

## Structure and Composition of GaAs(001) Surfaces

J. Falta, R. M. Tromp, M. Copel, G. D. Pettit, and P. D. Kirchner

IBM Research Division, Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598

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The structure and composition of the GaAs(001) surface was studied with high-resolution medium-energy ion scattering, from As-rich to Ga-rich reconstructions. In contrast to commonly accepted models, we find that first and second layers in the surface may contain *both* Ga and As atoms. The surfaces are more Ga-rich than previously believed, with Ga atoms occupying As sites. Such mixed compositions are explained by consideration of charge neutrality, as well as Coulomb repulsion between surface electrons. Implications for heteroepitaxial growth on GaAs(001) are discussed.

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The GaAs(001) surface has been studied extensively in the past, as it provides the growth surface for many structures of great scientific and technological interest [1-3]. Depending on the preparation conditions the surface may be relatively rich in either Ga or As, due to different vapor pressures of the two constituents. Variations in surface composition are accompanied with changes in surface structure, as can be easily observed with low-energy electron-diffraction (LEED) patterns.

During the last decade much progress has been made in determining the structure and composition of the various GaAs(001) surfaces [4-12]. However, the exact elemental composition of these surfaces has not been accurately determined. In particular, information obtained from Auger electron spectroscopy (AES) [4] and core-level spectroscopy [7] experiments depends sensitively on the value of the electron escape depth, a quantity not known with high accuracy. This lack of accurate composition information has precluded full surface structure determination. Indeed, a quantitative comparison between experimental results and specific models has not been previously attempted. However, it has been widely assumed that the alternating Ga-As sequence, going from the bulk to the surface in layer-by-layer fashion, is maintained up to the very surface, without any Ga-As mixing *within* a given atomic layer.

In this Letter we present high-resolution medium-energy ion scattering (MEIS) results of the first fully quantitative determination of the elemental compositions of a number of structures. We find that the surfaces contain more Ga than previously assumed, and that Ga-As mixing in a given atomic layer is common. We propose specific atomic models to explain these results and discuss implications on heteroepitaxial growth of Ge and Si on GaAs.

Previous MEIS studies of GaAs surfaces by Smit, Derry, and van der Veen did not resolve the Ga and As surface peaks due to limited mass resolution with the  $H^+$  beam used [13]. The use of a  $Li^+$  beam, along with recent improvements in ion detection [14], have enabled us to perform a quantitative determination of the structure and composition of GaAs surfaces.

GaAs(001) samples were prepared with an *ex situ* molecular-beam-epitaxy (MBE) grown GaAs buffer layer, capped with an As layer for protection during air transfer. The samples were decapped by carefully annealing until the As capping layer desorbed ( $\sim 300^\circ C$ ), resulting in a surface with a good  $c(4\times 4)$  LEED pattern. This procedure was very reproducible; we found no difference with or without  $As_4$  flux supplied during decapping. Annealing to  $490^\circ C$  for 5 min changed the LEED pattern to  $c(2\times 8)$ . Lower annealing temperatures resulted in a  $(2\times 4)$  LEED pattern, which can be explained as a disordered  $c(2\times 8)$  [10]. Subsequent annealing of the  $c(2\times 8)$  for short times to higher temperatures lead to the formation of the increasingly Ga-rich  $c(8\times 2)$  and  $(2\times 6)$  surfaces.

Figure 1(a) shows an energy spectrum of 200-keV  $Li^+$  ions, scattered from the GaAs(001)- $c(2\times 8)$  surface, at a scattering angle of  $90^\circ$ . The dashed line shows the raw data, with the  $^{69}Ga$ ,  $^{71}Ga$ , and  $^{75}As$  isotopes clearly resolved. Since the Ga isotope ratios are accurately known, the isotope splitting of the  $^{71}Ga$  and  $^{69}Ga$  surface peaks can be easily removed (similar to removal of spin-orbit splitting in core-level electron spectra), resulting in the solid line in Fig. 1(a). The Ga and As surface peak intensities can be converted to the number of Ga and As monolayers, visible to beam and detector, by standard quantitative procedures, with an accuracy of about 5%.

The angular dependence of the Ga and As scattering intensities for the  $c(2\times 8)$  surface is shown in Fig. 1(b). The shaded bands are the results of Monte Carlo calculations for this surface, discussed later. The scattering geometry is shown by the inset of Fig. 1(b). In double alignment ( $90^\circ$  scattering) the incident ion beam is aligned to the  $[1\bar{1}1]$  direction (channeling) and the detector is aligned to  $[\bar{1}12]$  (blocking). For single alignment only the ion detection angle is changed by a few degrees. A review of the principles of MEIS is given in Ref. [15]. From data like those shown in Fig. 1(b), the As and Ga areal densities can be determined both in double and single alignment. The results for a number of structures are shown in Fig. 2(a), from the most As-rich  $c(4\times 4)$  surface, to the most Ga-rich  $(2\times 6)$  surface. We find that

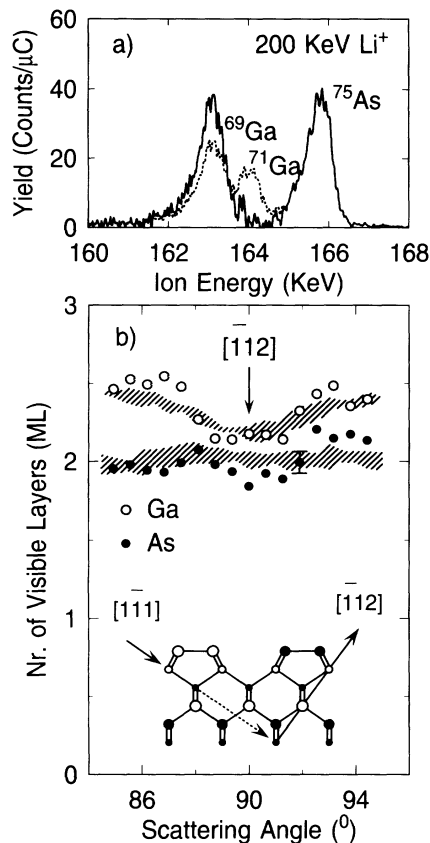


FIG. 1. (a) MEIS spectrum of GaAs(001)-c(2x8) in double alignment, before (dashed line) and after removal of the isotope splitting of the <sup>71</sup>Ga and <sup>69</sup>Ga surface peaks (solid line). (b) Angular profile of the As and Ga surface peaks: The scattering geometry is shown in the inset. The shaded bands display the results of Monte Carlo simulations (see text).

decreasing As density is compensated by increasing Ga density, in a simple 1:1 ratio, as indicated by the solid and dashed lines. Of course, the exchange of surface As by Ga is accompanied with changes in the overall structure and symmetry of the surface, as manifested by the changes in the LEED pattern.

In the following, we perform a quantitative comparison of our results with current structural models from the literature. Figure 3(a) shows an atomic model of the As-rich c(4x4) surface, proposed by Biegelsen *et al.* [11] on the basis of atomic-resolution scanning tunneling microscope (STM) observations. The model consists of an As-terminated GaAs(001) surface, capped with As dimers in a c(4x4) pattern. The dimers were directly observed in the STM experiments; the second-layer atoms of course were not. Some possible dimer locations are left vacant, allowing the surface to only expose fully occupied lone-pair orbitals to the vacuum, preventing the presence of surface states in the GaAs band gap [16]. These missing dimer locations leave a “gap” in the first layer, exposing second-layer atoms (indicated by half-open/half-solid circles), which we will refer to as “gap

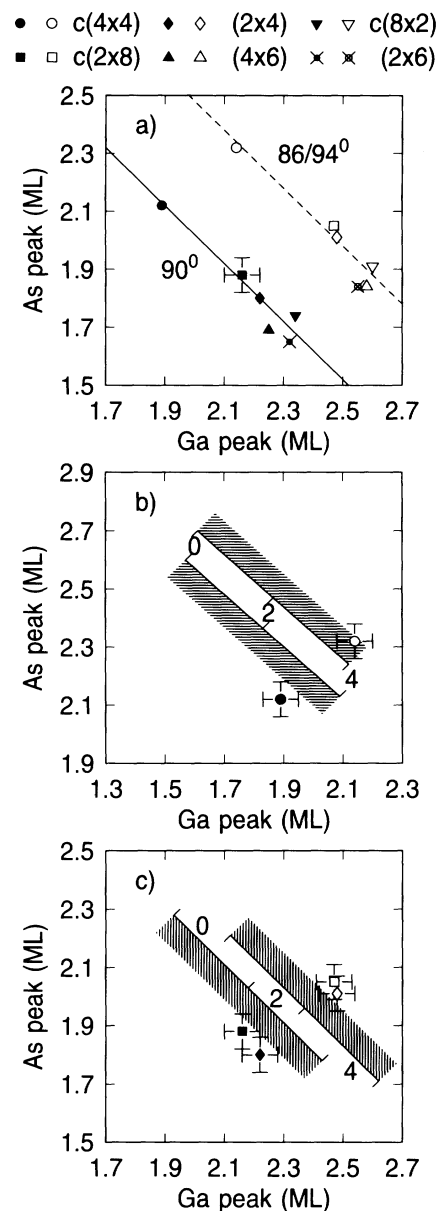


FIG. 2. (a) Number of surface As vs Ga layers, visible to the ion beam in single (86°/94°) and double alignment (90°) for different surface structures of GaAs(001). (b),(c) Comparison of the data for the c(4x4), c(2x8), and (2x4) reconstructions and the results of Monte Carlo simulations (shaded bands). The number of Ga atoms replacing As atoms is indicated with the Monte Carlo results, per reconstructed unit cell.

atoms.” Agreement with our data can only be achieved if first- or second-layer As is replaced by Ga. As already noted in Ref. [11], replacing the gap atoms with Ga is consistent with electron counting arguments. We regard this as more likely than As/Ga replacement in the first layer for the following reason: Like the As dimer atoms, As gap atoms carry a lone-pair orbital. Replacement of As gap atoms with Ga would be accompanied by the removal of two valence electrons, exchanging a lone-pair

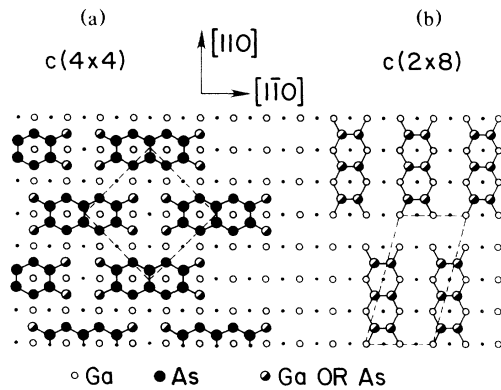


FIG. 3. Models of the structure and composition of two GaAs(001) surface reconstructions: (a) The  $c(4 \times 4)$  consist of two rearranged layers on the bulklike Ga plane. The second layer is formed of As and Ga, with Ga atoms at "gap" sites (half-solid circles). (b) The  $c(2 \times 8)$  is made up of rows of dimers on a bulklike Ga plane. We find a mixed surface layer of As and Ga dimers (half-solid circles) in a ratio of  $\sim 2:1$ .

state with an empty surface state orbital, keeping the surface states out of the band gap. We believe that the proximity of neighboring As gap atoms is energetically unfavorable due to Coulomb repulsion between the lone-pair states. (Partial) replacement with Ga atoms is favorable for this reason. Figure 2(b) shows the results of Monte Carlo simulations for this structure, with the number of Ga atoms per  $c(4 \times 4)$  unit cell in the second layer as a parameter. If no As sites are replaced with Ga the As/Ga ratio is far higher than observed experimentally. In fact, the comparison between calculated and measured densities shows that almost all gap atoms [3–4 per  $c(4 \times 4)$  unit cell] are replaced with Ga, resulting in an almost 50-50 Ga-As composition of the second layer.

Similar results are shown in Fig. 2(c) for the less As-rich  $c(2 \times 8)$  and  $(2 \times 4)$  structures. Figure 3(b) shows an atomic model, based on STM observations by Pashley *et al.* [10]. Monte Carlo calculations for As dimers only [0 Ga atoms replaced in Fig. 2(c)] show an As/Ga ratio well above the experimental results. For the  $c(2 \times 8)$  structure we find about 1 out of 3 As dimers are replaced by Ga. For the  $(2 \times 4)$  surface this number increases slightly. Full surface blocking profiles for the  $c(2 \times 8)$  structure, with 1 out of 3 dimers being a Ga dimer, are shown in Fig. 1(b), indicated by the shaded bands. Notice that in both structures the second-layer gap atoms are already Ga atoms, and As-Ga exchange is not expected. The "two-missing-dimer"  $c(2 \times 8)$  structure suggested by Pashley, Haberern, and Gaines [17] is incompatible with our data. The Ga signal expected for this surface is too low by 0.25 monolayer (ML).

Next we consider the  $c(8 \times 2)$  structure, on the Ga-rich side. Geometrically, the structure is similar to the  $c(2 \times 8)$  [Fig. 3(b)], but the dimers are now adsorbed on an As-terminated bulklike sample, instead of a Ga-

terminated sample. Thus, the reconstruction is rotated by  $90^\circ$ . As before, Monte Carlo simulations show that the surface contains more Ga than predicted by the simple model. As in the  $c(4 \times 4)$  surface, the second layer is not fully covered by dimers in the first layer, leaving lone-pair orbitals of second-layer As atoms in proximity. (Partial) replacement of such second-layer As atoms with Ga is consistent with our experimental results. The data cannot be explained *without* replacement of second-layer As by Ga.

Finally, we have analyzed the data for the  $(2 \times 6)$  surface, using the STM observations by Biegelsen *et al.* [11], and their proposed structure, as a starting point. Again, this structure contains threefold-coordinated As atoms in a layer capped with dimers. As in the  $c(4 \times 4)$  and  $c(2 \times 8)$  structures, the As lone-pair orbitals are too close to each other. We find that the surface contains less As and more Ga than predicted by the model. Excellent agreement is obtained when all threefold-coordinated, second-layer As atoms are replaced with Ga, but the data agree with a partial replacement of As dimers by Ga dimers as well [18].

The composition and structure of the GaAs(001) surface, serving as a template for epitaxial growth, will certainly affect aspects of the overlayer. To investigate this we have studied growth of Ge on the GaAs(001)- $c(2 \times 8)$  surface [19], which—as discussed above—contains a 2:1 ratio of As and Ga in the outer monolayer. Segregation of As and Ga on the growing Ge film is quite favorable, because a single atomic layer of these elements at the Ge surface eliminates all dangling bonds. This phenomenon has recently led to the use of group III and V elements as a surfactant in Si/Ge heteroepitaxial growth to eliminate interdiffusion and islanding [20]. After growth of 20 ML of Ge on the GaAs(001)- $c(2 \times 8)$  surface we observe segregation of *both* As and Ga, at 0.6 and 0.3 ML coverage, respectively. This ratio corresponds quite closely to the As/Ga ratio in the  $c(2 \times 8)$  surface. Apparently, the surface layer simply "floats" up as Ge is deposited on the GaAs. The ion scattering spectra show no signal at the Ge/GaAs interface, indicating excellent crystal quality without significant disruption at the interface.

In this study we have performed the first quantitative determination of the elemental composition of a variety of GaAs(001) surface structures. We find that these structures are much more rich in Ga than previously believed or assumed. In the  $c(4 \times 4)$  structure second-layer As gap atoms are replaced with Ga atoms, avoiding overlap of and Coulomb repulsion between As-related lone-pair orbitals. In the  $c(2 \times 8)$  and  $(2 \times 4)$  structures the dimer layer shows a  $\sim 2:1$  mix of As and Ga dimers. For the  $c(8 \times 2)$  surface our results suggest Ga/As mixing in both the first and second surface layers. In the most Ga-rich  $(2 \times 6)$  surface exchange of As with Ga occurs, similar to the  $c(4 \times 4)$  surface.

The implications of these results for our understanding

of the detailed processes at work in MBE of GaAs, AlGaAs, and AlAs on GaAs(001), as well as in other growth methods, such as MOCVD and ALE, need to be addressed in future studies. Here we have shown that the composition of the surface layer determines the segregation of Ga and As during epitaxial growth [19]. Furthermore a mixed Ga/As surface composition and the possibility of a variable Ga/As coverage for a given structure could have profound influence on electronic properties, such as work function or Schottky barrier heights. It is already clear that simple assumptions about the elemental composition of these surfaces during growth need to be considered with care, and that the true structure and composition are more complicated than previously assumed.

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