Metalorganic Vapor-Phase Epitaxial Growth and
Characterization of Quaternary AlGaInN

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Abstract

In this letter we report the growth (by MOVPE) and characterization of quaternary AlGaInN. A combination of PL, high-resolution XRD, and RBS characterizations enables us to explore and delineate the contours of equilibrium emission energy and lattice parameter as functions of the quaternary compositions. The observation of room temperature PL emission as short as 351nm (with 20% Al and 5% In) renders initial evidence that the quaternary could be used to provide confinement for GaInN (and possibly GaN). AlGaInN/GaInN MQW heterostructures have also been grown; both x-ray diffraction and PL measurement suggest the possibility of incorporating this quaternary into optoelectronic devices.

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It is frequently cited that the III-nitride family possesses direct energy gaps spanning from 1.9 (InN) to 6.2 eV (AlN). Large lattice mismatches, however, exist among the three binary compounds. For example, AlN and InN have 2.4% tensile and 11% compressive mismatches, respectively, to GaN.¹ Mismatch-induced strain and the associated structural degradation often dictate the practical, accessible range of III-N materials in device construction. Published designs of light-emitting diodes (LEDs) and laser diodes (LDs), in which GaInN serves as the active medium and AlGaInN the barrier/cladding layers, often represent a compromise between maximizing electrical/optical confinement and minimizing mismatch-induced strain. Quaternary AlGaInN compound semiconductors are expected to enclose a finite (non-zero) area on the plot of energy gap versus lattice constant.¹ In principle the growth of quaternary AlGaInN compounds should render flexibility in tailoring bandgap profile while maintaining lattice matching and structural integrity.²

Exploration of semiconductor alloy system always commences in establishing the correlation between lattice parameter and band gap, which serves as a guideline for epitaxial growth and heterojunction design. Since Vegard's law for the lattice parameter is generally applicable to numerous alloy systems and is assumed to hold for the III-nitride family,³ the main objective in the current study of AlGaInN is to correlate bandgap energy with the quaternary composition. Wright et al.⁴ calculated the bowing parameters for ternaries GaInN, AlGaIn, and AlInN, though the calculation has not been extended to AlGaInN quaternary system. Matsuoka⁵ predicted the presence of an unstable mixing region (spinodal phase separation) in wurtzite AlGaInN as the indium

content increases. In the experimental field, AlGaInN epilayers have been prepared by metalorganic vapor-phase epitaxy (MOVPE).^{3, 6} Aiming at proof-of-concept demonstrations of the physical incorporation of Al and In into GaN, little information was provided in either work concerning the bandgap versus alloy compositions. The functional feasibility of AlGaInN as a confinement barrier remained ambiguous in these studies since photoluminescence (PL) emission from the quaternary did not exceed the emission wavelength of GaN (~363 nm). The concern is reiterated by Peng et al⁷ in stating, based on optical absorption measurements of sputtered polycrystalline films, that AlInN and AlGaInN do not seem to provide good confinement (to GaInN) due to a very strong bowing effect.

In this paper we intend to address two issues related to the quaternary AlGaInN material family: i) The possibility of using AlGaInN for confinement to GaN and GaInN, and ii) the bandgap bowing behavior of AlGaInN. Instead of exploring the whole composition range of AlGaInN, in which factors such as structural defects and phase separation would make the extraction of bandgap data challenging (and misleading),^{3, 6, 8} we confine this study to compositions where pseudomorphic growth on GaN can be easily maintained. The compositions of Al and In were limited to 25% and 14%, respectively, to preserve structural quality. We demonstrate in this paper that AlGaInN is capable of providing confinement to GaInN (and possibly GaN). The contours of constant “band gap”, defined operationally in this paper as the emission energy measured by PL, are delineated by measuring a series of alloy (ternary and quaternary) epilayers.

The MOVPE growth is carried out in a vertical rotating-disc reactor. All of the quaternary epilayers and multiple quantum well structures were grown on 1- μ m GaN

epilayers (grown at 1050°C) using a standard 2-step nucleation procedure with low-temperature GaN grown at 550°C.⁹ The growth temperature of the quaternary AlGaInN was varied between 750 and 820 °C. The reactor pressure was held constant at 200 Torr. The NH₃ and N₂ flows were set at 6 l/min each. An additional flow of H₂ (~400 cm³/min) was employed as a carrier gas. Trimethylgallium (TMGa), triethylaluminum (TEAl), and trimethylindium (TMIn) are employed as metalorganic precursors. Given the scarcity of reliable information concerning the quaternary, it is imperative to accurately determine the compositions of the constituent elements. Compositions of In and Al in the films were measured using Rutherford backscattering spectrometry (RBS)¹⁰ with a 2.5 MeV ⁴He⁺ ion beam. Ion-channeling effects in the RBS spectra were randomized by tilting the sample 10° from normal to the analysis beam and continuously rotating the sample about its normal during the analysis. Al and In concentrations were then extracted from the spectra using the SIMNRA (ver. 4.4) simulation program.¹¹ The large backscattering yield from In, coupled with the accurately known nuclear cross section, results in a relatively high accuracy for the determination of the In composition. We estimate an uncertainty of ±0.002 at an In composition of 0.01, and ±0.005 for a composition of 0.10. Because the backscattering yield from Al is much smaller, the Al composition was determined less directly by measuring a reduction, or dip, in the yield from Ga, due to the presence of the Al and In in the layer. An uncertainty of ±0.01 at an Al concentration of 0.10, and ±0.015 for a concentration of 0.20 was estimated for the cited data. A high-resolution triple-axis x-ray diffractometer (Philips X'Pert System) was employed to assess the structural quality and determine both in-plane (*a*) and out-of-plane (*c*) lattice parameters. Room temperature (RT) PL was measured using a HeCd laser

(325 nm) as the excitation source in conjunction with a 0.3 meter spectrometer and a UV enhanced CCD detector.

Figure 1 shows (0002) $2\theta-\omega$ x-ray diffraction (XRD) scans (with an analyzer-crystal detector) for several AlGaInN (a, c-f) and GaInN (b) samples. Thickness of the samples varied from 0.14 to 0.20 μm , as indicated by the change of the period of the diffraction fringes. By adjusting the relative Al and In compositions, one observes a change of the out-of-plane lattice parameter from being larger (top trace) to smaller (bottom trace) than that of GaN. One should take caution that, unlike the case in zincblende semiconductor heterostructure, the appearance of an overlap between the (0002) diffraction peak from the quaternary and the peak from GaN (a condition between scans (d) and (e)) does not necessarily imply a lattice-matched strain-free epitaxy as the in-plane and out-of-plane lattice parameters of AlN, GaN, and InN do not vary in a linear manner. Using the published lattice parameters,¹ exact match of the a lattice constant of AlInN to GaN should occur at an Al fraction of 18% while it takes approximately 28% Al in AlInN to match the out-of-plane (c) lattice parameter of GaN. A quaternary compound with a c lattice parameter matched to GaN is speculated to be under biaxial compression during growth.

Optical properties of the AlGaInN samples (d and f in Figure 1) were investigated with RT PL (Figure 2). The PL from a “standard” GaN epilayer⁹ was included for reference. In attempting to designate the band gap energy from PL measurement for the quaternary system, one is reminded that the presence of a large Stoke’s shift in ternary GaInN (on the order of 100 to 300 meV)¹² has created much discrepancy and controversy among various research groups.¹³ We can, nevertheless, consider the PL emission energy

as a lower bound to the bandgap energy. It is clear from Figure 2 that the AlGaInN epilayer emits with energy higher than that of GaN. The $\text{Al}_{0.14}\text{Ga}_{0.82}\text{In}_{0.04}\text{N}$ epilayer (sample (d) in Figures 1 and 2) gives the indication that one can synthesize a wider bandgap (than GaN) quaternary AlGaInN compound yet with an in-plane lattice constant *larger* than that of GaN. There has been much empirical observation and speculation that the presence of indium in GaInN ternary layers seems to preserve the optical efficiency from otherwise heavily dislocated samples. Mukai et al¹⁴ reported, in the development of ultra-violet LEDs, a rapid reduction of optical efficiency as the In content in the GaInN active region decreases below a certain value. It is worth noting that the integrated PL intensity from this quaternary is about three times brighter than that from GaN. An implication is that the carrier-localization effect,¹² possibly due to the presence of a compositional fluctuation of indium, could make AlGaInN an alternative (to GaN or AlGaIn) as a short-wavelength ($\lambda < 360\text{nm}$) light-emitting medium.

For the design and implementation of quaternary heterostructure devices, it is helpful to superimpose contours of constant lattice constant and bandgap energy as functions of the alloy compositions.² A series of AlGaInN, GaInN, and AlGaIn epilayers have been grown and the characterizations are summarized in Figure 3. $\text{Al}_y\text{Ga}_{1-x-y}\text{In}_x\text{N}$ is described in this work by a right-angle triangle with AlGaIn and GaInN forming the two sides around the right-angle vortex. (The hypotenuse corresponds to the ternary AlInN, not shown in Figure 3.) The location of any $\text{Al}_y\text{Ga}_{1-x-y}\text{In}_x\text{N}$ quaternary is uniquely specified by the In (x) and Al (y) fractions and the display in Figure 3 is limited to 0.3 for both x and y. The triangles, diamonds, and circles represent the data points for AlGaIn, GaInN, and AlGaInN, respectively. The compositions of the ternaries were determined primarily

by x-ray diffraction and independently confirmed by RBS, the quaternary compositions were determined by RBS. The solid line with a slope of around 4.44 defines the quaternary alloys that are lattice matched to GaN; one can construct an array of parallel lines for lattice-matched growth with different in-plane lattice parameters. (Vegard's law predicts that the in-plane lattice parameter will remain unchanged when the increments of Al (ΔAl) and In (ΔIn) maintain a ratio of 4.44.) Quaternary alloys located to the lower right half of the straight line are expected to be under compression on a GaN template. The distance between a given data point on this plot and the solid line gives a qualitative measure of mismatch-induced strain.

As mentioned earlier, the use of PL in probing the near bandedge emission in GaInN is subject to an underestimation of band gap energy of up to 0.3 eV due to compositional inhomogeneity.¹² The attempt to determine the bandgap energy is therefore transformed to a direct construction of the contours of *the PL emission energy*, taken as an operational measure of the bandgap, versus alloy compositions in this preliminary investigation. The dashed contours are derived based on two assumptions: i) all the data points should be fitted by contours with nearly identical forms, and ii) the contours should be consistent with the available (theoretical⁴ and experimental⁸) bowing information of ternary AlInN. Along each dashed line, the emission wavelength remains constant while the in-plane lattice parameter (and therefore grown-in strain) can be adjusted by varying the Al and In fractions. It is worth adding that the dashed curves represent contours of *constant emission energy*. It has been shown that the PL emission wavelength of AlGaInN (and GaN) is very close to the bandgap, while the PL emission wavelengths from AlGaInN

and GaInN tend to be red-shifted as the In-content increases. It is conjectured that the actual contours for constant band gap might exhibit reduced slopes.

To demonstrate the possibility of heterostructures incorporating quaternary AlGaInN, we have grown a multiple quantum well (MQW) structure consisting of 10 periods of AlGaInN barriers (Al~14%, In~4%, ~100Å) and GaInN wells (In~4%, ~45Å). Figure 4 shows the (0002) $2\theta-\omega$ XRD from the MQW structure. The presence of satellite peaks and other interference fringes is indicative of structural order and coherency (along the growth direction). The 0th order peak at the lower-angle side indicates that the overall MQW is under compression. A comparative study of PL intensity between the MQW structure and a 2000 Å GaInN epilayer (grown with an identical condition as the well of the MQW) is shown in the inset of Figure 4. In spite of the expected disparity in the absorption of the pump laser in the two samples, the MQW sample shows a distinct enhancement of more than a factor of three and yet with an active volume of much less than the epilayer.

In conclusion, we reported the MOVPE growth and characterization of quaternary AlGaInN. Qualitative bowing behavior of the energy gap for AlGaInN (with Al and In compositions less than 30%) is established. We confirmed that the employment of this novel quaternary compound could facilitate tailoring of both energy gap and lattice mismatch for flexibility in device design. In spite of the previous speculation that strong bowing could hinder the usage as a short-wavelength light emitter, we observed PL emission as short as 351 nm from a layer with about 20% Al and 5% In. The possibility of replacing AlGaIn as an alternative barrier material was demonstrated through an AlGaInN/GaInN MQW structure.

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Figure Caption

Figure 1. (0002) 2θ - ω x-ray diffraction of AlGaInN (solid traces) and GaInN (dashed line) epilayers showing a range of lattice parameters bracketing the GaN lattice parameter.

Figure 2. Room-temperature photoluminescence from a GaN (solid line) epilayer and two AlGaInN epilayers (dashed and dotted lines).

Figure 3. Contour plot of constant (in-plane) lattice parameter and emission energy versus Al and In compositions for AlGaInN epilayers.

Figure 4. (0002) 2θ - ω x-ray diffraction of an AlGaInN (100Å)/GaInN (45Å) multiple quantum well structure with 10 periods. The inset shows RT PL emission from the MQW sample (upper trace) which is more than three times more intense than that from a GaInN epilayer (~2000 Å) of similar composition to the quantum wells.

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