstructions coexist. Such an image is shown in Fig. 1(a) for the 1×1 and 3×3 phases. This surface had a slight excess of Ga, but not enough to form a complete 3×3. Considerable atomic motion is apparent at the interface, as indicated by the glitchy behavior there. Additionally, we have observed in many cases like this one that the 3×3 area grows as Ga atoms from nearby areas on the surface are drawn into the area just beneath the STM tip. Figure 1(b) shows the interface between 3×3 and 6×6 regions. While the 3×3 appears as a hexagonal arrangement of corrugation maxima, the 6×6 has the appearance of ring-like structures. Figure 1(c) shows the interface between 6×6 and c(6×12). In the c(6×12), all rotational symmetry is broken which results in three different directional domains, one of which is shown here. It has a row structure with rows parallel to the $<1\bar{1}00>$ crystal directions.

In this case, the rows are perpendicular to the interface with the 6×6 region. Each row is made up of pairs of circular-looking maxima superimposed on a trough-valley background (shown more clearly below). A line drawn through each pair of maxima is oriented at either + or - 60° with respect to the row direction, giving a total of 6 possible types of c(6×12) domains. Once enough Ga has been deposited to form the c(6×12), further deposition does not lead to any additional reconstructions.

Each reconstruction has a unique RHEED pattern. As Ga is incrementally deposited onto the 1×1 surface, the one-third order ((1/3 0), (-1/3 0), (2/3 0), and (-2/3 0)) streaks gradually increase in intensity until the 3×3 reconstruction is fully formed. After additional deposition, the one-sixth order streaks ((1/6 0), etc.) begin to appear in a similar fashion, growing in intensity until the 6×6 reconstruction is fully formed. A similar evolution of streaks unique to the c(6×12) occurs as well. By measuring and recording these intensities as a function of the deposition time, a quantitative determination of the number of Ga atoms in the various structures can be made. We have recently reported quantitative results of such a study for the 3×3 reconstruction.[8] Here we extend these results to include the 6×6 and c(6×12) reconstructions.

In our study, Ga was deposited onto the 1×1 in increments of 0.025 ML at a sample temperature of 60° C. The Ga flux was calibrated using a quartz crystal thickness monitor in the growth chamber. For each deposition increment, the intensity of the relevant fractional RHEED streak was normalized to the intensity of the first order streak (e.g. the (2/3 0) to the (1 0) in the case of the 3×3). The coverage at which this ratio began to plateau for the 3×3 was 0.145 ± 0.025 ML, slightly larger than 1/9 ML which corresponds to one Ga adatom per 3×3 cell. For the 6×6, the result was 0.433 ± 0.025 ML or about 16 Ga atoms per 6×6 unit cell, and for the c(6×12), the result was 0.577 ± 0.025 or about 42 Ga atoms per c(6×12) unit cell. Since we know that the number of atoms per unit cell must be an integer, we conclude the 3×3 has 1/9 ML Ga adatom coverage, and furthermore, that the sticking coefficient for the deposited Ga is about 0.77. Assuming the sticking coefficient does not change significantly over the range of coverage from 1×1 to c(6×12), we correct the estimates for the 6×6 and c(6×12) to arrive at 0.333 (1/3 ML) and 0.444 (4/9 ML), respectively. However, it is well known that sticking coefficients fall off with increasing coverage as probable sticking sites become occupied so that these values are probably still overestimates.[10] Additional deposition experiments, possibly at even lower temperatures, will be required to obtain more reliable estimates of Ga coverage for these structures.

The RHEED patterns observed for the 3×3, 6×6, and c(6×12) structures are all observed to convert to 1×1 above temperatures in the range 200–300° C, which we attribute to order-disorder transitions of the adatoms which comprise the structures. The 1×1 RHEED pattern for the annealed surface stays sharp all the way up to the decomposition temperature at around 850° C, which reflects the relative high stability of this structure. The 3×3 RHEED pattern disappears, on the other hand, at about 300° C, at which point the adatom arrangement becomes totally disordered. Each successive higher order reconstruction has a slightly lower disordering temperature. The 6×6 disorders at about 250° C, and the c(6×12) disorders at around 200° C. These disordering temperatures are measured by means of a thermocouple located on the MBE growth stage. We estimate the absolute error in the measurements to be ± 25° C. Our qualitative picture for this behavior is that the relevant bonding strengths for each successive reconstruction are slightly smaller than those for

the previous structure. This picture makes sense over the whole range of coverage, starting with the strongest bonds of the 1×1 adlayer, where Ga atoms are directly bonded to N atoms, all the way up to a relatively thick layer of Ga, e.g. several ML, where the bonding strengths between Ga atoms will be close to those for bulk Ga metal, which has a melting temperature of 29.7° C.

Figure 2 shows atomic-resolution zoom-in views of the 1×1 and 3×3 reconstructions (on the same length scale for comparison). The spacing between the atoms of the 1×1 agrees very well with the lateral lattice constant of GaN, 3.19 Å. A model for the 1×1 structure has recently been proposed,[8] and is shown below in Fig. 2(c). This novel structure consists of a single monolayer of Ga atoms, referred to as the Ga adlayer, sitting 1.99 Å above the nitrogen atoms of the last GaN bilayer, as indicated in the figure. Our experimental results indicate one additional atom per unit cell for the 3×3 structure, and theoretical calculations[8] suggest this additional atom resides as an adatom in a three-fold coordinated site on top of the adlayer. As shown in the model for the 3×3 in Fig. 2(d), the adlayer atoms relax laterally as the Ga adatoms sink into the surface at 3-fold coordinated sites to a final height of only 0.9 Å above the adlayer plane. In good agreement, the height difference measured by STM between the 1×1 and 3×3 surfaces is about 0.8 Å. The largest lateral relaxation occurs for the three adlayer atoms nearest to the 3×3 adatom, which move away in the radial direction by 0.51 Å. It is interesting to note that both the 1×1 and 3×3 models contains only 3-fold rotational symmetry, a consequence of the fact that each GaN bilayer in bulk GaN has only 3-fold rotational symmetry. But while this effect is weak for the 1×1, it is very apparent for the 3×3. Indeed, upon crossing a single bilayer-high step on a surface with 3×3 reconstruction, the asymmetry reverses (as it should), while it does not reverse upon traversing a double bilayer-high step (1 unit cell in the c direction).

A zoom-in view of the 6×6 reconstruction, along with a six-atom ring model, are shown in Fig. 3(a) and 3(b). From the STM image, it appears that each ring is made up of three interconnected lobes; these lobes could possibly arise from some type of dimerization of pairs of atoms in the rings. This dimerization has been indicated schematically in the model by ellipses connecting pairs of Ga atoms. This model corresponds to a Ga adatom coverage of only 1/6 ML which seems appropriate since it is less than 1/4 ML, which was found to be unstable with respect to the Ga adlayer.[8] This dimerization produces an inequivalence between the three corrugation minima, one of which occurs at each corner of the unit cell and two others which occur near the centers of each half of the unit cell, labeled M1-M3 in Fig. 3(b). Such an inequivalence agrees with the experimental observations, where we observe three different types of corrugation minima in the 6×6 images. As mentioned elsewhere,[8] on rare occasions we also observe small regions of a similar-looking six-fold adatom ring structure on surfaces containing 3×3 and 6×6. We have referred to this structure as a somewhat disordered $4\sqrt{3} \times 4\sqrt{3}$ -*R30*° reconstruction. This is because the $4\sqrt{3}$ periodicity is maintained only for one or two unit cells; after this, the structure typically shifts along the primitive lattice directions by a single GaN lattice constant, which reduces the average spacing to be close to that of the 6×6 structure.

The c(6×12) structure is shown in Fig. 4(a), where several interesting features of this reconstruction are displayed. First, all three of the possible different directional domains are present, as indicated in the image by D1, D2, and D3. In the upper middle portion is a translational domain boundary, labeled T, where the two largest domains in the image come together slightly out of phase. As a result, two entire rows appear distorted. Near the upper right and lower left of the image

are regions where the rows shift by half a unit cell in the direction normal to the row direction (indicated by S), which also results in a reversal of the orientation of the bright maxima with respect to the row direction. Finally, glitchy behavior near domain boundaries is observed which is characteristic of a surface in a pre-melting state, as has been studied in detail by STM for Ge(111) surfaces.[11] Atomic disorder and atomic motion at room temperature both reflect the low order-disorder temperature and high adatom mobility for these structures.

Out of all of the reconstructions reported here, the c(6×12) shows the strongest bias dependence. Figures 4(b) and 4(c) show simultaneously-acquired filled and empty states images, respectively, which look quite different from each other at first glance. Closer inspection reveals the correspondence, where it is seen that the bright maxima in the filled states image lie in the same positions as those in the empty states image. However, the additional distribution of charge density evident in the filled states image gives it the very different appearance. There is an enhancement to the local maxima between the bright features straddling rows and additional minima between the bright features within the rows. More work will be required to understand these differences.

We present a preliminary model for the c(6×12) structure in Fig. 4(d). It is arrived at by slightly rearranging the rings of the 6×6 model so that they form rows along the $<1\bar{1}00>$ crystal directions, which has the effect of giving the structure a c(6×12) unit cell as well as simulating the trough-valley appearance in the images. We then add two additional adatoms in bridging sites per 6×6 ring. This gives the model an adatom coverage of 2/9 ML, still less than the 1/4 ML upper limit suggested in the discussion of the 6×6 model previously. Still, the model presented here may not be entirely correct. For example, there are other possibilities for where the additional adatoms could be placed, such as in three-fold sites to make a triplet of adatoms which would then correspond to the bright features in the image. However, the model does convey a picture of the translational periodicity and rotational orientation of the structure.

4 Conclusions

In conclusion, we have used scanning tunneling microscopy to study the four main reconstructions which occur on the GaN$(000\bar{1})$ surface. We have found that these reconstructions can be produced reliably and repeatably by depositing submonolayer quantities of Ga atoms onto the 1×1 surface. The 1×1 surface is formed by annealing the as-grown GaN film to desorb excess Ga atoms and appears to be a stable surface all the way up to the decomposition temperature. The 3×3, 6×6, and c(6×12) reconstructions are all adatom-on-adlayer structures[8] with order-disorder temperatures in the range 200-300 °C. These relatively low disordering temperatures are also consistent with significant atomic motion observed on these surfaces during STM imaging at room temperature, especially in the vicinity of domain boundaries. It has been determined experimentally that the 3×3 structure involves a single Ga adatom per 3×3 unit cell. Upper bounds for the number of Ga atoms per 6×6 and c(6×12) unit cell have been estimated to be 1/3 ML and 4/9 ML, respectively. For the 6×6, a six-adatom ring model including dimerization has been proposed for the 6×6 structure which agrees well with the observed STM images. A schematic model has also been presented for the c(6×12) structure which has the correct translational periodicity and rotational symmetry. Although coverages for the latter two models are smaller by factors of two compared to the experimental estimates, the experimental estimates may still be overestimates due to the likelihood of a coverage-dependent sticking coefficient.

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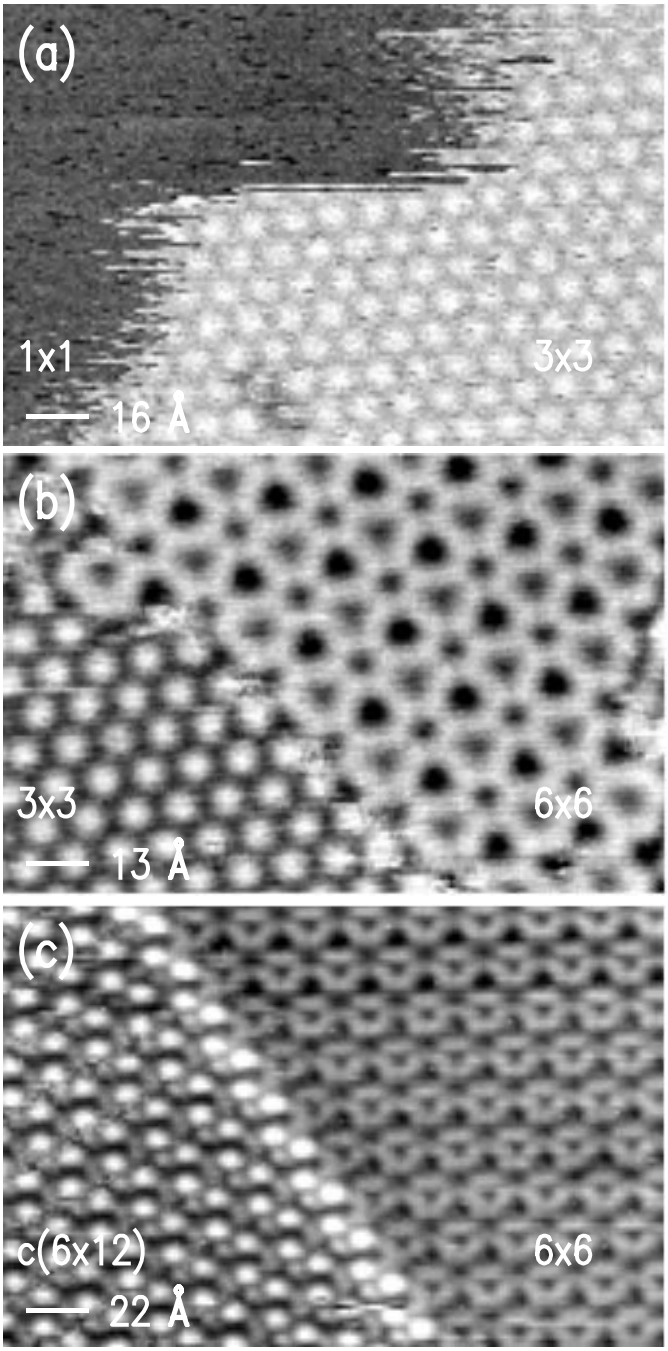

Figure 1 STM images of the GaN(000$\bar{1}$) surfaces displaying (a) 1×1 and 3×3 reconstructions, (b) 3×3 and 6×6 reconstructions, and (c) 6×6 and c(6×12) reconstructions. Sample bias voltages are +2.0, +1.5, and +1.0 V; tunnel currents are 0.02, 0.03, and 0.09 nA; and gray scale ranges are 1.42, 0.72, and 0.83 Å, respectively.

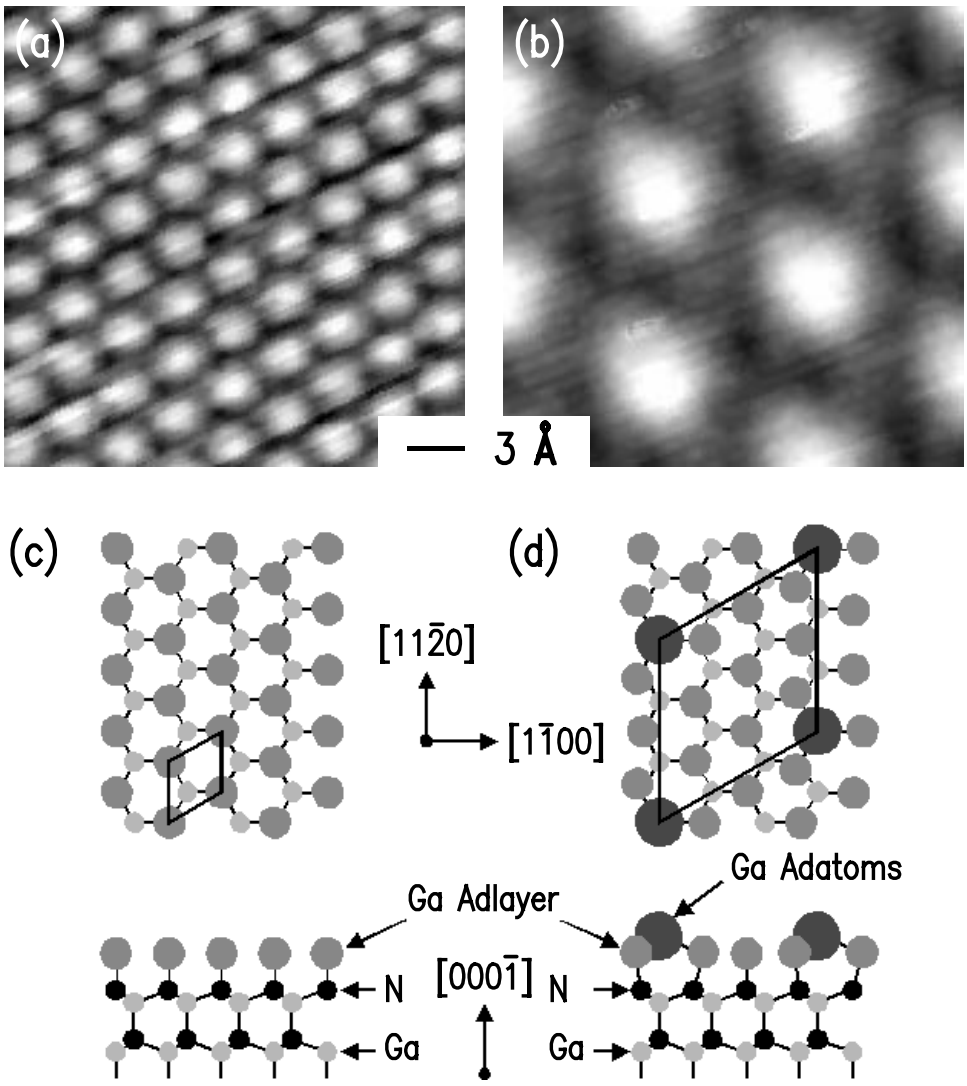

Figure 2 STM images of the (a) 1×1 and (b) 3×3 reconstructions. Sample bias voltages are -0.75 and -0.1 V; tunneling currents are 0.1 and 0.11 nA; and gray scale ranges are 0.16 and 0.74 Å, respectively. To-scale models for each structure are shown directly beneath the images in (c) and (d). Notice the lateral relaxation of the adlayer atoms in the 3×3 model.

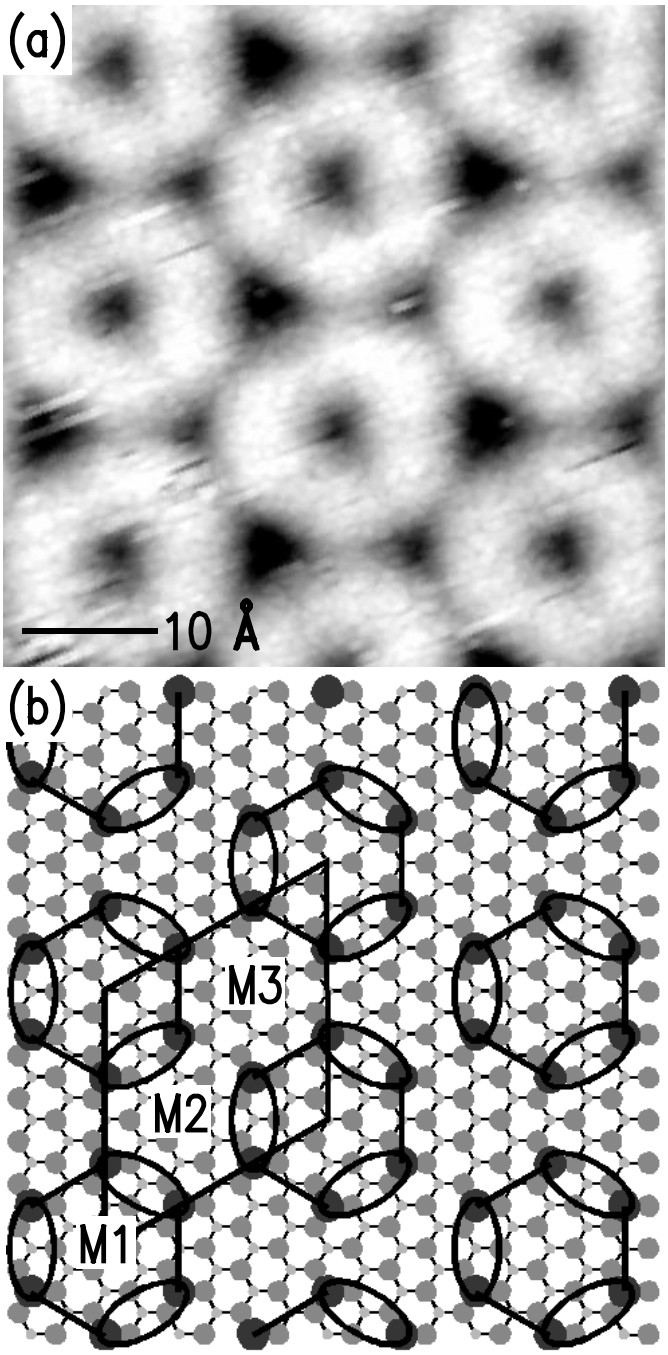

Figure 3 (a) STM image of the 6×6 reconstruction. Sample bias voltage is +1.5 V with tunnel current of 0.03 nA and gray scale range of 1.1 Å. (b) Schematic model. Ga adatoms are shown by dark gray circles with ellipses illustrating two-atom dimerization. Locations of inequivalent minima are indicated by M1, M2, and M3.

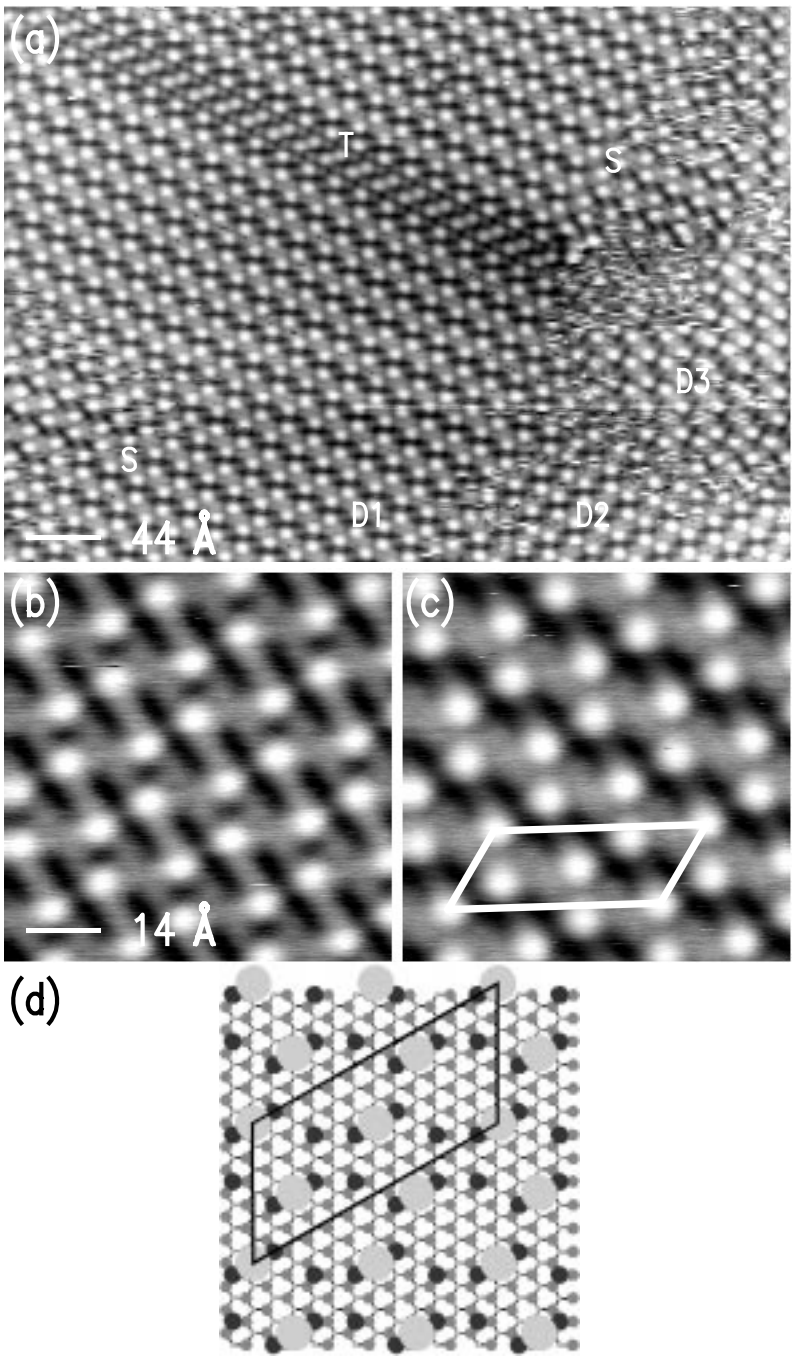

Figure 4 (a) STM image of multiple domains D1, D2, and D3 of the c(6×12) reconstruction. Sample bias voltage is +1.0 V with tunnel current of 0.1 nA and gray scale range of 1.3 Å. A translational domain boundary is indicated by T with orthogonal domain boundaries indicated by S. (b) and (c) are simultaneously recorded filled and empty states images acquired at sample biases of -1 and +1 V, respectively. Tunnel currents are each 0.1 nA. Gray scale ranges are 0.66 Å and 0.93 Å.(d) Schematic model, consisting of a slightly rearranged six-atom ring model plus two additional adatoms, indicated by the large, light gray circles.