

## Location of Atoms in the First Monolayer of GaAs on Si

J. R. Patel, P. E. Freeland, M. S. Hybertsen, and D. C. Jacobson  
*AT&T Bell Laboratories, Murray Hill, New Jersey 07974*

and

J. A. Golovchenko

*Division of Applied Physics and Department of Physics, Harvard University, Cambridge, Massachusetts 02139*  
(Received 12 March 1987)

The position of Ga and As atoms at monolayer coverages of heteroepitaxial GaAs on clean Si(111) have been measured by x-ray standing waves in UHV. Though both As and Ga are incident on the surface, As atoms choose to occupy the upper half of the (111) double plane about 5% higher on the average, relative to the Si(111)  $d$  spacing, than the bulk silicon position. Ga atoms are exclusively located on the lower half of the (111) plane about 3% higher than the corresponding bulk positions.

PACS numbers: 68.55.Jk

In recent years there have been many advances in our understanding of the growth of heteroepitaxial layers on crystal surfaces. However, the problem of atom location in the first monolayer of the crystal, which must influence subsequent growth, has remained elusive. We consider as a concrete example the growth of GaAs on a silicon substrate, a problem that has received a great deal of attention recently because of its obvious fundamental and technological importance. If we direct a beam of Ga and As atoms at a clean (111) surface of silicon we may legitimately ask the question, "which atom occupies the top crystal layer?" In this Letter we demonstrate how questions such as these may be addressed with the x-ray standing-wave technique.<sup>1</sup> We will show that with a high degree of coherence, Ga and As atoms occupy mutually exclusive sites on the (111) double plane with As atoms occupying the upper half. Furthermore, the surface structure of heteroepitaxial GaAs on Si(111) differs markedly from homoepitaxial GaAs on  $(\bar{1}\bar{1}\bar{1})$  (As face) GaAs.

In earlier nonvacuum experiments we have shown that a crystal terminated with impurities in the monolayer range is an optimum system for atom location studies with x-ray standing waves.<sup>2</sup> Under ideal conditions, atoms at the surface, and their registration<sup>3</sup> to the crystal below, can be located with an accuracy of 0.01 of the relevant atomic planar spacing. In the following we will present direct evidence for the location of both As and Ga in UHV on a clean reconstructed (111) face of silicon. Some observations on the conditions under which these surfaces show a remarkable chemical stability will also be presented.

The arrangement of the x-ray standing-wave experiment was similar to that originally proposed by Batterman<sup>1</sup> with modifications and advances. The fine-focus beam from an x-ray rotating-anode generator was collimated by an asymmetric (111) silicon crystal. After passing through a thin beryllium window, the beam from

the monochromator was reflected from the specimen crystal in UHV. Both fluorescence and reflected x-ray intensities were recorded as the feedback-stabilized<sup>4</sup> monochromator crystal in air was scanned repeatedly back and forth through the Bragg reflection region. A lithium-drifted silicon x-ray detector monitored the inelastic x rays scattered from the crystal surface. In particular, the Ga and As fluorescence x-ray yield from the crystal surface was monitored as a function of the reflection angle.

Silicon crystals for the UHV substrates were prepared by Syton polishing of a well-oriented (111) silicon crystal surface. The polishing was followed by a chemical cleaning procedure described by Ishizaka, Nakagawa, and Shiraki.<sup>5</sup> After chemical cleaning, only a modest heating at  $\approx 850^\circ\text{C}$  in a UHV chamber (base pressure  $8 \times 10^{-11}$  Torr) is required to produce sharp  $(7 \times 7)$  LEED (low-energy electron diffraction) patterns. The Auger spectrum of the cleaned surface was free of oxygen and showed only a trace carbon peak. Experience from experimenting with various growth conditions led to the following procedure for well-defined first monolayer growth. The silicon substrate was heated to  $600^\circ\text{C}$  and positioned to face an effusion oven containing a crystal of GaAs heated to  $\approx 800^\circ\text{C}$ . At this temperature the As/Ga flux is 12:1.<sup>6</sup> A coverage of the order of a monolayer (ML) of Ga and As was deposited on the  $(7 \times 7)$  (111) silicon surface. Following deposition, the  $(7 \times 7)$  reconstruction of the original silicon surface disappeared completely and was replaced by a clear  $(1 \times 1)$  LEED pattern. *In situ* x-ray fluorescence measurements indicate about 3 times as much As as Ga on the Si surface. The coverage estimated from the As and Ga *LMM* Auger lines was 0.5-ML Ga and 1.5-ML As (1 ML  $= 7.8 \times 10^{14}$  atoms/cm<sup>2</sup>). Coverages could also be determined with x-ray fluorescence measurements against standard implanted samples calibrated by Rutherford backscattering. The estimated uncertainty in the cover-

age measurement is of the order of 10%–15%.

An angular scan of the reflectivity together with the As and Ga fluorescence yield in the region of the (111) Bragg reflection from silicon is shown in Fig. 1. The fluorescence yield curves for the Ga and As fluorescence may be understood with the aid of the inset in Fig. 1 which shows the two inequivalent (111) surface planes marked as (a) and (b). The maxima of the (111) Fourier component of the charge density will lie between the (a) and (b) planes (dashed lines). Consequently, the nodes of the standing-wave field due to the interaction of the incident and diffracted beams will coincide with the maxima on the low-angle side of the Bragg reflection. As the crystal is tilted through the Bragg reflection, the nodes move in the direction of the inward drawn normal to the crystal surface and will pass through the lower (b) plane. Thus the observed (b) fluorescence will pass through a minimum as indicated by the curve with open circles in Fig. 1. On the high-angle side of the Bragg gap the antinodes will move through the (a) positions in the inset of Fig. 1 and a large peak should be observed in the (a) fluorescence as illustrated by the curve with filled circles in Fig. 1. The Bragg reflectivity is also shown in Fig. 1 and indicates that in the Bragg gap, the reflectivity is very close to unity. The solid lines for both reflectivity and fluorescence are calculated from dynamical theory with accurately known x-ray scattering factors. The calculated position (POS) and coherent fractions (FRAC) are also indicated in Fig. 1. FRAC is defined as the fraction of atoms at position POS that would yield a signal of the observed strength. For a perfect termination of the bulk silicon lattice [plane (a) in inset], POS=1.125 and FRAC=1.0. For As, the experimental result is POS=1.18 and FRAC=0.95. Thus, on average, the As atoms occupy a position  $\approx 5\%$  higher relative to the Si(111)  $d$  spacing than the perfectly terminated silicon lattice. The coherent fraction 0.95 indi-

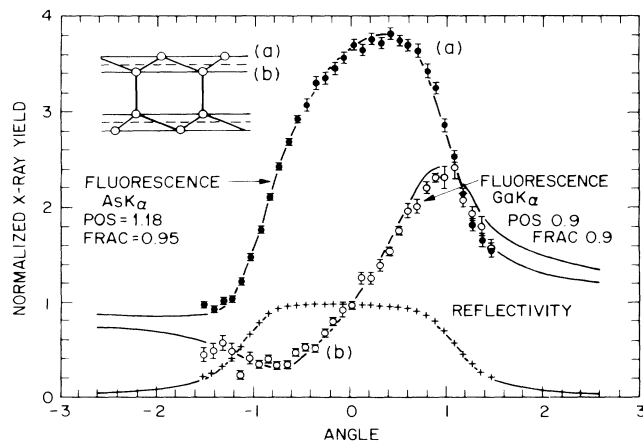


FIG. 1. Reflectivity and fluorescence yield for 0.5 ML of GaAs epitaxially grown on a Si(111) surface.

cates the overwhelming tendency for As atoms to lie in the *upper half* of the (111) double layers.

The position and coherent fraction for the Ga atoms are also indicated in Fig. 1. The position of the lower half of the (111) plane in the perfectly terminated silicon bulk lattice is POS=0.875 and FRAC=1.0. For Ga the experimental result is POS=0.90 and FRAC=0.90. Thus, on average, the Ga position is  $\approx 3\%$  higher than that for a perfectly terminated silicon position relative to the Si(111)  $d$  spacing and the Ga atoms occupy only the *bottom half* of the (111) double plane.

A remarkable property of the GaAs/silicon surface is its stability upon limited exposure to various contaminating environments. For instance, after exposure to pure oxygen { $10^6$  L [1 L (Langmuir) =  $10^{-6}$  Torr sec]} in the UHV chamber, the As and Ga positions hardly changed from the results shown in Fig. 1. Although an oxygen Auger peak was clearly observed on the sample surface, the LEED pattern was still ( $1 \times 1$ ). Subsequent exposure to humid air ( $10^6$  L) a day later, still in the UHV chamber, resulted in slight changes in the As and Ga fluorescence yields as indicated in Fig. 2. In the inset is shown a portion of the Auger spectra showing C and O lines on a magnified scale after exposure to humid air. While the As and Ga curves look substantially the same as those in Fig. 1 some change has occurred. Compare curves (a) and (b) of Fig. 2 with their counterparts in Fig. 1. Curve (c) was obtained after storage of the specimen under ambient conditions for some months and shows that most of the atoms are in random positions. Only the Ga result is shown in curve (c); however, an

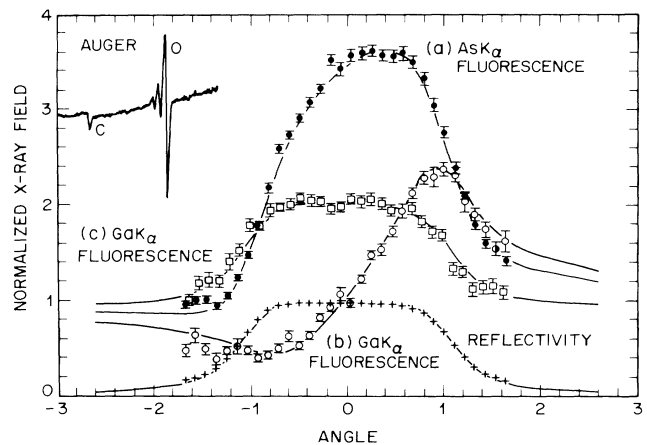


FIG. 2. Reflectivity and fluorescence yield for 0.5 ML of GaAs epitaxially grown on a Si(111) surface showing the influence of exposure to various ambient conditions. Inset: A portion of the Auger spectrum after exposure to humid air. (a) As  $K\alpha$  fluorescence yield, POS=1.17, FRAC=0.85, and (b) Ga  $K\alpha$  fluorescence yield, POS=0.9, FRAC=0.83, after exposure to humid air. (c) Ga  $K\alpha$  fluorescence yield, POS=1.30, FRAC=0.83, after storage some months under ambient conditions.

analogous result was obtained for the As positions. The results suggest a low-energy passive surface configuration which we will discuss later.

From the above results severe constraints are placed on the first monolayer of growth of GaAs on silicon. When a clean ( $7\times 7$ ) silicon surface, held at high temperature ( $\approx 600^\circ\text{C}$ ), is exposed to a flux of As and Ga atoms the complete ( $7\times 7$ ) reconstruction of the original silicon surface is destroyed and is replaced by a sharp ( $1\times 1$ ) LEED pattern. It is remarkable that even though both species of atoms arrive at the silicon surface it is only the As atoms that occupy the topmost site, i.e., the *upper half* of the double (111) plane, while the Ga atoms are confined exclusively to the *lower half* plane. We therefore can report that on an atomic scale, anti-phase domains are essentially absent in the first monolayer stages of heteroepitaxial growth of GaAs on Si. Furthermore, it is *the polar ( $\bar{1}\bar{1}\bar{1}$ ) or B face that initially terminates the epitaxial crystal*.

A simple model, involving just Ga and As in the top double (111) plane with Ga atoms in the lower half, is not consistent with several experimental facts. With the observed Ga coverage of 0.5 ML the 3:1 As/Ga ratio cannot be accounted for. Furthermore, such a layer would have a single dangling bond associated with the topmost As atoms which is hard to reconcile with the ( $1\times 1$ ) periodicity observed by LEED and the chemical passivity of the surface. Finally the simple model predicts bonding between Ga/Si at the interface. However, recent core-level spectroscopy data<sup>7</sup> show that bonding at the GaAs/Si interface is predominantly between As and Si atoms.

A model consistent with our detailed measurement of both arsenic and gallium positions and the above facts is shown in Fig. 3. The silicon crystal is everywhere terminated with arsenic atoms which occupy upper-level (111) double-layer positions. This layer is partially covered with a gallium layer in which gallium atoms alone occupy the lower positions in the (111) double layer. Finally these regions are again terminated with ar-

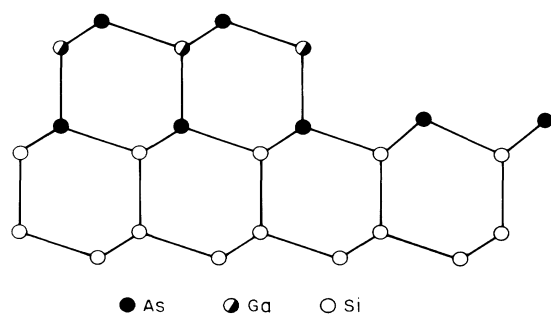


FIG. 3. Schematic of a GaAs on Si(111) surface viewed edge on along a  $[\bar{1}10]$  projection. Note that only As-Si bonds are present at the interface.

senic atoms in upper-level positions. Since only half a monolayer of gallium is present on the surface, steps of the type indicated are presumably present.

In regions where arsenic atoms alone terminate the silicon surface, a POS value of 1.18 may be taken which is identical to that found for arsenic atom termination in the absence of gallium arsenide.<sup>8</sup> The remaining atom positions can only be accounted for by our slightly contracting the arsenic atoms below the gallium-arsenide layer to POS=1.12 and expanding those above to POS=2.24 ( $=1.0+1.24$ ). Gallium atoms are at POS=0.9 as earlier indicated. With this configuration all gallium-arsenide bond lengths are as in the bulk and no appreciable subsurface silicon relaxation is required to explain the results. We note that the extremely high coherent fractions observed place such hard constraints on the model that we are quite confident in our deduction of the configuration with only a single reflection for this study.

The model is also consistent with the core-level shift data,<sup>7</sup> since only Si-As bonds are present at the interface. Furthermore, since the As atoms under the Ga can donate an extra electron to satisfy the fourfold coordination of the Ga atoms, the As atoms above the Ga can have a lone-pair state consistent with the observed passivity of the surface. Of course As atoms which terminate the Si surface also have a lone-pair configuration as discussed by Bringans *et al.*<sup>9</sup> The passivity and lack of reconstruction is not expected to persist as the layer thickens. Misfit locations will be introduced as a result of lattice mismatch of Si and GaAs, and the simple chemical arguments are no longer valid.

Further general support for the ideas in Fig. 3 is found in the direct transmission-electron-microscopy observations of *in situ* growth of GaAs on Ge(111).<sup>10</sup> Qualitative LEED observations<sup>11</sup> are also consistent with stepped features of the order of  $d(111)$ . From the arguments given above we conclude that the model in Fig. 3 describes our results accurately and is the preferred arrangement of atoms at the surface and interface.

Some general remarks on the growth of GaAs on silicon surfaces are in order. Recently it has been found<sup>12</sup> that the presence of double steps on (100) surfaces of silicon allows the growth of GaAs without antiphase domains. Because of the nature of double (111) planes, such a structure appears to be naturally built into these surfaces and provides the selectivity to allow As and Ga atoms preferentially to choose the correct site. Of course the chemical-site selectivity is driven by the chemical stability of the As termination of the (111) surface with its full occupancy of lone-pair states. We have discussed above that this places strong constraints on the atomic arrangements at the surface and interface of the adsorbed species. It also determines the crystal polarity which turns out to be the ( $\bar{1}\bar{1}\bar{1}$ ) or B face of GaAs. Our results show that growth of GaAs on well-oriented (111)

Si should suppress the formation of antiphase domains relative to growth on (100) Si. These observations may well be applicable to the heteroepitaxial growth of other III-V compounds on silicon.

We gratefully acknowledge discussions with L. C. Kimmerling, E. G. McRae, R. D. Bringans, M. A. Olmstead, and J. F. Northrup.

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