CORE
Metadata, citation and similar papers at core.ac.uk
Provided by Warwick Research Archives Portal Repository

THE UNIVERSITY OF WARWICK

University of Warwick institutional repository: http://go.warwick.ac.uk/wrap
This paper is made available online in accordance with publisher policies. Please scroll down to view the document itself. Please refer to the repository record for this item and our policy information available from the repository home page for further information.

To see the final version of this paper please visit the publisher's website. Access to the published version may require a subscription.

Author(s): T. D. Veal, I. Mahboob, L. F. J. Piper, C. F. McConville, and M. Hopkinson
Article Title: Core-level photoemission spectroscopy of nitrogen bonding in GaN_xAs_{1-x} alloys
Year of publication: 2004
Link to published version: http://dx.doi.org/10.1063/1.1784886
Publisher statement: None

HTML ABSTRACT * LINKS

APPLIED PHYSICS LETTERS VOLUME 85, NUMBER 9 30 AUGUST 2004

Core-level photoemission spectroscopy of nitrogen bonding in GaN_xAs_{1-x} alloys

T. D. Veal, I. Mahboob, L. F. J. Piper, and C. F. McConville[a)]
Department of Physics, University of Warwick, Coventry, CV4 7AL, United Kingdom

M. Hopkinson
Department of Electronic and Electrical Engineering, University of Sheffield, Mappin Street, Sheffield S1 3JD, United Kingdom

(Received 18 February 2004; accepted 21 June 2004)

The nitrogen bonding configurations in GaN_xAs_{1-x} alloys grown by molecular beam epitaxy with $0.07 < x < 0.11$ have been studied using x-ray photoelectron spectroscopy (XPS). In contrast to previous studies of alloys with $x \geq 0.03$, the nitrogen is found to exist in a single bonding configuration – the Ga–N bond; no interstitial nitrogen complexes are present. The amount of nitrogen in the alloys is estimated from the XPS using the N 1*s* photoelectron and Ga LMM Auger lines and is found to be in agreement with the composition determined by x-ray diffraction. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1784886]

Dilute nitride alloys, III–V semiconductors with a few per cent of the anions replaced by nitrogen, are promising materials for optoelectronic devices in 1.3 and 1.55 μm telecommunications. Most importantly, these applications rely upon the nitrogen-induced dramatic reduction of the band gap to obtain the technologically important emission wavelengths. Additionally, the fact that GaInNAs, with a composition to give the appropriate band gap, can be lattice matched to GaAs substrates enables high quality epitaxial growth and incorporation into the existing electronic technology infrastructure.[1]

Post-growth annealing is normally required to produce device quality dilute nitride material, enhancing luminescence efficiency by removing interstitial nitrogen complexes, but also causing a blueshift of the emission due to out-diffusion of nitrogen[2] or diffusion of nitrogen inside the material.[3] Evidence of non-substitutional nitrogen in GaN_xAs_{1-x} has been provided by comparison of data from high-resolution x-ray diffraction (HRXRD) and secondary ion mass spectrometry (SIMS). While SIMS measures the total nitrogen content irrespective of the location of the nitrogen atoms, HRXRD gives the change in the lattice constant caused by substitution of nitrogen on anion lattice sites. Nitrogen concentrations measured by SIMS have been found to differ from those determined using HRXRD by up to 30% for $x \geq 2.5\%$, indicating the presence of significant concentrations of non-substitutional nitrogen.[4,5] Using XPS and ion channeling experiments, Spruytte *et al.* confirmed the existence of interstitial nitrogen in GaN_xAs_{1-x} grown by molecular beam epitaxy (MBE) for $x \geq 2.9\%$.[2] Upon rapid thermal annealing (60 s at 760 °C), all of the nitrogen was found to be located substitutionally on anion lattice sites.

In this letter, the nitrogen bonding configurations in GaN_xAs_{1-x} grown by MBE are investigated using x-ray photoelectron spectroscopy. The nitrogen is found to exist in a single bonding configuration; the Ga–N bond. No interstitial nitrogen is observed, in contrast to previous studies of high nitrogen content GaN_xAs_{1-x}, where up to 30% of the nitrogen was found to be located non-substitutionally.[2,4,5]

The GaN_xAs_{1-x} epilayers were grown to a thickness of 300 nm on semi-insulating GaAs(001) substrates by molecular beam epitaxy using a turbo-pumped Vacuum Generators V80 system equipped with an Oxford Applied Research (OAR) HD25 RF plasma nitrogen source. A regulated supply of purified nitrogen gas was provided to the RF source by means of a piezoelectric-controlled leak valve. The samples were all grown with a substrate temperature of 375 °C. The nitrogen content of the three GaN_xAs_{1-x} samples used in the XPS study was determined by x-ray diffraction using Cu $K\alpha$ ($\lambda = 1.54178$ Å) as the radiation source. X-ray diffraction curves around the (004) Bragg reflections, recorded to measure the lattice constants of the epilayers, are shown in Fig. 1. The N contents, estimated from the epilayer lattice constants assuming Vegard's law, are $x = 0.073$, 0.083, and 0.104. The variations in XRD peak intensity for the different samples correspond to different crystalline qualities. From this small set of samples no trend relating crystalline quality to nitrogen content is apparent. The XRD indicates that the

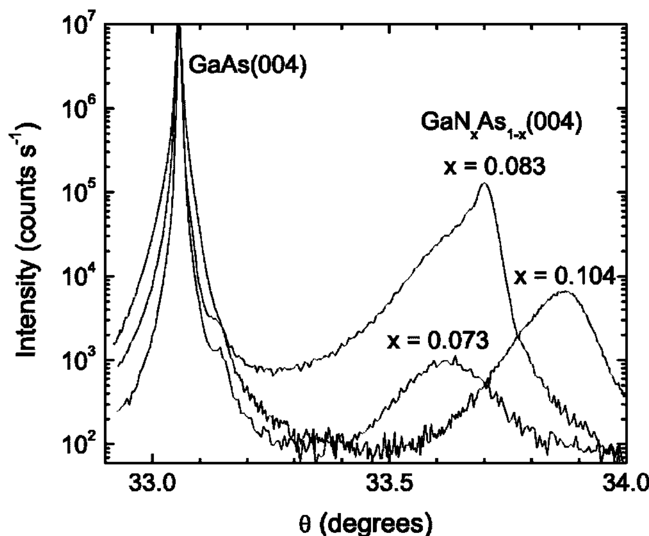

FIG. 1. (004) XRD spectra of GaNAs layers MBE-grown on GaAs(001) at 375 °C, indicating N contents of 7.3%, 8.3%, and 10.4%.

[a)]Author to whom correspondence should be addressed; electronic mail: c.f.mcconville@warwick.ac.uk

0003-6951/2004/85(9)/1550/3/$22.00 © 2004 American Institute of Physics
Downloaded 06 Jul 2009 to 137.205.202.8. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp

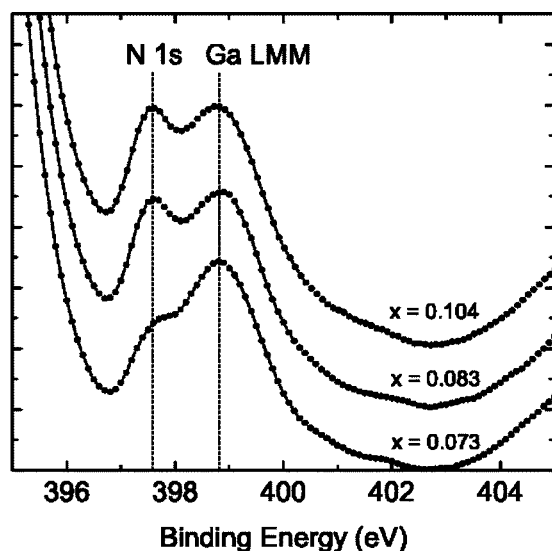

FIG. 2. X-ray photoelectron spectra of N 1*s* photoelectron and Ga LMM Auger lines from GaNAs samples with $x=0.073$, 0.083, and 0.104. Each spectrum is normalized to the intensity of the Ga $L_2M_{45}M_{45}$ Auger line at 393.7 eV.

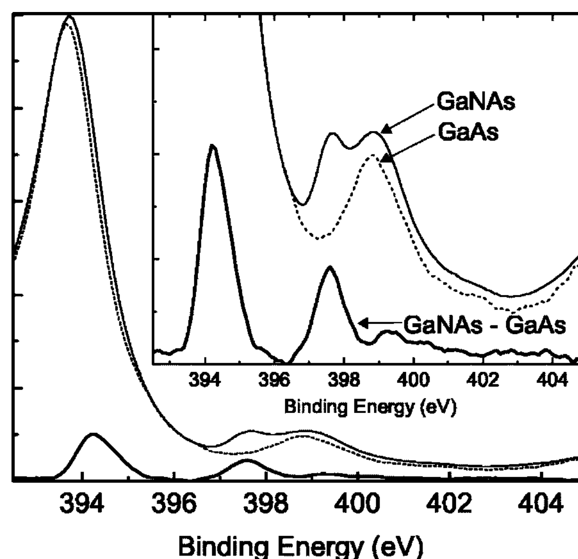

FIG. 3. XPS spectra from the GaNAs sample with $x=0.104$ (light solid line) and GaAs (light dashed line). The difference spectrum (the result of subtracting the GaAs spectrum from the GaNAs spectrum) is also shown (heavy solid line).

sample with $x=0.083$ has better crystalline quality than the sample with $x=0.104$, which in turn is better than the sample with $x=0.073$.

XPS analysis of the Ga 2*p*, Ga 3*d*, As 2*p*, As 3*d*, and N 1*s* photoelectron spectra and the Ga LMM Auger spectra was performed using a Scienta ESCA300 spectrometer at the National Centre for Electron Spectroscopy and Surface Analysis, Daresbury Laboratory, UK. This incorporates a rotating anode Al $K\alpha$ x-ray source ($h\nu=1486.6$ eV), x-ray monochromator and 300 mm mean radius spherical-sector electron energy analyzer and parallel elecron detection system. The analyzer was operated with 0.8 mm slits and at a pass energy of 150 eV. Gaussian convolution of the analyzer broadening with an effective line width of the 0.27 eV for the x-ray source gives an effective instrument resolution of 0.45 eV. XPS analysis of samples that contain Ga and N is complicated by the fact that, for both commonly used x-ray source anode materials (Al and Mg), Ga Auger peaks occur in the same region of the spectrum as the N 1*s* photoelectron peaks. A GaAs(001) reference sample was also analyzed so that the nitrogen-related features in the GaNAs spectra could be distinguished from the Ga Auger lines of GaAs.

The surfaces of the GaN_xAs_{1-x} epilayers and GaAs reference sample were prepared *in situ* for the XPS analysis by a two-stage atomic hydrogen cleaning process consisting of a 10 kL dose of H_2 at room temperature followed by a 10 kL dose at a sample temperature of 350 °C. Each 10 kL dose took 40 min using a hydrogen gas pressure of $\sim 5 \times 10^{-6}$ mbar. The molecular hydrogen was thermally cracked with ~50% efficiency using an OAR TC-50 thermal gas cracker. The samples were radiatively annealed using a tungsten filament mounted behind them. The removal of atmospheric contamination was confirmed using XPS by the absence of C 1*s* and O 1*s* photoelectron peaks and the lack of oxide-related chemically shifted components in the As 3*d*, As 2*p*, Ga 3*d*, and Ga 2*p* spectra.

A series of normalized core-level photoelectron spectra recorded from the GaN_xAs_{1-x} alloys are shown in Fig. 2. The spectral region shown includes the low binding energy tail of a Ga LMM Auger peak centered at 393.7 eV, another Ga LMM Auger peak at 398.9 eV (Ref. 6), and the N 1*s* core level photoemission peak at a binding energy of 397.6 eV.[2] The variation of the intensity of the N 1*s* peak with respect to the Ga LMM peaks reflects the different nitrogen contents of the samples.

To determine the different nitrogen bonding configurations, the N 1*s* and Ga LMM peaks have been analyzed in more detail to resolve any chemically shifted components. For this, the same spectral region was also analyzed for a GaAs(001) sample prepared in the same way. This GaAs spectrum is shown in Fig. 3, along with that of the most nitrogen-rich sample. The Ga LMM Auger peak at 393.7 eV referred to above is shown in full in this figure. The nitrogen-related contributions to the GaNAs spectra are then revealed at the bottom of this figure by subtracting the normalized GaAs spectrum from that of GaNAs. The original spectra and this difference spectrum are also shown with an expanded intensity scale in the inset of Fig. 3. The N 1*s* peak at 397.6 eV is now clearly resolved. However, two further peaks at 394.2 and 399.4 eV are also revealed. These are chemically shifted components of the Ga LMM lines associated with the Ga–N bonding.

Curve fitting of the difference spectra has been performed using a Shirley background and Voigt functions, each with a full width at half-maximum of 0.9 eV and consisting of 20% Lorentzian and 80% Gaussian line shapes. The curve fit of the difference spectrum for $GaN_{0.104}As_{0.896}$ is shown in Fig. 4. The ratio of the areas of the two Ga LMM peaks associated with the Ga–N bonding was set in the curve fitting, to be equal to that of the Ga LMM peaks from the Ga–As bonding in the spectra recorded from GaAs (see Fig. 3). This provides a good fit to the peaks at 394.2 and 399.4 eV in the difference spectrum, confirming that these spectral features are due solely to Ga LMM lines chemically shifted (by 0.5 eV to higher binding energy with respect to the GaAs LMM lines) as a result of the Ga being bonded to N. The remaining peak in the difference spectrum is also well fitted by a single component, indicating that all of the

Downloaded 06 Jul 2009 to 137.205.202.8. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp

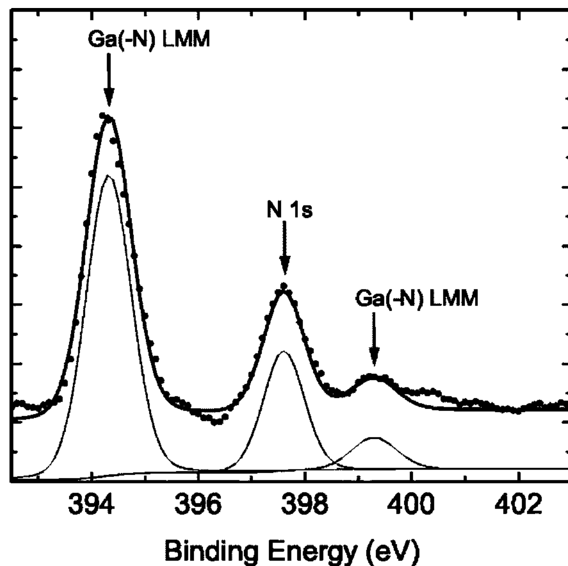

FIG. 4. Curve fit (heavy solid line) of the difference spectrum (points) shown in Fig. 3. The two Ga(–N) LMM Auger peaks and the single component of the N 1*s* peak (light solid lines) are vertically offset.

nitrogen is bonded to Ga and is located on group V lattice sites. The photoemission spectra can also be used to estimate the composition of the GaNAs epilayers. For example, the area of the Ga–N component at 394.2 eV in Fig. 4 is 10.6% of the total Ga LMM Auger peak area. This value is in excellent agreement with the alloy composition of $x=0.104$ determined from the lattice constant obtained from the XRD spectrum, assuming Vegard's law. The same analysis was also applied to the photoemission spectra from the other two samples. The compositions determined from the peak areas were again found to be in agreement (within the error of ±0.3%) with the values obtained from XRD. The recent results of Bisognin *et al.* found that Vegard's law is obeyed in GaN_xAs_{1-x} up to at least $x=0.045$.[7] Our findings extend this result, allowing us to conclude that, in the absence of non-substitutional nitrogen, Vegard's law is valid up to at least ~10.5% nitrogen.

In previous photoemission spectroscopy of MBE-grown GaNAs, an additional component in the N 1*s* spectrum has been observed at a higher binding energy of ~398.5 eV.[2] This was attributed to the presence of a nitrogen complex in which N is less strongly bonded to Ga. The absence of such a component in Fig. 4 indicates that, inspite of the high N content of these samples, the concentration of interstitial N is below the detection limit of XPS.

While in the majority of cases incorporating more than 3% N in GaNAs epilayers leads to the existence of interstitial N complexes,[2,4,5] alloys with a high N content but free of non-substitutional N have been achieved in at least two previous studies. First, Qiu *et al.* used metal-organic MBE to grow GaN_xAs_{1-x} alloys with $x=0.10$, as determined by both SIMS and XRD.[8] Second, Bisognin *et al.* have very recently found all of the N to be substitutional in GaNAs samples with x up to 0.045. This was determined using a combination of nuclear reaction analysis, Rutherford backscattering spectroscopy, and HRXRD.[7] The high nitrogen contents of our alloys and those of both Bisognin *et al.* and Qiu *et al.* with x up to ~0.10 were achieved by growing at the relative low temperatures of 375 and ~400 °C, respectively; GaNAs is typically grown at between 450 and 550 °C. However, the reason for the lack of interstitial nitrogen in these high nitrogen content alloys is unclear.

Photoemission spectroscopy has been used to determine the nitrogen bonding configurations in GaN_xAs_{1-x} alloys ($x=0.073$, 0.083, and 0.104) grown by molecular beam epitaxy. All of the nitrogen is bonded to gallium and is located substitutionally on group V lattice sites. In contrast to previous studies of GaN_xAs_{1-x} alloys with $x \geqslant 0.003$, no component in the N 1*s* spectrum associated with interstitial nitrogen was observed. The alloy compositions determined from the photoemission spectra are in good agreement with those obtained from XRD analysis.

The authors would like to thank Dr. D. S.-L. Law for his assistance with the XPS experiments at the National Centre for Electron Spectroscopy and Surface Analysis, Daresbury Laboratories, UK. The Engineering and Physical Sciences Research Council, UK is acknowledged for financial support under Grant Nos. GR/S56030/01 and GR/S14252/01, and for the provision of research studentships for I.M. and L.F.J.P.

[1]M. Kondow, K. Uomi, A. Niva, T. Kitatani, and Y. Yazawa, Jpn. J. Appl. Phys., Part 1 **35**, 1273 (1996).
[2]S. G. Spruytte, C. W. Coldren, J. S. Harris, W. Wampler, P. Krispin, K. Ploog, and M. C. Larson, J. Appl. Phys. **89**, 4401 (2001).
[3]L. Grenouillet, C. Bru-Chevallier, G. Guillot, P. Gilet, P. Ballet, P. Duvaut, G. Rolland, and A. Million, J. Appl. Phys. **91**, 5902 (2002).
[4]W. Li, M. Pessa, and J. Likonen, Appl. Phys. Lett. **78**, 2864 (2001).
[5]W. J. Fan, S. F. Yoon, T. K. Ng, S. Z. Wang, W. K. Loke, T. Liu, and A. Wee, Appl. Phys. Lett. **80**, 4136 (2002).
[6]J. F. Moulder, W. F. Stickle, P. E. Sobol, and K. D. Bomben, *Handbook of X-Ray Photoelectron Spectroscopy* (Perkin-Elmer, Eden Prairie, MN, 1992).
[7]G. Bisognin, D. D. Salvador, C. Mattevi, M. Berti, A. V. Drigo, G. Ciatto, L. Grenouillet, P. Duvaut, P. Gilet, and H. Mariette, J. Appl. Phys. **95**, 48 (2004).
[8]Y. Qui, S. A. Nikishin, H. Temkin, N. N. Faleev, and Y. A. Kudriavtsev, Appl. Phys. Lett. **70**, 3242 (1997).

Downloaded 06 Jul 2009 to 137.205.202.8. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp