Reconstructions of GaAs($\bar{1}\bar{1}\bar{1}$) Surfaces Observed by Scanning Tunneling Microscopy

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We present scanning tunneling microscopy images of the As-rich (2×2) and the Ga-rich ($\sqrt{19}\times\sqrt{19}$) reconstructions of the GaAs($\bar{1}\bar{1}\bar{1}$) surface produced *in situ* by molecular-beam epitaxy. From the experimental results and total-energy calculations we show that the (2×2) surface consists of As adatom trimers bonded to the underlying surface. The ($\sqrt{19}\times\sqrt{19}$) unit cell is dominated by a two-layer hexagonal ring.

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The main driving force for reconstruction in diamond-structured elemental semiconductors is the minimization of the number of dangling bonds with their energy near midgap. In III–V semiconductors the energy of a dangling bond on the column V (III) element is pulled from midgap to the valence- (conduction-) band edge (see, for example, Refs. 1 and 2). The surface energy is therefore minimized by filling group-V and emptying group-III dangling bonds. Certain surface compositions of GaAs, to be specific, allow this autocompensation to be complete resulting in a locally neutral, semiconducting surface. In fact, all of the GaAs surfaces for which structures are well accepted are consistent with this notion (see Refs. 3–5 for examples). For the GaAs($\bar{1}\bar{1}\bar{1}$) surface a (2×2) structure is found during and after molecular-beam epitaxy (MBE) growth under As-rich conditions, and subsequent annealing of this surface in UHV results in a transition to a ($\sqrt{19}\times\sqrt{19}$)-R23.4° reconstruction.[6,7] The latter surface, with an odd number of atoms per unit cell, cannot be fully autocompensated. In this Letter we present the first reported scanning tunneling microscopy (STM) results for the GaAs($\bar{1}\bar{1}\bar{1}$) reconstructions. We show that the (2×2) reconstruction again satisfies the autocompensation ansatz; however, for the ($\sqrt{19}\times\sqrt{19}$) surface a different behavior is evident, namely, the presence of twofold-coordinated Ga atoms and the occupation of Ga-derived surface states. The existence of this structure implies an alternative mechanism for energy minimization.

The experimental system has been described elsewhere.[5] Samples of n-type GaAs (Si doped, 3×10^{18} cm^{-3}) with surfaces parallel to ($\bar{1}\bar{1}\bar{1}$) within 0.5° were prepared in the same way as described previously for GaAs(100).[5] After insertion into UHV, samples were prebaked for several hours at 500 °C. After oxide sublimation at 640 °C, a homoepitaxial layer 300 nm thick was grown by MBE. Samples were cooled to room temperature in the As_4 ambient and then, except where specifically stated, heated to 300 °C for 2 min in UHV to sublime any excess As accumulated on the surfaces.

The as-grown samples showed sharp (2×2) low-energy electron-diffraction (LEED) patterns. STM was performed at room temperature; all images presented here are raw data. Figure 1(a) is a typical constant-current STM empty-state image (sample bias $V_s=+1.8$ V and tunneling current $I_T=100$ pA), reflecting the (2×2) symmetry. Spacing between peaks is 8 Å, in agreement with the unit-cell dimension. Both filled- and empty-state images had peaks at the same positions.

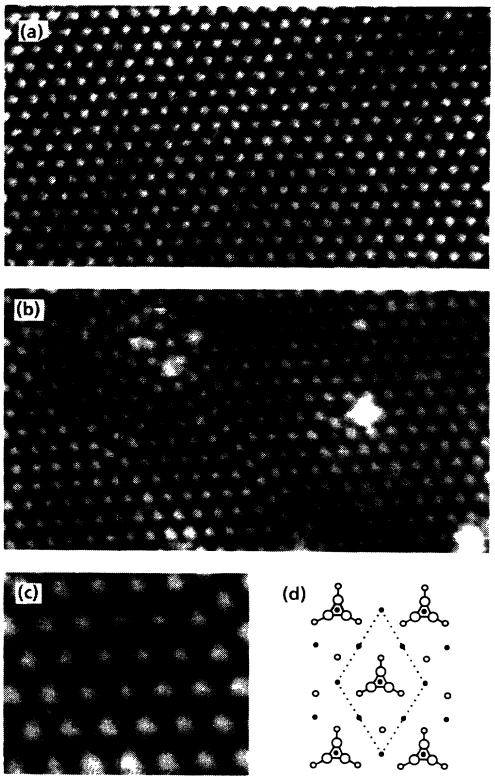

FIG. 1. GaAs($\bar{1}\bar{1}\bar{1}$) (2×2) reconstruction. (a) STM empty-state image, 11 nm×20 nm ($V_s=+1.8$ V, $I_T=100$ pA); (b) filled-state image ($V_s=-1.8$ V, $I_T=100$ pA) with surface stacking faults observable; (c) 2× enlargement of (b) to show triangular adatom structure and rest atom feature; (d) As trimer model: large open circles denote adsorbed As trimer atoms, small open circles denote first-layer As atoms, and small closed circles denote second-layer Ga atoms.

The same topographic topology, namely, an isolated adatom structure, surrounded by a connected lower layer can therefore be inferred. Vacancy models[8,9] for the reconstruction are thus immediately ruled out. Figure 1(b) is a filled-state image with $V_s = -1.8$ V. Although tip artifacts cannot be ruled out, the adatom structure looks consistently triangular in the highest corrugation filled-state images and a satellite spot is observed lying between the triangles [see enlarged area in Fig. 1(c)]. Frequently, surface stacking faults were seen to occur over short lengths as can be seen in Fig. 1(b). With respect to the underlying layers the local structure around the adatoms is equivalent in the faulted and unfaulted regions. The same structure was found even when excess As, observed as a distribution of small localized clusters, was allowed to remain.

Grown surfaces were isochronally annealed and tracked with LEED, x-ray photoemission spectroscopy (XPS), and STM. The intensity ratio ρ of the (As $2p$)/(Ga $2p$) core levels (the most surface sensitive available with Al $K\alpha$ radiation) decreased by less than 5% from room temperature to 450 °C. The (2×2) symmetry converted to the $(\sqrt{19}\times\sqrt{19})$ after annealing at 500 °C for ~10 min. At the transition, ρ decreased by ~45%. The sharpness of this transition in the As concentration indicates that there is only a single form of (2×2) reconstruction present before conversion takes place to the $(\sqrt{19}\times\sqrt{19})$ structure. A large-area scan of the resulting $(\sqrt{19}\times\sqrt{19})$ surface is shown in Fig. 2(a). The image, which is 120-nm square, is typical of the sur-

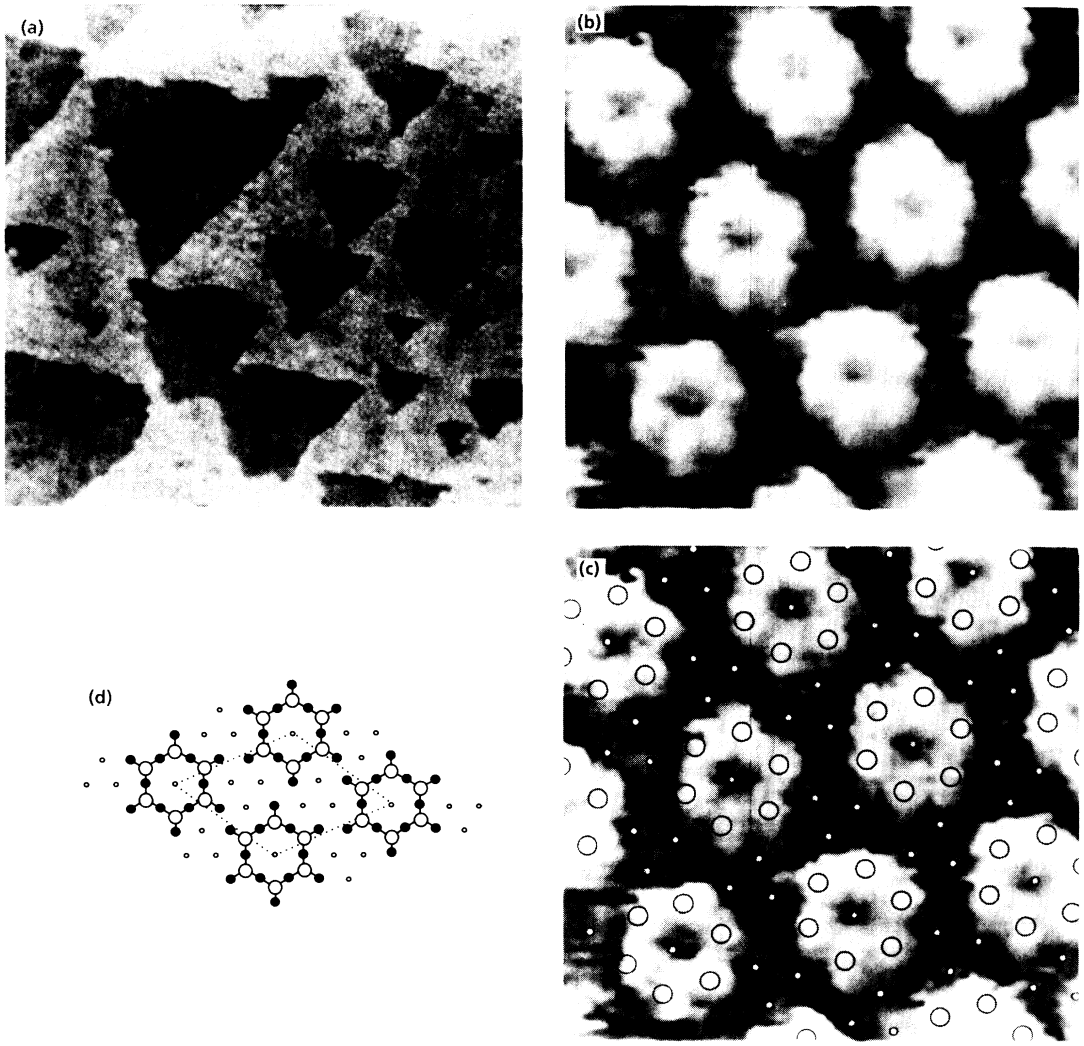

FIG. 2. GaAs($\bar{1}\bar{1}\bar{1}$) $(\sqrt{19}\times\sqrt{19})$ reconstruction. (a) Filled-state image ($V_s = -1.8$ V, $I_T = 100$ pA) 120-nm-square scan; (b) 4.9-nm-square scan; (c) same as (b) with overlay of threefold As atoms from unrelaxed model; (d) detailed model: large open circles denote top As atoms, medium closed circles denote second-layer Ga atoms, and small open circles denote third-layer threefold-coordinated As atoms.

face. Brighter regions are terraces 3.3 Å higher (a bilayer step) than the equivalent lower terrace. The observable disorder also leads to significant broadening of the LEED spots. In Fig. 2(b) we show a higher magnification image. (The predominantly hexagonal units are found as raised features also in the empty states; however, in that case the center of the hexagon is filled in.) We can also make out atomic structure ~ 3 Å below the hexagons. A simple, unrelaxed model for the surface is overlaid on the image in Fig. 2(c) and will be described in more detail below. Tunneling became unstable for applied bias voltages in the range $-0.3 < V_s < +0.3$ V, consistent with a small surface gap or metallic surface. The equivalent range for (2×2) was $-1.7 < V_s < +1.7$ V. It should be noted that inequivalent domains can be generated ($\pm 23.4°$ rotation of the cell translation vectors). Disorder from the coexistence of these structures and substructures is evident here. Higher-temperature anneals led to slightly greater order before Ga droplet formation sets in.

The STM results for the MBE grown surface show a 2×2 array of adatoms or adatom clusters. Although the triangular aspect of the adatom units in the filled-state images is quite suggestive, experimental resolution is not adequate to determine structure internal to the adatom species unambiguously. We should therefore consider that models consisting of a single As (or Ga) adatom[2] or a triplet[9] of As (or Ga) atoms are consistent with the images. To decide between various possibilities, calculations of the atomic structure and relative surface energies of these four models and an As vacancy model were performed. The local-density approximation and first-principles pseudopotential method were employed in these calculations as in previous work.[10] In each case the adatom or adatom clusters were placed in the T_4 site, in which the adatom unit has a Ga neighbor two planes below. Forces were calculated to obtain the coordinates which minimize the total energies. The surface formation energies $\Omega = E - TS - n_{Ga}\mu_{Ga} - n_{As}\mu_{As}$ depend on the chemical potentials of the As and Ga atoms and a meaningful comparison of formation energies necessitates a calculation of the bulk energies of As, Ga, and GaAs to place appropriate limits on the allowed range of chemical potentials.[10,11] The assumption that the MBE grown surface is in equilibrium with bulk GaAs, and that $\mu_{As} < \mu_{As(bulk)}$ and $\mu_{Ga} < \mu_{Ga(bulk)}$ leads to the following constraints: $\mu_{Ga} + \mu_{As} = \mu_{GaAs(bulk)}$ and $\Delta\mu_b - \Delta H < \Delta\mu < \Delta\mu_b + \Delta H$. Here $\Delta\mu_b = \mu_{Ga(bulk)} - \mu_{As(bulk)}$, ΔH is the heat of formation of GaAs from Ga and As, and $\Delta\mu = \mu_{Ga} - \mu_{As}$.

The surface energies, relative to the As vacancy structure, are shown in Fig. 3 as a function of $\Delta\mu$ over its allowed range, which is $2\Delta H$. Several conclusions can be obtained from these results. First, the As adatom structure, the Ga trimer structure, and the As vacancy structure are thermodynamically unstable over the entire

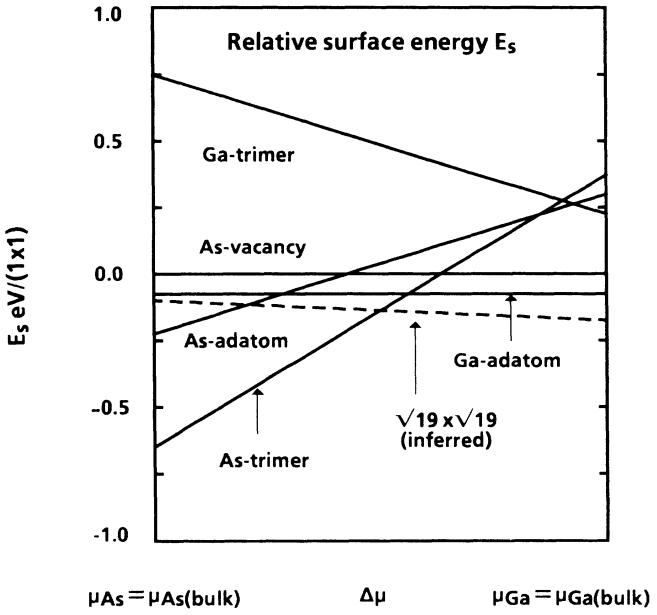

FIG. 3. Surface formation energies relative to the As vacancy model for four GaAs($\bar{1}\bar{1}\bar{1}$) (2×2) models. The dashed line has the correct slope (Ref. 12) for the ($\sqrt{19}\times\sqrt{19}$) model but the height is undetermined.

range of allowed $\Delta\mu$. In the As-rich limit the As trimer [Fig. 1(d)] is stable,[9] but it becomes unstable with respect to the Ga adatom model in the Ga-rich regime. These results together with the assumption that MBE growth of GaAs occurs in the As-rich regime imply that the observed (2×2) structure is an As trimer. Additional total-energy calculations predict that the As trimer is slightly more stable [by (0.06 eV)/(2×2 cell)] in the T_4 position that in the hollow site (H_3) position. The As-As bond length in the trimer is 2.44 Å. This bond length is actually shorter than that found in bulk As, thus the intratrimer bonding is quite strong. The As atoms in the trimer are each bonded to one As atom in the first layer (bond length = 2.42 Å), and the plane of the trimer is 2.28 Å above the plane defined by these three atoms. The remaining first-layer As atom in the unit cell (the rest atom) is 1.89 Å below the plane of the trimer. In the adatom models, the As adatom plane is 1.12 Å above the As rest atoms, and the corresponding distance for the Ga adatom model is 0.98 Å. In the Ga trimer model, the Ga trimer plane is 1.90 Å above the As rest atom.

Both the triangular adatom structure and the satellite feature are consistent with the trimer model [cf. Figs. 1(c) and 1(d)]. We can also use the experimental tip-height variations in conjunction with the calculated atomic positions to discriminate between the models. The measured corrugation was found to be 1.3 ± 0.1 Å (at $V_s = -1.8$ V) by averaging many traces passing diagonally through unit cells. 1.3 Å is larger than one would estimate for the simple adatom model. Moreover,

in the case of nonflat surfaces, tip-height displacements are a lower bound on the actual topographic corrugation because the tip does not track to the bottom of a hole with radius of curvature smaller than the tip. The degree of this underestimation can be inferred from the $(\sqrt{19}\times\sqrt{19})$ images and we find a correction of $\sim 60\%$. The (2×2) electronic corrugation would then be 2.2 Å, in close agreement with the 1.9 Å of the trimer topography and significantly larger than the 1.1 Å of the adatom model. In summary, we believe that the shape of the images in Fig. 1(c), the corrugation measurements, and the theory, each favors the As trimer structure. Furthermore, our XPS results imply that only this one (2×2) structure is stable as $\Delta\mu$ is varied from the point where excess As is found on the surface until the surface converts to $(\sqrt{19}\times\sqrt{19})$.

When the (2×2) is annealed under UHV conditions, a stoichiometrically abrupt structural transition to a $(\sqrt{19}\times\sqrt{19})$ structure occurs. On the basis of the STM images [cf. Fig. 2(c)] we propose the model shown in Fig. 2(d). In this model the primary structural unit consists of six As atoms in the top layer and twelve Ga atoms in the second layer. We refer to this as a hexagonal ring. However, the rotational symmetry is strictly threefold, so the six As atoms in the top layer occupy two inequivalent sites relative to the underlying layer as do the six twofold Ga atoms at the vertices. We therefore expect some inequivalent relaxation of these atoms. The third layer consists entirely of As atoms, twelve of these As are fourfold coordinated, bonded to four Ga atoms, and seven are threefold coordinated, bonded to three Ga atoms. The unit cell is too large for us currently to perform total-energy calculations as above. However, according to the experimental results, the $(\sqrt{19}\times\sqrt{19})$ is the most stable structure in the Ga-rich regime, and a transition from the (2×2) As trimer to the $(\sqrt{19}\times\sqrt{19})$ structure occurs as the surface is depleted of As. We indicate this by the dashed line in Fig. 3.[12] According to the models, this transition requires the desorption of 1.07 monolayers of As and migration of 0.37 monolayer of GaAs to steps. This is in reasonable consistency with estimates by Arthur[7] given the difficulties in making absolute measurements. It is also compatible with the terraced structure seen in the large-area scan, Fig. 2(a). The surface, under the constraint of high $\mu_{Ga}-\mu_{As}$, lowers its energy by introducing relaxed twofold Ga atoms thereby also allowing the hexagon As atoms to approach their ideal p^3 configurations. We note that an array of identical hexagons packed in a 2×2 configuration by merging twofold Ga atoms into single-bridging Ga atoms would result in Chadi's alternating vacancy structure,[8] but experiment shows that separation of the hexagons results in an energy lowering probably by freeing the otherwise frustrated relaxation of the capping As atoms. This energy reduction comes at the expense of occupying Ga-derived states, thus violating the autocompensation ansatz.

In summary, we have presented STM images and first-principles total-energy calculations which determine the atomic structures of the GaAs$(\bar{1}\bar{1}\bar{1})$ (2×2) and $(\sqrt{19}\times\sqrt{19})$ reconstructed surfaces. We conclude that the (2×2) consists of one adsorbed As trimer (T_4 site) per cell, and the $(\sqrt{19}\times\sqrt{19})$ is a complex structure featuring a strongly relaxed As-capped hexagonal ring.

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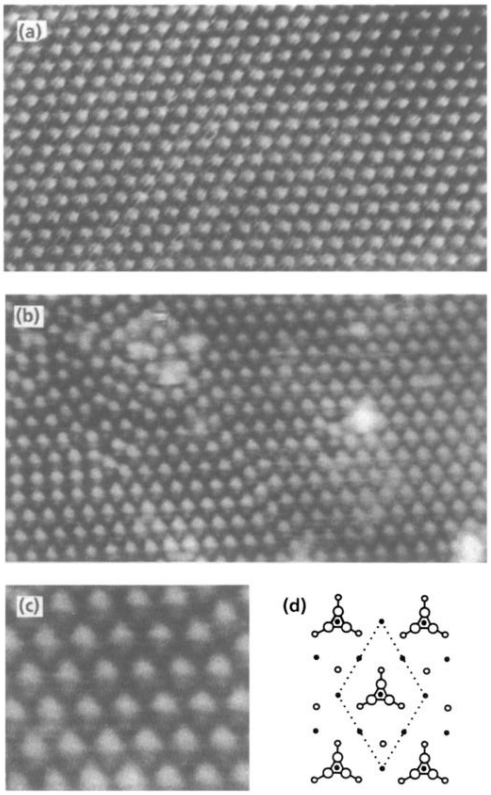
[12]Note that $\Omega = E - TS - \frac{1}{2}(n_{Ga}+n_{As})\mu_{GaAs(bulk)} - \frac{1}{2}(n_{Ga}-n_{As})\Delta\mu$. Thus, the surface energies of structures with the same $n_{Ga}-n_{As}$ have the same dependence on $\Delta\mu$.



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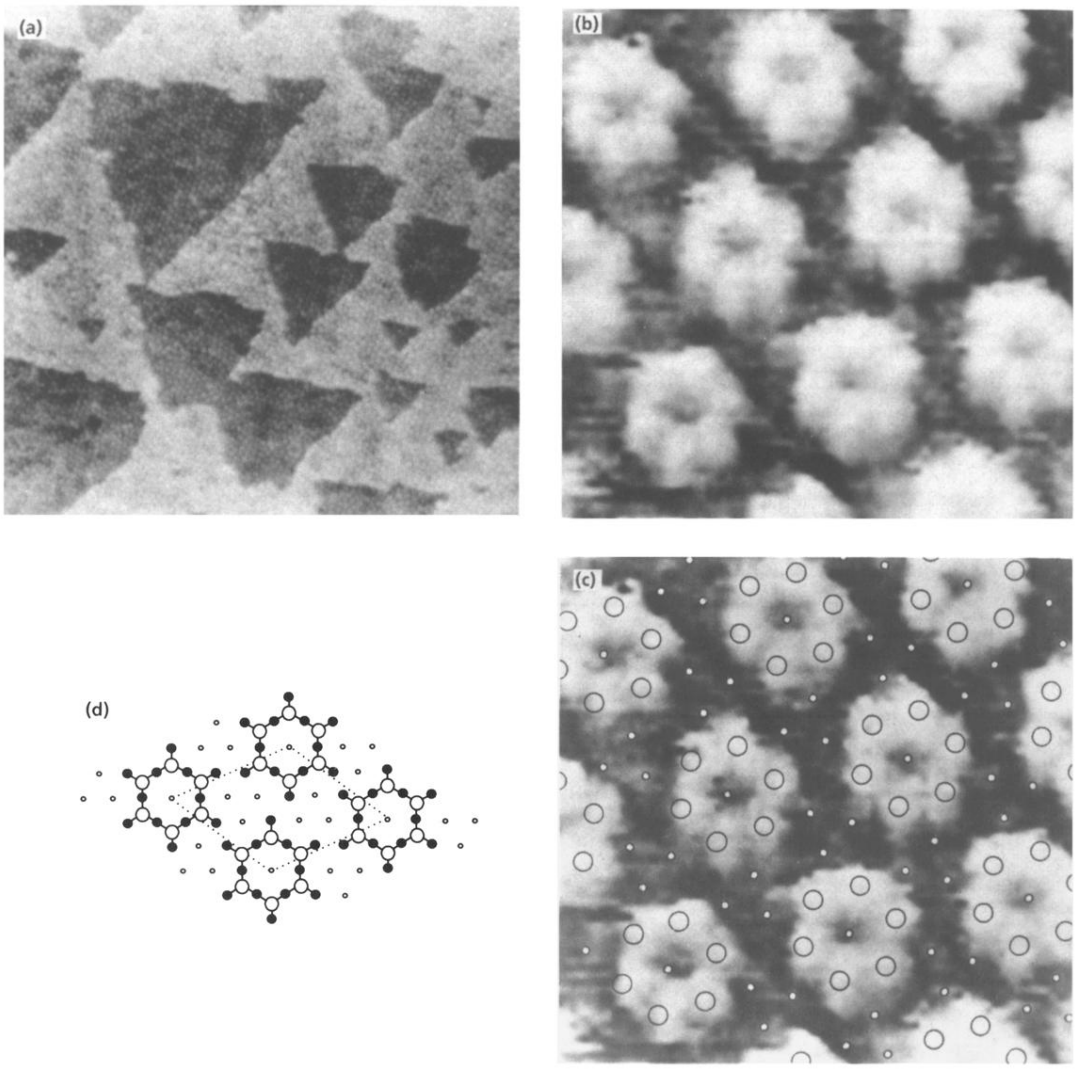

FIG. 2. GaAs($\bar{1}\bar{1}\bar{1}$) ($\sqrt{19}\times\sqrt{19}$) reconstruction. (a) Filled-state image ($V_s=-1.8$ V, $I_T=100$ pA) 120-nm-square scan; (b) 4.9-nm-square scan; (c) same as (b) with overlay of threefold As atoms from unrelaxed model; (d) detailed model: large open circles denote top As atoms, medium closed circles denote second-layer Ga atoms, and small open circles denote third-layer threefold-coordinated As atoms.