

Mechanism of enhanced luminescence in $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ quaternary alloys

C. H. Chen, L. Y. Huang, Y. F. Chen, H. X. Jiang, and J. Y. Lin

Citation: *Applied Physics Letters* **80**, 1397 (2002); doi: 10.1063/1.1455147

View online: <http://dx.doi.org/10.1063/1.1455147>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/80/8?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

[Mechanism of enhanced luminescence in \$\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}\$ quaternary epilayers](#)

Appl. Phys. Lett. **84**, 1480 (2004); 10.1063/1.1650549

[Luminescence mechanisms in quaternary \$\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}\$ materials](#)

Appl. Phys. Lett. **80**, 3730 (2002); 10.1063/1.1481766

[Enhanced luminescence in InGaN multiple quantum wells with quaternary AlInGaN barriers](#)

Appl. Phys. Lett. **77**, 2668 (2000); 10.1063/1.1319531

[Mechanism of luminescence in InGaN/GaN multiple quantum wells](#)

Appl. Phys. Lett. **76**, 3712 (2000); 10.1063/1.126758

[Resonant Raman scattering from buried \$\text{Al}_x\text{Ga}_{1-x}\text{N}\$ \(\$x \approx 0.17\$ \) layers in \(Al,Ga,In\)N heterostructures](#)

J. Appl. Phys. **87**, 2853 (2000); 10.1063/1.372268

The banner features a blue background with a molecular structure of spheres and rods. On the left is a thumbnail of an 'AIP Applied Physics Reviews' journal cover, which shows a diagram of a layered material structure. To the right of the thumbnail, the text 'NEW Special Topic Sections' is written in large, white, bold letters. Below this, in yellow, is the text 'NOW ONLINE'. Underneath that, in white, is the text 'Lithium Niobate Properties and Applications: Reviews of Emerging Trends'. On the far right, the 'AIP Applied Physics Reviews' logo is displayed in white.

Mechanism of enhanced luminescence in $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ quaternary alloys

C. H. Chen, L. Y. Huang, and Y. F. Chen

Department of Physics, National Taiwan University, Taipei, Taiwan, Republic of China

H. X. Jiang and J. Y. Lin

Department of Physics, Kansas State University, Manhattan, Kansas 6506-2601

(Received 10 October 2001; accepted for publication 19 December 2001)

We report a firm evidence of enhanced luminescence from InGaN-like clusters in $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ quaternary alloys. Photoluminescence (PL) and Raman scattering measurements have been employed to study the optical properties of these alloys. The excellent correlation between the phonon replica structures accompanying luminescence line and the observed InGaN-related phonon modes in Raman spectra provide a powerful evidence showing that the existence of InGaN-like clusters is responsible for the enhanced luminescence in $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ quaternary alloys. In addition, the dependence of the PL emission energy on temperature in the low-temperature regime and on excitation power density can also be explained consistently with recombination mechanisms involving the localized states attributed to InGaN-like cluster size fluctuations. © 2002 American Institute of Physics. [DOI: 10.1063/1.1455147]

The group III-nitride wide-band-gap semiconductors have been recognized as very important materials for many optoelectronic devices, such as blue ultraviolet (UV) light-emitting diodes, laser diodes, and high-temperature/high-power electronic devices.^{1–3} It has been demonstrated that most nitride based devices must take advantage of multiple quantum wells and heterostructures such as GaN/AlGaIn (Refs. 4 and 5) and InGaN/GaN (Refs. 6–8) as well as the tunability of the band gaps in the alloys from InN (1.9 eV) to GaN (3.4 eV) and to AlN (6.2 eV). Recently, $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ quaternary alloys have also been recognized to have the potential to overcome some shortfall of GaN epilayers, InGaN, and AlGaIn alloys.^{1–8} By varying In and Al compositions x and y in $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$, one can change the energy band gap while keep lattice matched with GaN, which can be used to reduce dislocation density as well as piezoelectric field. In addition to the key features of lattice match with GaN and tunability in energy band gap, $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ quaternary alloys also have the potential to provide a better thermal match to GaN, which could be an important advantage in epitaxial growth. The potential application of $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ quaternary alloys as InGaN/InAlGaIn quantum well light emitters,⁹ GaN/InAlGaIn heterojunction field-effect transistors,¹⁰ and UV detectors have been demonstrated recently.¹¹ It is also found that the quantum efficiency (QE) of $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ is enhanced significantly over AlGaIn with a comparable Al content.¹² However, the physical origin of this enhanced QE is not clear.

In this letter, a set of $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ quaternary alloys with different Al concentration has been grown by metalorganic chemical vapor deposition (MOCVD). A 1.0 μm GaN epilayer was first deposited on the sapphire substrate with 25 nm low-temperature GaN buffer layer, followed by the deposition of 0.1 μm $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ quaternary alloy epilayer by the low pressure MOCVD. The growth temperature and pressure for the underneath GaN epilayer were 1050 °C and

300 Torr, respectively. For $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ quaternary alloys, the growth temperature 780 °C and In and Al compositions were controlled by varying the flow rates of TMIn and TMAI. Contents of In and Al were determined by different methods including x-ray diffraction (XRD), energy dispersive system, and Rutherford backscattering.¹² It was found that $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ quaternary alloys, which are lattice matched with GaN epilayers ($y \sim 4.8x$, which is very close to the theoretical value), have the highest photoluminescence (PL) intensity as well as the narrowest XRD linewidth.

The PL spectra were recorded by a SPEX 0.85 m double spectrometer, and a photomultiplier tube. The sample was placed inside a closed-cycle He cryostat. A He–Cd laser working at 325 nm was used as the excitation source. The Raman signal was measured by a Jobin–Yvon T64000 micro-Raman system working in the triple-subtractive mode. The Raman spectra of the samples were measured at room temperature using a solid-state laser with a 532 nm wavelength, and they were measured in backscattering geometry. The incident and scattered light propagated parallel to the c axis, which in turn was normal to the growth surface.

Figure 1 shows the typical PL spectra of $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ quaternary alloy samples with different Al composition at temperature 15 K. The spectrum of lattice-matched sample is dominated by a sharp emission and the full width at half maximum is about 34 meV. The lower emission peak at 3.483 eV is due to the underneath GaN epilayer. It is worth noting that we can achieve not only higher emission energies but also higher emission intensity in $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ quaternary alloys than that of high quality GaN epilayer.¹² The QE of $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ quaternary alloys is also significantly enhanced over AlGaIn alloys with a comparable Al content.¹² In addition, several phonon replicas can be clearly observed on the low energy shoulder of the main PL peak. As shown in the inset of Fig. 1, we took a multi-Gaussian fit of the PL line of lattice-matched sample,

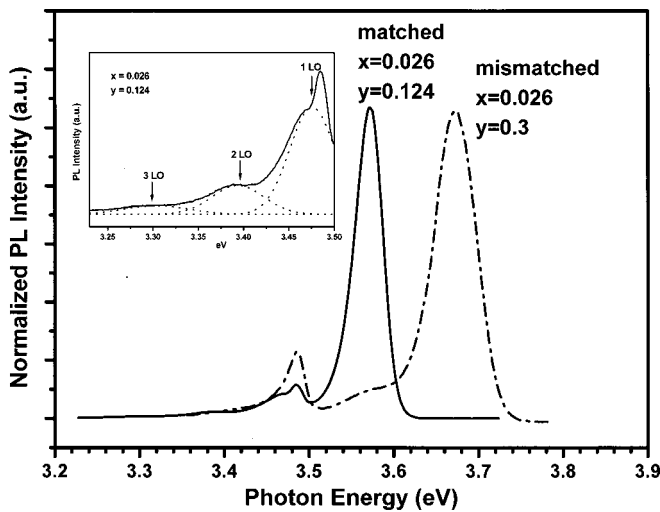


FIG. 1. PL spectra of the $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ quaternary alloys at 15 K. In the inset, the enlarged PL spectrum of lattice-matched sample was fitted by Gaussian curves (dotted lines). By the fitting result, the energy of LO-phonon replicas is 86 meV.

and we found that the separation between adjacent peaks is about 86 meV which is in excellent agreement with the InGaN-like longitudinal optical (LO) phonon energy measured by Raman scattering as shown next. This result strongly implies that the InGaN-like regions do exist in the $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ matrix, and the electron-hole pairs responsible for the bright luminescence in $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ quaternary alloys are confined in the InGaN-like region. The situation here is similar to the existence of InN clusters in InGaN quantum wells.^{6–8} Because the electron-hole pairs are confined in InGaN-like clusters, which enhance the wave function overlap and thus the transition probability, the $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ alloys therefore can overcome the influence of a large number of defects and provide the bright emission. In addition, due to the confinement of electron-hole pairs in InGaN-like regions, there will be a strong interaction between electron-hole pairs and InGaN-like lattice. Therefore, the PL spectra display the InGaN-like phonon replicas.

Due to the strong immiscibility of the InGaN and AlGaN system, it is expected that the InGaN-like clusters can be easily found in $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ quaternary alloy. According to previous reports, the cluster formation is very sensitive to the growth temperature¹³ as well as constituent atom mole fraction.¹⁴ With the increase of growth temperature, due to the movement of the constituent atoms, the alloy segregation tendency is enhanced. With different constituent composition, the stress field in the material is changed. It is believed that the stress field may provide the driving force for the migration of constituent atoms and lead to the formation of InGaN-like clusters.

As shown in Fig. 1, with the increase of Al composition, the transition energy of $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ quaternary alloys blueshifts to higher energy. The higher transition energy of lattice-mismatched $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ sample can be attributed to a sum of three possible contributions: (i) composition, (ii) strain, and (iii) quantum size. Firstly, because of the high Al composition, the confinement effect of InGaN-like clusters due to the larger band offset is stronger and the

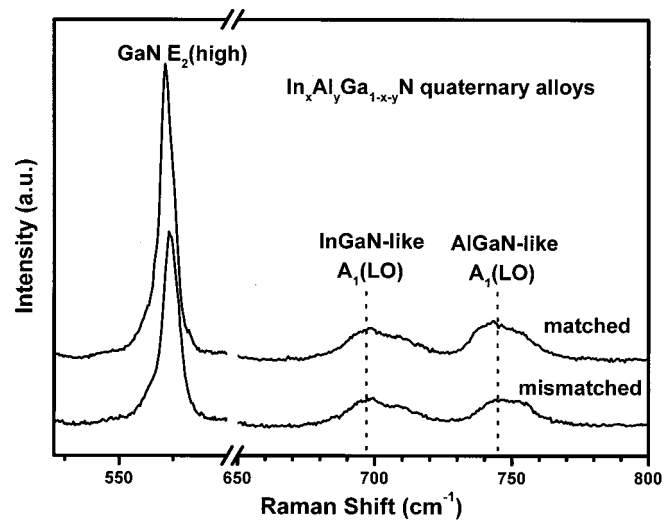


FIG. 2. Room-temperature micro-Raman spectra of the $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ quaternary alloy samples probed with a solid-state laser (532 nm).

transition energy is higher. Secondly, because of the high Al composition, the enhanced strain between the interface of InGaN-like region and $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ matrix can result in a higher transition energy. Lastly, due to the increase of Al concentration, the size of InGaN-like region gets smaller. Because of the stronger confinement effect, the transition energy is higher when the Al concentration increases.

In order to confirm the aforementioned argument, we have performed the Raman measurements. In Fig. 2, we showed the room-temperature Raman spectra of $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ quaternary alloys. There are three resolved phonon structures observed in each Raman spectrum of $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ quaternary alloys. The 569 cm^{-1} peak is from E_2 mode of h -GaN. The broaden line in 696 cm^{-1} is the InGaN-like $A_1(\text{LO})$ mode and that in 745 cm^{-1} is AlGaN-like $A_1(\text{LO})$ mode. This assignment of both InGaN-like A_1 mode and AlGaN-like A_1 mode is based on the energy of GaN $A_1(\text{LO})$ phonon^{15,16} at 735 cm^{-1} and the phonon modes of InGaN and AlGaN alloys given in previous reports.^{17–19} Thus, this finding provides direct evidence to support the existence of InGaN-like clusters in $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ quaternary alloys. Moreover, the energy of the InGaN-related $A_1(\text{LO})$ obtained in Raman spectra is consistent with that obtained from PL spectrum. Therefore, the excellent correlation between PL and Raman spectra strongly suggests that the electron-hole pairs responsible for the enhanced emission in $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ alloys are confined in InGaN-like regions.

A plot of the PL peak position versus temperature is shown in Fig. 3. The spectrum exhibits an anomalous behavior, in which the peak energy decreases, then increases with increasing temperature, and finally decreases with temperature rapidly. The same behavior has been observed previously in materials containing localized states such as disordered superlattices²⁰ and ternary QWs.²¹ Here, we suggest that the localized states lead to the unusual behavior coming from the size fluctuations due to the inhomogeneous distribution of InGaN-like clusters. The larger InGaN-like cluster has the lower energy state corresponding to the stronger localized effect. At low temperature, the radiative recombina-

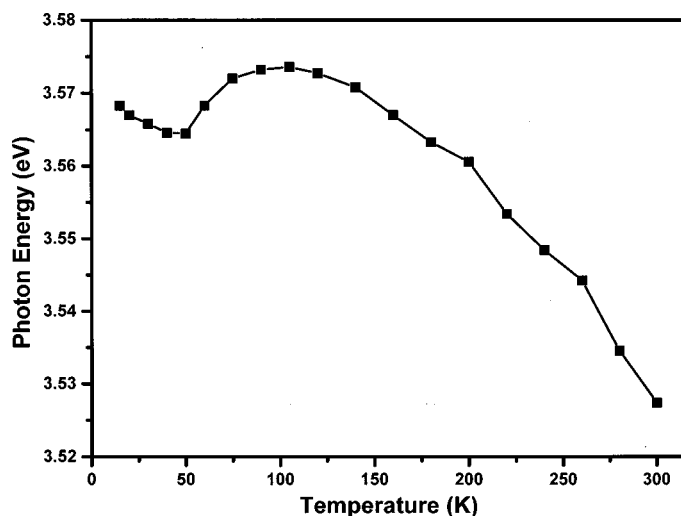


FIG. 3. Temperature dependence of the PL peak position of the lattice-matched sample.

tion occurs around the localized states with local potential minima. That is, PL arises from the sum of emission of many different cluster sizes. When the temperature increases slightly, the weakly localized carriers can repopulate thermally to other stronger localized states. The PL peak therefore decreases with increasing temperature in the range of 15–50 K. When the temperature increases further, the thermalized carriers are activated to higher energy states and hence PL peak energy is blueshift. As the temperature exceeds 100 K, a “normal” temperature-induced band gap shrinkage becomes stronger than the effect of thermal excitation. Thus, the temperature dependence of the emission energy is dominated by the property of the band gap which decreases with increasing temperature.

Additional evidence of the existence of the localized states due to size fluctuations is the measurement of the excitation intensity dependence of the PL spectra as shown in Fig. 4. It is seen that the PL peak energy increases with increasing excitation intensity. This peculiar result can also be understood by the localized states due to size fluctuations. Because the localized states located at the band edge are limited in number, they can be easily occupied by the photoexcited carriers. Increasing the excitation intensity will increase the state filling, and hence the emission energy is also increased. Therefore, all our PL measurements can be explained by the localized states due to size fluctuations in a consistent way.

In summary, the optical properties of $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ quaternary alloys with different Al content have been investigated. We have reported that the enhanced emission in $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ alloys originates from the radiative recombination within InGaN-like clusters. Both the phonon replica structures accompanying the luminescence line and the observed InGaN-related phonon modes in Raman spectra provide a powerful evidence that the electron–hole pairs responsible for the bright emission in $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ alloys are confined in InGaN-like clusters. The inhomogeneous distribution of cluster sizes leads to the anomalous behavior of temperature-dependence PL peak energy and the blueshift of PL with increasing excitation power density. Similar to other

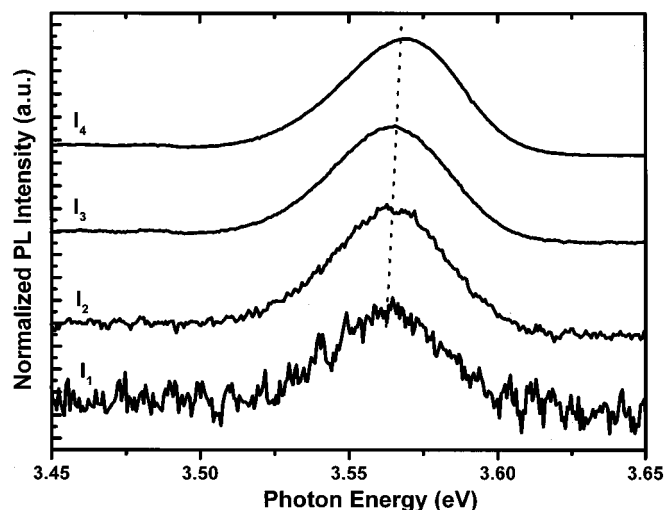


FIG. 4. Excitation intensity dependence of the PL spectra of the lattice-matched sample taken at 15 K. The PL energy increases with increasing excitation intensity I , where I_1 , I_2 , I_3 , and I_4 are 0.007, 0.035, 0.126, and 0.4 W cm^{-2} .

nitride alloys, our results thus support the fact that the clusters due to phase segregation can strongly influence the optical properties of $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ quaternary alloys.

This work was partly supported by the National Science Council and Ministry of Education of Republic of China.

- ¹M. A. Khan, A. Bhattarai, J. N. Kuznia, and D. T. Olson, *Appl. Phys. Lett.* **63**, 1214 (1993).
- ²H. Morkoc, S. Strite, G. B. Gao, M. E. Lin, B. Sverdlov, and M. Burns, *J. Appl. Phys.* **76**, 1363 (1994).
- ³S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H. Kiyoko, and Y. Sugimoto, *Jpn. J. Appl. Phys., Part 2* **35**, L74 (1996).
- ⁴C. H. Chen, Y. F. Chen, A. Shih, S. C. Chen, and H. X. Jiang, *Appl. Phys. Lett.* **78**, 3035 (2001).
- ⁵D. R. Hang, C. H. Chen, Y. F. Chen, H. X. Jiang, and J. Y. Lin, *J. Appl. Phys.* **90**, 1887 (2001).
- ⁶Y. Narukawa, Y. Kawakami, M. Funato, S. Fujita, S. Fujita, and S. Nakamura, *Appl. Phys. Lett.* **70**, 981 (1997).
- ⁷S. Chichibu, T. Azuhata, T. Sota, and S. Nakamura, *Appl. Phys. Lett.* **70**, 2822 (1997).
- ⁸H. C. Yang, P. F. Kuo, T. Y. Lin, and Y. F. Chen, K. H. Chen, L. C. Chen, and J.-I. Chyi, *Appl. Phys. Lett.* **76**, 3712 (2000).
- ⁹M. E. Aumer, S. F. LeBoeuf, S. M. Bedair, M. Smith, J. Y. Lin, and H. X. Jiang, *Appl. Phys. Lett.* **77**, 821 (2000).
- ¹⁰M. A. Khan, J. W. Yang, G. Simin, R. Gaska, M. S. Shur, G. Tamulaitis, A. Zukauskas, D. J. Smith, D. Chandrasekhar, and R. Bicknell-Tassius, *Appl. Phys. Lett.* **76**, 1161 (2000).
- ¹¹T. N. Odgers, J. Li, J. Y. Lin, and H. X. Jiang, *Appl. Phys. Lett.* **77**, 791 (2000).
- ¹²J. Li, K. B. Nam, K. H. Kim, J. Y. Lin, and H. X. Jiang, *Appl. Phys. Lett.* **78**, 61 (2001).
- ¹³T. Matsuoka, *J. Cryst. Growth* **189**, 19 (1998).
- ¹⁴I.-H. Ho and G. B. Stringfellow, *Appl. Phys. Lett.* **69**, 2701 (1996).
- ¹⁵H. Siegle, G. Kaczmarczyk, L. Filippidis, A. P. Litvinchuk, A. Hoffmann, and C. Thomsen, *Phys. Rev. B* **55**, 7000 (1997).
- ¹⁶G. Wei, J. Zi, K. Zhang, and X. Xie, *J. Appl. Phys.* **82**, 4693 (1997).
- ¹⁷J. Wagner, A. Ramakrishnan, H. Obloh, and M. Maier, *Appl. Phys. Lett.* **74**, 3863 (1999).
- ¹⁸D. Behr, R. Niebuhr, J. Wagner, K.-H. Bachem, and U. Kaufmann, *Appl. Phys. Lett.* **70**, 363 (1997).
- ¹⁹F. Demangeot, J. Groenen, J. Frandon, M. A. Renucci, O. Briot, S. Clur, and R. L. Aulombard, *Appl. Phys. Lett.* **72**, 2674 (1998).
- ²⁰H. Nashiki, I. Suemune, H. Suzuki, T. Obinata, K. Vesugi, and J. Nakahara, *Appl. Phys. Lett.* **70**, 2350 (1997).
- ²¹P. G. Eliseev, P. Perlin, J. Lee, and M. Osinski, *Appl. Phys. Lett.* **71**, 569 (1997).