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HTML ABSTRACT + LINKS

In-rich $In_{1-x}Ga_xN$ films by metalorganic vapor phase epitaxy

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Single crystalline $In_{1-x}Ga_xN$ films containing high In content (70%–100%) were grown by metalorganic vapor phase epitaxy. A linear relation was observed between the lattice constants and gas phase Ga/In ratios. The surface morphology changed from pyramid for InN to more planar ones for the InGaN alloys with increasing Ga content. The electron mobility decreased rapidly from 1200 cm^2/V s for InN to less than 100 cm^2/V s for $In_{0.7}Ga_{0.3}N$, with a carrier concentration of low-10^{19} cm^{-3} for all the as-grown films. Using photoluminescence a single emission peak was observed at 1.4–1.6 μm for the In-rich InGaN with decreasing wavelengths up to below 20% of Ga. Two peaks were observed for the $In_{0.80}Ga_{0.20}N$, however, indicating possible phase separation. The x-ray photoelectron spectroscopic measurement showed shifts to higher binding energies for both In and Ga with increasing Ga content. The estimated alloy composition, however, depended sensitively on the sputtering conditions of the samples. © *2004 American Institute of Physics*.
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InN has attracted an extensive interest in recent years due to its possible narrow band gap that makes InN suitable for the optical communication in the long wavelength region.[1] A narrow band gap of 0.7–1 eV has been reported by many groups[2–6] that is much smaller than the 1.9 eV value reported earlier.[7–9] A very recent report indicated possible wide band gap of InN, with the small band-gap values likely caused by the In clusters present.[10] An additional challenge to the study of InN is the growth of high quality InGaN films with low Ga content. This has several scientific and technological implications. The phase separation of InGaN near the GaN side makes it difficult to grow InGaN with high In content for the optical devices. This difficulty could be circumvented by studying pure InN and In-rich InGaN for an in-depth understanding of the intriguing phase separation issue. The growth of high quality In-rich InGaN is also essential to the fabrication of optical devices employing InN–InGaN or InGaN–InGaN heterostructures and quantum wells. In addition, the study of In-rich InGaN also provides valuable information regarding the band gap of such materials.

In this letter we report the growth of In-rich InGaN with Ga content up to about 30%. Single crystalline films were grown throughout such alloy compositions. The correlations with the gas phase Ga/In ratio, however, depended sensitively on the analytical techniques used. The alloy films were analyzed for electrical, optical, structural and binding characteristics, and were correlated with those of InN and GaN.

InGaN films were grown on (0001) sapphire substrates using metalorganic vapor phase epitaxy (MOVPE) in an Aixtron rf-200/4 reactor. A low temperature GaN nucleation layer, 20 nm, was first deposited at 500 °C. This was followed by a 2 μm GaN grown at 1000 °C. The surface polarity of GaN was Ga by choosing proper V/III ratios. The substrate was then cooled to 600 °C for the InN and InGaN growth. Metalorganic precursors used were triethylgallium (TEG) for Ga, trimethylindium (TMI) for In, and NH_3 for nitrogen, with hydrogen carrier gases. Typical flow rates used were 400 sccm for TMI, varying rates for TEG, and 18 000 sccm for NH_3. The thickness of the InGaN films grown was around 150 nm. Details of the growth were reported elsewhere.[6] The films were analyzed with x-ray diffraction (XRD), Hall measurement, photoluminescence (PL), x-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and scanning electron microscopy (SEM).

For the growth of InGaN alloys, the gas phase TEG/(TMI+TEG) ratio was varied from 0% to over 30%. The correlations between the alloy compositions determined by different analyses and the gas phase Ga/In ratios are shown in Fig. 1. The numbers of the vertical axis of Fig. 1

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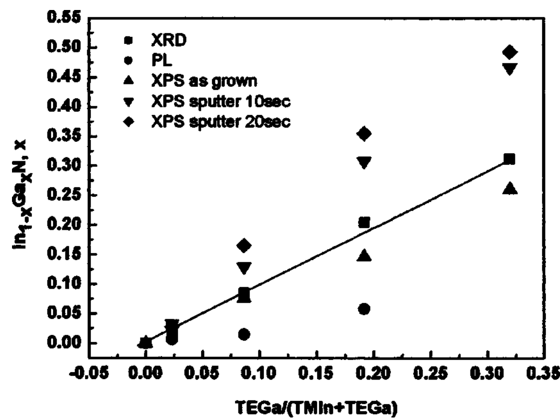


FIG. 1. Correlation of InGaN compositions with gas phase Ga/In ratios using x-ray diffraction (XRD), photoluminescence (PL), and x-ray photoelectron spectroscopy (XPS). The vertical axis is based on Vegards's rule for each property. The XPS analysis showed increasing Ga contents due to sputtering.

were adopted assuming Vegard's law for each property analyzed over this InGaN alloy range. This resulted in a linear relation between the XRD data with the gas phase Ga/In ratios. It is also interesting to notice that the alloy compositions determined by the XRD measurement agreed very well with those using the gas phase flow rate ratios. All the films grown were single crystalline, as shown in Fig. 2. Two major diffraction peaks were observed, attributing to the (0002) diffraction of GaN at 34.56° and InGaN over the angles of 31.33°–32.27°. The two weak side peaks near 33° and 34.6° were likely due to interference from the x-ray source used. Unless otherwise indicated, the alloy compositions assigned to the films in this report were based on the XRD correlation shown in Fig. 1.

The surface morphology was analyzed using SEM and AFM. A pyramid morphology was observed for the InN films, as already reported.[6] The surface became increasingly flattened with the addition of Ga, as revealed by both SEM and AFM. The mean surface roughness measured by AFM was 66.8, 64.4, 31.4, 16.4, and 13.0 nm for the InGaN films containing 0%, 2%, 8%, 20%, and 30% Ga, respectively. The Hall measurement of the InGaN samples showed donor concentrations of $1-3\times10^{19}$ cm^{-3} for the as-grown films, typical for all the MOVPE grown InN films reported.[1] The electron mobility was 1100–1200 cm^2/V s for the InN films, but rapidly decreased for the InGaN films with increasing Ga content. For example, the electron mobilities were 1100, 500,

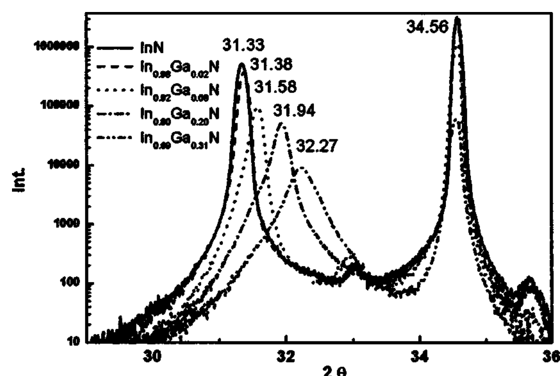
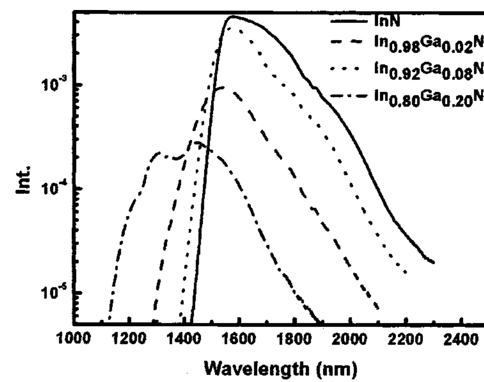


FIG. 2. X-ray diffraction patterns of InGaN films with different Ga contents, showing InGaN (0002) and GaN (0002) peaks.



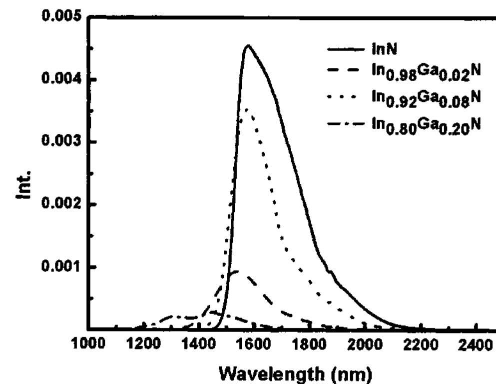


FIG. 3. Photoluminescence spectra of different InGaN films, showing shift toward shorter wavelength with increasing Ga contents. The $In_{0.8}Ga_{0.2}N$ films showed double emission peaks due to possible phase separation. Both log and linear scales are shown for comparison.

and 110 cm^2/V s for the InGaN films containing 2%, 8%, and 20% Ga, respectively.

The photoluminescence measurement showed emission peaks in the vicinity of 1.6–1.2 μm for the InGaN alloys grown. This is shown in Fig. 3 for the four samples containing 0%, 2%, 8%, and 20% Ga. The spectra shown were taken at 20 K, with the room temperature emission intensities about 20–80 times smaller. A single, rather broad peak was seen for the first three samples, but two peaks were noted for the sample containing 20% Ga at 1.4 and 1.28 μm, with a likely shoulder peak near 1.2 μm. The emission energies from the PL measurements were compared with the gas phase TEG/(TEG+TMI) ratios, and are also shown in Fig. 1. A much smaller slope was noted for such a correlation than that using the XRD results. This observation and the appearance of more than one emission peaks for the InGaN containing 20% Ga will be discussed later.

The XPS measurement revealed a clear correlation of the binding energies of In and Ga with the alloy compositions, as shown in Fig. 4 for the as-grown InGaN samples. Both the In and Ga peaks showed increasing binding energies with increasing Ga content. An estimate of the Ga content using the Ga/In intensity ratio, however, was found to be sensitive to the surface treatment of the samples. For example, a sputtering treatment with Ar^+ ions to remove the surface carbon and oxygen contaminants led to increased Ga/In ratios. The correlations with the gas phase (TEG)/(TEG+TMI) ratios are also shown in Fig. 1 for both the as-grown and sputtered samples. The sputtering treatment resulted in a continuing increase of the estimated Ga content in the films.

The observed electron mobility of InN films was likely the highest among the reported MOVPE grown InN films, all

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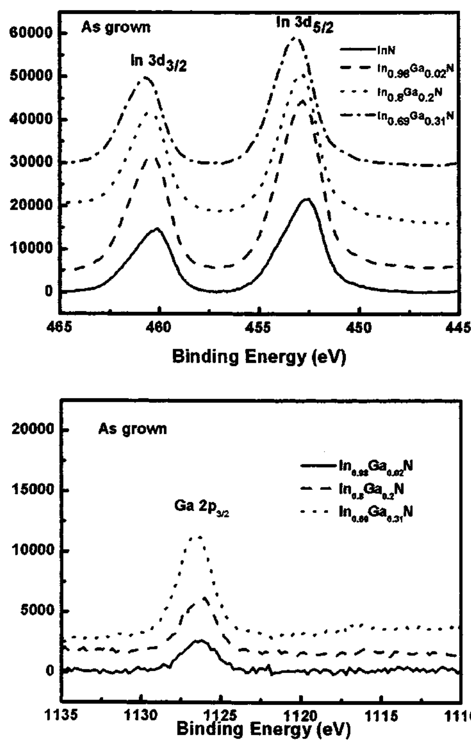

FIG. 4. X-ray photoelectron spectroscopy measurement of the binding energies of In and Ga for different InGaN films. All binding energies show chemical shift toward higher energies for increasing Ga contents in the films.

with a similar carrier concentration of $1-2\times10^{19}$ cm^{-3}.[1,4] The electron mobility was found to decrease rapidly with increasing Ga content in the InGaN films. The likely reasons included random alloy structures, decreasing crystalline quality, and nonoptimization of the growth conditions for the InGaN alloys. GaN is known to grow at a much higher temperature, 1000 °C, than InN, 500–600 °C. In this study, both the InN and InGaN films were grown at the same temperatures. With increasing Ga content, the electronic properties of the films grown would be expected to improve using higher growth temperatures. Work is in progress to optimize the growth, along with the growth of InN/InGaN quantum well structures, to better understand the properties of In-rich InGaN.

The actively pursued quest of band gap of InN was also explored with the addition of Ga. The photoluminescence measurement showed a shift of emission toward shorter wavelengths with increasing content of Ga in the InGaN films. For the InGaN films containing up to 20% Ga where PL was measurable, the emissions were all in the long wavelength region of 1.2–1.6 μm. This corresponded to narrow band gaps, in agreement with most recent reports on pure InN.[2–6] The PL measurement seemed to indicate a phase separation for the $In_{0.8}Ga_{0.2}N$ alloy where two major emission peaks were observed. This is not surprising in view of the widely reported phase separation of the InGaN films close to the GaN end.[11] The phase separation for the latter case has to vanish as the InGaN alloys approach pure InN. The assessment of this property from the InN end is thus interesting to both the fundamental understanding of the In-rich InGaN alloys and their use as optical devices. A determination of the alloy range without a phase separation could lead to controlled properties of the quantum well structures at such long wavelengths. An exploration of the two-dimensional properties in such structures, both optical and electronic, could be of high interest in view of the reported superconductivity of InN at very low temperatures.[12] We have observed similar changes in electrical conductivity for pure InN films.[13] An analysis of the InN/InGaN quantum wells should also shed light on the fundamental properties of InN. In this regard, the relation shown in Fig. 1 involving the PL measurement could be partly due to the phase separation and the band-gap bowing of the alloys.[11] Davydov and coworkers studied In-rich $In_xGa_{1-x}N$, with x ranging from 1 to 0.36.[14] A monotonic change was observed for both the lattice constant and PL emission wavelength with increasing Ga content, but with no phase separation noted. It thus requires further detailed growth and analysis to determine the onset and range of phase separation for the InGaN alloys containing high content of In.

The XPS analysis provided further understanding of the InGaN alloys grown. The binding energies of In $3d_{3/2}$ and $3d_{5/2}$ states, and that of Ga $2p_{3/2}$ all increased with increasing Ga content in the alloys. Using the Ga/In peak intensities, the estimated Ga contents in the as-grown samples were rather close to that using the XRD measurement. The estimated Ga contents, however, increased with increasing sputtering time for all the samples analyzed. We attributed the changes to a preferred loss of In to Ga by sputtering. The bond energy of InN, 7.7 eV/atom, is weaker than that of GaN, 8.9 eV/atom.[15] This could lead to a preferred sputtering of In and result in the increased Ga contents for the sputtered samples. One should thus be cautious in using the XPS measurement for the composition determination for such alloys. In this regard, the XRD measurement is least disturbed by the sample treatment.

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