2004

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Ramaiah, K.S., Su, Y.K., Chang, S.J., et al. Characterization of InGaN/GaN multi-quantum-well blue-light-emitting diodes grown by metal organic chemical vapor deposition. Applied Physics Letters, 84, 3307 (2004). Copyright © 2004 AIP Publishing LLC.

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APPLIED PHYSICS LETTERS VOLUME 84, NUMBER 17 26 APRIL 2004

Characterization of InGaN/GaN multi-quantum-well blue-light-emitting diodes grown by metal organic chemical vapor deposition

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(Received 5 December 2003; accepted 9 March 2004)

The structural, surface morphology, and the temperature dependence photoluminescence of InGaN(3 nm)/GaN(7 nm) 5 period multi-quantum-well blue-light-emitting diode (LED) structures grown by metal organic chemical vapor deposition (MOCVD) have been studied. Quantum dot-like structures and strain contrast evident by black lumps were observed in the quantum wells using high-resolution transmission electron microscopy (HRTEM) analysis. Double-crystal high-resolution x-ray diffraction (HRXRD) spectra of blue LED were simulated using kinematical theory method, to obtain composition, and period thickness of well and barrier. The ''S'' shape character shift as red–blue–redshift of the quantum-well emission line, i.e., blue emission peak 2.667 eV at 10 K, was observed with variation of temperature in the photoluminescence (PL) spectra. The shift is assigned to the potential fluctuations due to alloy inhomogeneous distribution in the quantum wells. The In composition in the quantum wells obtained by two independent techniques, namely HRXRD and PL, was 8% and 19%, respectively. The reason for this large difference in composition is explained in this letter. [DOI: 10.1063/1.1728302]

Nitride-based blue and green light-emitting diodes illuminating with high brightness are now commercially available, despite high dislocation density of 10^8–10^9 cm^{-2} in the epilayers.[1] The InGaN/GaN multi-quantum-well structures are being used as active layers in the light-emitting diodes (LED) because the emission spectrum can be tailored from ultraviolet to visible region by varying In composition. The blue LEDs, which showed higher efficiency than that of green LEDs, have been widely used in the communication and information technologies. The In mole fraction of 0.1–0.2 and 0.45 is required for blue and green LEDs, respectively. The phase separation or segregation of In is a major problem in the InGaN system due to solid phase immiscibility between InN and GaN. This segregation is due to a large difference in interatomic spacing, and other physical properties such as thermodynamical and chemical instabilities, etc., which are very different between InN and GaN. The experimental and theoretical studies revealed that the solid-phase immiscibility is high in InGaN.[2] At normal growth temperatures, the alloy is unstable over the entire composition. The formation of phase separation leads to a quantum dot-like structure, which is highly beneficial to obtain high external quantum efficiency from the InGaN/GaN LEDs structures.[3] Due to a lack of understanding of this phase segregation, LED structures have to be investigated with respect to structural, optical properties, etc., to know the role of In in the wells.

The blue LEDs studied were prepared on c-plane sapphire substrates by using conventional MOCVD technique. The GaN buffer layer with thickness of 25 nm was grown at a low temperature of 560 °C, followed by 2 μm thick Si-doped GaN layer at a higher temperature of 1060 °C, on which a 5 period of 3 nm InGaN well (W)/7 nm GaN barrier (B) was grown at a temperature of 780 °C using N_2 only as a carrier gas. This structure was capped with p-GaN having a thickness of 0.5 μm. Trimethyl-gallium, trimethyl-indium, and NH_3 were used as precursors for Ga, In, and radical nitrogen, respectively. N_2 and H_2 were chosen as carrier gases to grow layers. The entire deposition process was described in detail elsewhere.[4]

The samples were mechanically polished and then thinned by employing Ar^+ laser to study their microstructures. Philips transmission electron microscope was operated at 200 kV to obtain structural data. Crystal structure was characterized using a Philips X-pert double-crystal x-ray diffractometer with Ge (220) single crystal, operated at 40 kV and 50 mA with radiation of 1.540 56 Å. Nanoscope atomic microscope was used to scan the surface of the LED structure. For PL measurements, a He–Cd laser operated at 325 nm, a GaAs-based photodetector used to record excited emission, and a closed-loop He cryostat for low temperature were employed.

AFM analysis showed the root-mean-square (rms) surface roughness of 1 nm of the quantum well sample. TEM analysis revealed that an average width of the period was found to be 10.2 nm, i.e., well width ~3 nm and barrier width ~7.2 nm from a micrograph. Figure 1(a) shows dark contrast regions formed between the intermixing of InGaN quantum wells and GaN barriers by relaxation of strain, known as strain contrast. The quantum dot-like structures are

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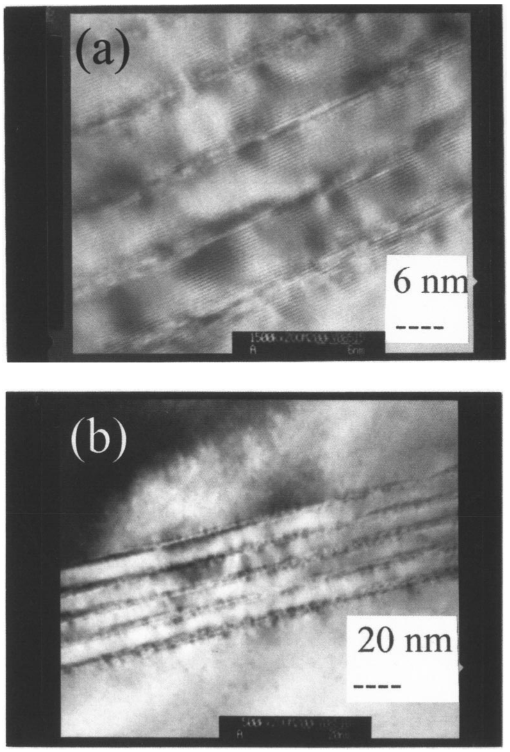

FIG. 1. Transmission electron micrographs of quantum-well structure: (a) high-resolution transmission electron micrograph bright field images, showing well and barrier width of 10.2 nm, black contrast resulting in strain between the well and barrier regions, and (b) quantum dot-like structures very clearly visible in the well regions.

clearly visible in the well regions but not in the barriers, as shown in Fig. 1(b). The formation of quantum dot-like structure in the InGaN multiquantum well is evident due to the low miscibility of InN in GaN.

The experimental $\omega/2\theta$ XRD scan for LED structure was simulated by using the kinematical theory method, which gave an approximate average indium composition of 8% in the wells, as shown in Fig. 2. Surprisingly, PL analysis indicated an In composition of ~19% in the wells. The anomalous behavior could be a quantum-confined Stark effect (QCSE)[5] due to piezoelectric field caused by strain between well and barrier. In general, the intense PL emission is provided by the quantum dot-like structures, which have efficient radiative recombination centers when compared to the usual layers. The In-rich GaN matrix favors longer wavelength emission, whereas XRD analysis showed an approximate average In composition in the well layers giving a lower value. Tran *et al.*[6] also observed that In composition in the multiquantum well structures is less than that in the individual or usual InGaN layers. The width of the period (well and barrier) was determined to be 10 nm by using the simple relation $n\lambda/[2(\sin\theta_i-\sin\theta_j)]$, where λ is the wavelength of x-ray radiation, θ_i, θ_j are angles of the adjacent i and j satellite peaks, and n is the order between the adjacent satellite peaks of i and j. The occurrence of well-resolved sharp diffraction or satellite peaks indicates that the interface between well and barrier is abrupt; however, the right-hand-side satellite peaks are less pronounced, which is common in quantum well structures because the periods are not in phase and unequal in compositions at micro levels. In the case of green LEDs, satellite peaks are less pronounced due to high-In composition fluctuations in the layers.

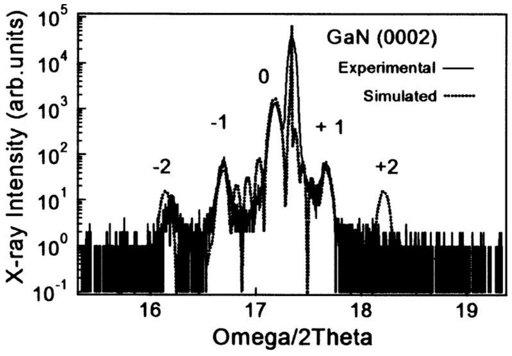

FIG. 2. Double-crystal x-ray diffraction spectrum $\omega/2\theta$ scan of the InGaN/GaN multi quantum-well blue LED structure: (a) Experimental (solid line) and (b) Simulation (dashed line), giving In composition of 8% in the wells.

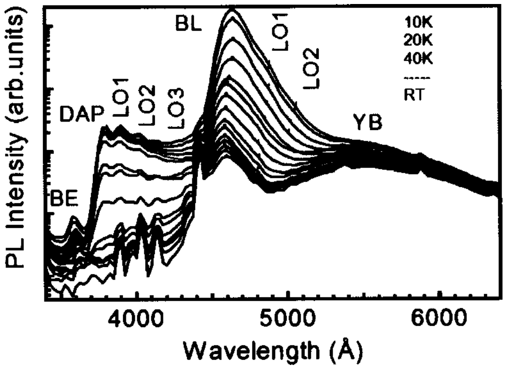

FIG. 3. PL spectra of the InGaN/GaN multi-quantum-well blue LED structure measured at different low temperatures; the quantum-well peak shows "S" shape character shift red–blue–redshift with variation of temperature.

In order to obtain blue emission (BL) at 465 nm (2.667 eV) from the LEDs, the required In mole fraction in the quantum well structures is 0.2. Recent results confirmed that the band gap of InN is ~0.77 eV with a bowing parameter determined to be 1.43, as shown in the equation,[7] $Eg(x)=3.42x+0.77(1-x)-x(1-x)1.43$. The band gap (Eg) of InGaN can be calculated from the InGaN quantum-well ground-level emission (E_{1e1h}) i.e., blue emission peak at 2.667 eV, using the relation $E_{1e1h}=E_g-eF_WL_W+(9\pi\hbar eF_W/8\sqrt{2})^{2/3}((1/m_e)+(1/m_h))^{1/3}$. From these relations, In composition in the InGaN wells was found to be ~19%, which is not necessarily equal to that of XRD results because the QSCE could be involved in the quantum-well emission, unlike absorption measurements; thus, the In composition obtained from the PL measurements might be larger than that of XRD measurements. The emission peak showed "S"-shape character shift, as temperature decreased from room temperature to 10 K and two phonon (LO) replicas existed with energy difference of about 91 meV, as shown in Fig. 3. The other emission peaks such as band edge emission (BE) at 3.469 eV, donor acceptor pair (DAP) at 3.285 eV, and its (phonon) replicas pronounced at 3.192, 3.099, and 3.008 eV with a difference of about 91 meV and yellow band (YB) emission at 2.214 eV, which are mainly from GaN. The S-shape character shift is due to potential fluctuations caused by inhomogeneous compositional and interface fluctuations in the quantum-well structures. As temperature increased from 10 to 60 K, the peak showed redshift with respect to photon energy because the (electron hole pairs) carriers, which are randomly distributed in the potential minima at low temperature, do not have sufficient thermal energy so that they relax down to lower energy level states by reducing higher energy emission. As temperature further increased (80–140 K), the emission peak showed blueshift, indicating the carriers do have sufficient thermal energy to occupy higher energy level states by emitting higher energy radiation. For the temperature range of 160–303 K, there is again redshift, which is commonly accepted to be due to nonradiative recombination rates, which dominate radiative recombination rates at room temperature.[8,9] We observed that the PL intensity of quantum wells without a capping layer was higher than that of *p*-GaN capped quantum-well structures because there is intraband absorption in the capped layer.[10] The PL quantum efficiency and full width at half maximum of the QW peak for the LED structure were found to be 0.05% at room temperature and 62 meV at 10 K. The blue emission peak intensity versus inverse temperature gave the activation energy of 43 meV, indicating the localization of the carriers in the structure. The activation energy was increased with increasing In composition, resulting in deep localization energies of excitons due to potential fluctuations.[11] However, PL quantum efficiency is higher in the blue LEDs as compared to that in the green LEDs, which is due to domination of stronger intrinsic radiative recombination rather than nonradiative recombination. The decrease of PL intensity with increasing temperature can be attributed to the thermionic emission of the excited photocarriers due to potential fluctuations, which arise from the compositional fluctuations in the well and also from the interface roughness fluctuations between well and barrier.

In conclusion, the essence of the results is that the strain, quantum dot-like structures, and the widths of well and barrier were observed from TEM analysis for blue LEDs. AFM analysis showed rms roughness of 1 nm resulting in good quality of the layers. The low-temperature PL studies showed that ‘‘S’’-shaped character shift, i.e., red–blue–redshift of quantum-well emission is attributed to the potential fluctuations due to alloy inhomogeneity and interface roughness in the quantum wells. The higher activation energy of 43 meV is indication of deep localization energies of excitons.

The authors would like to thank National Science Council (NSC) Taipei, for partial financial support under Contract No. NSC 85-2215-E-006-004. We thank Professor H. Morkoç and Professor D. Johnstone for fruitful discussions.

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