Optical Band Gap Dependence on Composition and Thickness of $In_xGa_{1-x}N$ ($0<x<0.25$) Grown on GaN

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Abstract

Band gap measurements have been carried out in strained and relaxed $In_xGa_{1-x}N$ epilayers with $x<0.25$. Values of x were determined from x-ray diffraction of relaxed films. The lowest energy absorption threshold, measured by transmittance, was found to occur at the same energy as the peak of the photoluminescence spectrum. Bowing parameters for both strained and relaxed films were determined to be 3.42 eV and 4.11 eV, respectively. The dependence of the band gap shift, ΔE_g, on strain is presented. The dependence of the optical properties of InGaN on film thickness will also be discussed.

Significant strides in the growth of III-Nitride semiconductor films have led to the recent achievement of extremely bright blue and green light-emitting diodes (LEDs) [1] and blue lasers from InGaN/GaN/AlGaN based heterostructures [2]. These developments have occurred in spite of the fact that there is still much not understood concerning the growth and properties of these III-

Nitride films, especially In based compounds [3]. For example, reports in the literature on $In_xGa_{1-x}N$ ternary alloys have primarily focused on thin films of low x values since thick and/or high InN percentage films result in alloys of poor structural and optical properties. As a result, values of band gap, E_g, published in the literature are deduced from the experimental data for strained films [4,5] within the limited composition range of $0<x<0.15$. Determining the composition of these strained films via x-ray diffraction (XRD) requires reliance on elastic properties of InGaN which are not directly known but, rather, deduced from interpolation of values for InN and GaN binary alloys. Values of E_g for relaxed films are then calculated based on the amount of strain in thin films with the same composition [4]. Other techniques have been used to determine the value of x, such as Rutherford Back Scattering [4] and Secondary Ion Mass Spectrometry [6]. Also, the band gaps of relaxed films have been deduced from the shift of experimental excitonic transition energies of strained InGaN films using formulas that were deduced from GaN, since the corresponding InGaN values were not known.

In this letter we report on methods for the growth of $In_xGa_{1-x}N$ up to 1 μm thick, with $0<x<0.25$. This study is limited to the stated composition range to avoid any complications due to ordering [7] or phase separation [8] that have been observed for values of x larger than 0.25. These films were then used for the direct determination of x using XRD, and determination of E_g using Photoluminescence (PL) and transmission measurements.

For this study, $In_xGa_{1-x}N$ films were grown by atmospheric metalorganic chemical vapor deposition (MOCVD) on *c*-plane sapphire substrates in a RF inductively heated vertical chamber. Trimethylgallium(TMGa), Ethyldimethylindium(EdMIn), and ammonia(NH_3) were used as the Ga, In, and N precursors, respectively, while purified N_2, rather than H_2, was used as the carrier gas to facilitate In incorporation in the epitaxial films [9]. Thermocouple temperature readings of the

susceptor were calibrated by an infrared pyrometer while a temperature controller was employed to maintain a constant temperature. Growth proceeded after annealing the sapphire substrates at 1050°C. A thin GaN nucleation layer was deposited at 550°C followed by a 1-2 μm GaN layer grown at 1000°C. Following the GaN growth, the susceptor was cooled to 750-820 °C to grow the InGaN layers. Films with InN mole fractions in the $0<x<0.25$ range and thickness between 30 nm and 1 μm were grown. XRD, room temperature PL using a He-Cd laser pump source, and transmission electron microscopy (TEM) were used to characterize the InGaN films. Transmittance spectra of several $In_xGa_{1-x}N$ films were also measured. The measured transmittance (T) was converted to absorbance (A) with the relation A = -ln(T).

XRD θ–2θ and rocking curve scans were used to determine values of x using d-spacing. Measurements were made on a high resolution double-crystal diffractometer outfitted with a channel-cut-collimator and a Si(111) monochromatic crystal set for $Cu_{k\alpha 1}$ radiation. The (0002) symmetric reflection of the c-plane sapphire substrate at $\theta = 20.8425^o$ was used as a reference for locating all other peaks. The c-spacing of the $In_xGa_{1-x}N$ films was determined from the (0002) reflection in conjunction with Bragg's law. Experimentally determined values of c and $d_{11\text{-}24}$ were then substituted into the equation below in order to calculate the a spacing for the $In_xGa_{1-x}N$ crystal:

$$a = [(h^2+hk+k^2)(d_{hkl}^{-2}+l^2c^{-2})^{-3/4}]^{1/2}$$

where h, k and l are the indices of the plane (hkl). The XRD measurements were carried out for several fairly thick InGaN films ($t \approx 0.3$ μm or higher). These films were determined to be unstrained since the a- and c-spacing were independent of film thickness, and the value of the a spacing was larger than that of a_{GaN} and corresponds to that of relaxed $In_xGa_{1-x}N$ for a given value of c and x. Therefore, d-spacing in the c-direction was used to calculate values of x for thick InGaN films, assuming Vegard's law is valid. Films too thin for this XRD analysis were assumed to have

the same composition as their thicker counterparts produced under the same growth conditions (e.g., temperature, NH_3, TMG, EDMIn flows).

Figure 1 shows the room temperature PL spectra of InGaN alloys of various compositions. The PL spectra obtained for relaxed films are shown in Figure 1(a) and those for strained films in Figure 1(b). The 3.4 eV peak in the spectra of the strained films arises from the underlying GaN layer. The optical quality, as determined from PL, seems to deteriorate with increasing thickness as evidenced by the increased prominence of deep levels relative to band edge emission in the thick films. The highest-energy peak in each spectrum (excluding the 3.4 eV peak if present) is assumed to correspond to the band gap energy of the InGaN layer. Also, the band gap energies of the thick films are lower than their thinner counterparts. This shift in band gap energy can be explained in terms of strain. If the thin films are coherently strained to the GaN surface, the compressive, biaxial strain is likely to cause an increase in band gap, as in most other III-V semiconductors.[9a] As In content increases, the mismatch between the InGaN and the GaN increases, which, in turn, increases the strain and shift in band gap energy.

We have also observed that the PL emission spectra have three distinct regions depending on InGaN film thickness. These regions correspond to thin, intermediate, and thick films. Band edge emission dominates for the thin (strained) and thick (relaxed) regions, while emission from deep levels is prominent in the transition region, as shown in Figure 2. This transition behavior is observed for all compositions from x=0.05 to x=0.25. In addition, films with higher x exhibit the transition region at a lower thickness than films of lower x. The nature and origin of the transition region deep levels are currently under investigation and the presence of these defective regions, presumably, at the InGaN/GaN interface will be discussed in more detail in relation to the onset of relaxation and critical layer thickness [10]. The InGaN film surfaces were imaged in plan-view by

scanning electron microscopy. Smooth surfaces were observed for strained films, whereas rough surfaces were observed for film thickness corresponding to the transition and relaxed regions.

Figure 3 shows the variation of band edge related emission with composition for strained and relaxed InGaN films. (The uncertainty in the band gap energies measured by PL is estimated to be ±0.03 eV from examination of the sharpness of features in the PL spectra. The same estimated uncertainty applies to the band gap energies measured by transmittance, discussed below.) In order to calculate the E_g for coherently strained InN, we assumed that the deformation potentials for GaN and InN are the same. Thus, the band gap for InN coherently strained to match GaN is estimated as 2.77 eV [11]. The band gap for relaxed InN is assumed to be 1.89 eV, as reported in the literature. This calculated energy, along with the experimentally determined values of E_g for strained films, were fit with a second order polynomial (dotted line):

$$E_{g(strained)} = 3.42-0.65x-3.42x(1-x) \qquad (1)$$

The empirically determined bowing parameter of 3.42 eV is consistent with previously published data for strained InGaN [4,5]. The solid curve shows the corresponding E_g data versus. x for relaxed InGaN films:

$$E_{g(relaxed)} = 3.42-(1.53)x-4.11x(1-x) \qquad (2)$$

A bowing parameter of 4.11 eV was determined for relaxed InGaN films. This is higher than previously reported bowing parameters, which were extrapolated from strained data [4,12]. Recent reports indicate that InGaN's bowing parameters are compositionally dependent and decrease with increasing x [4]. Considering this, bowing parameters of 5.02 eV and 3.97 eV were found by parabolic fits to the relaxed $In_xGa_{1-x}N$ films for $0.05<x<0.12$ and $0.12<x<0.25$, respectively. Also, the shift in band gap energy, ΔE_g, due to strain in InGaN films was deduced from Equation (1) and

Equation (2), where $\Delta E_g = E_g$ (strained) – E_g (relaxed) for the same value of x. In terms of strain ΔE_g is as follows:

$$\Delta E_g = -14.8\varepsilon_{\|} - 51.1\varepsilon_{\|}^2 \qquad (3)$$

The shift in energy was converted from a function of composition to a function of strain using the relation $\varepsilon_{\|} = [a_{GaN} - a_{InGaN(relaxed)}]/a_{InGaN(relaxed)}$, where $a_{InGaN(relaxed)}$ is a function of x. This shift in E_g between the curves fitted to the strained and relaxed film data is plotted as a function of absolute strain in Figure 4. A monotonic increase in ΔE_g is observed with increasing strain.

The band gap of InGaN was also determined by optical transmission measurements. Absorbance spectra of three $In_xGa_{1-x}N$ samples, with x values (estimated from XRD) of 0.06, 0.13, and 0.14, are shown in Figure 5. The spectra show a characteristic "turning point" energy such that the absorbance increases more rapidly with energy above the turning point than below. We use the observed "turning point" energy as a measure of the electronic band gap in each sample. Three effects may contribute to the observed increase of absorbance with energy below the band gap: (a) absorption by defect and impurity states in the film, whose density increases with energy as the band gap is approached from below; (b) optical scatter from the rough top surface of the film, which increases with decreasing wavelength; (c) reflection losses from the film and substrate surfaces, which increase with energy because the refractive indices of the materials increase with energy for energies below the band gap. The origin of the broad absorption edge is currently under investigation.

When the absorbance band gap (or "turning point" energy) is not sharply defined, it is difficult to obtain a quantitative estimate of this energy from the data. To facilitate the data analysis, the following empirical criterion was used: the absorbance band gap is defined as the energy where the curvature of the logarithm of the absorbance (as a function of energy) is

maximum, $\partial^2 \ln(A)/\partial E^2$ = maximum. A 4th-order Savitzky-Golay filter with a windowing width of 0.1 eV was used to numerically calculate the second logarithmic derivative of the data, as defined here. The band gap values obtained with this definition correspond well to estimates from visual inspection of the data; the results are E_g=3.07 eV for the x = 0.06 sample, E_g=2.67 eV for the x = 0.13 sample, and E_g=2.63 eV for the x = 0.14 sample. The calculated $\partial^2 \ln(A)/\partial E^2$ function for the x = 0.14 sample is also shown in Figure 5.

Band gaps deduced from these optical transmission measurements are shown in Table I and plotted in Figure 3. These results indicate that the E_g of relaxed InGaN films have about the same values whether they are deduced from PL or from optical transmission measurements, indicating the absence of a Stokes shift between the highest-energy PL emission peak and the lowest-energy optical absorption threshold. A summary of the agreement of these results can be seen in Table 1.

In conclusion, the variations of the band gap with composition in the InGaN ternary alloys for both strained and relaxed films are measured. Band gaps were obtained from both room temperature PL and optical transmission measurements. We have also observed that an intermediate thickness range always accompanies the transition of the films from the strained to relaxed condition where the PL spectra are dominated by deep levels.

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Figure captions

Figure 1 Room temperature PL spectra of $In_xGa_{1-x}N$ films with different values of *x*. The InN% and InGaN thickness are indicated next to each spectrum. (a) Relaxed films (b) Strained films.

Figure 2 Dependence of the dominant PL emission energy on the thickness of the $In_xGa_{1-x}N$ films. Lower figures are PL spectra, from left to right, for strained, transitional, and relaxed InGaN films.

Figure 3 Band gaps of strained (open circle) and relaxed (solid diamond) $In_xGa_{1-x}N$ epitaxial films obtained from room temperature PL. Dotted and solid lines represent the least square fit to the strained and relaxed band gap respectively. Also shown is the band gap obtained from optical transmission measurements (stars). The uncertainty in the measured band gap energies is estimated to be ±0.03 eV (for both PL and transmission).

Figure 4 Variation of band gap energy shift, "ΔE_g", with strain between pseudomorphically strained and relaxed InGaN epitaxial films grown on GaN substrates

$\Delta E_g = E_g$ (strained) – E_g (relaxed)

Figure 5 Absorbance spectra of $In_xGa_{1-x}N$ samples with *x* (from XRD) equal to (a) 0.06; (b) 0.13; (c) 0.14. Vertical dashed lines indicate the band gap energies determined numerically from the equation $\partial^2 \ln(A)/\partial E^2$ = maximum (where A is absorbance). Curve (d) is the calculated $\partial^2 \ln(A)/\partial E^2$ function for the $x = 0.14$ sample shown on an arbitrary y-axis and arbitrary offset.

Table I: Values of the band gap E_g (eV) obtained from PL and optical transmission measurements on thick ($t > 0.3\mu m$) $In_xGa_{1-x}N$ for a given composition, x. Data shows good agreement between the two techniques. The uncertainty in the measured band gap energies is estimated to be ±0.03 eV (for both PL and transmission).

	SampleA	SampleB	SampleC	SampleD	SampleE
x	0.06	0.07	0.08	0.13	0.14
E_g (PL)	3.09	3.02	2.95	2.69	2.62
E_g (Transmission measurement)	3.07	3.01	3.05	2.67	2.63