

Deep ultraviolet emitting AlGa_N quantum wells with high internal quantum efficiency

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We report the development of Al_{0.7}Ga_{0.3}N/AlN quantum wells with high internal quantum efficiency. All samples had identical well and barrier thickness but the III/V flux ratio was varied during growth by increasing the Ga flux. The luminescence spectra show single peaks which vary from 220 nm (III/V ~ 1) to 250 nm (III/V ≫ 1) with internal quantum efficiency varying from 5% to 50%, respectively. To account for these results, a growth model was proposed in which at III/V ~ 1 the growth proceeds via vapor phase epitaxy, while at III/V ≫ 1 the growth proceeds via liquid phase epitaxy. © 2009 American Institute of Physics. [DOI: 10.1063/1.3130755]

High Al-content AlGa_N alloys and their quantum wells (QWs) can be used for the development of emitters in the deep-UV spectral region. The external quantum efficiency of deep UV light-emitting diodes was found to be relatively low (0.01%–0.2% at 250 nm).¹ This result can be accounted for by low internal quantum efficiency (IQE), current injection efficiency, light extraction efficiency, or a combination of these three factors. The IQEs at room temperature of AlGa_N alloys, with Al content varying from 10% to 60%, were reported to vary from 0.4% to 0.05%, respectively, as opposed to indium-containing nitride QWs emitting in the blue, with IQEs of 70%.² This is attributed to compositional inhomogeneities in the InGa_N alloys³ due to either spinodal decomposition^{4,5} or statistical fluctuations,² which give rise to potential fluctuations, leading to exciton localization and thus efficient radiative recombination.³ On the other hand, compositional inhomogeneities due to spinodal decomposition are not expected in AlGa_N alloys since Al and Ga atoms have the same ionic radius in tetrahedral environments. In this paper, we report the growth and characterization of Al_{0.7}Ga_{0.3}N/AlN multiple quantum wells (MQWs) emitting in the wavelength region 220 to 250 nm, with IQEs varying from 5% to 50%, respectively.

All samples were deposited on (0001) sapphire by plasma-assisted molecular beam epitaxy (PAMBE), using an rf plasma source for nitrogen activation. Growth was conducted using a three-step deposition process. First, the substrate was heated to 870 °C and exposed to nitrogen plasma. This nitridation process converted the surface of the sapphire to AlN, as was monitored by observing the reflection-high-energy electron diffraction pattern.^{6,7} A thick AlN film was then deposited at the same substrate temperature using an Al beam equivalent pressure of 5.1×10^{-7} Torr, a plasma power of 300 W, and a nitrogen flow rate of 1.2 SCCM (SCCM denotes standard cubic centimeter per minute), which lead to group III to group V ratio close to unity. On top of the 1- μ m-thick AlN layer, 100 pairs of Al_{0.7}Ga_{0.3}N/AlN MQWs were deposited at 770 °C. The thickness of the barriers and wells were 12 and 2–3 ML,

respectively. The group III to V flux ratio during growth of the AlN barriers was the same for all samples, while that for the AlGa_N wells was varied from close to unity to significantly greater than unity. This was done by keeping the Al flux for the well layer fixed at 3.8×10^{-7} Torr and increasing the Ga flux from 4.5×10^{-7} to 7.5×10^{-7} Torr. Indium was employed during the deposition of QWs in some samples to act as a surfactant.⁸ Prior to the growth of the MQWs, a series of bulk Al_{0.7}Ga_{0.3}N films were grown under similar conditions, and their composition as well as their optical gap were determined by x-ray diffraction and optical absorption measurements. All these bulk AlGa_N films were found to have the same composition (AlN mole fraction 72%) and the same optical gap (240 nm).^{9,10} Based on these results on bulk AlGa_N, we expect the AlGa_N wells to have the same composition.

The microstructure of the samples was determined by transmission electron microscopy (TEM) employing a JEM-4000 EX operating at 400 KV. The luminescence properties were studied by room and temperature-dependent cathodoluminescence and photoluminescence (PL) measurements. A Photon System He–Ag laser emitting at 224 nm was employed as an excitation source for PL measurements.

The normalized luminescence spectra from all samples are presented in Fig. 1. These data show that all MQW samples exhibit only a sharp near band-edge emission. It is important to stress that although the thicknesses and compositions of the wells and barriers were the same for all samples, the emission wavelengths vary from 220 to 250 nm as the Ga flux increased from III/V close to one to much greater than one. We also observed that the luminescence spectra of samples with wells grown under excess gallium were blueshifted if indium was employed as a surfactant.

To understand why the composition of the AlGa_N films is the same independent of the employed Ga flux, we refer to studies of the kinetics of growth for PAMBE of AlGa_N alloys by Iliopoulos and Moustakas.¹¹ These authors have reported that the kinetics of Al_xGa_{1-x}N growth is fundamentally different from the kinetics of Al_xGa_{1-x}As growth. They attributed this to the difference in Al–N and Ga–N bond strengths versus the closely similar Al–As and Ga–As bond

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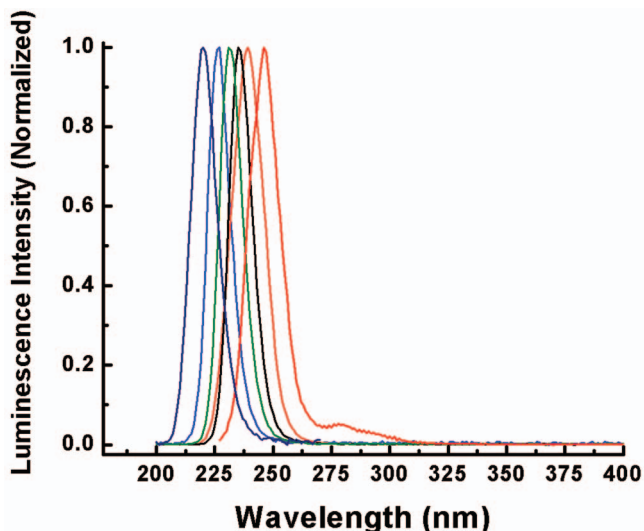


FIG. 1. (Color) Room-temperature luminescence from $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}/\text{AlN}$ MQWs, with identical well and barrier widths. All spectra consist of a single peak, which varies from 220 to 250 nm.

strengths. For the group III nitrides, Al incorporates with high probability in both group III and N-rich growth regimes. Thus, the incorporation of Ga is controlled solely by the available N flux that is not consumed by Al atoms. As a result, the Ga flux can be increased significantly without affecting the Al mole fraction of the films. The excess Ga forms a thin overlayer on the surface during growth. The steady state thickness of this liquid Ga layer is determined by the Ga arrival, incorporation, and evaporation rates, the latter being strongly dependent on the substrate temperature. Although the Ga overlayer on the surface does not incorporate and hence does not alter the alloy composition, the presence and thickness of this liquid Ga film must play an important role in the growth and optoelectronic properties of the final AlGa_{0.3}N alloy.

It remains now to explain as to why identical $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}/\text{AlN}$ MQWs with wells grown with different Ga flux emit at different wavelengths. To account for these results, we propose that the growth mechanism changes from a vapor phase epitaxy in the absence of excess Ga to a liquid phase epitaxy in the presence of excess Ga in the surface of the growing film as the Ga flux increases. In the latter case, the alloy growth proceeds by dissolving the arriving Al and active N species in the metallic Ga film, and the deposition

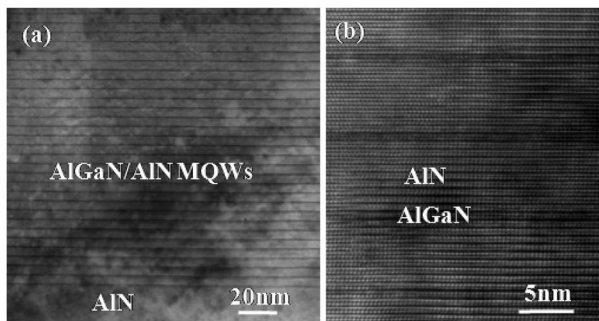


FIG. 2. (a) Bright-field TEM image showing the $\text{AlGa}_{0.3}\text{N}/\text{AlN}$ MQW structure. (b) High-resolution electron micrograph taken in $[11\bar{2}0]$ zone axis projection showing well-defined $\text{AlGa}_{0.3}\text{N}$ QWs and abrupt $\text{AlGa}_{0.3}\text{N}/\text{AlN}$ interfaces.

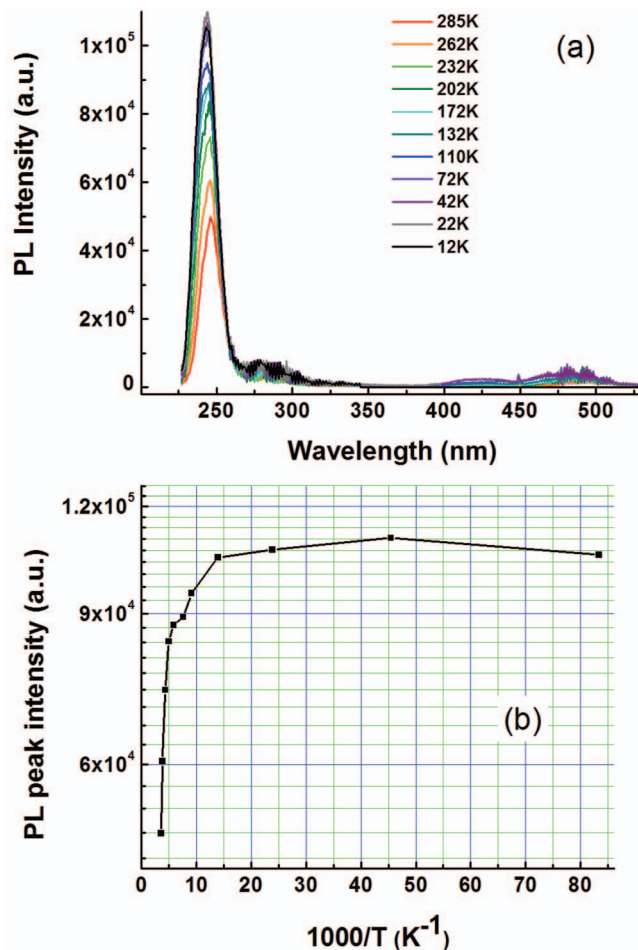


FIG. 3. (Color) (a) Temperature dependent PL spectra for the $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}/\text{AlN}$ MQW sample emitting at 250 nm, and (b) the integrated PL intensity vs inverse temperature for the same sample.

of the alloy proceeds from the liquid phase.¹² It should be pointed out that although the solubility of molecular N_2 in Ga at the growth temperature of AlGa_{0.3}N alloys is very low, the solubility of active N (atomic, anionic and N_2^*) is expected to be very high. In this growth mode, deposition in the growing front occurs when the Ga solution is saturated with N and Al, and this unavoidably leads to vertical and lateral compositional inhomogeneities in the film. For example, we have reported previously that bulk AlGa_{0.3}N films grown under Ga-rich conditions were found to exhibit ordered superlattice structures that are incommensurate with the wurtzite crystal lattice.⁹ Furthermore, the same AlGa_{0.3}N films exhibit strong Stokes shift in the luminescence peak compared to the absorption edge, a result also consistent with compositional inhomogeneities in the films.¹⁰ Thus, the observed redshift in the luminescence spectra from 220 to 250 nm from $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}/\text{AlN}$ MQWs with identical well and barrier widths is attributed to the compositional inhomogeneities introduced during growth of the wells under excess Ga. Consistent with this interpretation is also the increase in the spectral width from 11 to 16 nm.

A potential explanation of the observed blueshift in the luminescence spectra of the $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}/\text{AlN}$ MQWs, when the wells are grown under excess Ga as well as indium, is the surfactant action of indium.⁸ We postulate that the films produced this way have less compositional inhomogeneities, which cause the redshift in the luminescence spectra.

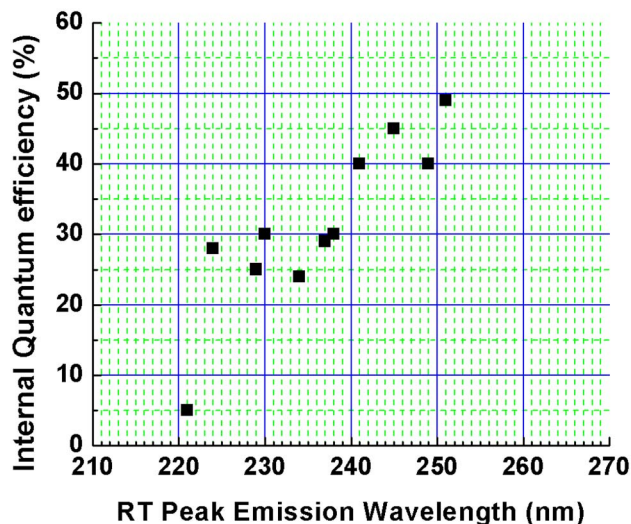


FIG. 4. (Color online) IQE for all $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}/\text{AlN}$ MQWs investigated. The IQE of these nominally identical MQWs varies from 5% at 220 nm to 50% at 250 nm.

Figure 2 shows cross-sectional TEM micrographs of a MQW sample which was deposited under a group III to group V ratio close to unity, using indium as a surfactant. Figure 2(a) is a relatively low magnification image, which shows the AlN buffer and the plurality of the QWs. The quality of the heterointerfaces does not degrade with the increasing number of QWs, and the QWs are very flat, indicating that the growth surface was atomically smooth throughout the deposition process. The high-resolution image presented in Fig. 2(b) shows sharp, distinct, and flat QWs with well widths of 2–3 ML and barriers of 12 ML.

The brightness of the AlGaN/AIN QWs is a function of the IQE as well as the light extraction efficiency. Experimental and theoretical results show that light extraction from the surface of (0001) AlGaN alloys depends strongly on the alloy composition due to changes in the band structure.^{13,14} In this paper, however, we are addressing only the IQE, which is measured by taking the ratio of the luminescence intensity at room temperature to that measured at low temperature.

Figure 3 presents the temperature-dependent PL spectra for the $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}/\text{AlN}$ MQWs emitting at 250 nm, as well as the integrated PL intensity as a function of inverse temperature. The IQE, as measured by the ratio of PL intensity at room temperature to that measured at 11 K, is 50%. The IQEs for the samples discussed in Fig. 1 are presented in Fig.

4. Thus, the IQE for these MQWs varies from 5% for emission at 220 nm, to 50% for emission at 250 nm. This increase in the IQE for $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}/\text{AlN}$ MQWs with identical well and barrier widths is attributed to the localization of the excitons due to the compositional inhomogeneities introduced during the growth of the wells under excess Ga.

In conclusion, we have reported the growth by PAMBE and characterization of $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}/\text{AlN}$ MQWs with identical well and barrier widths grown under different amounts of excess Ga. The luminescence spectra from these nominally identical MQWs vary from 220 to 250 nm as the Ga flux during growth increases. Furthermore, the IQE of the same samples increases from 5% to 50%, respectively. To account for these observations, as well as the relatively high IQE, we have proposed a model in which growth of the well under excess Ga occurs via liquid phase rather than vapor phase epitaxy. These results demonstrate that the AlGaN alloys hold the same promise as InGaN alloys for the development of deep-UV optoelectronic devices.

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