Published in Appl. Phys. Lett. 78, 82 (2001).

Arrangement of Nitrogen Atoms in GaAsN Alloys determined by Scanning Tunneling Microscopy

H. A. McKay and R. M. Feenstra
Department of Physics, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213
T. Schmidtling and U. W. Pohl
Technische Universität Berlin, Hardenbergstr. 36, D-10623 Berlin, Germany

Abstract

The pair distribution function of nitrogen atoms in $GaAs_{0.983}N_{0.017}$ has been determined by scanning tunneling microscopy. Nitrogen atoms in the first and third planes relative to the cleaved $(1\bar{1}0)$ surface are imaged. A modest enhancement in the number of nearest-neighbor pairs particularly with [001] orientation is found, although at larger separations the distribution of N pair separations is found to be random.

Considerable interest has developed in recent years concerning GaAsN and InGaAsN alloys with low N content, typically a few %. The large predicted band gap bowing in this system of highly mismatched anions leads to the possibility of considerable band gap reduction with modest N content [1,2]. Important applications include lasers with wavelength in the 1.3–1.55 μm range, as well as solar cells with band gap around 1.0 eV [3]. Generally speaking the GaAsN and InGaAsN alloys have displayed evidence of inhomogeneities, such as broad photoluminescence (PL) line widths, variable PL decay times, and short minority carrier diffusion lengths [4-7]. Such observations are often taken as an indicator of compositional fluctuations in the materials, although direct structural characterization of such fluctuations is lacking.

In this work we use cross-sectional scanning tunneling microscopy (STM) to directly probe the arrangement of N atoms in $GaAs_{0.983}N_{0.017}$ alloys. Nitrogen atoms of two distinct contrast levels are imaged, which we assign to occupation in the first and third surface planes relative to the $(1\bar{1}0)$ surface. From an accurate determination of the position of about 1000 N atoms in a continuous strip of alloy material, we compute the distribution function of pair separations. The arrangement of N atoms is found to be quite consistent with that expected from random occupation, with the exception that an enhanced occurrence of nearest-neighbor N pairs is found.

The GaAsN alloys studied here were grown on GaAs(001) substrates by metal organic vapor phase epitaxy (MOVPE) at temperatures between 530 and 570 °C using TMGa, TBAs or AsH_3, and tertiarybutylhydrazine (TBHy) under hydrogen carrier gas. Additional details of the growth and characterization of the material can be found in Ref. [8]. The particular film studied here consists of a GaAs buffer layer followed by a $GaAs_{0.983}N_{0.017}$ layer, a 52 nm thick GaAs spacer layer, a $GaAs_{0.972}N_{0.028}$ layer, and a 370 nm thick GaAs cap layer. The thickness of the GaAsN layers was determined by high-resolution x-ray diffraction (HRXRD) to be about 18 nm; STM measurements of their thickness gave results of 14–19 nm depending on location in the wafer. The N contents quoted above were also determined by HRXRD; STM measurements for those quantities gave similar results. The GaAs substrate, buffer layer, and cap layer were doped with Si at a con-

centration of about 2×10^{18} cm^{-3}, and all other layers are undoped. STM measurements were performed by cleaving the sample *in situ* on a $(1\bar{1}0)$ plane. Obtaining atomically flat cleavage faces was relatively difficult, probably due to the mismatch in strain and/or elastic constants between the GaAs and the GaAsN. Large cleavage steps located in or near the alloy layers often occurred, and smaller cleavage related defects within the GaAsN layers were also seen as discussed in more detail below (these cleavage related defects were more numerous in the high N-content layer, and for that reason our study has focussed on the low N-content layer). The STM studies were performed using PtIr probe tips, at a constant current of 0.1 nA. All images presented here are filled state images obtained with negative sample-tip bias voltages.

Figure 1(a) shows an STM image of the $GaAs_{0.983}N_{0.017}$ layer. The anion sublattice is imaged in this filled state image, and some of the anions appear to be darker, *i.e.* lower, than others. We associate these darker unit cells with N atoms which are substitutional for As in the alloy layer; the N atom contrast is similar to that previously observed in delta-doped N layers in GaAs [9]. There appears to be two distinct gray levels for most of the N atoms in Fig. 1(a); we mark two or the darkest cells A, and two less dark cells B. The depth of the unit cells can be measured as the difference between their topographic height compared to that of their neighboring cells (neglecting neighbors which also contain N atoms). Applying this procedure to about 10 images of similar size to that of Fig. 1(a) yields the histogram shown in Fig. 1(b). We see that there are two distinct depths, 0.40 Å and 0.17 Å, for the unit cells containing nitrogen atoms [10]. Nearly the same number of each type occurs in the images. Following prior cross-sectional STM studies [11,12], we associate these two types of features with N atoms residing on different planes relative to the $(1\bar{1}0)$ surface. In the [110] direction, practically all of the dark unit cells we observe are located centrally on an anion sublattice unit cell (*i.e.* not between unit cells), indicating that they are associated with a substitutional N atom residing in the first atomic plane (*i.e.* the surface layer), or the third plane, or a deeper odd numbered plane [11,12]. We thus associate the observed deepest unit cells with N atoms in the first plane, and the shallower cells with N atoms in the third plane.

Our interpretation of the STM images as revealing first- and third-plane N atoms is consistent with recent computations involving the analogous case of anion vacancies imaged on $(1\bar{1}0)$ cleaved III-V surfaces [13]. The well known case of a surface vacancy produces a depression in filled state images [14], and we expect similar behavior for a N atom since it is so much smaller than the As atom it replaces. For the case of anion vacancies in deeper planes, the theory indicates that their appearance in STM images will be relatively small [13]. Second-plane vacancies (or N atoms) are expected to produce a slight *lateral* shift in an [110]-oriented pair of corrugation maxima leading to a slight opening of the gap between corrugation rows; we observe such features in our data, as seen faintly at the locations marked C in Fig. 1(a) and shown in more detail in Fig. 2(a). For third-plane vacancies the theory predicts only a very small reduction in height, ≤ 0.1 Å; the fact that we observe third-plane N atoms with somewhat greater depth (0.17 Å) is a matter which we believe requires detailed calculation to understand.

In addition to the features marked A, B, or C in Fig. 1(a), another commonly observed structure in the alloy layers are rows of either missing or extra atoms, extending along the [110] direction. Figures 2(b) and (c) show examples of such features. We observe about the same number of missing rows as extra rows. The height (or depth) of the features is 2.0 Å, corresponding to a single atomic step in the $(1\bar{1}0)$ direction. We interpret these features as being cleavage induced

surface defects, in which a row of GaAs is torn out from one side of the cleavage plane and added to the opposite side. Detailed inspection of the ends of these defects often reveals what appears to be one or two or more N atoms with a [110] relative orientation. We thus believe that the stress associated with those N atoms leads to these cleavage induced surface defects. Finally, the only other type of defect observed on the cleavage surface of the alloy layers are occasional stray atoms, such as that marked D in Fig. 1(a). Such atoms presumably arise from the cleavage induced defects just mentioned, or from residual surface contamination.

Having established the identity of the observed N containing unit cells above, we can now proceed with a detailed analysis of arrangement of the N atoms. This analysis is performed on a sequence of large-scale STM images extending over a contiguous 400 nm length of the $GaAs_{0.983}N_{0.017}$ layer. All images clearly show the two types of unit cells containing N atoms, as seen in Fig. 1(a). We associate each observed N atom with a specific unit cell location, and we then count the number of pairs of a given separation (with separations determined from the unit cell dimensions, 5.65 Å $\times$ 4.00 Å). For simplicity we do not consider here the different vertical positions (first or third plane) of the N atoms, although including that information does not change any of our conclusions, as discussed elsewhere [15]. The results of our analysis are shown in Fig. 3. We plot the distribution of pair separations [16] which is the observed pairs of N atoms of a specified separation divided by the number of equivalent sites of each separation (2 or 4). Uncertainties in these values are given simply by the counting statistics, and are shown on a few selected points. The dominant feature seen in Fig. 3 is that the distribution function is spread over a range of values, *e.g.* at a separation of 100 Å, the distribution values range from about 3 to 22. This spread results simply from the fact that the width of the $GaAs_{0.083}N_{0.017}$ layer is finite (that is, ≈ 18 nm). The number of [001] oriented pairs thus falls off as the separation increases, whereas in the [110] direction we have analyzed a 400 nm length of layer so that such finite size effects are negligible.

For a truly random arrangement of N atoms, the distribution function would have some constant value independent of separation. The maximal values in Fig. 3 do indeed indicate a constant value of about 20 as indicated by the dashed line, which equals $m\,\sigma / 2$ where m is the number of N atoms studied and σ is their fractional occupation of surface unit cells. Examining specific points of the distribution function which deviate from this constant, we note that the number of [001]-oriented second nearest-neighbor (5.65 Å separation) pairs is significantly higher (2.7 error bars) than expected, indicating enhanced formation probability for those pairs. The observed number of [110]-oriented first nearest-neighbor (4.00 Å separation) pairs is *not* higher than expected, although those specific pairs were probably undercounted since we did *not* count any of them associated with the formation of the cleavage induced defects (extra or missing rows) discussed above. If we associate a single [110]-oriented first nearest-neighbor pair with each cleavage induced defect, the total number of those pairs increases to a similar value as for the [001]-oriented nearest-neighbor pairs. All the only other values in Fig. 3 are statistically indistinguishable from that expected from a random arrangement of N atoms.

Perhaps the most important conclusion to be drawn from our computed pair correlation function is that, aside from the slight enhancement of nearest-neighbor pairs, all other pair separations appear to occur with essentially a uniform probability. The same conclusion results if we consider the number of N atoms, N_W, in a window of fixed size, and move that window over the alloy layer; we find fluctuations in the values of N_W which equal, within a few %, the expected value of

$\langle N_W \rangle^{1/2}$ where $\langle N_W \rangle$ is the average value of N_W [15]. Thus, we find no evidence for medium- or long-range compositional fluctuations of the N atoms, as has been suggested in some recent studies [4,7]. To model GaAsN alloys, at least of the type grown here, our results indicate that one can simply assume a modest ($\leq 50\,\%$) enhancement of the number of second (and possibly also the first) nearest-neighbor pairs, together with a random distribution of all other pairs. Such a model would, of course, still display random fluctuations in local N content, strain, band gap, *etc.* which would be reflected in the optical properties of such a system. The enhanced number of nearest-neighbor pairs will produce additional fluctuations in strain and band gap [17].

Discussions with J. Geisz, J. Neugebauer, J. Northrup, and G. Schwarz are gratefully acknowledged. This work was supported by the National Science Foundation (grant DMR-9985898).

[1] M. Weyers, M. Sato, and H. Ando, Jpn. J. Appl. Phys., Part 2, **31**, L853 (1992).

[2] S.-H. Wei and A. Zunger, Phys. Rev. Lett. **76**, 664 (1996).

[3] S. R. Kurtz, A. A. Allerman, E. D. Jones, J. M. Gee, J. J. Banas, B. E. Hammons, Appl. Phys. Lett. **74**, 729 (1999).

[4] Y. Qiu, S. A. Nikishin, H. Temkin, N. N. Faleev, and Yu. A. Kudriavtsev, Appl. Phys. Lett. **70**, 3242 (1997).

[5] I. A. Buyanova, W. M. Chen, B. Monemar, H. P. Xin, and C. W. Tu, Appl. Phys. Lett. **75**, 3781 (1999).

[6] R. A. Mair, J. Y. Lin, H. X. Jiang, E. D. Jones, A. A. Allerman, and S. R. Kurtz, Appl. Phys. Lett. **76**, 188 (2000).

[7] S. R. Kurtz, A. A. Allerman, C. H. Seager, R. M. Sieg, and E. D. Jones, Appl. Phys. Lett. **77**, 400 (2000).

[8] T. Schmidtling M. Klein, U. W. Pohl, and W. Richter, MRS Internet J. Nitride Semicond. Res. **5S1**, W3.43 (2000).

[9] R. S. Goldman, B. G. Briner, R. M. Feenstra, M. L. O'Steen, and R. J. Hauenstein, Appl. Phys. Lett. **69**, 3698 (1996).

[10] The observed depth of the N-containing unit cells does, of course, depend on the probe tip sharpness. Concerning electronic effects, filled state images always shows depressions for the N atoms whereas empty state images (revealing the cations) display relatively little height variation around the N atoms.

[11] R. M. Feenstra, J. M. Woodall, and G. D. Pettit, Phys. Rev. Lett. **71**, 1176 (1993).

[12] C. Domke, Ph. Ebert, and K. Urban, Surf. Sci. **415**, 285 (1998).

[13] G. Schwarz, A. Kley, J. Neugebauer, and M. Scheffler, Phys. Rev. B **58**, 1392 (1998).

[14] G. Lengel, R. Wilkins, G. Brown, M. Weimer, J. Gryko, and R. E. Allen, Phys. Rev. Lett. **72**, 836 (1994).

[15] H. A. McKay, R. M. Feenstra, T. Schmidtling, and U. W. Pohl, to be published.

[16] K.-J. Chao, C. K. Shih, D. W. Gotthold, and B. G. Streetman, Phys. Rev. Lett. **79**, 4822 (1997).

[17] L. Bellaiche and A. Zunger, Phys. Rev. B **57**, 4425 (1998).

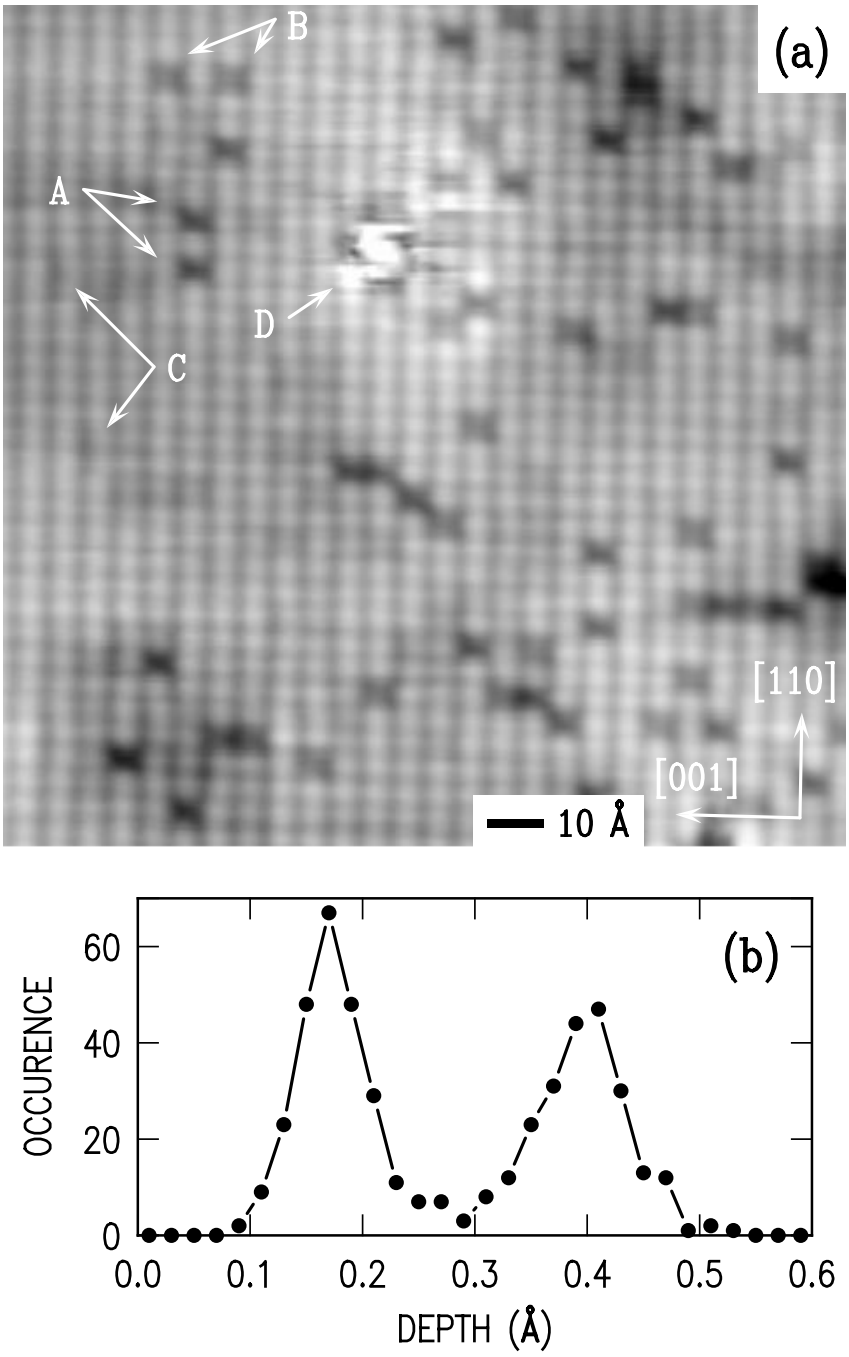

Figure 1 (a) STM image of $GaAs_{0.983}N_{0.017}$ alloy, acquired with sample voltage of -2.3 V and displayed with gray scale range of 0.6 Å. Growth direction is from right to left. Dark unit cells (A and B) correspond to N atom locations; other marked positions (C and D) are discussed in the text. (b) Histogram of depths of observed locations of N atoms.

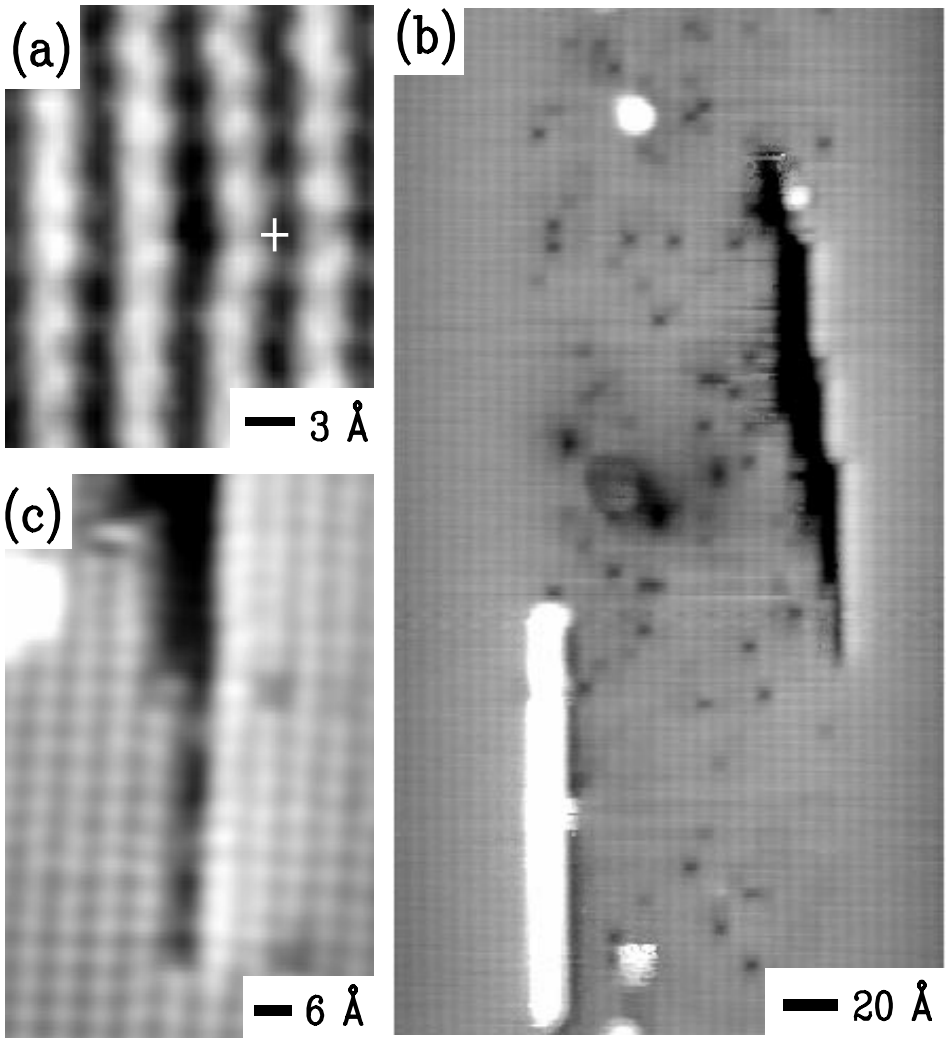

Figure 2 STM images of the $GaAs_{0.983}N_{0.017}$ layer: (a) detailed view of a C-type feature associated with a second-plane N atom whose deduced position is marked by "+"; the two corrugation maxima to the left of the N atom are shifted slightly to the right, (b) large-scale view of alloy layer containing cleavage induced defects (trenches and raised rows), with the GaAs layers seen on either side of the alloy layer, and (c) detailed view of one of the cleavage induced trenches. Images were acquired with sample voltage of -2.5, -2.3, and -2.3 V respectively, and are displayed with gray scale ranges of 0.14, 1.8, and 1.8 Å respectively.

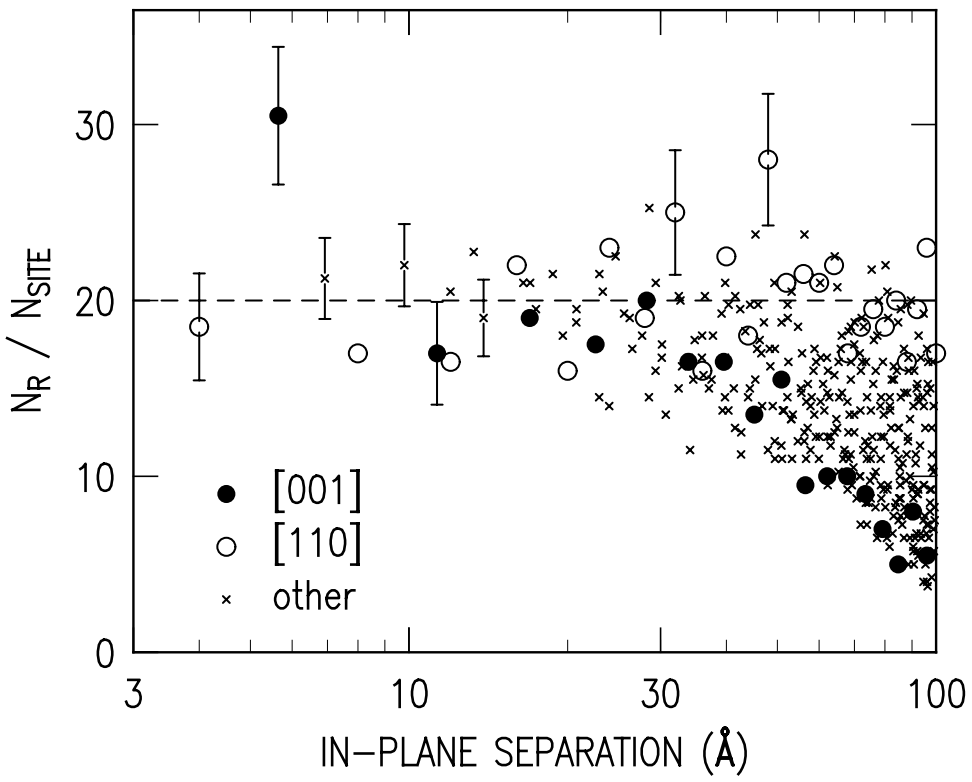

Figure 3 Observed number of N-N pairs N_R of a given separation R. The orientation of the pairs is indicated by the different types of symbols. Uncertainty in the values arises from counting statistics. The dashed line indicates the expected result for a random arrangement of N atoms.