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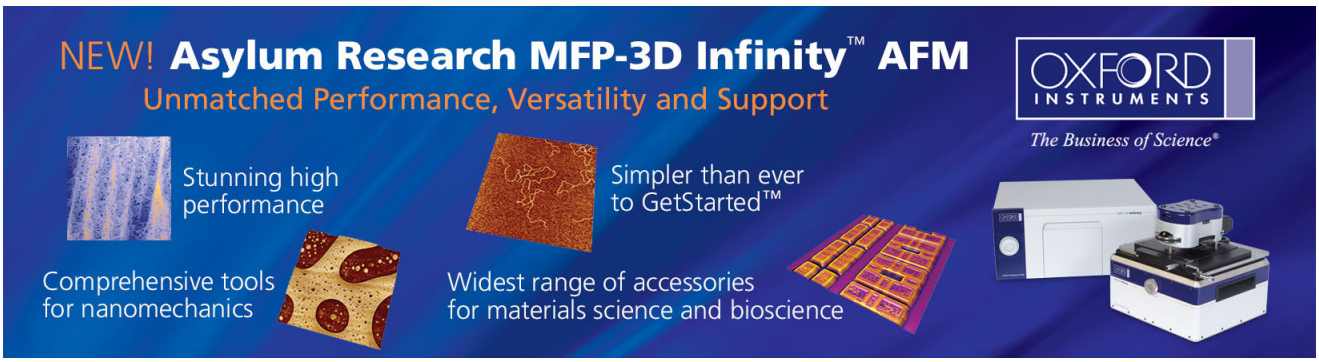

Thermal annealing effects on an InGaN film with an average indium mole fraction of 0.31

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We compared the optical and material properties of an InGaN thin film with an average indium content at 0.31 between as-grown and postgrowth thermally annealed conditions. The major part of the photoluminescence spectrum was shifted from the original yellow band into the blue range upon thermal annealing. Cathodoluminescence (CL) spectra showed that the spectral shift occurred essentially in a shallow layer of the InGaN film. The deeper layer in the as-grown sample contributed blue emission because it had been thermally annealed during the growth of the shallow layer. The spectral change was attributed to the general trends of cluster size reduction and possibly quantum-confined Stark effect relaxation upon thermal annealing. The attribution was supported by the observations in the CL, x-ray diffraction, and high-resolution transmission electron microscopy results. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1625434]

Recently, InGaN compounds of relatively high indium contents have caught much attention in research.[1,2] However, study has mainly focused on bowing effects.[2] The optical characteristics and material microstructures of such a compound, particularly after thermal annealing, have not been well studied yet. Because of the large lattice mismatch between InN and GaN, leading to the low miscibility between them, indium aggregation and phase separation usually occur in InGaN through the process of spinodal decomposition.[3] Such a process results in indium composition fluctuation and the formation of InGaN or InN clusters of quantum dot nature. With such clusters, carriers are localized in potential minima for effective radiative recombination.[4–6] Typically, the process of aggregation, and hence the effect of carrier localization, becomes stronger with increasing average indium content.[3,7] With the effect of carrier localization, it has been widely observed that the photoluminescence (PL) spectral peak showed an S-shaped variation with temperature.[1,8] Such an S-shaped variation was also interpreted as the result of the quantum-confined Stark effect (QCSE) in an InGaN/GaN quantum well (QW) structure.[9,10]

In this letter, we report the thermal annealing effects on the optical and material characteristics of an InGaN film with luminescence in the yellow range. Postgrowth thermal annealing can provide thermal energy for atomic rearrangement to reach a thermal equilibrium state. The induced spinodal decomposition process upon thermal annealing can result in more stable cluster structures in InGaN and enhance photon emission efficiency.[11–14] In our research, it was observed that after thermal annealing, the PL peak shifted from the yellow band into the blue range. This shift is particularly clear for photons emitted from the shallow portion of the InGaN thin film. The spectral change was attributed to the general trends of cluster size reduction and possibly QCSE relaxation upon thermal annealing.

The sample used in this study was grown in a low-pressure metal–organic chemical vapor deposition reactor. A $\sim$1.2 μm GaN layer was deposited on a sapphire substrate with a 25 nm GaN buffer layer. The GaN layer growth was followed by the deposition of an $In_xGa_{1-x}N$ film with a thickness of $\sim$0.2 μm. The average indium content, x, was estimated to be 0.31. Thermal annealing was conducted with 800 °C for 30 min in ambient nitrogen.

Figure 1 shows the PL and photoluminescence excitation (PLE) spectra at 10 K of the as-grown and annealed samples. It is interesting to note that PL spectral peak has shifted from the yellow band (around 2.2 eV) to the blue band (around 2.75 eV) after thermal annealing. The blue emission contribution as a small sidelobe can also be observed in the PL spectrum of the as-grown sample. It is believed that PL emission essentially comes from a shallow layer of the sample. Its peak shifts due to nanostructure alteration in the InGaN layer upon thermal annealing. This argument excludes the possibility that the yellow-band emission originates from defects in GaN.[15] The PLE spectrum of the as-grown sample shows multiple InGaN absorption peaks corresponding to clusters

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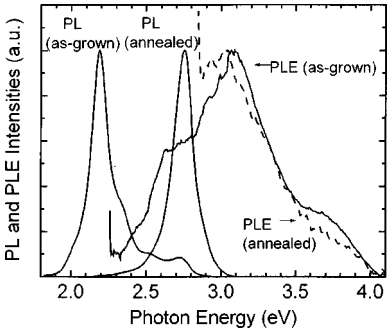

FIG. 1. PL and PLE spectra at 10 K before and after thermal annealing.

of different geometries and compositions. The Stokes shift (SS) is as large as around 1 eV, indicating the strong indium composition fluctuation and/or strong QCSE. After thermal annealing, the spectral position of the major absorption peak near 3.05 eV is unchanged. This energy level may correspond to the background indium composition, on top of which the higher indium composition fluctuates in the as-grown and annealed samples. The distribution of the higher indium composition fluctuation varied upon thermal annealing such that the PL spectrum blueshifted and the SS became quite small (around 200 meV). From this result, we may conclude that the indium composition fluctuation range was decreased and/or the QCSE within clusters was reduced upon thermal annealing.

Figures 2(a) and 2(b) show the cathodoluminescence (CL) spectra of the as-grown and annealed samples, respectively. In each sample, the four different electron acceleration voltages correspond to electron penetration depths of 88, 210, 450, and 1300 nm, respectively. In the as-grown sample, only the luminescence in the yellow band is observed in a shallow layer. However, as the electron voltage increases, not only the strong luminescence of the GaN layer (around 3.4 eV) can be seen, but also a small peak of blue luminescence is observed. Hence, it is speculated that a certain structure existing deep in the InGaN film can emit photons in the blue range (between 2.7 and 2.85 eV). This result is consistent with the sidelobe of the PL spectrum in the as-grown sample,

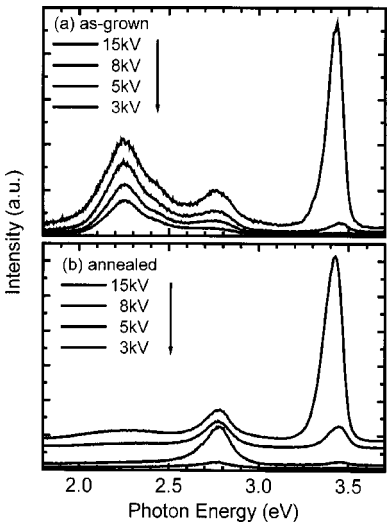

FIG. 2. CL spectra with four different electron voltage levels for the samples before (a) and after (b) thermal annealing.

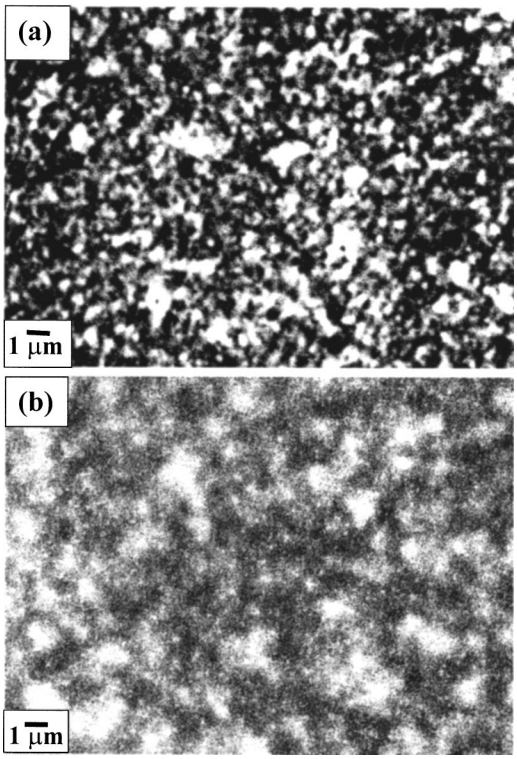

FIG. 3. (a) Typical CL image before thermal annealing; (b) typical CL image after thermal annealing.

as shown in Fig. 1. After thermal annealing, in the shallow layer of InGaN (3 kV probe), only the blue luminescence exists, which is again consistent with the PL measurement. With higher energy electron excitation, the blue luminescence is enhanced and the GaN emission peak appears. Also, a broad yellow luminescence is observed. This yellow luminescence is believed to originate from the defects in the GaN layer, instead of the cluster luminescence in the InGaN film. From the results described above, we speculate that after thermal annealing, the nanostructure of the shallow layer of the InGaN film has been changed into that similar to the structure resulting in blue luminescence in the deeper portion. Hence, the whole InGaN film emits blue light. The different structures between the shallow and deep portions in the as-grown InGaN film are due to the fact that in growing the shallow portion the high growth temperature had the effect of thermally annealing the deep portion.

Figure 3 shows typical CL images of the as-grown (a) and annealed (b) samples, both with the excitation of 15 kV electrons. Light spots of a few μm in size confirm the cluster

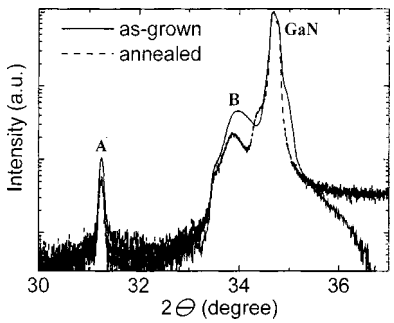

FIG. 4. XRD patterns before and after thermal annealing.

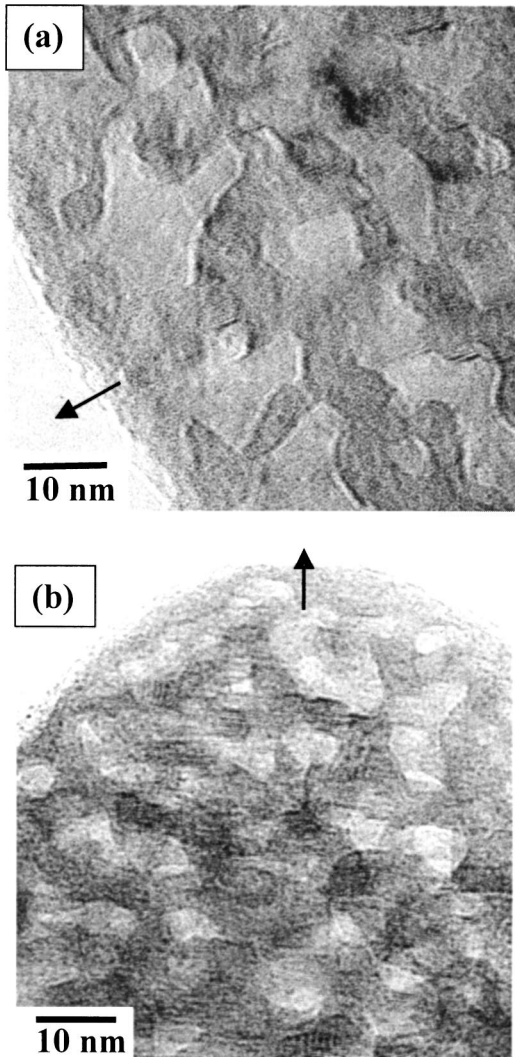

FIG. 5. Typical HRTEM images before (a) and after (b) thermal annealing. Arrows show crystal growth directions.

structures in the as-grown sample. After thermal annealing, the CL image [see Fig. 3(b)] becomes blurred because many tiny light spots of sub-μm in size were generated. In this situation, large bright areas in the μm scale also exist. The large bright areas may originate from three possibilities: clustering of small light spots, accumulation of emission along the depth, and μm-scale emission areas. Since such large bright areas also exist before thermal annealing, the key variation upon thermal annealing is the generation of tiny light spots. Those tiny light spots essentially emit blue light. The generation of those tiny light spots implies that the cluster sizes in the InGaN film, at least for part of clusters, have been reduced upon thermal annealing, particularly in the shallow portion.

Figure 4 shows the x-ray diffraction (XRD) patterns of the as-grown and annealed samples. The InN peak (A) and the distribution (B), corresponding to InGaN of indium composition fluctuation, clearly confirm a strong indium aggregation process in the as-grown and annealed samples. In distribution B, the signal splits into two components after thermal annealing. The low-indium component is attached to the GaN peak. This phenomenon may imply a larger contrast of indium concentration between a cluster and the surrounding region. In addition, Figs. 5(a) and 5(b) show the high-resolution transmission electron microscopy (HRTEM) images of the as-grown and annealed samples, respectively. The cluster domain structures in both samples can be clearly seen. Although the domain geometry in either sample is quite random, one can still observe that the domain size in the annealed sample is smaller.[16,17]

Based on the observations described above, we can assume that during thermal annealing, spinodal decomposition tends to reduce the sizes of at least part of the clusters. In this process, the indium content in an InGaN cluster can be enhanced, which may lead to a smaller material band gap. However, the shrinkage of cluster size results in stronger quantum confinement and increases the effective band gap of the quantum dot. From our calculations, based on a quantum box model, it is found that the effective band gap is increased, which is consistent with the significant blueshift in PL spectrum. Furthermore, the strain within a cluster may be partly relaxed during the spinodal decomposition process upon thermal annealing. The reduction of QCSE can also contribute to the blueshift of the PL peak.

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