5-20-2002

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Publication Info

Published in *Applied Physics Letters*, Volume 80, Issue 20, 2002, pages 3730-3732.

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Citation: Applied Physics Letters **80**, 3730 (2002); doi: 10.1063/1.1481766
View online: http://dx.doi.org/10.1063/1.1481766
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/80/20?ver=pdfcov
Published by the AIP Publishing

Luminescence mechanisms in quaternary $Al_xIn_yGa_{1-x-y}N$ materials

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(Received 24 January 2002; accepted for publication 27 March 2002)

Low-temperature photoluminescence investigations have been carried out in the quaternary AlInGaN epilayers and AlInGaN/AlInGaN multiple quantum wells (MQWs) grown by pulsed metalorganic chemical-vapor deposition (PMOCVD). With increasing excitation power density, the emission peaks in both AlInGaN epilayers and MQWs show a strong blueshift and their linewidths increase. The luminescence of the samples grown by PMOCVD is attributed to recombination of carriers/excitons localized at band-tail states. We also demonstrate the luminescence properties of AlInGaN and AlGaN materials grown by a pulsed atomic-layer epitaxy and conventional MOCVD, respectively. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1481766]

III-nitride-based deep ultraviolet (UV) light-emitting diodes (LEDs) and laser diodes (LDs) are key for solid-state white-lighting and chembiodetection applications. They require the use of ternary $Al_xGa_{1-x}N$ or quaternary $Al_xIn_yGa_{1-x-y}N$ layers in the active region.[1–3] In the past, we reported deep-UV LEDs with peak emission wavelengths from 305 to 340 nm.[1,2,4–6] The active layers for these LEDs consisted of quaternary AlInGaN layers that were deposited on sapphire substrates using a pulsed atomic-layer epitaxy (PALE) procedure.[1,2,6] Recently, we have also reported on a pulsed metalorganic chemical-vapor deposition (PMOCVD) procedure.[7] The two procedures differed mainly in the group-V (NH_3) precursor supply. In PMOCVD, the group-III metalorganic (MO) precursors were pulsed and the NH_3 supply was kept on all the time, whereas in PALE both the MO and the NH_3 were pulsed and alternatively supplied in the growth chamber. High-quality quaternary AlInGaN layers would be grown by either of the two procedures. However, the spontaneous photoluminescence (PL) intensity of the PMOCVD layer was, in general, higher than that of the PALE-deposited material. In this letter, we present a detailed comparative study of the PL emission from quaternary AlInGaN epilayers and quaternary–alloy-based multiple quantum wells (MQWs) grown by the PMOCVD technique.

The quaternary samples used in this study were grown on a (0001)-oriented sapphire substrate by PMOCVD. The growth was carried out at a temperature of 750 °C by keeping a constant ammonia flux while pulsing trimethyl–aluminum (TMA), trimethyl–indium (TMIn), and triethyl–gallium (TEGa). Prior to the deposition of the quaternary AlInGaN epilayers or MQWs, about a 1-μm-thick intrinsic GaN epilayer was deposited on a sapphire substrate with a 25-nm-thick AlN buffer layer by using conventional low-pressure MOCVD. The AlInGaN layers and MQWs were grown by the PMOCVD process at 750 °C. In order to elucidate the effects of indium (In) incorporation in AlInGaN materials, bulk AlGaN epilayers grown by PMOCVD have been studied and compared with bulk AlInGaN epilayers. The quantum-well (QW) regions of the MQWs were made up of three QWs consisting of 5-nm-thick AlInGaN wells and 7-nm-thick AlInGaN barriers. Al molar fractions in the wells and barriers are about 10% and 16%, respectively, and In content in both wells and barriers does not exceed 2%. The composition of quaternary epilayers is identical with those of the well materials of the MQWs.

For PL measurements, the samples were mounted on a sample holder in a helium closed-circuit cryostat. The PL was measured by using a pulsed excimer laser ($\lambda = 193$ nm, $\tau = 8$ ns) as an excitation source. The luminescence was dispersed by a monochromator (SPEX550) and detected by a liquid-nitrogen-cooled charge-coupled-device array. The excitation power density dependence was controlled by using a set of UV neutral density filters. The maximum excitation power density of ~ 2 MW/cm^2 could be reached by focusing the laser beam on the surface of the sample to a spot of about 0.1 mm diam.

Figures 1(a) and 1(b) show the PL spectra of the $Al_{0.10}Ga_{0.90}N$ and $Al_{0.10}In_{0.02}Ga_{0.88}N$ epilayers, respectively, obtained under low (open circles, $I_{exc} = 2.1\times10^{-4}\ I_0$) and high (closed circles, $I_{exc} = I_0 = \sim 2$ MW/cm^2) excitation power densities at 10 K. The PL peak position in the AlGaN

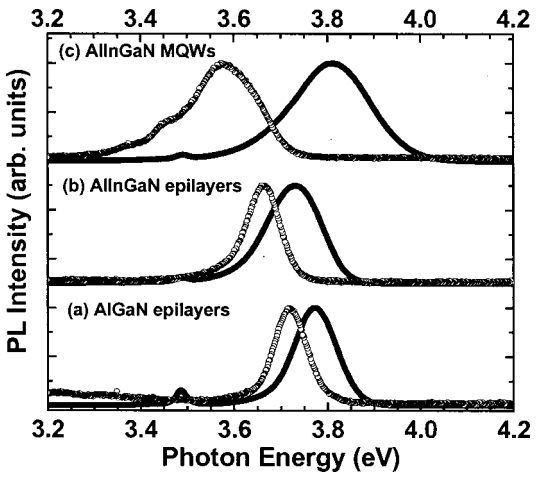

FIG. 1. Normalized PL spectra of the $Al_{0.10}Ga_{0.90}N$ epilayer (a), $Al_{0.10}In_{0.02}Ga_{0.88}N$ epilayer (b), and $Al_{0.10}In_{0.02}Ga_{0.88}N/Al_{0.16}In_{0.02}Ga_{0.82}N$ MQWs (c) obtained under low (open circles) and high (closed circles) excitation power densities at 10 K.

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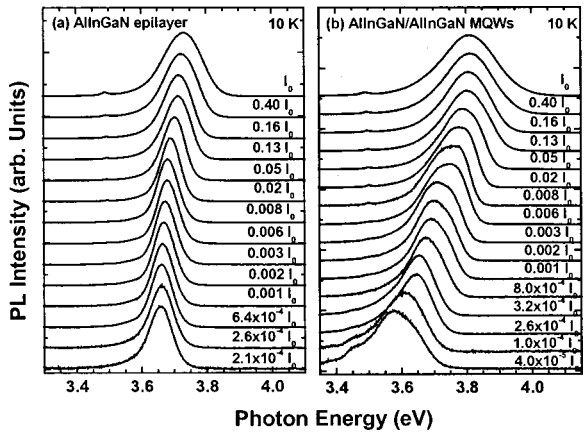

FIG. 2. PL spectra of the quaternary epilayer (a) and MQWs (b) for various excitation power densities at 10 K. All spectra are normalized and shifted vertically for clarity.

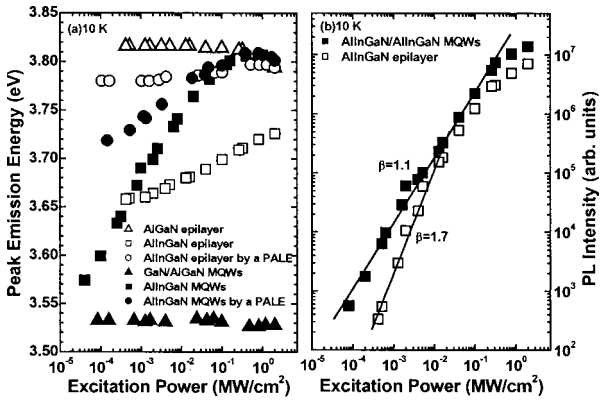

FIG. 3. Excitation power density dependence of the PL emission peak energy (a) and intensity (b) of the AlInGaN epilayer and MQWs measured at 10 K. In (a), the emission peak energies of the $Al_{0.13}Ga_{0.87}N$ epilayer and $GaN/Al_{0.08}Ga_{0.92}N$ MQWs have also been displayed for comparison.

(AlInGaN) epilayer is at about 3.72 (3.66) eV with a full width at half maximum (FWHM) of about 85 (86) meV under low excitation. The difference of the spectral peak positions in these two samples can be explained by the incorporation of In into the AlInGaN epilayer, or by slightly different Al uncontrolled composition in two samples although we intend to grow the same Al-containing samples. With increasing excitation power density from $2.1\times10^{-4}\ I_0$ to I_0, the emission peak position of the AlGaN (AlInGaN) layer shifts toward the high-energy side in the amount of 50 (70) meV. The FWHM of the emission peak for the AlGaN (AlInGaN) layer simultaneously increases from 85 (86) to 106 (139) meV. Figure 2(a) shows the PL spectra of the AlInGaN epilayer as a function of I_{exc} measured at 10 K. Incorporation of In into the quaternary AlInGaN epilayer resulted in a stronger PL maximum blueshift and larger FWHM broadening with excitation, lower peak emission energy, and higher emission intensity compared with those of a ternary AlGaN epilayer.

The blueshift and FWHM broadening of the PL spectra in alloy bulk materials with increasing I_{exc} can be explained by the band filling of band-tail states caused by spatial potential fluctuations due to alloy disorder.[8–10] From the above results, we have verified the presence of band-tail states in the AlGaN and AlInGaN bulk materials grown by PMOCVD. In addition, incorporation of In into AlInGaN material in order to fabricate smooth layers with strong PL emission creates more band-tail states, which cause a stronger excitation-induced blueshift and larger FWHM broadening of PL spectra for the AlInGaN epilayers than those for the AlGaN epilayer. On the other hand, we did not observe these phenomena for AlGaN samples grown by conventional MOCVD. Samples grown by PMOCVD at 750 °C have more inhomogeneous surfaces than samples grown at temperatures over 1000 °C required for conventional MOCVD. The growth at lower temperature may lead to the disordering of AlGaN, and thus to the formation of the band-tail states in the Al(In)GaN materials grown by PMOCVD. In addition to that, the AlInGaN bulk materials grown by PALE also show little or no blueshift with increasing I_{exc}, which means that the PALE technique does not create significant concentration of band-tail states.[11]

In Fig. 1(c), the PL peak position of the MQWs is at 3.57 eV with a FWHM of about 171 meV under low excitation ($I_{\text{exc}}=4.0\times10^{-5}\ I_0$). Compared to the bulk well material shown in Fig. 1(b), the MQWs show a 90 meV redshift and an 85 meV FWHM broadening of the emission band. With increasing I_{exc} from $4.0\times10^{-5}\ I_0$ to I_0, the emission peak of the MQWs also shifts toward the high-energy side from 3.57 to 3.81 eV, whereas the FWHM slightly increases from 171 to 175 meV.

Figures 2(a) and 2(b) show the PL spectra of the AlInGaN epilayer and MQWs, respectively, as a function of I_{exc} measured at 10 K. As I_{exc} increases from $2.1\times10^{-4}\ I_0$ ($4.0\times10^{-5}\ I_0$) to I_0 (I_0), the blueshift and FWHM broadening of the emission band of the epilayer (MQWs) are about 70 (240) and 53 (4) meV, respectively. As can be seen in Figs. 1 and 2, the blueshift of the MQWs is much stronger than that of the bulk well material while the FWHM broadening of the MQWs is much smaller than that of the bulk well material.

Figure 3(a) gives the emission peak energies of the AlInGaN epilayer (open squares) and MQWs (closed squares) grown by PMOCVD as a function of I_{exc}. The emission peak energies of the quaternary epilayer (open circles) and MQWs (closed circles) grown by the PALE technique and those of the $Al_{0.13}Ga_{0.87}N$ epilayer (open triangles) and $GaN/Al_{0.08}Ga_{0.92}N$ MQWs (closed triangles) grown by conventional MOCVD are shown in Fig. 3(a) for comparison. Unlike the quaternary samples, the emission peak energies of the AlGaN samples do not show any blueshift, but at high excitation a redshift due to band-gap renormalization is observed. In the case of the quaternary samples grown by PMOCVD, the emission peak energies of the epilayer and MQWs exhibit a strong blueshift. On the other hand, the quaternary epilayer and MQWs samples grown by PALE show dissimilar results such as little or no shift for the epilayer samples and a small blueshift for the MQWs. The active layers grown by the PALE process were found to have far fewer band-tail states and they exhibited predominantly UV band-to-band emission.[6,11]

The observed differences in the PL properties of the quaternary epilayers and MQWs arise from the quantum-confinement effects. In the MQWs, we should take into account the quantum-confined Stark effect (QCSE) caused by built-in internal electric fields due to spontaneous and piezo-

electric polarization[12,13] as well as the band-filling effect of band-tail states induced by alloy disorder and/or interface disorders.[8–10,14] The effects of the QCSE in the QW sample are a redshift and FWHM broadening of the peak in comparison with bulk material. As I_{exc} increases, the built-in electric field is screened, thus a blueshift and FWHM narrowing should be observed. This was obtained in the InGaN system.[15] Therefore, the FWHM of the MQWs, which is almost unchanged, is ascribed to the combined effects of the FWHM broadening due to band filling and the narrowing due to the screening of the QCSE. A strong blueshift of PL spectra of the MQWs grown by PMOCVD is also attributed to the combined results of band filling of tail states and the Coulomb screening of the internal electric field due to the intense optical excitation.

The PL intensities of the AlInGaN epilayer and MQWs as a function of I_{exc} are shown in Fig. 3(b). The PL emission intensities (I_{emi}) in both samples increase superlinearly with I_{exc}, following a power-law form, $I_{emi} \propto I_{exc}^{\beta}$. The exponent β is about 1.7 and 1.1 for the epilayer and MQWs, respectively. The superlinear increase of I_{emi} with I_{exc} has also been observed for localized exciton recombination in the InGaN epilayer[8] and InGaN/AlGaN single QW.[16] The dependence of I_{emi} on I_{exc} generally depends on whether radiative or nonradiative recombination dominates giving a slope between 1 and 2 in an intermediate case involving excitons and free carriers.[17] The smaller value of exponent β for the MQWs may be due to the localization of carriers/excitons at interfaces due to the QCSE and reduction of nonradiative decay of carriers/excitons. This should lead to the predominating radiative recombination and smaller slope exponent β.

We report the low-temperature PL investigation of the AlInGaN epilayers and MQWs grown by PMOCVD. The luminescence of the samples grown by PMOCVD is attributed to recombination of carriers/excitons localized at band-tail states, which is beneficial to obtain a strong spontaneous emission for UV LEDs. The obtained properties of AlInGaN materials for LEDs agree well with those in InGaN materials. This indicates that the AlInGaN system is promising materials for UV applications such as the InGaN system for blue LED and LD applications.

This work at USC was supported by the Ballistic Missile Defense Organization (BMDO) under Army SMDC Contract No. DASG60-98-1-0004, monitored by Terry Bauer, Dr. Brian Strickland, and Dr. Kepi Wu. This work was supported in part by a postdoctoral fellowship program from KOSEF.

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