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K. Wang,[1,a)] R. W. Martin,[1] D. Amabile,[1] P. R. Edwards,[1] S. Hernandez,[1] E. Nogales,[1]
K. P. O'Donnell,[1] K. Lorenz,[2] E. Alves,[2] V. Matias,[3] A. Vantomme,[3] D. Wolverson,[4]
and I. M. Watson[5]

[1]*Department of Physics, SUPA, University of Strathclyde, Glasgow G4 0NG, United Kingdom*
[2]*ITN, Estrada Nacional 10, 2686-953 Sacavém, Portugal*
[3]*Instituut voor Kern- en Stralingsfysica and INPAC, KULeuven, Belgium*
[4]*Department of Physics, University of Bath, Bath BA2 7AY, United Kingdom*
[5]*Institute of Photonics, SUPA, University of Strathclyde, Glasgow G4 0NW, United Kingdom*

Optical energy gaps are measured for high-quality $Al_{1-x}In_xN$-on-GaN epilayers with a range of compositions around the lattice match point using photoluminescence and photoluminescence excitation spectroscopy. These data are combined with structural data to determine the compositional dependence of emission and absorption energies. The trend indicates a very large bowing parameter of ≈ 6 eV and differences with earlier reports are discussed. Very large Stokes' shifts of $0.4-0.8$ eV are observed in the composition range $0.13 < x < 0.24$, increasing approximately linearly with InN fraction despite the change of sign of the piezoelectric field. © *2008 American Institute of Physics.* [DOI: 10.1063/1.2898533]

I. INTRODUCTION

The ternary group III-nitrides $In_xGa_{1-x}N$ and $Al_xGa_{1-x}N$ have been extensively studied for light emitting devices operating across the entire visible and ultraviolet spectral regions.[1] The third III-nitride ternary alloy $Al_{1-x}In_xN$ is relatively unexplored but offers potential for light emitting and electronic devices. In addition to a band gap covering a very wide energy range $(0.7-6.2$ eV$)$ it has the advantage that it can be lattice matched to GaN.[2,3] This occurs at an InN fraction of about 17% and, coupled with the increasing availability of GaN substrates, offers significant potential for improved devices based on strain-free $Al_{0.83}In_{0.17}N-GaN$ heterostructures. Recently, several applications of such structures have been reported, including distributed Bragg reflectors,[2] field effect transistors,[4] and facilitation layers in pseudomorphic epitaxy.[5] A further, quite surprising, advantage is the observed resistance to thermal degradation. $Al_{1-x}In_xN$ layers survive annealing at 1100 °C, hundreds of degrees above the growth temperature[6] and lattice matched $Al_{0.83}In_{0.17}N$ has been shown to be stable up to at least 960 °C.[7] Despite these positive attributes, key optical parameters of $Al_{1-x}In_xN$ are not well known, in part caused by the difficulty in growing high quality layers following from the large difference in size between Al and In atoms.

This letter examines the relationship between $Al_{1-x}In_xN$ composition and optical properties in high quality layers with a range of compositions close to lattice match with GaN. Photoluminescence (PL), cathodoluminescence (CL), and PL excitation (PLE) spectra measure the optical energies and compositions are assayed by Rutherford backscattering spectrometry (RBS) and wavelength dispersive x-ray (WDX) analysis. Previous reports on the optical band gaps of $Al_{1-x}In_xN$ have quoted widely differing values. The investigated material appears not to have been always of the highest crystal quality. The uncertainty concerning the composition dependence of the optical band gaps is perhaps unsurprising given the challenges faced when growing $Al_{1-x}In_xN$. Low adatom mobilities and slow bulk diffusion tend to impair the crystal quality,[4] and it is likely that surface indium atoms act as surfactants in optimized $Al_{1-x}In_xN$ growth. Methodologies reliant upon the growth temperature to control In incorporation in the growing layer are likely to result in a general worsening of crystal quality as the InN fraction increases, particularly away from the lattice matching point.

II. EXPERIMENT

A series of high quality $Al_{1-x}In_xN$ epilayers, with InN fractions ranging from 0.13 to 0.24 were grown in an Aixtron 200 series metal-organic chemical vapor deposition (MOCVD) reactor on GaN buffer layers on c-plane sapphire substrates. The films are ≈ 130 nm thick and their growth rate was close to 65 nm/h. The InN/AlN ratio of the epilayers was controlled mainly by the substrate setpoint temperature, which was varied between 760 and 840 °C. The InN fractions were estimated using RBS and WDX microanalysis.[8] X-ray diffraction and RBS channeling (RBS/C) data provided information on the crystalline quality and elastic strain.[3] The sample details and measured compositions are summarized in Table I. Room temperature (RT) PL was excited using a frequency-doubled Ar ion laser (244 nm) with a power density at the sample of ≈ 2000 mW/mm^2. A 1000 W Xe lamp in combination with a monochromator was used as a tunable excitation source to measure PL and PLE spectra at 15 K. The lamp excites an area of about 2×5 mm^2 at ≈ 0.02 mW/mm^2.

The InN fractions extracted from the RBS data using simulations are consistently 1%–2% lower than those obtained from WDX analyses and are to be preferred here due to limitations associated with available Al calibration standards for WDX. The minimum yield χ_{min}, defined as the In

a)Electronic mail: k.wang@strath.ac.uk.

TABLE I. $Al_{1-x}In_xN$ sample details and measured compositions. The RBS data for S760 revealed a lower InN fraction layer above one with higher InN fraction.

Sample number	$Al_{1-x}In_xN$ growth temperature (°C)	TMAl and TMIn flow rates (μmol/min)	InN mole fraction: RBS (± 0.005)	χ_{min} (%) RBS
S760	760	22 and 14	0.24 and 0.19	≈ 40
S800	800	22 and 14	0.194	6.3
S800a	800	29.5 and 14	0.181	7.0
S820	820	22 and 14	0.153	4.0
S840	840	22 and 14	0.132	4.4

yield in the $\langle 0001 \rangle$ aligned RBS/C spectrum divided by that in the random spectrum, provides information on the $Al_{1-x}In_xN$ crystalline quality. Here, values for χ_{min} of 4%–7% for the samples grown at temperatures $\geqslant 800$ °C reveal a good single crystalline quality. The quality of the film deteriorates for lower growth temperatures. For sample S760, grown at 760 °C, χ_{min} is as high as 40%. For this sample, the RBS data reveal an initially grown layer of higher quality $Al_{0.76}In_{0.24}N$ underlying a layer with a lower InN content.[9]

III. RESULTS AND DISCUSSION

The laser-excited RT PL spectra are shown in Fig. 1(a). They have a relatively sharp band-edge emission peak near 362 nm from the underlying GaN layer and, apart from S760, a broad emission band at shorter wavelength attributed to band-to-band emission from the $Al_{1-x}In_xN$ epilayers. The linewidths are reasonably small for recombination emission in random alloys, where composition fluctuations dominate, and neither widths nor intensities correlate with the quality factors obtained by RBS. A clear redshift of the $Al_{1-x}In_xN$ emission peak with increasing InN fraction is observed in the first four samples. For the low quality S760 sample, a broad weak peak underlying the GaN emission might originate from $Al_{1-x}In_xN$. RT CL spectra (Fig. 1) also show this peak in S760, but not in the other samples, and it is tentatively assigned to the higher quality lower $Al_{1-x}In_xN$ sublayer.[9]
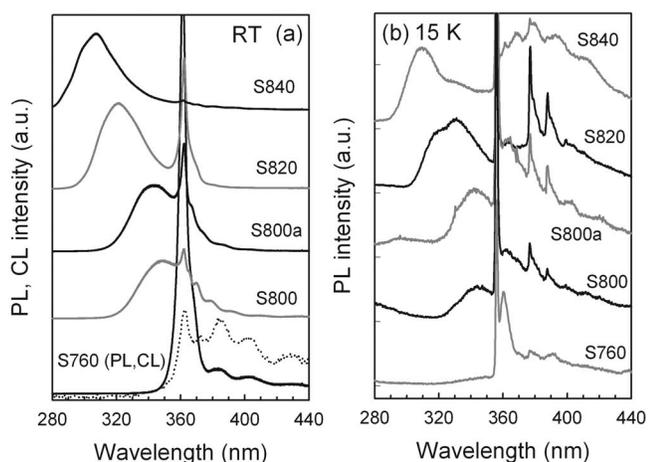

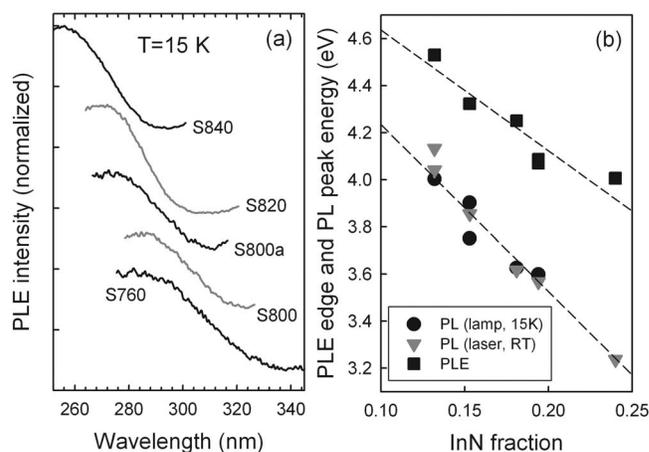FIG. 1. PL excited by (a) the laser at RT and (b) by the lamp at 15 K. The dotted line in (a) shows RT CL of S760.

FIG. 2. (a) PLE spectra from the $Al_{1-x}In_xN$ epilayers. In the case of S760, the PLE is monitored using the 622 nm line in a Eu-doped sample (b) PL peak energy and effective band gap as a function of InN content.

Figure 1(b) shows 15 K PL spectra excited by 250 nm light from the monochromated Xe lamp. The differences in relative peak heights compared to the RT laser-excited spectra are in large part due to the much lower power density. In addition to the band shifting with AlN content, as seen in Fig. 1(a), a broad band at longer wavelength is resolved. Reference 2 also mentions such lower energy PL bands, appearing for poorer quality samples and enhanced for lower excitation powers or thicker samples.

Figure 2 shows PLE spectra recorded at 15 K with the detection monochromator set at the peak of the higher energy PL band. For sample S760, the overlapping GaN luminescence precludes reliable detection of the $Al_{1-x}In_xN$ excitation spectra and the PLE data shown are measured using the 622 nm Eu luminescence of an ion-implanted sample.[10] The sigmoidal shape is reminiscent of PLE spectra of $In_xGa_{1-x}N$ (Ref. 11) and an effective energy gap is estimated as described in Ref. 12. As with the PL peak, the absorption edge shows a clear redshift with increasing InN fraction. PLE spectra detected on the shorter wavelength side of the emission bands show the same absorption edges for each sample. This is true even for S820 despite the two overlapped PL bands and is noticeably different from the PLE results reported for $In_xGa_{1-x}N$ epilayers,[11] which showed a redshift of the absorption edge when detecting at the lower energy regions of the emission bands. PLE spectra detected on the lower energy bands, below the GaN energy gap, show the broad background to be related to $Al_{1-x}In_xN$ while the sharp peaks are associated with the GaN buffer layer.

The peak PL emission energies and effective PLE band gaps are plotted as a function of the measured InN fractions in Fig. 2(b). Both display a linear dependence in this restricted composition range, similar to that observed for $In_xGa_{1-x}N$ epilayers and diodes.[12] The difference between the effective band gap and PL peak energy, referred to as Stokes' shift, is plotted in Fig. 3(a) which reproduces earlier data[12] from $In_xGa_{1-x}N$ for comparison. The $Al_{1-x}In_xN$ Stokes' shifts are seen to be considerably (two times) larger than those for $In_xGa_{1-x}N$ with the same InN fraction. The variation is roughly linear but a significant extra consider-

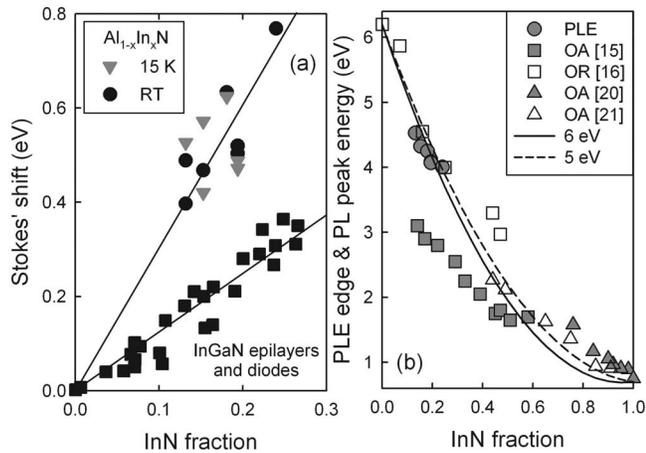FIG. 3. (a) $Al_{1-x}In_xN$ and $Ga_{1-x}In_xN$ Stokes' shifts plotted against InN composition. (b) Measured and reported $Al_{1-x}In_xN$ optical energy gaps for $0 < x < 1$. The lines plot energy gap dependencies with bowing parameters of 6 and 5 eV as described in the text.

ation is the dependence of in-built electric field strength on InN content and strain. For $In_xGa_{1-x}N/GaN$ both piezoelectric and spontaneous polarization fields increase with InN content whereas with $Al_{1-x}In_xN/GaN$, the piezoelectric field goes to zero at the lattice-match point. The field due to spontaneous polarization in $Al_{1-x}In_xN/GaN$ remains large[2,13] but the additional piezoelectric field changes sign either side of this zero. Large Stokes' shifts are generally associated with a high degree of exciton localization but supporting structural evidence in MOCVD-grown $Al_{1-x}In_xN$ is so far lacking. One recent report has described an unusual lateral phase separation on the nanoscale in layers grown by molecular beam epitaxy at much lower temperature.[14]

Figure 3(b) compares $Al_{1-x}In_xN$ data from this work with those from several earlier reports. Yamaguchi *et al.*[15] described PL from $Al_{1-x}In_xN$ layers with InN fractions up to 0.5. The peak of the PL emission tends toward 1.8 eV for InN-rich layers and is near 3 eV at the lattice-match point, both values differing significantly from currently accepted values. Some early papers[16–18] report transmission measurements on $Al_{1-x}In_xN$ layers over wider composition ranges. For high InN contents, the data again trend toward the formerly accepted InN band gap near 2 eV, suggesting that these $Al_{1-x}In_xN$ films were of quite low quality. Onuma *et al.*[19] reported optical reflectance and PL data over the range $0.07 < x < 0.5$ to indicate extremely large Stokes' shifts (1–2 eV) and a lattice-matched band gap of approximately 5 eV. Carlin *et al.*[2] recently reported high quality $Al_{1-x}In_xN$ on GaN layers, with compositions near the lattice-match point, with somewhat smaller Stokes' shifts and a lattice-matched band gap of ≈ 4.3 eV. The PLE data reported here allow a more accurate estimation of the absorption gap than is achievable by use of the fringes in reflectivity spectra.[2,19] Figure 3(b) also reproduces optical absorption data on InN-rich $Al_{1-x}In_xN$ from two recent reports.[20,21] Fitting the excitation data for $0.13 < x < 0.24$ (together with the accepted values of the binary endpoints) yields a very high bowing

parameter of ≈ 6 eV, as plotted in Figure 3(b) along with the slightly lower value of 5 eV obtained using InN-rich layers in Ref. 21.

IV. CONCLUSION

In summary, the optical energy gaps, emission peak energies and Stokes' shifts for a series of high quality $Al_{1-x}In_xN$-on-GaN epilayers have been measured as a function of composition by using PL and PLE spectroscopy. The observed trend fits with a bowing parameter of 6 eV and differences with earlier reports are discussed. Very large Stokes' shifts are observed and their dependence on composition reflects both the variation of in-built electric fields within the layers and the degree of exciton localization.

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