

Atomic-scale structure and electronic properties of GaN/GaAs superlattices

R.S. Goldman,^a B.G. Briner,^{b,*} R.M. Feenstra,^{a,b} M.L. O'Steen,^c and R.J. Hauenstein^c
(a) Department of Physics, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213
(b) IBM Research Division, Yorktown Heights, New York 10598
(c) Department of Physics, Oklahoma State University, Stillwater Oklahoma 74078

Abstract

We have investigated the atomic-scale structure and electronic properties of GaN/GaAs superlattices produced by nitridation of a molecular beam epitaxially grown GaAs surface. Using cross-sectional scanning tunneling microscopy (STM) and spectroscopy, we show that the nitrided layers are laterally inhomogeneous, consisting of groups of atomic-scale defects and larger clusters. Analysis of x-ray diffraction data in terms of fractional area of clusters (determined by STM), reveals a cluster lattice constant similar to bulk GaN. In addition, tunneling spectroscopy on the defects indicates a conduction band state associated with an acceptor level of N_{As} in GaAs. Therefore, we identify the clusters and defects as GaN and N_{As}, respectively. Together, the results reveal phase segregation in these arsenide/nitride structures, in agreement with the large miscibility gap predicted for GaAsN.

Nitride-based III-V compound semiconductor heterostructures are promising for optoelectronic devices, such as blue light-emitting diodes¹ and lasers.² In principle, mixed anion nitride/arsenide alloys would enable the fabrication of light emitters operating in the entire visible spectrum. However, for the GaAsN system, calculations predict a limited miscibility of N in GaAs,³ and experiments have presented conflicting results concerning the formation of GaAsN alloys. Apparently, thick layers (>0.5 μm) of dilute GaAs_{1-x}N_x (x ≤ 0.03) alloys have been produced by nitride growth,^{4,5} and attempts to increase the nitrogen composition in the alloy using GaAs surface nitridation resulted in GaAs/GaN/GaAs thin-layer structures⁶ and GaAs_{1-x}N_x/GaAs superlattices (0.04 ≤ x ≤ 0.33).^{7,8} The identification of the nitride/arsenide structures as binary or ternary alloys has relied upon x-ray diffraction (XRD), which has spatial resolution of hundreds of μm and averages over many surface layers parallel to the interfaces. Thus, standard interpretations may lead to misleading results in terms of ternary alloy formation if the structures are not continuous films of homogeneous material. Therefore, a detailed study of the atomic-scale structure and electronic properties at nitride/arsenide interfaces is essential for the understanding of alloy formation in this materials system.

In this letter, we present cross-sectional scanning tunneling microscopy (STM) and spectroscopy investigations of GaN/GaAs superlattices produced by nitridation of a molecular beam epitaxially (MBE) grown GaAs surface. Our cross-sectional studies indicate that the nitrided layers are not continuous films, but consist of regions with

* Present address: Fritz-Haber-Inst. der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany.

sparse N content and larger clusters. Analysis of x-ray diffraction data in terms of fractional area of clusters reveals a cluster lattice constant similar to bulk GaN, indicating that the nitrated regions consist of pure GaN. Spectroscopic studies on the atomic-scale defects reveal a state in the conduction band associated with an acceptor level of N_{As} in GaAs, which allows us to identify the defects as N_{As} . The observed lateral inhomogeneity and lack of ternary alloy formation indicate that phase segregation has occurred, in agreement with the prediction of a large miscibility gap in the GaAsN system.³ In addition, spectroscopy on the clusters reveals band gap narrowing associated with highly strained GaN, and an upward shift of the band edges due to band bending at the cluster/GaAs interface.

The samples were prepared using a combination of solid Ga and As_2 effusion and ECR-plasma-excited N_2 gaseous sources; details of the growth apparatus have been described elsewhere.⁷ Thirty-six period superlattices were produced by a 3-step process, based on the principle of N-As surface anion exchange, which consisted of (1) 4 second exposures of the (001) GaAs surface to a radical-nitrogen flux, (2) 100 second overgrowth of GaAs (simultaneous exposures to Ga, As_2 , and Si fluxes), and (3) 30 second "As-soak" (As_2 flux only). This sequence was expected to result in monolayers of $GaAs_{1-x}N_x$ separated by spacers of 200 Å Si-doped ($N_d \approx 5 \times 10^{18} \text{ cm}^{-3}$) GaAs. During the growth and nitridation of the samples described in this paper, the substrate temperature typically ranged from 540–560°C. Reflection high energy electron diffraction obtained during surface nitridation revealed a specular, commensurate (3x3) pattern, indicating coherent growth.⁷ Simulations of XRD data suggested that the structures consist of coherently strained superlattices, with monolayer thickness $GaAs_{0.79}N_{0.21}$ embedded in 192 Å GaAs layers. For STM studies, the samples were cleaved to expose a (110) surface, in an ultra-high-vacuum chamber with base pressure $< 4 \times 10^{-11}$ Torr. STM was performed with both electrochemically etched single crystal $\langle 111 \rangle$ -oriented W tips cleaned by in-situ electron bombardment and characterized by in-situ field-emission microscopy. Images were obtained with a constant tunnel current of 0.1 nA. Details of the STM design,⁹ cleavage procedure,¹⁰ and spectroscopic methods¹¹ have been described previously.

Figures 1(a) and 2(a) show STM topographic images of the GaN/GaAs superlattices, displayed with the growth direction from right to left. In these empty state images, the nitrated regions appear as depressions (darker regions) in the surrounding GaAs (brighter regions). The large-scale image in Fig. 1(a), acquired at sample bias voltage of +2.2 V, indicates that the nitrated layers are not continuous films, but consist of groups of atomic-scale defects and clusters of various sizes. In Fig. 2(a), we present a high-resolution view of the superlattices, acquired at a sample bias voltage of +2.5 V. Fringes with a spacing of 5.65 Å, corresponding to the (001) lattice planes of GaAs, are observed in the bright regions of the image. The image consists primarily of one nitrated layer sandwiched by 160 Å GaAs layers, with tails of additional nitrated layers on the edges of the image. This nitrated layer contains one small cluster and a group of atomic scale defects. It is evident that the extent of nitrogen incorporation in the growth direction is ≥ 30 Å, considerably greater than the simulated monolayer thickness. In filled state images (negative sample bias voltage), the nitrated regions appear bright in comparison with the surrounding GaAs.¹² Since the contrast of the defects and clusters is dependent on the

sign of the bias voltage, both features are of electronic rather than topographic origin. In other words, the dark (bright) features in the empty (filled) state images are not pits (protrusions) in the surface but instead regions with different electronic structure.

In order to quantify the nitrogen content in the structures, we have determined the fractional area of clusters in several large-scale images such as Fig. 1(a). We used an algorithm to count pixels in regions of the image with tip height below a specified value. We estimate a tip height (depth) criterion based on the tip height profile in the vicinity of a cluster. Figure 2(c) is a line cut of the tip height, taken through the center of a cluster, defined by the arrows in Fig. 2(a). The line cut indicates a region of decreased tip height at the cluster, surrounded by a gradual increase in tip height, presumably due to band bending at the cluster/GaAs interface. It is evident from this line cut that the band bending is partly superposed on the GaAs atomic corrugation. This effect is further illustrated for the small cluster outlined by a white box in Fig. 2(a). In Fig. 2(b), the grey-scales in the white box region are expanded from 2.7 to 4.7 Å, and the apparent size of the cluster is significantly reduced. Thus, part of the contrast displayed in the clusters in Figs. 1(a) and 2(a) is due to band bending and must be taken into account when counting up the total cluster area. Therefore, the tip height cutoff is defined as the depth at which the atomic corrugation is not observed, approximately 2 Å below the unperturbed GaAs regions. In Figs. 1(b) and (c) we show our analysis of cluster density performed on several large-scale images such as Fig. 1(a). In Fig. 1(b), the grey-scales of Fig. 1(a) are expanded from 2.1 to 4.7 Å. In Fig. 1(c), image pixels with tip height more than 2 Å below the nominal GaAs height are displayed as black, while all other image pixels are white. The fraction of black regions is $4.45 \pm 0.05 \times 10^{-3}$, which corresponds to only about (1/5) monolayer of GaN per deposited layer, rather than the full monolayer assumed earlier.⁸ A similar fractional area of clusters is obtained in several large-scale images, with total area $> 0.2 \mu\text{m}^2$. High resolution x-ray diffraction data of these GaN/GaAs superlattices indicates an average superlattice lattice constant, 5.6499 Å, previously interpreted in terms of (continuous) monolayers of $\text{GaAs}_{0.79}\text{N}_{0.21}$ embedded in 192 Å GaAs layers.⁸ With the knowledge of the fractional area of the clusters, we estimate a cluster lattice constant of 4.6 ± 0.1 Å, similar to bulk GaN. Therefore, we conclude that the nitrated regions consist of pure GaN, as opposed to some alloy composition with 20% – 30% N.

In order to chemically identify the atomic-scale defects and clusters, we performed spectroscopic measurements on individual defects and clusters of various sizes. In Figs. 3(a) and (b), the normalized conductance versus sample bias voltage are plotted for an atomic scale defect (GaAs:N) and large cluster (lateral extent > 50 Å), respectively, and compared with regions of clean GaAs. The GaAs spectra, shown at the bottom of both figures, display well-defined band edges (the band edge positions are determined by assuming a linear onset in the normalized conductance¹³), with a band gap of 1.43 ± 0.10 eV, comparable to that of bulk GaAs. The nonzero conductance within the GaAs gap in Fig. 3(b) is the "dopant-induced" component, which arises from electrons tunneling out of filled conduction band states.¹³ In Fig. 3(a), the spectrum corresponding to atomic scale defects displays well-defined band edges and band gap similar to GaAs. However, in this case, a state is observed at 0.40 ± 0.05 eV above the conduction band edge. The

position of this state with respect to the conduction band edge is consistent with the predictions of Wolford et al.¹⁴ for N isoelectronic traps in GaAs. Therefore, we associate the state with an acceptor level of N_{As} in GaAs, and identify the atomic-scale defects as N_{As} .

The spectrum corresponding to a large cluster displays several features which are different from the clean GaAs spectrum. The most prominent difference is the reduced band gap of 1.23 ± 0.10 eV, which is significantly smaller than band gaps of GaAs (1.43 eV) and GaN (3.5 eV). Recently, a number of theoretical works have predicted band gap bowing in the $GaAs_{1-x}N_x$ alloy system,^{3,15-17} The calculated bowing parameters would suggest that the reduced band gap corresponds to a few percent nitrogen or arsenic in $GaAs_{1-x}N_x$. However, our analysis of x-ray diffraction data discussed earlier suggests that the clusters are pure GaN. Thus, the band gap reduction may be due in part to a few percent As in GaN with additional reduction due to the high lattice-mismatch strain between the clusters and GaAs.^{12,18-21} In addition to the reduced band gap, the band edges of the cluster spectrum are shifted upward in comparison to the GaAs spectrum. Similar effects are observed in spatially resolved spectroscopy of a small cluster (lateral extent < 50 Å), where the band edges are shifted upward as one moves towards the GaAs/cluster interface.¹² The band edge shifts are attributed to electrostatic charging which results in band bending at the cluster/GaAs interface, similar to that observed previously in studies of arsenic precipitates in low-temperature GaAs.²² The upward shift of the band edges of the cluster is consistent with the contrast observed in the bias-dependent images mentioned earlier.¹²

We thank C.G. Van de Walle for useful discussions. M.L.O. and R.J.H. acknowledge the support of AFOSR.

References

1. S. Nakamura, T. Mukai, and M. Senoh, *Appl. Phys. Lett.* **64**, 1687 (1994).
2. S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H. Kiyoku, and Y. Sugimoto, *Jpn. J. Appl. Phys.* **35**, L74 (1996).
3. J. Neugebauer and C.G. Van de Walle, *Phys. Rev. B* **51**, 10568 (1995).
4. M. Weyers, M. Sato, and H. Ando, *Jpn. J. Appl. Phys.* **31**, L853 (1992).
5. M. Kondow, K. Uomi, K. Hosomi, and T. Mozume, *Jpn. J. Appl. Phys.* **33**, L1056 (1994).
6. M. Sato, *Jpn. J. Appl. Phys.* **34**, 1080 (1995).
7. R.J. Hauenstein, D.A. Collins, X.P. Cai, M.L. O'Steen, and T.C. McGill, *Appl. Phys. Lett.* **66**, 2861 (1995).
8. Z.Z. Bandic, R.J. Hauenstein, M.L. O'Steen, and T.C. McGill, *Appl. Phys. Lett.* **68**, 1510 (1996).
9. R.M. Feenstra, 21st Int. Conf. Phys. Semicond., ed. P. Jiang and H.-Z. Zheng (World Scientific, Singapore, 1992), p.357.
10. R.M. Feenstra, E.T. Yu, J.M. Woodall, P.D. Kirchner, C.L. Lin, and G.D. Pettit, *J. Vac. Sci. Technol. B* **61**, 795 (1992).
11. R.S. Goldman, B.G. Briner, R.M. Feenstra, M.L. O'Steen, and R.J. Hauenstein, unpublished.
12. P. Mårtensson and R.M. Feenstra, *Phys. Rev. B* **39**, 7744 (1988).
13. R.M. Feenstra, *Phys. Rev. B* **50**, 4561 (1994).
14. D.J. Wolford, J.A. Bradley, K. Fry, and J. Thompson, 17th Intl. Conf. Phys. Semicond., ed. J.D. Chadi and W.A. Harrison (Springer-Verlag, New York, 1985), p.627.
15. S. Sakai, Y. Ueta, and Y. Terauchi, *Jpn. J. Appl. Phys.* **32**, 4413 (1993).
16. S.-H. Wei and A. Zunger, *Phys. Rev. Lett.* **76**, 664 (1996).
17. L. Ballaiche, S.-H. Wei, and A. Zunger, unpublished.
18. K. Kim, W.R.L. Lambrecht, and B. Segall, *Phys. Rev. B* **50**, 1502 (1994).
19. C.G. Van de Walle, *Phys. Rev. B* **39**, 1871 (1989).
20. W. Shan, T.J. Schmidt, R.J. Hauenstein, J.J. Song, and B. Goldenberg, *Appl. Phys. Lett.* **66**, 3492 (1995).
21. C.G. Van de Walle, unpublished.
22. R.M. Feenstra, A. Vaterlaus, J.M. Woodall, and G.D. Pettit, *Appl. Phys. Lett.* **63**, 2528 (1993).

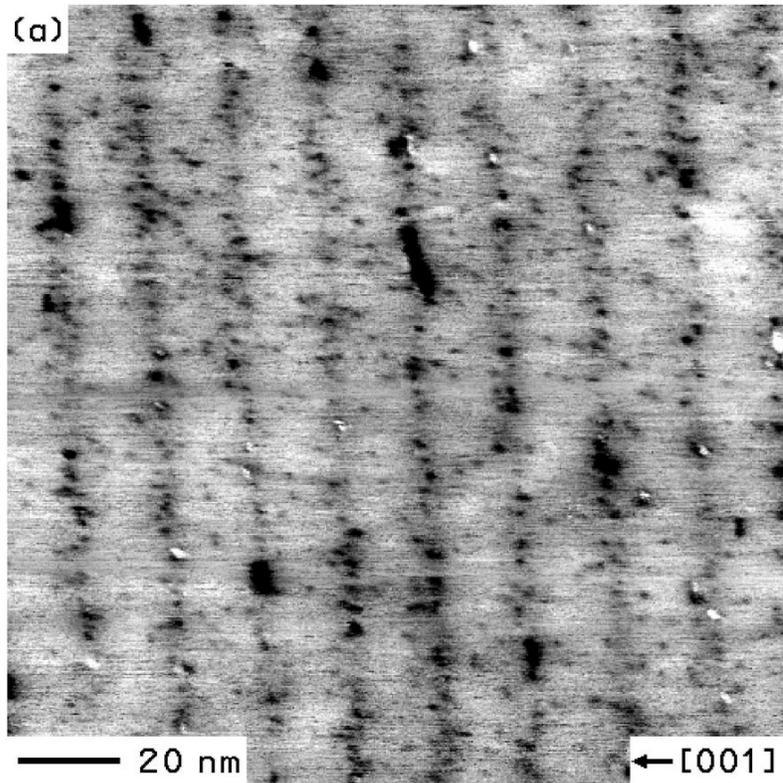
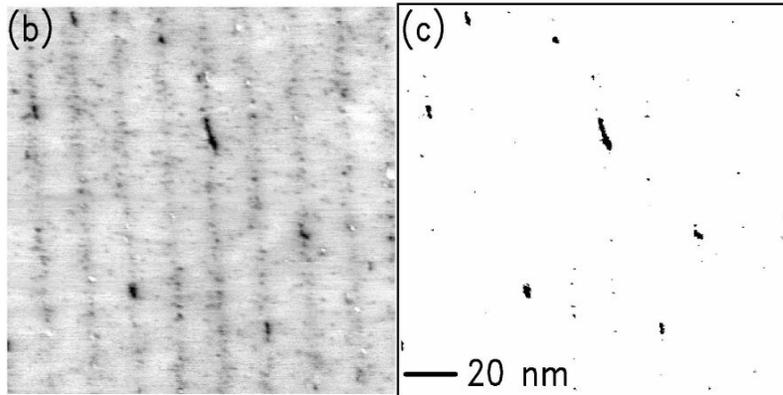


FIG 1 Large-scale topographic images of GaN/GaAs superlattices, acquired at a sample voltage of +2.2 V. The grey-scale ranges displayed in (a) and (b) are 2.1 and 4.7 Å, respectively. In (c), pixels with tip height more than 2 Å Below the nominal GaAs height are displayed as black, while all others are white.



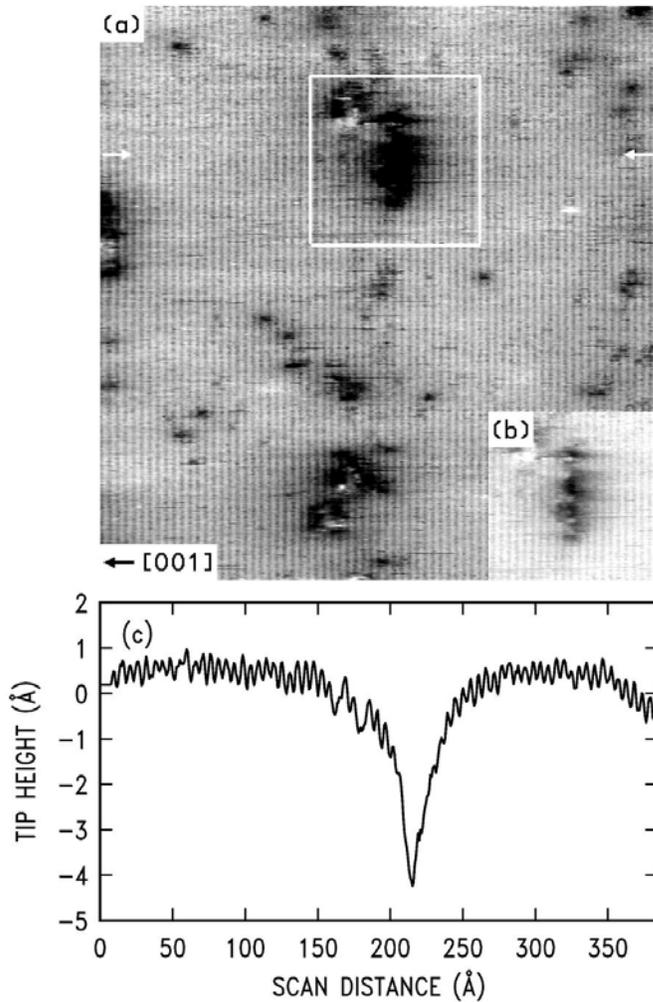


FIG 2 High resolution topographic image acquired at a sample voltage of +2.5 V. The grey-scale range displayed in (a) is 2.7 Å. A view of the region outlined by a white box in (a) is shown in (b), with a grey-scale range of 4.7 Å. A cut along the line indicated by arrows in (a) is displayed in (c).

FIG 3 STM spectra acquired on an atomic scale defect (GaAs:N) and large cluster (lateral extent > 50 Å), in comparison with regions of clean GaAs. The valence and conduction band edges are marked by E_V and E_C , respectively. The state associated with an acceptor level of N_{As} in GaAs is indicated by an upward pointing arrow. The sample voltage corresponds to the energy of the state relative to the Fermi level.

