Surface reconstructions of GaAs(100) observed by scanning tunneling microscopy

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We present atomic-resolution images, obtained with scanning tunneling microscopy (STM), of the various reconstructions of smooth, *in situ* grown GaAs(100) surfaces. The outermost layer of the $c(4\times4)$ reconstruction consists of three As-As adatom dimers parallel to [011]. Cells containing two or three As-As dimers have been observed on the 2×4 surface. The "1×6" surface seen in low-energy electron diffraction has a 2×6 unit cell containing two As-As dimers. Diffraction patterns implying 4×6 symmetry are seen to arise from the coexistence of 2×6 and 4×2 units. The $c(8\times2)$ surface is made up of two Ga-Ga dimers and two missing dimers per 4×2 cell. Atomic models, which are consistent with both the STM images and electron-counting heuristics, are also shown.

The (100) surface of GaAs is of intrinsic interest because it is known to manifest various surface reconstructions depending on the surface composition. The atomic structure of this surface is also of significant technological importance because most GaAs devices are grown epitaxially on the (100) face. Despite this interest, there has been little progress in obtaining a clear picture of the surface structure and its dependence on composition. In this paper we present atomically resolved real-space images of all of the known stable reconstructions. These surfaces were grown with state-of-the-art molecular-beam-epitaxy (MBE) techniques and imaged *in situ*.

Although no phase diagram of GaAs(100) has been mapped (or is known to exist in equilibrium), certain surface phases are generally observed during growth[1] or after growth and UHV annealing.[2,3] In order of decreasing [As]/[Ga] relative surface concentration, they have been assigned symmetries $c(4\times4)$, $c(2\times8)$, 1×6, 4×6, and $c(8\times2)$. The nature of the reconstructions has been surmised primarily from diffraction measurements and photoemission spectroscopy (PES) studies[4–6] of surface states. These techniques average over large areas, and the diffraction measurements are dominated by areas having long-range coherence. The results have been insufficient for the unique determination of surface reconstructions, particularly for large unit cells. Surface composition has generally been determined by Auger spectroscopy or PES (see, e.g., Refs. 2, 3, and 5). Here there also remains uncertainty as to the absolute concentrations, partly because knowledge of the structure is necessary to derive concentrations from signal heights and partly because inhomogeneity (e.g., local excesses of a species) are averaged over and cannot be discriminated from an intrinsic surface phase.

Recently, scanning tunneling microscopy (STM) has been applied to GaAs surfaces. Feenstra *et al.*[7] have studied the (110) cleavage face and ascertained that the surface is relaxed, but unreconstructed. Pashley *et al.*[8] have observed a GaAs(100) surface which had been grown by MBE and buried in amorphous As, then subsequently transferred through air into the ultrahigh-vacuum environment of the STM. The encapsulating layer was then removed by sublimation and a $c(2\times8)$ surface observed. The results, in agreement with Chadi's missing As-dimer model,[9] showed the coexistence of many possible alignments of 2×4 cells.

The apparatus which enables this study is unique in its ability to provide GaAs deposition and STM analysis in the same vacuum environment. The system consists of isolatable pods (all with base pressures $<10^{-10}$ mbar) disposed radially about a central UHV sample exchange manipulator. The pods are (1) a well-characterized MBE deposition system, (2) a chamber containing angle-resolved photoemission and Auger and low-energy electron diffraction (LEED) systems, and (3) a scanning tunneling microscope. The STM is suspended from an 8-inch flange with two-stage spring isolation. The isolation is so good that with turbopumps and cryopumps continuously in operation, STM images are not degraded. The STM uses a piezoelectric tube *XYZ* scanner mounted on an inertially driven "coarse" approach[10] which is capable of making 10-nm steps. Tips are W(111) wires prepared as described elsewhere.[11]

The GaAs(100) samples are prepared from nominally on-axis wafers by a sequence of cleaning steps[12] and then clipped by tungsten wires to sample holders which incorporate radiant heaters. After entry into vacuum via a loadlock, the doped GaAs (10^{18} Si) samples are prebaked at 500 °C for ~24 h. After transfer to the MBE chamber, surface oxides are sublimed off at 640 °C (Ref. 12) in either an As_4 or As_2 flux. Growth of ~300 nm of nominally undoped GaAs procedes at 300 nm/hr in an As-stabilized regime.

STM measurements have been performed in a variety of modes. However, in this paper a survey of the reconstructions is presented using only constant-current bias-voltage-dependent imaging. We report results for the reconstructed surfaces in order of decreasing [As]/[Ga] ratios. For all structures except the $c(8\times2)$, peaks in the effective surface height were centered at the same loca-

tions for both filled and empty states.

We prepared the $c(4\times4)$ surface reproducibly by cooling the grown GaAs epilayer to 300 °C in either an As_4 or As_2 flux, then removing the sample into UHV. Figure 1(a) is an STM image taken with the sample surface held at -2 V relative to the tip (electron emission from filled surface states) and a constant tunneling current of 100 pA. The $c(4\times4)$ symmetry is immediately evident. Figure 1(b) is an image with higher resolution showing that each of the rectangles in Fig. 1(a) consists of three indivi-

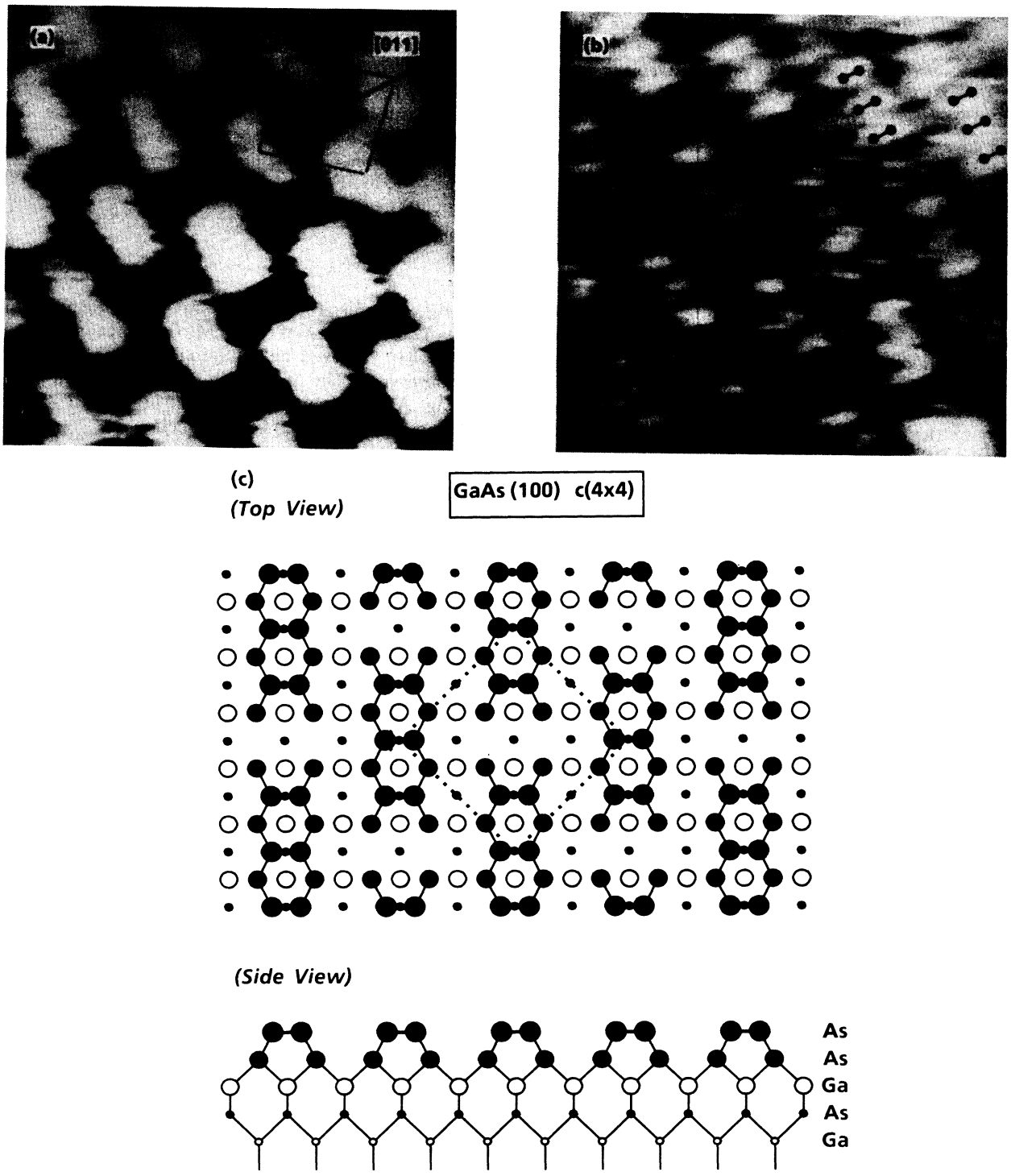

FIG. 1. (a) and (b) STM images of the GaAs(100)-$c(4\times4)$ reconstruction at (a) lower and (b) higher resolution. Electron emission is from filled surface states. The overlay is a $c(4\times4)$ unit cell, and the diagonal line is parallel to the [011] direction. White in the gray scale representation signifies highest surface elements. All images in this paper have the same crystallographic alignment and are raw data. Compensation for thermal drift or systematic skew was not applied. (c) Ball-and-stick model of the $c(4\times4)$ surface.

dual and essentially equivalent dimerlike features running in the [011] direction. These dimers are aligned perpendicular to the As dimers we observe on the $c(2\times8)$ structure, which in turn are parallel to the dimerization direction for a crystal terminated on the As plane. In Fig. 1(c) we show a ball-and-stick representation of a model which, as for all subsequent examples in this paper, is consistent with the STM images and satisfies electron-

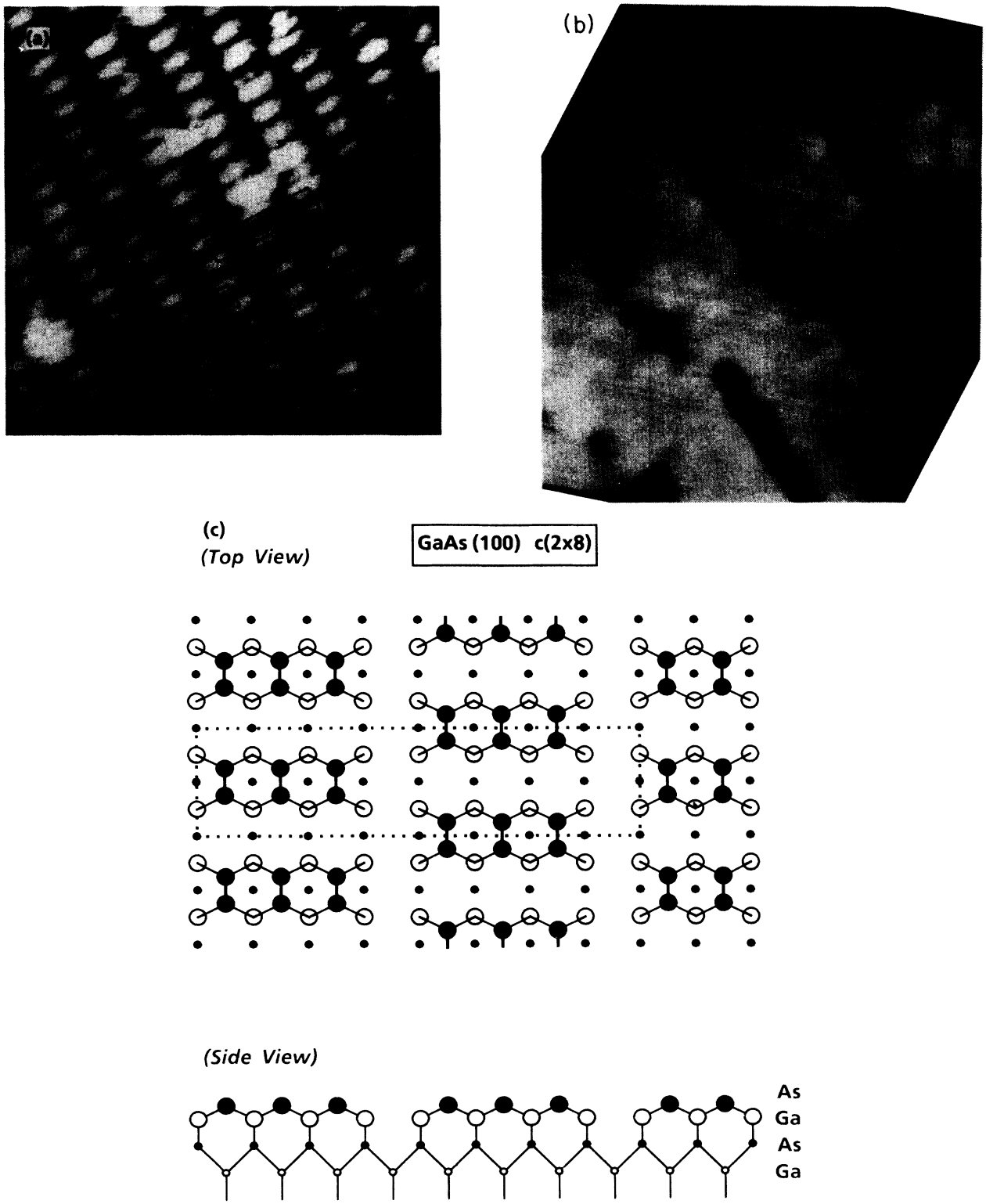

FIG. 2. (a) and (b) STM images of the GaAs(100)-(2×4) [or -$c(2\times8)$] reconstruction at (a) lower and (b) higher resolution. Domains of 2×4 and $c(2\times8)$ can be seen to coexist. (c) Ball-and-stick model of the $c(2\times8)$ surface with three dimers per (2×4) subcell.

counting (local-charge neutrality) heuristics. (All models shown in this paper are referenced to a common complete bulk layer.) This model for the $c(4\times4)$ is not necessarily unique. As an example, one other version, which also satisfies the above criteria, has the same As adatom-dimer structure but with half of the atoms in the underlying layer being Ga. These Ga atoms take the positions of the four central dark atoms of the underlying layer in the unit cell which is shown in Fig. 1(c). We have occasionally found a region with 2×2 symmetry coexisting with the much larger areas of $c(4\times4)$ (Ref. 13). [Note that 2×2 regions are not easily observed in LEED because their

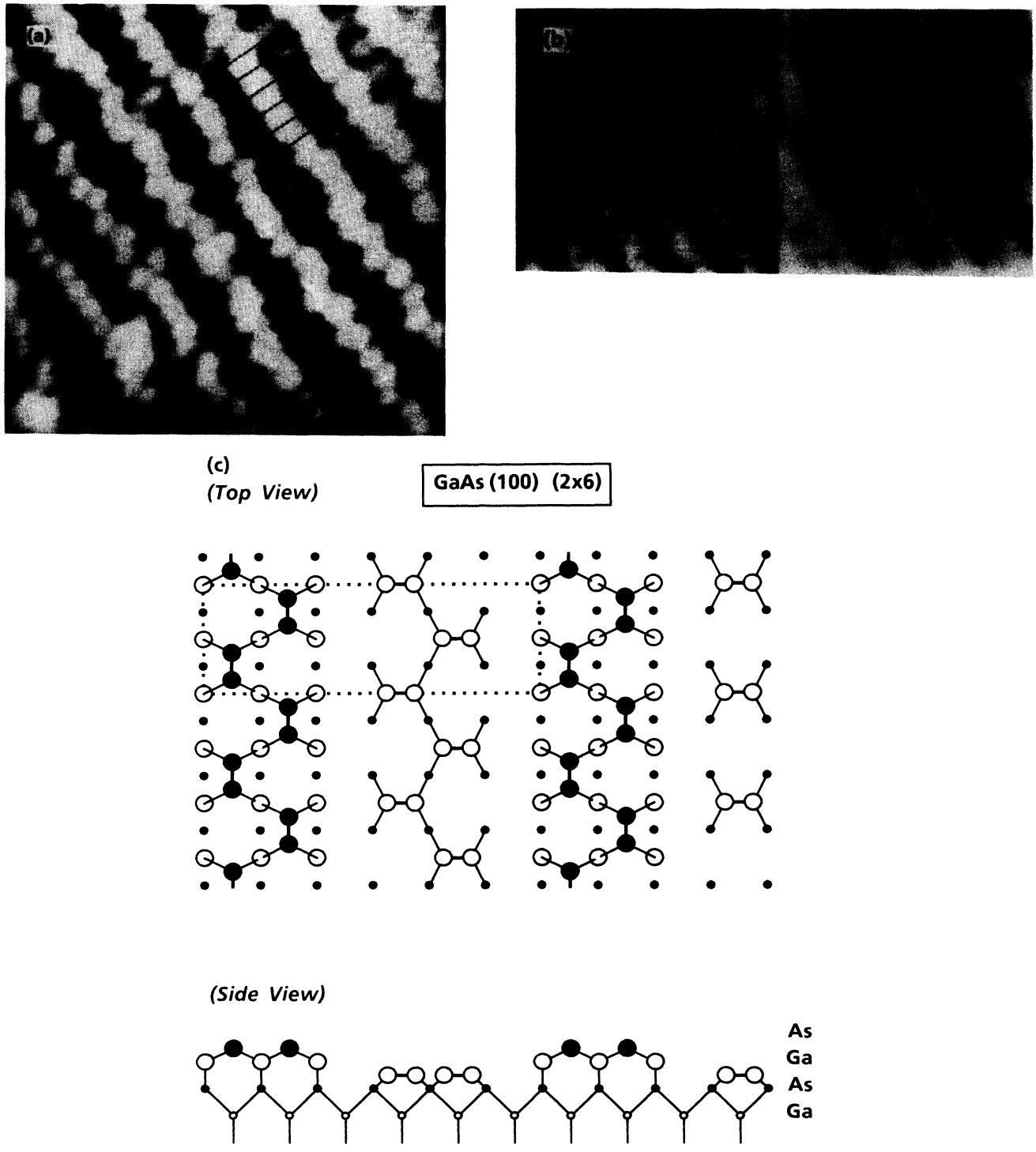

FIG. 3. (a) and (b) STM images of the GaAs(100)-(1×6) reconstruction. A grid corresponding to 2×6 unit cells is overlayed on part of (a) which was scanned at -2 V. Images from occupied (-1.5 V) and unoccupied ($+1.5$ V) surface states are shown on the left- and right-hand panels of (b), respectively. (c) A possible ball-and-stick model of the (2×6) surface.

spots are a coincident subset of those from $c(4\times4)$.]

Dimerization is a pervasive process for energy minimization on the {100} surfaces of diamond and zinc-blende semiconductors and is believed to be the major effect in this and all other GaAs(100) surfaces discussed below. The composition[14] ρ of the $c(4\times4)$ surface has been estimated to lie in the range $\rho\sim0.9-1.75$.[2,3,5] Structures with one, two, and three As-As dimers in $c(4\times4)$ arrays have been hypothesized previously for this surface.[5,15] Mixtures of unit cells with one and two dimers[5] and two and three dimers[15] have been invoked to explain the compositional variation observed. We have only seen evidence of the structure with three dimers. In principle, a large range in composition can be accounted for by a mixture of the $c(4\times4)$ and 2×2 units that we have directly observed. If the surface dimers are indeed As dimers, then the composition of the underlying plane may contain Ga as well as As atoms. We should point out that the apparent 2×1 dispersion of the surface states seen in PES (Refs. 5 and 6) is perpendicular to that one might expect from the direction of the dimers observed in the STM image.

We will now describe the one reconstruction whose morphology was previously well understood[8,9] and which is variously named 2×4 or $c(2\times8)$. We prepared these specimens by cooling the as-grown samples to 500 °C in the As flux and then quenching into UHV. Figure 2(a) is a filled state image of a typical array of 2×4 cells consisting of three As dimers and one missing As dimer. Areas with 2×4 and $c(2\times8)$ symmetry can be seen to coexist. Figure 2(b) shows, at atomic resolution, a more disordered region at higher magnification. Figure 2(c) is the ball-and-stick model for the $c(2\times8)$ cell.[8,9] We have evidence that surfaces annealed longer or at higher temperatures have 2×4 cells with only two neighboring As dimers and two missing dimers.[13] This is consistent with a range of surface stoichiometries for which the 2×4 symmetry can be stable (see Refs. 16–18, for example). We mention in passing that the preparation technique of As burial and subsequent sublimation[8] leads to much more disordered and roughened surfaces than these *in situ* grown epitaxial surfaces.

We move on now to the structure known as 1×6. We prepared these surfaces by annealing $c(2\times8)$ samples at 600 °C for 5 min in vacuum. As has been seen previously,[2] the LEED pattern for this reconstruction consistently shows sharp 1×6 spots plus weak intermediate streaks corresponding to $2\times$ and $3\times$ symmetry. The STM images also show considerable ordering in the $2\times$ direction, and the unit cell appears to be 2×6 as shown in Fig. 3(a). The surface cell is apparently two As dimers and four missing As dimers stacked along the $\times6$ direction. The stacking disorder in the $2\times$ direction must be such that the LEED shows only streaks corresponding to 2×6 and not spots. Features between the rows appear to be oriented along [010] and [001]. Figure 3(b) (taken at -1.5 and $+1.5$ V) and other images appear to show (i) that [0–11] oriented dimers [i.e., the same orientation as for the $c(2\times8)$ surface] tend to stagger along the [001] or [010] directions and (ii) that the empty surface states [right-hand side of Fig. 3(b)] are also centered on the dimer areas. Figure 3(c) is a ball-and-stick model for the 2×6 cell which is consistent with the images. Other related structures with the same basic components but with different orderings of the As-As and Ga-Ga dimers are also possible. The simultaneous presence of several similar structures is evident from the incomplete ordering in the STM and LEED data.

Surfaces with 4×6 LEED symmetry were produced by

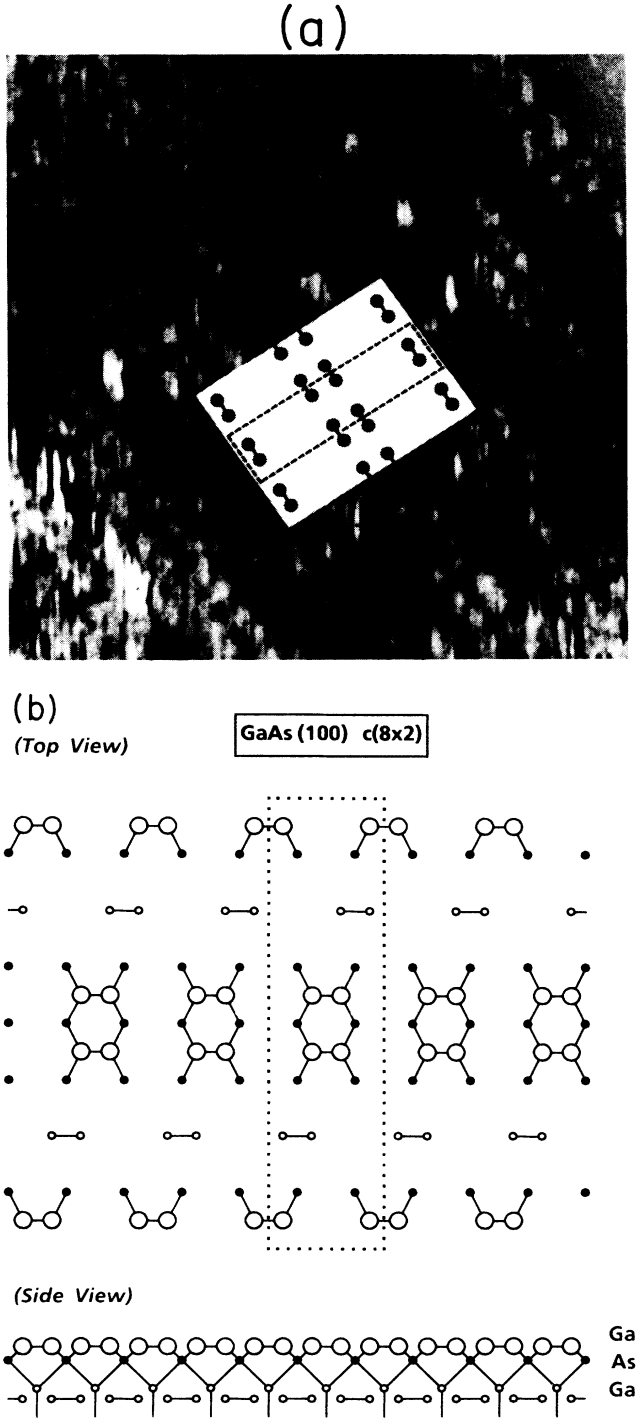

FIG. 4. (a) STM images of the GaAs(100)-$c(8\times2)$ reconstruction. Inset shows unit-cell and probable Ga-Ga dimerization. (b) A possible ball-and-stick model of the $c(8\times2)$ surface.

annealing at 670 °C for 5 min. The LEED patterns seen are consistent with a superposition of 4×1 and 1×6 domains.[2] In our STM images (not shown) we find no regions of 4×6 symmetry, but do observe the coexistence of domains of "4×1" and 2×6. The former areas consist of stripes with a repeat of four bulk lattice constants and appear to be regions of incompletely ordered $c(8\times2)$.

We have found that the more Ga-rich surfaces lead to rapid tip degradation and noise, probably due to Ga transfer to the tip. Nevertheless, we have obtained images of the $c(8\times2)$ surface, which is reported to have almost no surface-bonded As. Our samples were prepared by annealing in UHV at 690 °C. The STM images for occupied states are consistent with a $c(8\times2)$ cell as indicated in Fig. 4(a). The 4×2 subunit consists of two dimers adjacent to one another and two missing dimers. The dimer direction is the one expected for Ga—Ga dimers bonded to the last As plane of the bulk crystal. Figure 4(b) is a possible ball-and-stick model for the $c(8\times2)$ cell. Empty state images reveal a relatively low density of states over the dimers and a higher, but unresolved density in the rows between dimers.

We have also seen evidence both in LEED and STM of a reconstruction occurring at high-temperatures which has a true 4×6 symmetry. It is obtained after an anneal at temperatures higher than those necessary to obtain the $c(8\times2)$ reconstruction. Tunneling noise precluded capture of atomically resolved images.

In summary we have presented atomic-resolution images of a large number of different surface structures of the GaAs(100) surface. For the $c(4\times4)$ structure we show clear evidence that the building block on the outermost layer is a group of three [011]-oriented dimers. Images of the $c(2\times8)$ reconstruction show that the surface order from *in situ* grown surfaces is much better than that obtained using the As-capping technique. Domains of 2×4 cells having two and three As-As dimers per cell have been observed. For the (2×6) surface, two dimers plus four missing dimers can be seen, and for the Ga-rich $c(8\times2)$ structure we see what is most likely two Ga-Ga dimers per cell.

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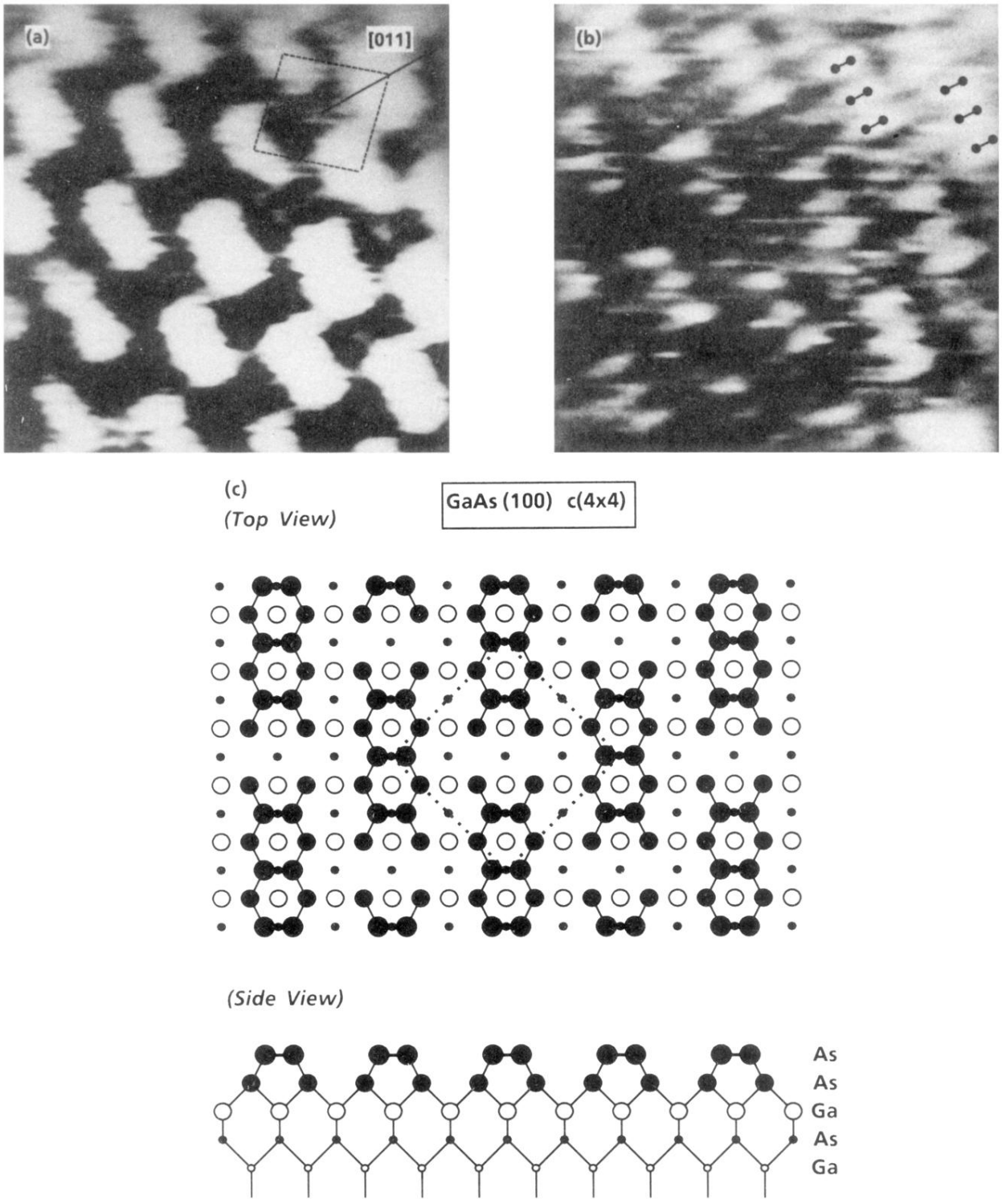

FIG. 1. (a) and (b) STM images of the GaAs(100)-$c(4\times4)$ reconstruction at (a) lower and (b) higher resolution. Electron emission is from filled surface states. The overlay is a $c(4\times4)$ unit cell, and the diagonal line is parallel to the [011] direction. White in the gray scale representation signifies highest surface elements. All images in this paper have the same crystallographic alignment and are raw data. Compensation for thermal drift or systematic skew was not applied. (c) Ball-and-stick model of the $c(4\times4)$ surface.

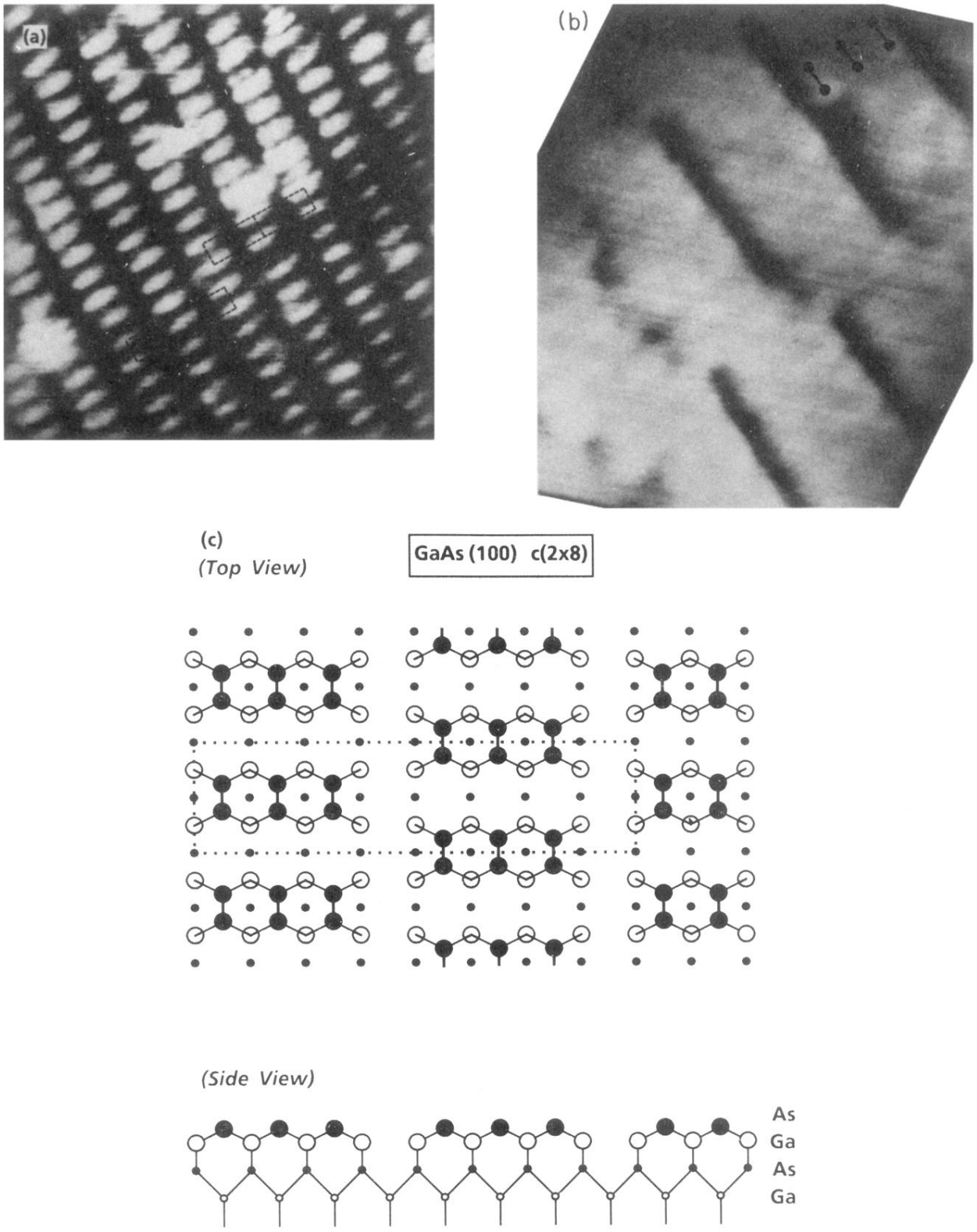

FIG. 2. (a) and (b) STM images of the GaAs(100)-(2×4) [or -c(2×8)] reconstruction at (a) lower and (b) higher resolution. Domains of 2×4 and c(2×8) can be seen to coexist. (c) Ball-and-stick model of the c(2×8) surface with three dimers per (2×4) subcell.

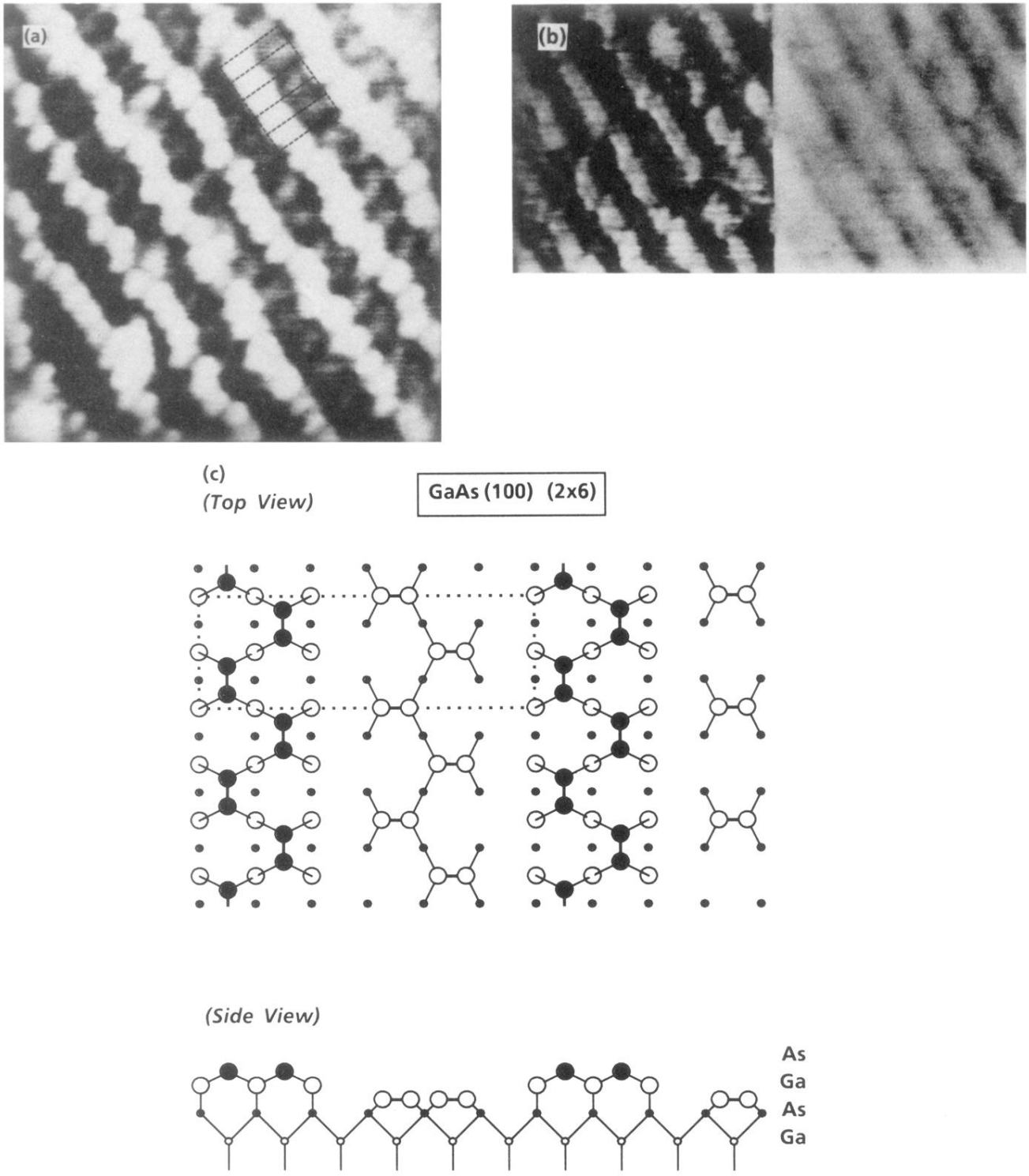

FIG. 3. (a) and (b) STM images of the GaAs(100)-(1×6) reconstruction. A grid corresponding to 2×6 unit cells is overlayed on part of (a) which was scanned at −2 V. Images from occupied (−1.5 V) and unoccupied (+1.5 V) surface states are shown on the left- and right-hand panels of (b), respectively. (c) A possible ball-and-stick model of the (2×6) surface.

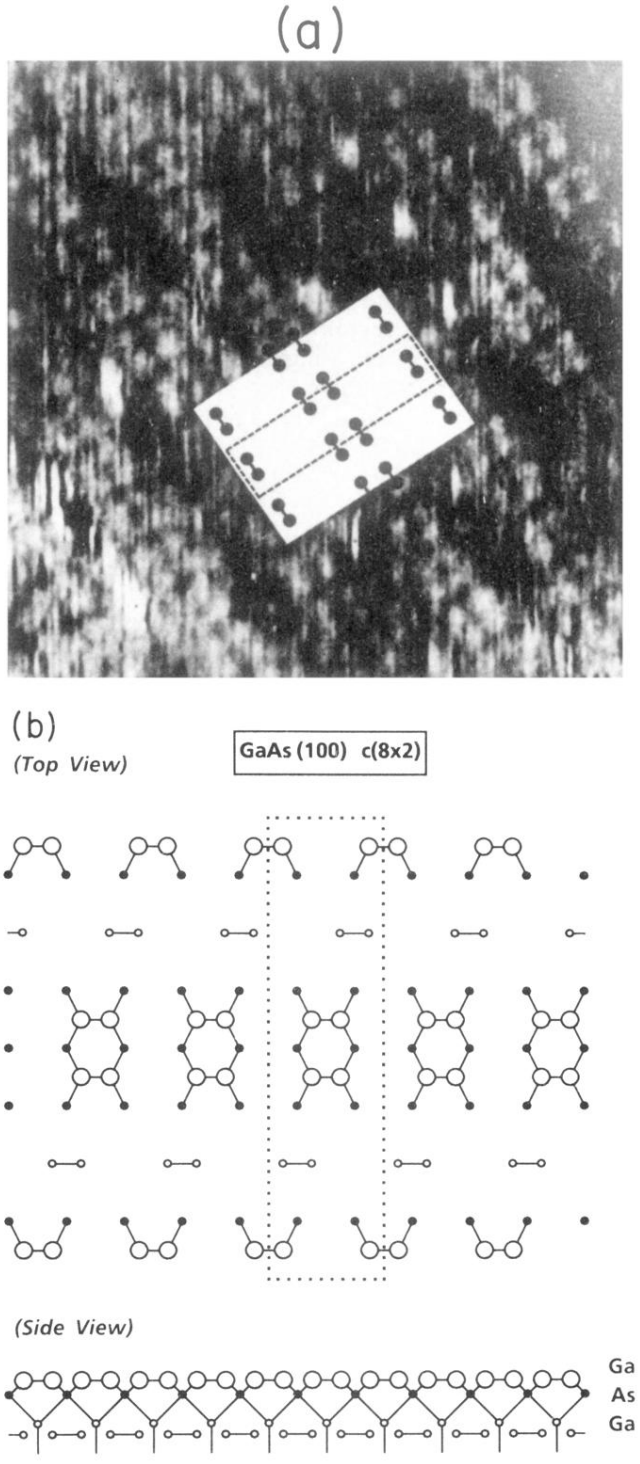

FIG. 4. (a) STM images of the GaAs(100)-$c(8\times2)$ reconstruction. Inset shows unit-cell and probable Ga-Ga dimerization. (b) A possible ball-and-stick model of the $c(8\times2)$ surface.