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Small band gap bowing in $In_{1-x}Ga_xN$ alloys

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High-quality wurtzite-structured In-rich $In_{1-x}Ga_xN$ films ($0 \leqslant x \leqslant 0.5$) have been grown on sapphire substrates by molecular beam epitaxy. Their optical properties were characterized by optical absorption and photoluminescence spectroscopy. The investigation reveals that the narrow fundamental band gap for InN is near 0.8 eV and that the band gap increases with increasing Ga content. Combined with previously reported results on the Ga-rich side, the band gap versus composition plot for $In_{1-x}Ga_xN$ alloys is well fit with a bowing parameter of ~1.4 eV. The direct band gap of the $In_{1-x}Ga_xN$ system covers a very broad spectral region ranging from near-infrared to near-ultraviolet. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1489481]

The $In_{1-x}Ga_xN$ alloy system has been studied extensively in recent years. An especially intense effort has been directed towards the studies of Ga-rich alloys, which are used as the active layer in blue and green light emitting diodes and lasers.[1–4] Another attribute of this alloy system is that the energy gap can be varied in a wide spectral range. For example, it has been shown that the band gap can be decreased from the GaN value, 3.4 eV, down to ~2.3 eV for $In_{0.4}Ga_{0.6}N$.[5–8] Studies of the optical properties of these Ga-rich alloys have shown a strong dependence of the fundamental band gap on the alloy composition. When a band gap of ~1.9 eV for InN is assumed as the end point value, large bowing parameters are required to fit the composition dependence of the fundamental band gap energy. For example, a bowing parameter of 2.5 eV was obtained from optical absorption measurements and a value of 4.4 eV was obtained from the location of the emission peaks.[5] The band gap value of ~1.9 eV for InN was determined in early studies mainly by interband optical absorptions performed on InN thin films deposited by sputtering techniques[9,10] and metalorganic vapor phase epitaxy.[11] The electron concentration in those films was usually over 10^{20} cm^{-3} and the room-temperature mobility was below 100 $cm^2/V\,s$. Despite extensive efforts, no reliable light emission associated with an energy gap near 1.9 eV has ever been reported in these early studies of InN.

Recent progress in epitaxial growth techniques has led to the availability of InN crystals with considerably lower electron concentrations and much higher electron mobilities. Films with electron concentrations in the low 10^{18} cm^{-3} range with room temperature mobilities well in excess of 1300 $cm^2/V\,s$ in InN have been grown by molecular beam epitaxy.[12–15] It has been reported very recently that these improved InN films show intense photoluminescence (PL) at energies around 0.8 eV at room temperature.[14–16] Along with the strong PL, a clear absorption edge[14–16] and a photomodulated reflectance transition feature have also been observed at this energy.[16] Thus, the fundamental band gap of InN has been determined to be near 0.8 eV.[15,16]

In this letter, we report our systematic study on the optical properties of In-rich $In_{1-x}Ga_xN$ alloys grown by improved epitaxial method. It was found that these alloys show strong infrared PL signal, as expected from an InN band gap of ~0.8 eV. The emission spectrum of the $In_{1-x}Ga_xN$ system thus extends to near-infrared. The bowing parameter in the entire composition range can be fit with a small bowing parameter of ~1.4 eV.

$In_{1-x}Ga_xN$ films (~240 nm) were grown on (0001) sapphire with an AlN buffer layer (~200 nm) by molecular beam epitaxy.[13] The growth temperature is in the range of 470 to 570 °C. The Ga atomic fraction was determined by x-ray diffraction (XRD) assuming a complete lattice relaxation. The XRD analysis shows that high-quality wurtzite-structured $In_{1-x}Ga_xN$ epitaxial layers formed with their *c* axis perpendicular to the substrate surface. The samples were characterized by conventional optical absorption (abs) and photoluminescence spectroscopy. The optical absorption measurements were performed on a CARY-2390 near-infrared-visible-UV spectrophotometer. The PL signals were generated in the backscattering geometry by excitation with the 476.5 nm line of an argon laser. The signals were then dispersed by a 1 m double-grating monochromator and detected by a Ge photodiode.

The samples exhibit strong infrared PL signal even at room temperature. Figure 1(a) shows the PL signals for samples with a wide range of Ga compositions from 0 to 0.5.

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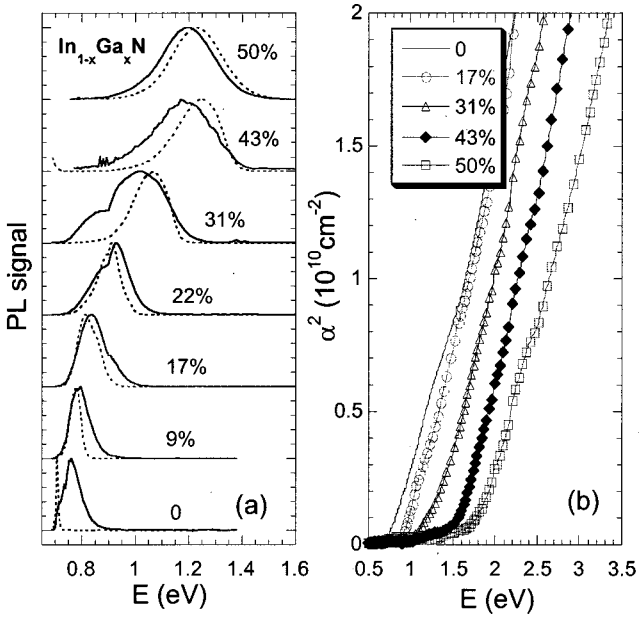

FIG. 1. (a) PL signal taken at room temperature (solid line) and 11 K (dashed line) for samples with Ga atomic fraction x ranging from 0% to 50%. All curves are normalized to equal height and offset vertically for clarity. (b) Room-temperature absorption coefficient squared as a function of photon energy.

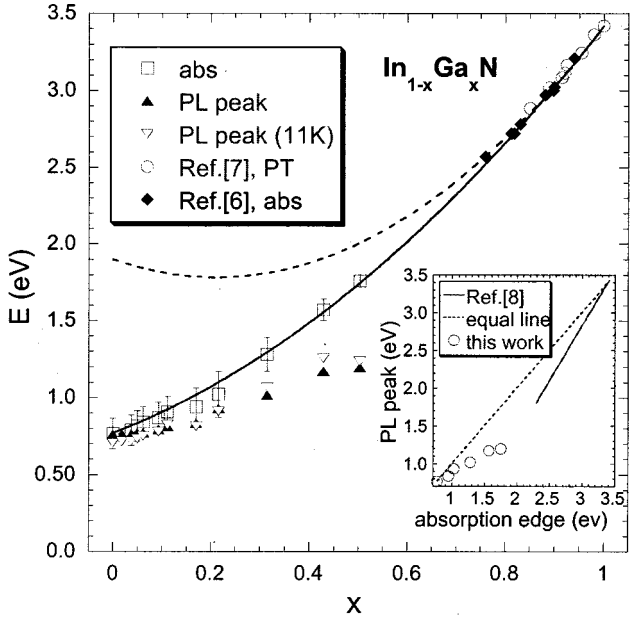

FIG. 2. PL peak energy and band gap determined by optical absorption as a function of composition. Some previously reported data on the Ga-rich side are also shown (Refs. 6 and 7). All data are taken at room temperature unless otherwise noted. The solid curve shows the fit to the band gap energies (abs and PT) using a bowing parameter $b=1.43$ eV. The dashed curve is the fit to the band gap energies on the Ga-rich side assuming a band gap of 1.9 eV for InN. Inset: PL peak energy plotted against absorption edge energy. The solid line is a least-square fit to experimental data on the Ga-rich side adopted from Ref. 8. The dashed straight line shows the relation when the Stokes shift is zero.

Both room temperature (295 K) and low temperature (11 K) results are shown. As expected, the PL peak energy shows a strong blueshift from the band gap of InN (0.77 eV at room temperature) with increasing Ga content. The linewidth of the PL peak is significantly broadened as x increases.

Figure 1(b) shows the absorption coefficient squared plotted as a function of photon energy. In all cases, the absorption coefficient reaches $\sim 10^5$ cm^{-1} for a photon energy of ~ 0.5 eV above the absorption edge, which is typical of direct semiconductors. The curves of absorption coefficient squared are essentially linear in the range of photon energy investigated, which also implies a direct fundamental band gap. The observed slight nonlinearity of the curves for small x can be attributed to the nonparabolicity of the conduction band resulting from the **k·p** interaction between the Γ_6-symmetry conduction band and the Γ_8-symmetry valence bands.[17]

The band gaps determined from the absorption edges in Fig. 1(b) are shown as a function of Ga concentration in Fig. 2. The absorption edge shifts rapidly to higher energy as x increases. In Ga-rich $In_{1-x}Ga_xN$ alloys, numerous studies have been done on the composition dependence of the band gap.[5–8] In order to see the composition dependence of the band gap in the entire composition range, two sets of previously reported data on the Ga-rich side are also shown in Fig. 2. These band gaps were measured by photomodulated transmission (PT)[7] and optical absorption,[6] respectively. It can be seen that our data on the In-rich side make a smooth transition to the data points on the Ga-rich side. This result further confirms that the absorption edge of InN observed near 0.77 eV indeed corresponds to the intrinsic fundamental band gap of InN.[15,16] As shown by the solid curve in Fig. 2, the composition dependence of the room-temperature band gap in the entire composition range can be well fit by the following standard equation:

$$E_G(x)=3.42x+0.77(1-x)-1.43x(1-x) \quad (1)$$

with a constant bowing parameter of $b=1.43$ eV. This value of b is much smaller than previously reported bowing coefficients for which a band gap of ~ 1.9 eV for InN was used as the lower-energy end point,[5,6] and is similar to that observed (1.3 eV) in the $Al_xGa_{1-x}N$ alloy system.[18] For example, for the two sets of data points on the Ga-rich side shown in Fig. 2, if an InN band gap of 1.9 eV is assumed instead of 0.77 eV, a bowing coefficient as large as 2.63 eV is needed to accommodate the composition dependence on the Ga-rich side. This fit is shown as a dashed curve in Fig. 2. This artificial large bowing effect has also been discussed in terms of a composition dependent bowing parameter.[19,20] It has been pointed out in Ref. 6 that the variety of experimental band gaps on the Ga-rich side can be better fit with a pseudolinear composition dependence. Our results show that this pseudolinear composition dependence on the Ga-rich side is just the direct evidence of the small bowing in the entire composition range. An additional significance of Fig. 2 is that it demonstrates that the fundamental band gap of this ternary alloy system alone covers a wide spectral region ranging from near-infrared at ~ 1.6 μm to near-ultraviolet at ~ 0.36 μm.

The composition dependence of the peak energy of the PL signal is also shown in Fig. 2. At higher Ga concentrations, the PL peak energy is shifted towards lower energy as compared with the absorption edge. The observed Stokes shift increases with increasing Ga content and is as large as 0.56 eV for $x=0.5$. In the inset of Fig. 2, the PL peak energy is plotted as a function of absorption edge energy. Also shown in solid line is a linear fit to experimental data on the

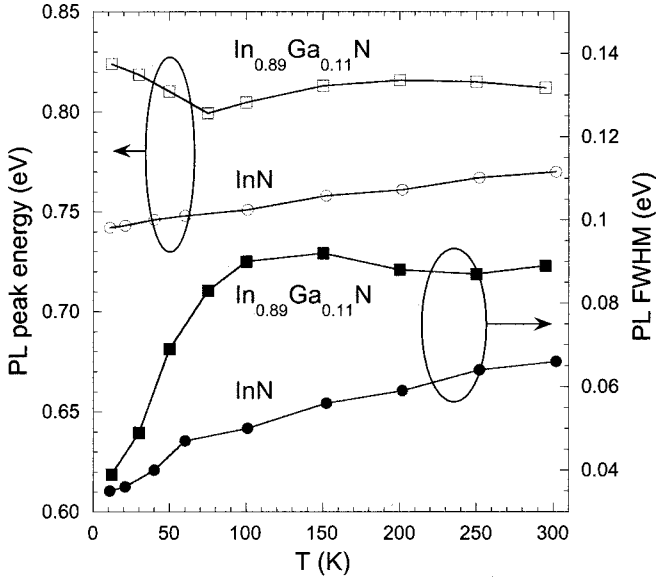

FIG. 3. Temperature dependencies of PL peak energy and FWHM for InN and $In_{0.89}Ga_{0.11}N$.

Ga-rich side.[8] The deviation from the linear interpolation (dashed line) represents the Stokes shift. It is clearly seen that the Stokes shift tends to reach the maximum near the middle of the composition, indicating inhomogeneous distribution of In and Ga atoms. The large, composition dependent, Stokes shift indicates that the PL measurement is not a reliable technique to determine the bowing parameter. It also explains the origin of much large bowing parameter of 2.5 eV determined in the most recent PL studies of $In_{1-x}Ga_xN$ alloys.[21]

The emission spectrum measured by PL spectroscopy reflects the distribution of localized states in smaller-gap regions that have larger-than-average In compositions,[19,22] while the absorption transition largely reflects the onset of the density of delocalized states. Therefore, the fact that the Stokes shift reaches the maximum around the middle of composition implies that the largest degree of composition fluctuation and/or structural disorder occurs near the middle. This is also consistent with the result that the linewidth of the PL signal increases with increasing Ga concentration, as is seen in Fig. 1(a). As discussed in Ref. 7, the PL linewidths of over 50 meV in $In_{1-x}Ga_xN$ cannot be explained by pure statistical randomness in the alloy composition without considering carrier localization caused by compositional inhomogeneity.

The temperature dependence of the peak energy and the full width at half maximum (FWHM) of the PL signal are shown in Fig. 3. Both samples exhibit an anomalous, although significantly different, behavior. In InN the PL peak energy increases monotonically with increasing temperature, whereas a so-called inverted ''S'' shaped dependence is observed for $In_{0.89}Ga_{0.11}N$. A strong temperature dependence of the FWHM is seen in $In_{0.89}Ga_{0.11}N$.

In summary, we have demonstrated that In-rich $In_{1-x}Ga_xN$ alloys with $x<0.5$ have small fundamental band gap energies ranging from around 0.77 to 1.75 eV. Strong infrared PL signals have been observed from these alloys. The composition dependence of the band gap can be well explained by a relatively small bowing parameter. The Stokes shift increases with increasing Ga concentration for the compositions investigated, suggesting spatial variation of the alloy composition and strong carrier localization in the samples.

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