

# Unique optical properties of AlGa<sub>x</sub>N alloys and related ultraviolet emitters

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Deep UV photoluminescence spectroscopy has been employed to study the optical properties of Al<sub>x</sub>Ga<sub>1-x</sub>N alloys ( $0 \leq x \leq 1$ ). The emission intensity with polarization of  $\mathbf{E} \perp \mathbf{c}$  and the degree of polarization were found to decrease with increasing  $x$ . This is a consequence of the fact that the dominant band edge emission in GaN (AlN) is with polarization of  $\mathbf{E} \perp \mathbf{c}(\mathbf{E} \parallel \mathbf{c})$ . Our experimental results suggest that the decreased emission efficiency in Al<sub>x</sub>Ga<sub>1-x</sub>N alloys and related UV emitters could also be related with their unique polarization property, i.e., the intensity of light emission with polarization of  $\mathbf{E} \perp \mathbf{c}$  decreases with  $x$ . It is thus concluded that UV emitters with AlGa<sub>x</sub>N alloys as active layers have very different properties from InGa<sub>x</sub>N and other semiconductor emitters. © 2004 American Institute of Physics. [DOI: 10.1063/1.1765208]

Recently, AlGa<sub>x</sub>N alloys, particularly Al-rich AlGa<sub>x</sub>N alloys have attracted much interest due to their applications in solid-state UV light sources for bioagent detection as well as for general lighting. However, it is well documented that the emission efficiency in Al<sub>x</sub>Ga<sub>1-x</sub>N alloys decreases with increasing  $x$ .<sup>1,2</sup> The efficiency of UV emitters using AlGa<sub>x</sub>N alloys as active layers is also lower than that of blue emitters using InGa<sub>x</sub>N alloys as active layers.<sup>3-5</sup> Recently, the properties of the fundamental optical transitions in AlN have been reported.<sup>6-8</sup> The band structure of wurzite AlN near the  $\Gamma$  point was found to be very different from GaN.<sup>8</sup> The recombination between the conduction band electrons and the holes in the top valence band is polarized along the direction of  $\mathbf{E} \parallel \mathbf{c}(\mathbf{E} \perp \mathbf{c})$  in AlN (GaN).<sup>8,9</sup> The unusual valence band structure of AlN gives rise to unique optical properties of AlGa<sub>x</sub>N alloys and their associated UV emitters.

In this letter, we present the results of the optical properties of Al<sub>x</sub>Ga<sub>1-x</sub>N alloys ( $0 \leq x \leq 1$ ). The 1- $\mu\text{m}$ -thick undoped AlGa<sub>x</sub>N epilayers were grown by metalorganic chemical vapor deposition (MOCVD) on sapphire (0001) substrates with low temperature AlN buffer layers. Trimethylgallium and trimethylaluminum were used as Ga and Al sources, respectively. The  $x$ -ray diffraction and secondary ion mass spectroscopy measurements (performed by Charles Evan & Associates) were employed to determine Al contents. The as-grown Al<sub>x</sub>Ga<sub>1-x</sub>N epilayers exhibited low degree of  $n$ -type conduction for  $x < 0.45$ . For GaN ( $x=0$ ), the unintentional carrier concentration was about  $6 \times 10^{16} \text{ cm}^{-3}$  and mobility was about  $650 \text{ cm}^2/\text{V s}$ . For  $x > 0.45$ , the conductivity of the films could not be measured. The deep UV laser spectroscopy system used for photoluminescence (PL) studies consisted of a frequency quadrupled 100 fs Ti: sapphire laser with an excitation photon energy set around 6.28 eV (with a 76 MHz repetition rate, a 3 mW average power, and vertical polarization), a monochromator (1.3 m), and a streak camera with detection capability ranging from 185 to 800 nm and time resolution of 2 ps.<sup>10</sup> The experimental geometry was depicted in the inset of Fig. 1, where the PL emission with either  $\mathbf{E} \parallel \mathbf{c}$  or  $\mathbf{E} \perp \mathbf{c}$  polarization orientation can be collected using a polarizer in front of the monochromator.

Figure 1 shows the low temperature (10 K) PL spectra for Al<sub>x</sub>Ga<sub>1-x</sub>N alloys ( $0 \leq x \leq 1$ ). We attribute the dominant emission lines to the localized exciton recombination.<sup>1</sup> The dotted (solid) lines indicate the emission spectra, collected with the polarization of  $\mathbf{E} \perp \mathbf{c}(\mathbf{E} \parallel \mathbf{c})$ . Several features are evident: (a) the emission peak position increases with increasing  $x$  for both polarization components and (b) the PL emission intensity,  $I_{\text{PL}}$ , decreases with increasing  $x$  for  $\mathbf{E} \perp \mathbf{c}$  polarization component. The PL emission component evolves for  $\mathbf{E} \perp \mathbf{c}$  being dominant for GaN to  $\mathbf{E} \parallel \mathbf{c}$  for AlN. The bowing parameter for AlGa<sub>x</sub>N alloys can be obtained by fitting data with the equation  $E_g(x) = (1-x)E_g(\text{GaN}) + xE_g(\text{AlN}) - bx(1-x)$ . The bowing parameter is determined to be  $b = 0.86 \text{ eV}$ , which is in good agreement with previous reported values.<sup>11-13</sup> It is interesting to note that we did not observe the PL spectral peak position shift between the  $\mathbf{E} \perp \mathbf{c}$  and  $\mathbf{E} \parallel \mathbf{c}$  components, as expected for the free electron-hole transition. This is primarily due to the fact that the exact selection rule only applies to the free-hole transition at  $\Gamma = 0$ , without considering the excitonic effect. The forbidden transition is not totally forbidden in the presence of the excitonic effect. Instead, one expects the forbidden transition appears at

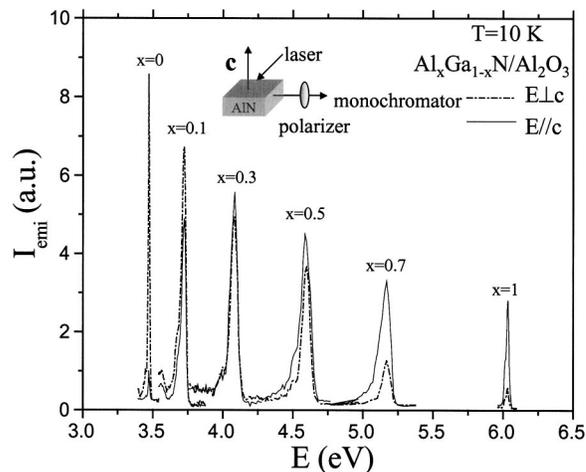


FIG. 1. Low temperature (10 K) PL spectra of Al<sub>x</sub>Ga<sub>1-x</sub>N alloys of varying  $x$ , for from  $x=0$  to 1. The experimental geometry was depicted in the inset, where the electrical field of PL emission ( $\mathbf{E}$ ) can be selected either parallel ( $\parallel$ ) or perpendicular ( $\perp$ ) to the  $\mathbf{c}$  axis.

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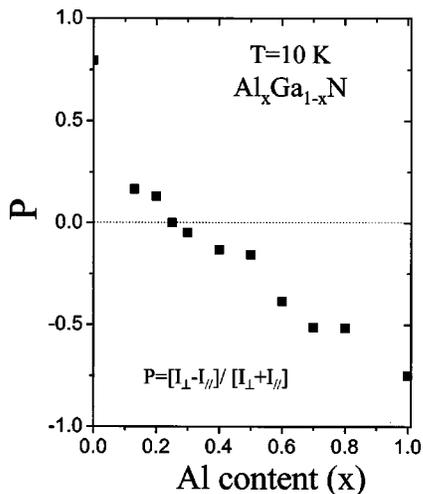


FIG. 2. The degree of polarization  $P$  vs  $x$  in  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  alloys.

the same energy position as the allowed transition, but with weaker emission intensity.<sup>14</sup> Moreover, strain effect and substrate misorientation can also relax the selection rule.

The degree of polarization ( $P$ ) is defined by  $P = (I_{\perp} - I_{\parallel}) / (I_{\perp} + I_{\parallel})$ , where  $I_{\perp}$  and  $I_{\parallel}$  are the integrated PL intensities for the polarization components of  $\mathbf{E} \perp \mathbf{c}$  and  $\mathbf{E} \parallel \mathbf{c}$ , respectively. Figure 2 plots  $P$  as a function of  $x$ .  $P$  decreases almost linearly with increasing  $x$ , and  $P=0$  at  $x=0.25$ . The representative band structures near the  $\Gamma$  point of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  alloys are depicted in Fig. 3 for (a)  $x=0$ , (b)  $x=0.25$ , and (c)

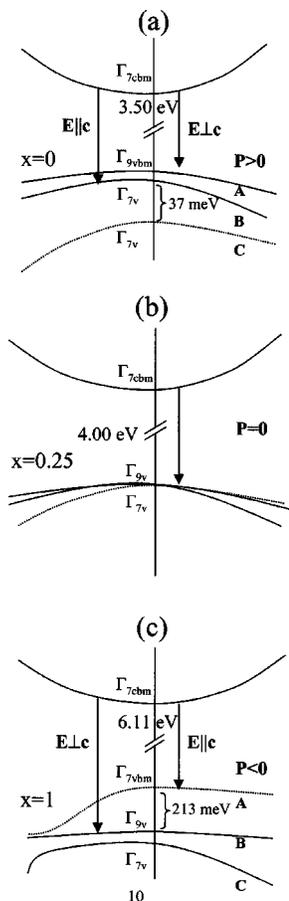


FIG. 3. The band structures near the  $\Gamma$  point of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  alloys for (a)  $x=0$ , (b)  $x=0.25$ , and (c)  $x=1$ .

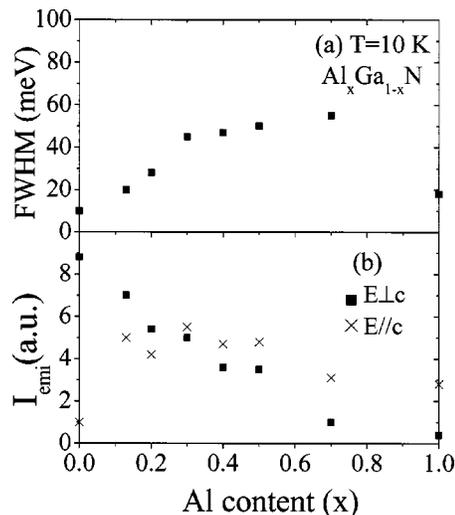


FIG. 4. (a) The FWHM of PL vs  $x$  in  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  alloys at 10 K. (b) PL emission intensities for  $\mathbf{E} \perp \mathbf{c}$  and  $\mathbf{E} \parallel \mathbf{c}$  vs  $x$  in  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  alloys measured at 10 K.

$x=1$ . The conduction bands have  $\Gamma_7$  symmetry in both AlN and GaN. Compared with the band structure of GaN, the most significant difference in AlN is the negative crystal-field splitting  $\Delta_{\text{CF}}$  ( $-219$  meV) compared with a positive value ( $+38$  meV) in GaN.<sup>8</sup> Because of this large negative  $\Delta_{\text{CF}}$  in AlN, the order of the valence bands in AlN is different from that in GaN. The top valence band has  $\Gamma_9$  ( $\Gamma_7$ ) symmetry in GaN (AlN) because of the positive (negative)  $\Delta_{\text{CF}}$ . Therefore, light emission due to the recombination between the conduction band electrons and the holes in the top valence band is polarized with  $\mathbf{E} \parallel \mathbf{c}$  in AlN, which is in contrast to that in GaN ( $\mathbf{E} \perp \mathbf{c}$ ). This unique band structure of AlN affects acutely the optical properties of AlGaN alloys, in particular of Al-rich AlGaN alloys. When Al content is increased from  $x=0$  to 0.25, the valence band with  $\Gamma_7$  symmetry evolves as the lowest valence band (C band) in GaN to the topmost valence band (A band) in  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  alloys ( $x > 0.25$ ). At  $x=0.25$ , three valence bands become degenerated at the  $\Gamma$  point and the degree of polarization  $P$  is thus zero.

Figure 4(a) shows the full width at half maxima (FWHM) of PL emission spectra of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  alloys versus  $x$  measured at 10 K. FWHM increases with increasing  $x$  and decreases again as  $x$  further increase from  $x=0.7$  to 1. The values of the PL linewidths we measure agree very well with those calculated using a model in which the broadening effect is assumed to be due to compositional disorder in completely random semiconductor alloys.<sup>15,16</sup> Figure 4(b) shows the variation of the integrated PL emission intensity of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  alloys with the Al content,  $I_{\text{PL}}$  vs  $x$ , measured at 10 K for both polarization orientations of  $\mathbf{E} \perp \mathbf{c}$  and  $\mathbf{E} \parallel \mathbf{c}$ . The emission intensity for  $\mathbf{E} \perp \mathbf{c}$  component decreases with increasing  $x$ , while  $I_{\text{PL}}$  for  $\mathbf{E} \parallel \mathbf{c}$  component decreases slightly with increasing  $x$  except for GaN. Our experimental results shown in Fig. 4(b) suggest that the unique optical property of AlGaN alloys is also partly responsible for the lower emission efficiency in  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  alloys and related UV emitters with higher  $x$ , i.e., the emission intensity of light with  $\mathbf{E} \perp \mathbf{c}$  decreases with increasing  $x$ . The fact that the emission intensity of the  $\mathbf{E} \parallel \mathbf{c}$  component is almost independent of  $x$  seems to preclude the dislocations and nonradiative centers being

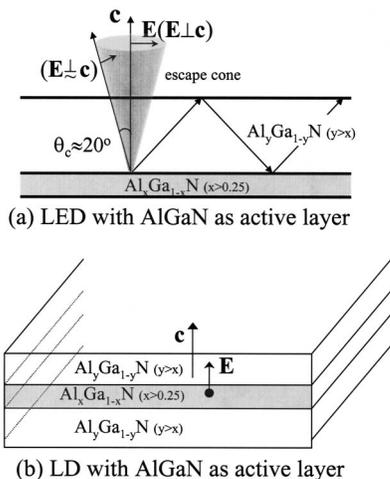


FIG. 5. (a) Schematic diagram of UV LEDs with  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  alloys as active layers. The light escape cone is about  $\theta_c \approx 20^\circ$ , within which any photons extracted are nearly polarized perpendicular to the  $c$  axis. (b) Schematic diagram of LDs with  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  alloys as active layers. In contrast with other semiconductor LDs with TE being the dominant models the TM mode is expected to be the dominant mode in AlGaIn UV LEDs.

the dominant cause for the reduced emission efficiency in  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  alloys with increasing  $x$ , as measured from the surfaces of the epilayers.

In terms of implications of our findings on device applications, the most significant effects include (i) the power output of light emitting diodes (LEDs) decreases and (ii) the light guiding for edge-emitting laser diodes (LDs) with a predominantly TM mode enhances with an increase of the Al content if AlGaIn alloys are being used as active layers, due to the negative crystal-field induced unique polarization property of AlGaIn alloys.

It is well known in conventional LEDs that the extraction efficiency is only about 5% from each side due to internal reflection. The light can only escape from the top and bottom surfaces when it is within a cone of about  $\theta_c \approx 20^\circ$ , where  $\theta_c$  is the critical angle of total internal reflection. For all types of existing LEDs from near infrared to blue color, emitted photons in this cone are able to escape since the polarization of emitted light is mainly perpendicular to the crystal axis within this cone ( $\mathbf{E} \perp \mathbf{c}$ ).<sup>17</sup> However, for UV LEDs using  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  ( $x > 0.25$ ) as active layers, the most dominant emission will be photons with polarization parallel to the  $c$  axis ( $\mathbf{E} \parallel \mathbf{c}$ ), which implies that UV photons can no longer be extracted easily from the escaping cone. Figure 5(a) illustrates this situation for UV LEDs using  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  alloys as active layers. The light escape cone is about  $\theta_c \approx 20^\circ$ , within which any photons extracted are nearly polarized perpendicular to the  $c$  axis ( $\mathbf{E} \perp \mathbf{c}$ ). Since the  $\mathbf{E} \perp \mathbf{c}$  emission component in Al-rich  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  alloys is almost forbidden, we thus emphasize that finding methods for enhancing the light extraction is more critical in UV LEDs with  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  active layers than in blue/green LEDs with InGaIn/GaN active layers. Techniques for extracting light of transverse propagation such as  $\mu$ -LEDs,<sup>18</sup> photonic crystals,<sup>19</sup> and other methods are not only recommended but also necessary for future high power short wavelength nitride UV emitters.

For edge-emitting LDs based on AlGaIn alloys, since light cannot leak out from the top and bottom layers due to their unique polarization property, the guiding effect is thus enhanced. Figure 5(b) shows the schematic diagram of LDs with  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  alloys as active layers. The transverse-electric TE mode is usually the dominant laser emission in all other semiconductor LDs, where the electric field of the mode is parallel to the layer interfaces. However, for LDs with  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  as active layers ( $x > 0.25$ ) the TM mode should be the dominant laser emission, in which the magnetic field is parallel to the layer interfaces.

In summary, we have investigated the optical properties of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  epilayers grown on sapphire by MOCVD. The dominant PL emission of GaN is with polarization of  $\mathbf{E} \perp \mathbf{c}$  while that of AlN is with polarization of  $\mathbf{E} \parallel \mathbf{c}$ . The emission intensity with polarization of  $\mathbf{E} \perp \mathbf{c}$  as well as the degree of polarization decreases with increasing  $x$ . It is argued that the poor emission efficiency of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  alloys and related UV emitters is also partly related with the unique optical property of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  alloys, i.e., the emission intensity of light with polarization of  $\mathbf{E} \perp \mathbf{c}$  decreases with  $x$ . UV emitters with AlGaIn alloys as active layers thus have very different properties than other existing semiconductor emitters.

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<sup>1</sup>H. S. Kim, R. A. Mair, J. Li, J. Y. Lin, and H. X. Jiang, Appl. Phys. Lett. **76**, 1252 (2000).

<sup>2</sup>K. B. Nam, J. Li, M. L. Nakarmi, J. Y. Lin, and H. X. Jiang, Appl. Phys. Lett. **81**, 1038 (2002).

<sup>3</sup>V. Adivarahan, J. Zhang, A. Chitnis, W. Shuai, J. Sun, R. Pachipulusu, M. Shatalov, and M. A. Khan, Jpn. J. Appl. Phys., Part 2 **41**, L435 (2002).

<sup>4</sup>A. Chitnis, J. Zhang, V. Adivarahan, W. Shuai, J. Sun, R. Pachipulusu, M. Shatalov, J. W. Yang, G. Simin, and M. A. Khan, Jpn. J. Appl. Phys., Part 2 **41**, L450 (2002).

<sup>5</sup>A. Yasan, R. McClintock, K. Mayes, D. Shiell, L. Gautero, S. R. Darvish, P. Kung, and M. Razeghi, Appl. Phys. Lett. **83**, 4701 (2003).

<sup>6</sup>J. Li, K. B. Nam, M. L. Nakarmi, J. Y. Lin, and H. X. Jiang, Appl. Phys. Lett. **81**, 3365 (2002).

<sup>7</sup>K. B. Nam, J. Li, M. L. Nakarmi, J. Y. Lin, and H. X. Jiang, Appl. Phys. Lett. **82**, 1694 (2003).

<sup>8</sup>J. Li, K. B. Nam, M. L. Nakarmi, J. Y. Lin, H. X. Jiang, P. Carrier and S. H. Wei, Appl. Phys. Lett. **83**, 5163 (2003).

<sup>9</sup>D. C. Reynolds, D. C. Look, B. Jogai, A. W. Saxler, S. S. Park, and J. Y. Hahn, Appl. Phys. Lett. **77**, 2879 (2000).

<sup>10</sup><http://www.phys.ksu.edu/area/GaNgroup>.

<sup>11</sup>W. Shan, J. W. Ager III, K. M. Yu, W. Walukiewicz, E. E. Haller, M. C. Martin, W. R. McKinney, and W. Yang, J. Appl. Phys. **85**, 8505 (1999).

<sup>12</sup>S. R. Lee, A. F. Wright, M. H. Crawford, G. A. Peterson, J. Han, and R. M. Biefeld, Appl. Phys. Lett. **74**, 3344 (1999).

<sup>13</sup>Q. S. Paduana, D. W. Weyburne, L. O. Bouthilllette, S. Q. Wang, and M. Alexander, Jpn. J. Appl. Phys., Part 1 **41**, 1936 (2002).

<sup>14</sup>Y. Zhang, A. Mascarenhas, P. Ernst, F. A. J. M. Driessen, D. J. Friedman, K. A. Bertness, and J. M. Olson, J. Appl. Phys. **81**, 6365 (1997).

<sup>15</sup>G. Coli, K. K. Bajaj, J. Li, J. Y. Lin, and H. X. Jiang, Appl. Phys. Lett. **78**, 1829 (2001).

<sup>16</sup>G. Coli, K. K. Bajaj, J. Li, J. Y. Lin, and H. X. Jiang, Appl. Phys. Lett. **80**, 2907 (2002).

<sup>17</sup>H. Morkoc, S. Strite, G. B. Gao, M. E. Lin, B. Sverdlov, and M. Burns, J. Appl. Phys. **76**, 1363 (1994).

<sup>18</sup>S. X. Jin, J. Li, J. Y. Lin, and H. X. Jiang, Appl. Phys. Lett. **77**, 3236 (2000).

<sup>19</sup>T. N. Oder, J. Shukya, J. Y. Lin, and H. X. Jiang, Appl. Phys. Lett. **83**, 1231 (2003); T. N. Oder, K. H. Kim, J. Y. Lin, and H. X. Jiang, *ibid.* **84**, 466 (2004).